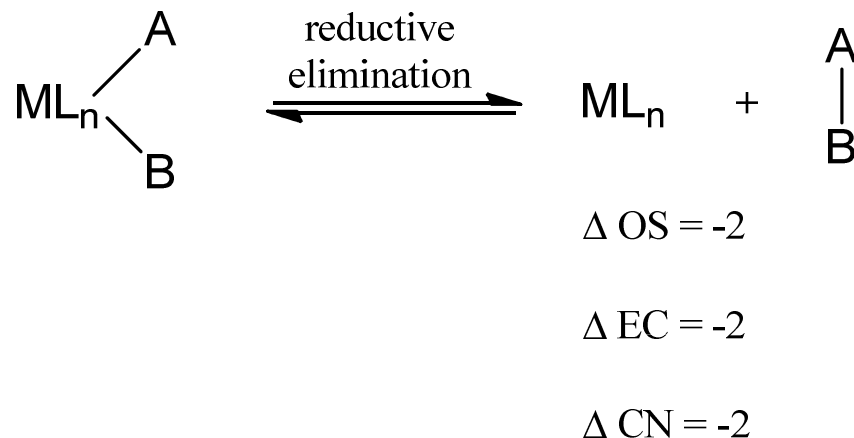


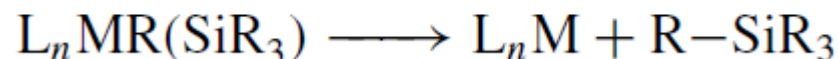
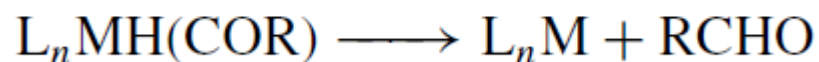
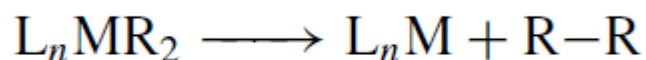
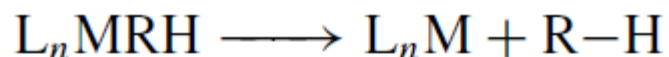
Reductive Elimination

- 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.



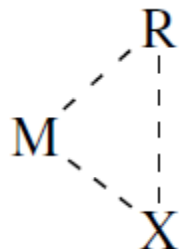
- The reaction is especially efficient for intermediate oxidation states, such as
 - the d^8 metals Ni(II), Pd(II), and Au(III)
 - the d^6 metals Pt(IV), Pd(IV), Ir(III), and Rh(III)
- Reductive elimination can be ***stimulated by oxidation or photolysis***.

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



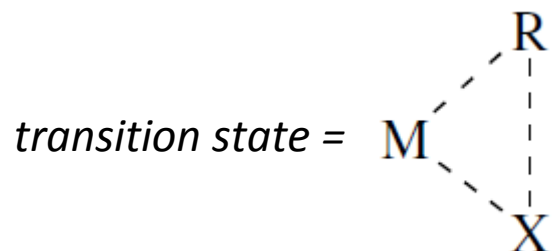
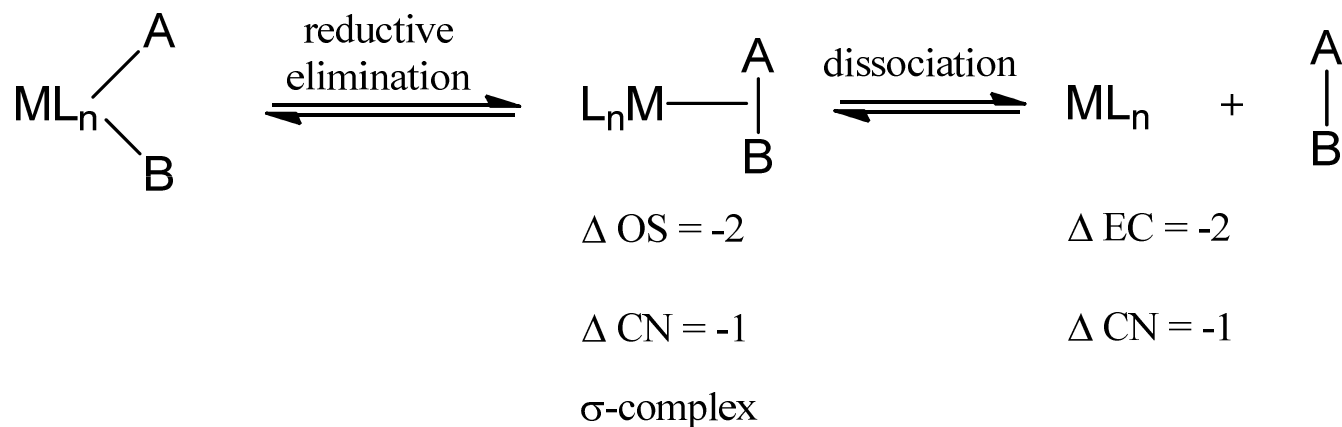
- **Reactions that involve H are particularly fast** (the first 3 above) , probably because the transition state energy is lowered by the formation of a relatively stable σ -bond complex $L_nM(H-X)$ along the pathway.
- Such complexes are known to be stable only where at least one H is eliminated.

