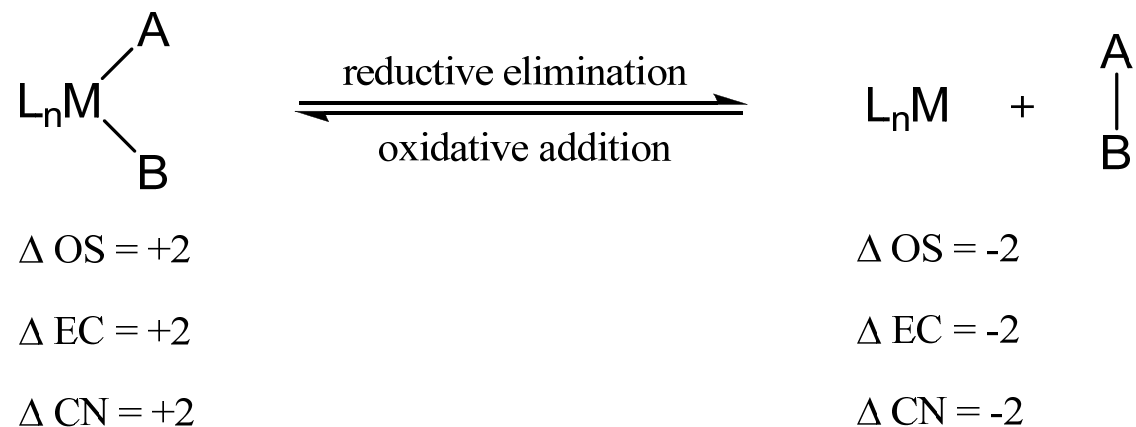


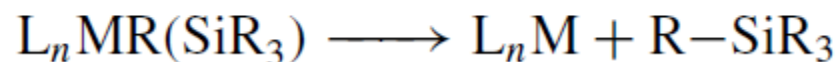
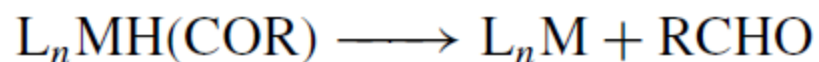
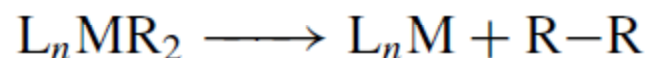
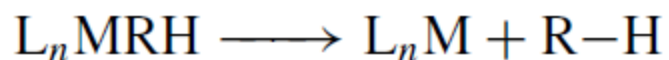
Reductive Elimination

- Reductive elimination, *the reverse of oxidative addition*, is most often seen in **higher oxidation states** because the formal oxidation state of the metal is reduced by two units in the reaction.



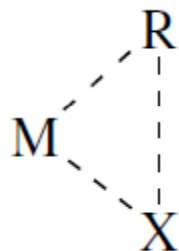
- The reaction is especially efficient for intermediate oxidation states, such as
 - **the d⁸ metals Ni(II), Pd(II), and Au(III)**
 - **the d⁶ metals Pt(IV), Pd(IV), Ir(III), and Rh(III)**
- Reductive elimination can be *stimulated by oxidation or photolysis*.

- Certain groups are more easily eliminated than others. The following reactions often proceed to the right for thermodynamic reasons:



- Reactions that involve H are particularly fast** (the first 3 above) , probably because the transition state energy is lowered by the formation of a relatively stable σ -bond complex $L_nM(H-X)$ along the pathway.
- It is often the case that reactions involving a hydrogen atom are much faster than those involving any other element; this is because H carries no electrons other than bonding electrons, and these are in a 1s orbital, which is capable of making and breaking bonds in any direction in the transition state.