- ***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 three-center transition state:



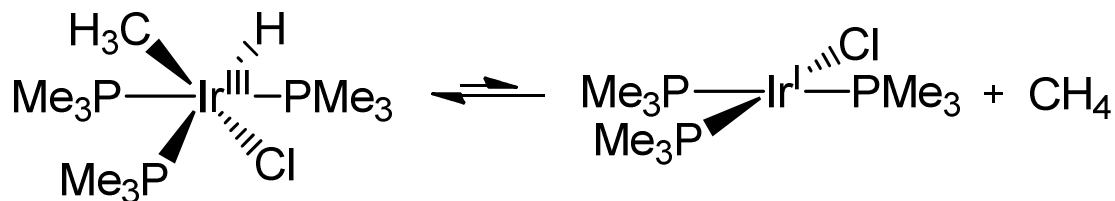
- ***Retention of stereochemistry at carbon*** is a characteristic feature of this group of reactions.

- 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 d⁶ 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.
- 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.



$$\Delta \text{ OS} = -2$$

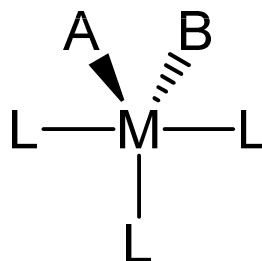
$$\Delta \text{ EC} = -2$$

$$\Delta \text{ CN} = -2$$

octahedral
18 electron

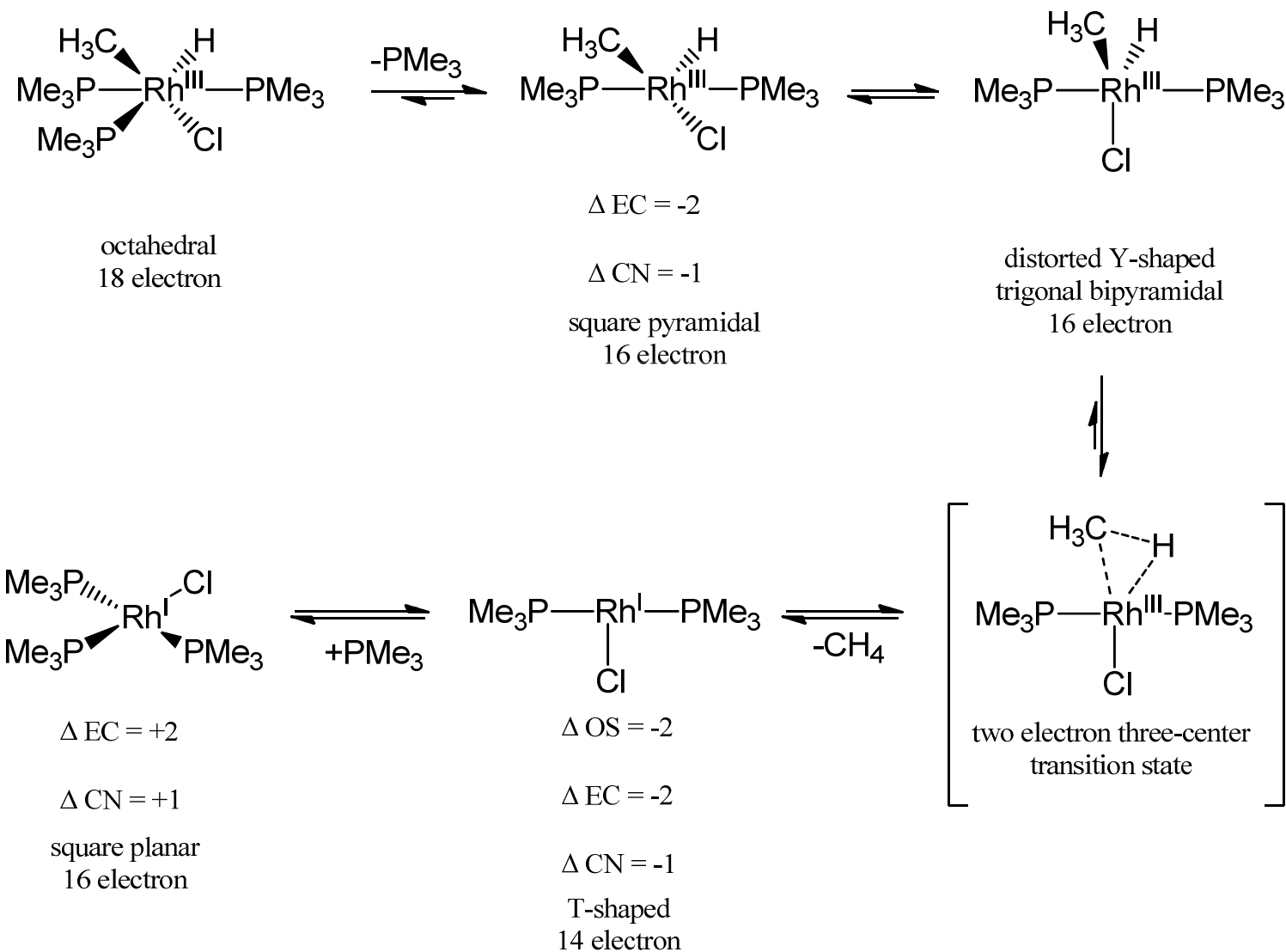
square pyramidal
16 electron

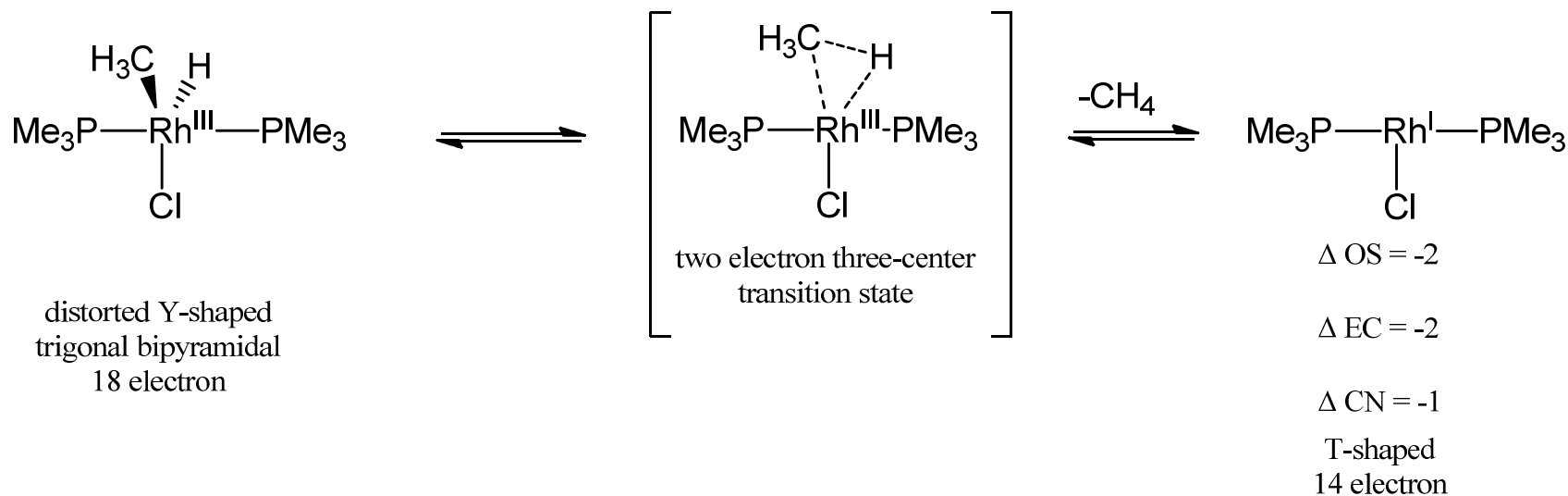
- The Rh analog with its weaker M-PMe₃ bonds, gives reductive elimination even at 30°C.
- It is the PMe₃ *trans* to the *high-trans-effect* hydride ligand that is lost.
- The 5-coordinate intermediate may be more reactive because it can more readily distort to reach the transition state for reductive elimination.
- It might be expected to be able to gain access to the **Y-type distorted trigonal bipyramidal structure**.