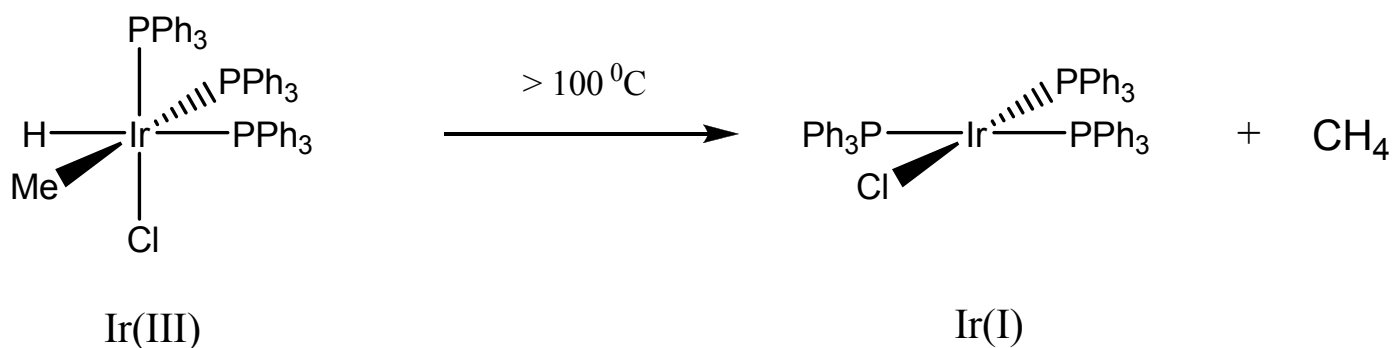
- In catalysis reactions, a reductive elimination is ***often the last step in a catalytic cycle***, and the resulting L_nM fragment must be able to survive long enough to react with the substrates for the organic reaction and so reenter the catalytic cycle.
- Reductive elimination is analogous to the concerted oxidative additions in that they are believed to go by a ***nonpolar, nonradical threecenter transition state***:



- ***Retention of stereochemistry at carbon*** is a characteristic feature of this group of reactions.
- Since there are several mechanisms for oxidative addition the principle of microscopic reversibility (which holds that a reversible reaction proceeds by the same mechanism in both forward and reverse directions) suggests that reductive eliminations should show the same variety. We will only discuss the concerted pathway.

Reductive Elimination – O_h complexes

- Octahedral d^6 complexes of Pt(IV), Pd(IV), Ir(III), and Rh(III) tend to undergo reductive elimination readily but often with **initial loss of a ligand to generate a 5-coordinate intermediate**, a much more reactive species than the starting 6-coordinate complex.
- When ligand dissociation does not occur, reductive elimination can be slow, even when it would otherwise be expected to be very favorable.
- For example, complexes with an alkyl group *cis* to a hydride are rare because reductive elimination of an alkane is usually very thermodynamically favorable.
- A stable example of this type is *mer*-[IrH(Me)Cl(PMe₃)₃], with H and Me *cis*, which survives heating to 100°C.



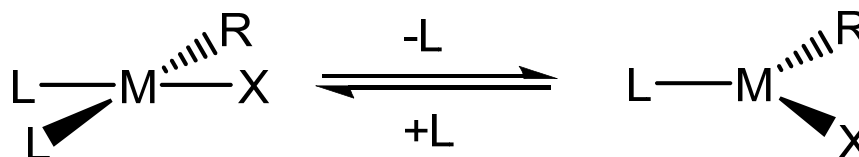
Reductive Elimination – Square Planar complexes

- Square planar d^8 complexes show a variety of reductive elimination mechanisms:

➤ dissociative

➤ Non-dissociative

➤ associative



- Sometimes a ligand dissociates from MRXL_2 , and the elimination occurs from the 3-coordinate MRXL intermediate, resulting in initial formation of a 1-coordinate ML metal fragment; this is the case for PdR_2L_2 and several Au(III) species.
- In some cases, the 4-coordinate *trans*- MRXL_2 species can reductively eliminate but usually only after initial isomerization from *trans* to *cis* to put the two groups to be eliminated next to one another.
- Occasionally, a fifth ligand associates, and elimination occurs from a 5-coordinate TBP intermediate; this has been found for Ni(II) .