distorted Y-shaped
trigonal bipyramidal

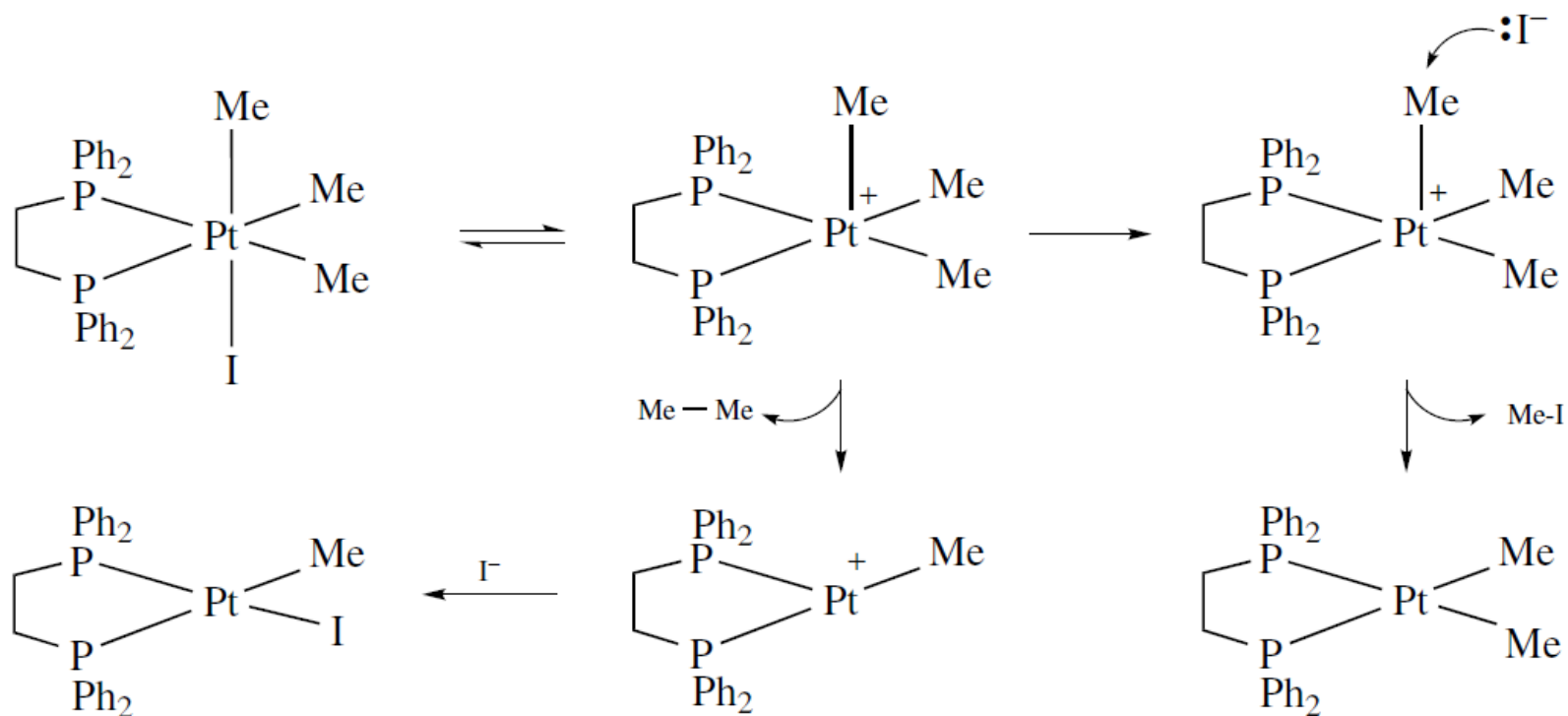
- Example of a common general mechanism for reductive elimination in Milstein's octahedral d^6 species ($L = \text{PMe}_3$; $R = \text{CH}_2\text{COMe}$).
- The reverse mechanism (dotted arrows) often holds for oxidative addition to square planar d^8 species (e.g., $R = \text{H}$).





- A Y structure is favored where one π -donor ligand, Cl in this case, is located at the basal position of the Y.
- This structure brings the two groups to be eliminated, R and H, very close together.
- The typical small R–M–H angle for these groups, 70° , may facilitate achievement of the proposed transition state for reductive elimination.
- After reductive elimination, a T-shaped 3-coordinate species is formed.

- If reductive elimination of 6-coordinate d^6 species goes by the Y-shaped t.b.p. *transition state* then the reverse reaction, oxidative addition to 4-coordinate d^8 species, is also expected to go by the same *transition state* by reversal of the same pathway.
- Indeed, Halpern showed that T-shaped $\text{RhCl}(\text{PPh}_3)_2$, formed by loss of a PPh_3 group from $\text{RhCl}(\text{PPh}_3)_3$, gives oxidative addition with hydrogen at a rate at least 104 times faster than the 4-coordinate complex.
- The reversibility argument also applies to reductive elimination of alkyl halides for which an $\text{S}_{\text{N}}2$ pathway applies for the oxidative addition direction.
- Iodide attacks the coordinated methyl *trans* to the open site and nucleophilically displaces the Pt complex, which is a good leaving group.
- The reactive 5-coordinate intermediate, which can even be isolated in some cases, can also undergo concerted reductive elimination of ethane if the I^- concentration is low.

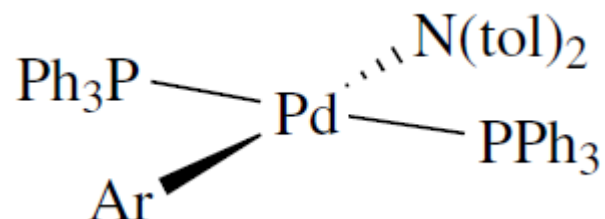


- The mechanism for reductive elimination to form C–C and C–Hal bonds in octahedral d^6 species in Goldberg's complex.
- The reverse mechanism holds for oxidative addition to square planar d^8 species.

Reductive Elimination – Square Planar complexes

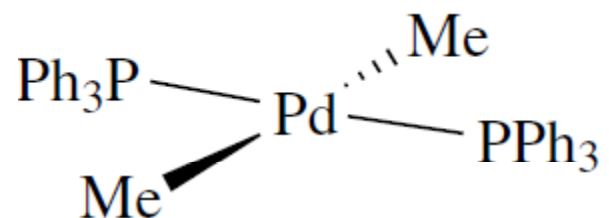
- Square planar d^8 complexes show a variety of reductive elimination mechanisms:
 - dissociative
 - non-dissociative
 - associative
- Sometimes a ligand dissociates from $MRXL_2$, and the elimination occurs from the 3-coordinate $MRXL$ intermediate, resulting in initial formation of a 1-coordinate ML 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 $Ni(II)$.

- Driver and Hartwig have analyzed the kinetics for the case of $\text{trans-[PdAr(N\{tolyl\}_2)(PPh_3)_2]}$ where reductive elimination of $\text{Ar-N\{tolyl\}_2}$ takes place via competing dissociative and non-dissociative pathways.



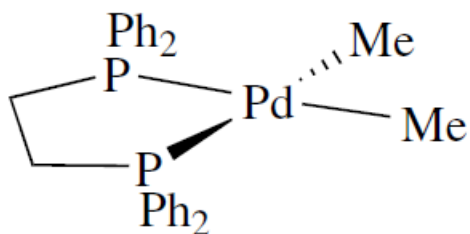
- Square planar Pt(II) is often slow to eliminate, perhaps because ligand dissociation is harder, but oxidative addition of RX to give a Pt(IV) intermediate can promote reductive elimination.

- Mechanisms are probed via the kinetics.
- For example, in the dissociative reductive elimination of Me–Me from trans-[PdMe₂(PPh₃)₂], added PPh₃ retards the reaction in an inverse first-order way (the rate is proportional to 1/[PPh₃]).

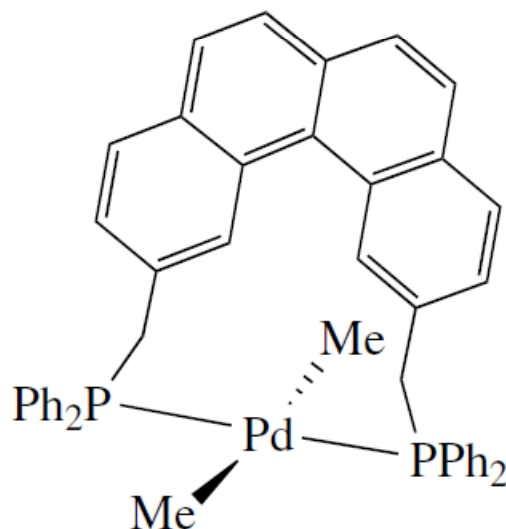


- This suggests that loss of phosphine takes place to give the 3-coordinate intermediate PdR₂L.
- The retardation might alternatively have been due to formation of PdR₂L₃, which would have to be less reactive than PdR₂L₂ itself.
- It was shown by NMR that this does not happen, however.

- The chelating diphosphine complex loses phosphine much less easily than do the analogs containing monodentate phosphines and undergoes elimination 100 times more slowly.



- The “transphos” complex **does not eliminate** ethane under conditions where the corresponding cis derivative **does so very** readily.

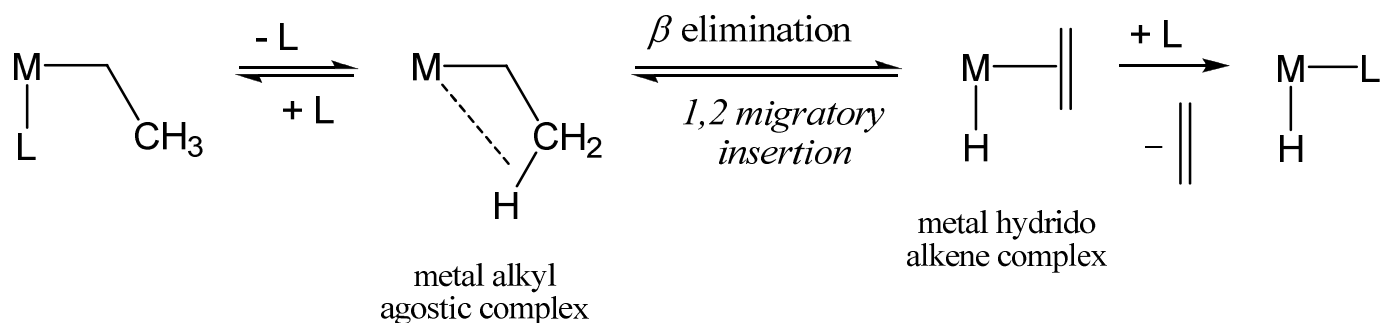


- The groups to be eliminated therefore need to be cis; transphos locks this system in a trans geometry.

α , β , γ , and σ elimination

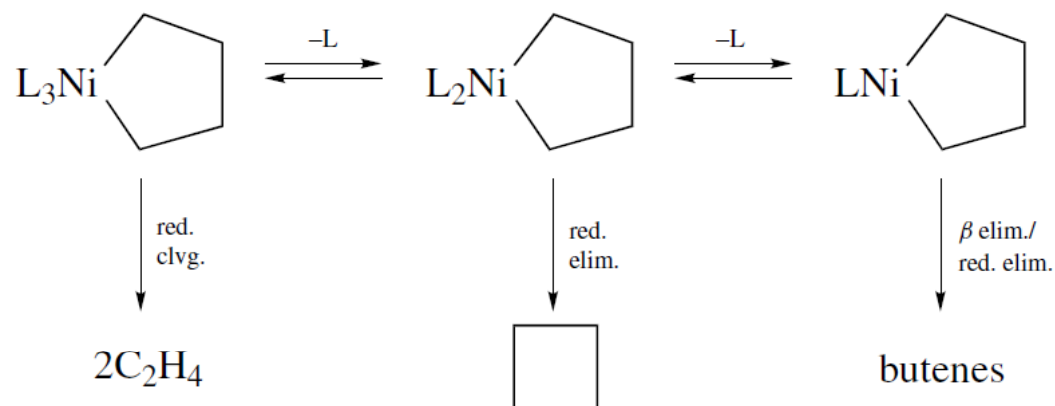
β elimination

- β elimination is the chief decomposition pathway for alkyls that have β -H substituents.*
- A 2e vacant site is required at the metal, and there has to be a roughly coplanar M-C-C-H arrangement that brings the β -H close to the metal.*
- A complicating feature of this process is that the alkene may reinsert into the metal hydride, and this can give rise to isomerization of the alkene or of the starting alkyl.*
- The alkene is rarely coordinated in the final products of a β elimination, however, because it is usually displaced by the ligand that originally dissociated to open up a 2e vacant site at the metal, or by some other ligand in the reaction mixture.*



- An 18e complex has to lose a ligand to open up a site for elimination. In each case the addition of excess ligand inhibits the reaction by quenching the open site.

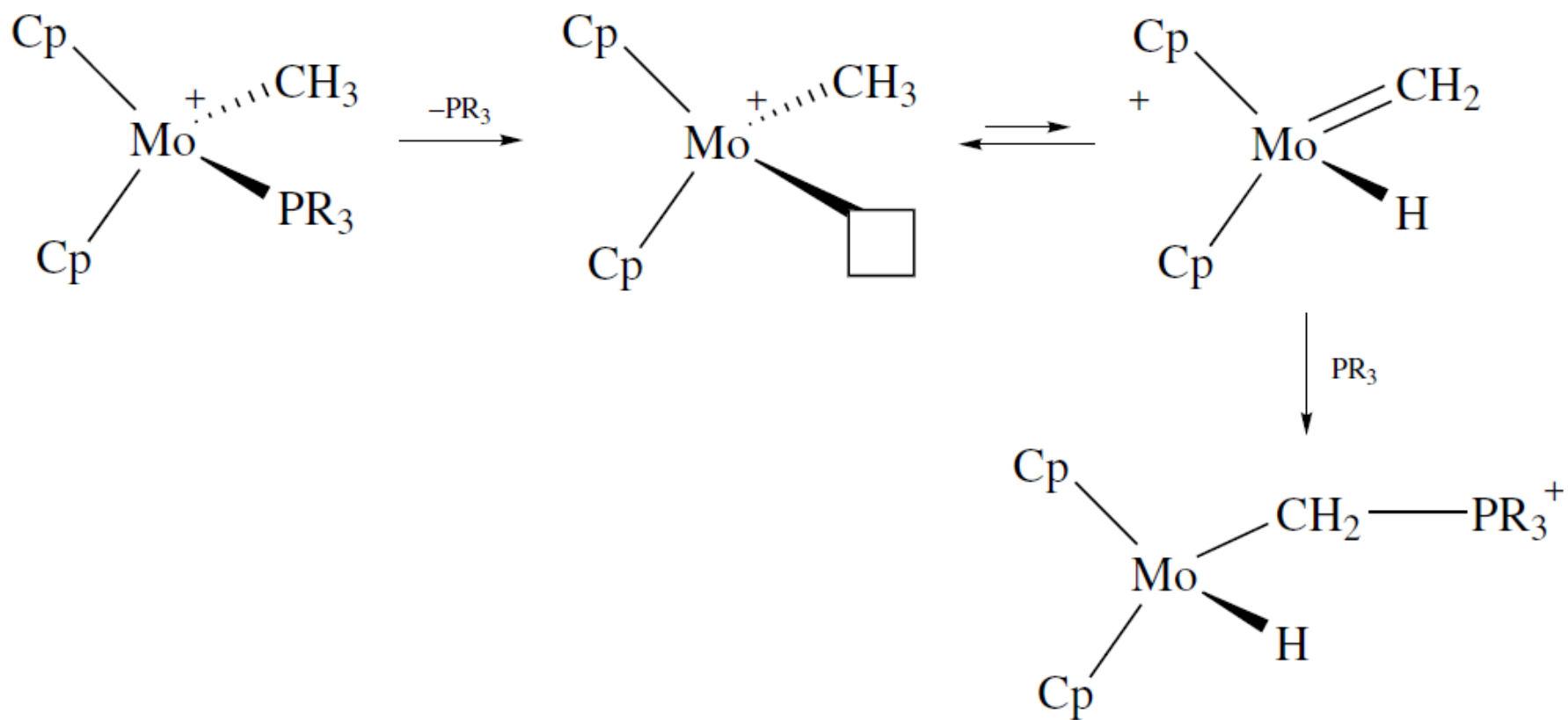
- Grubbs and co-workers have studied a series of nickel complexes in the presence and absence of excess phosphine and have found that there are three decomposition pathways, one for each of the different intermediates, 18e, 16e, and 14e, that can be formed.



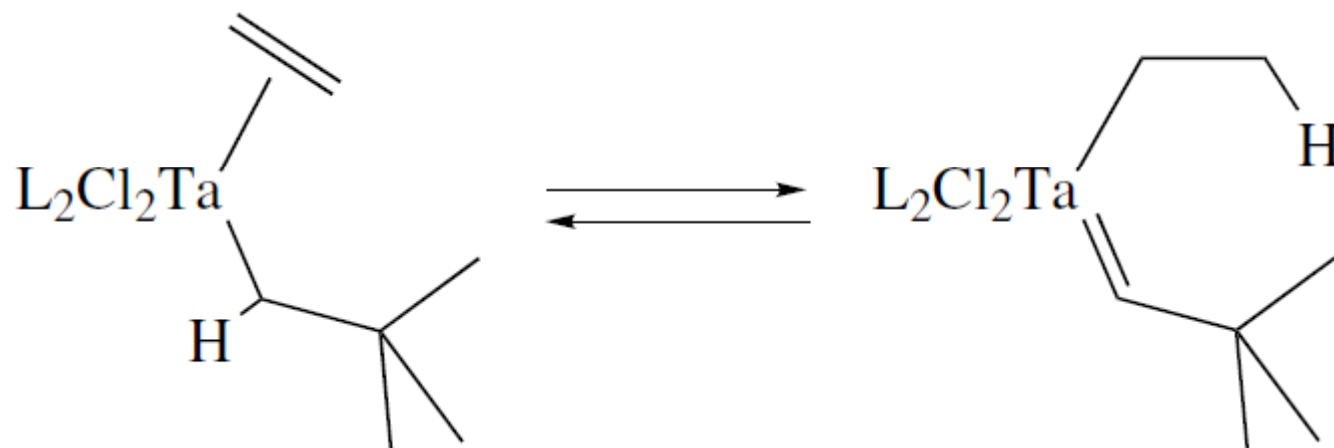
- Alkoxide complexes readily undergo β elimination to give ketones or aldehydes, accounting for the ability of basic isopropanol to reduce many metal halides to hydrides with formation of acetone.
- β Elimination of amides and amines to imines also occurs but tends to be slow.

α elimination

- If an alkyl has no β hydrogens, it may ***break a C–H bond in the α , γ , or δ position.***
- The simplest case is a methyl group, which has no β hydrogens and can undergo only α elimination to give the methylene hydride.
- While the β process gives an alkene, a stable species that can dissociate from the metal, the methylene ligand ($M=CH_2$) formed from the α elimination is very unstable in the free state and so does not dissociate.
- Methylene hydride complexes are unstable with respect to the starting methyl complex, and so the products of α elimination can be intermediates in a reaction but are seldom seen as isolable species.
- For this reason, the α -elimination process is less well characterized than β elimination.
- Studies of both molybdenum and tantalum alkyls suggest that α elimination can be up to 10^6 times faster than β elimination even in cases in which both α - and β -H substituents are present (Schrock carbene synthesis).
- In some cases, a coordinatively unsaturated methyl complex seems to be in equilibrium with a methylene hydride species, which can sometimes be trapped, either by nucleophilic attack at the carbene carbon or by removing the hydride by reductive elimination with a second alkyl present on the metal.

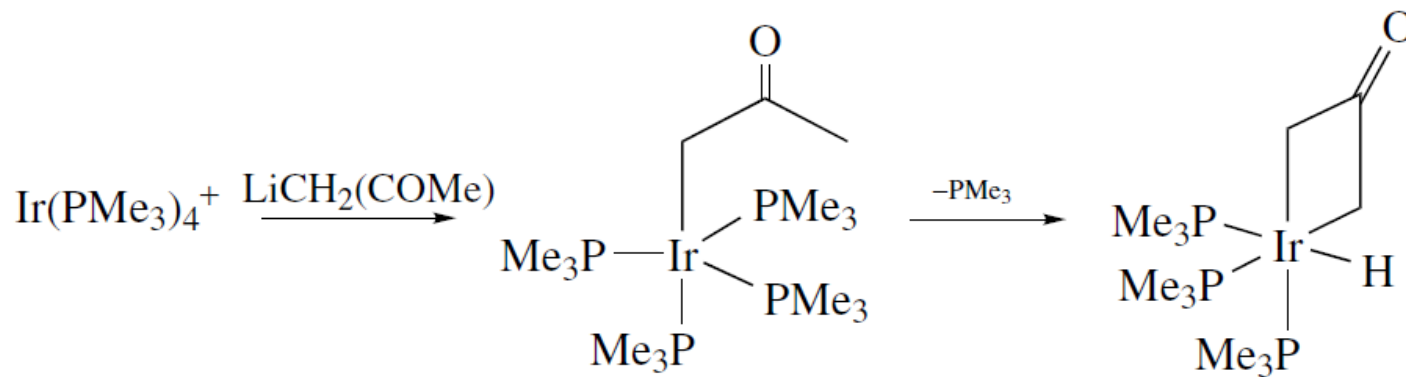
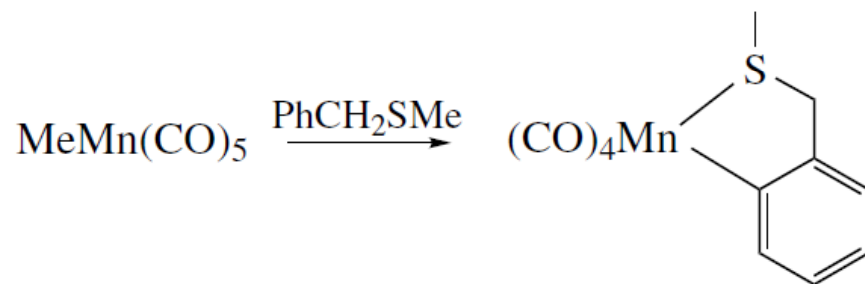
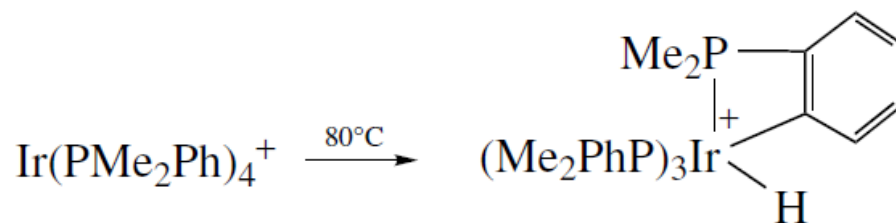


- Schrock and co-workers have found an interesting case of α and β elimination taking place competitively in a tantalum complex, the two tautomers of which can be observed in solution by ^1H NMR.

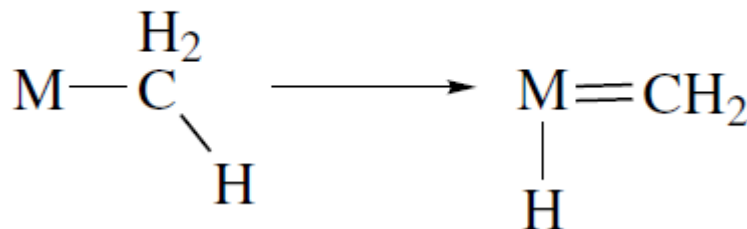


Other Eliminations

- In addition to alkyls, a great variety of other ligands have no β -H but do have γ or δ -H's and can undergo γ or δ elimination to give cyclic products.



- All these elimination reactions can be thought of as being related to oxidative additions of a C–H bond to the metal.
- This is seen more clearly for β elimination if we write the metalacyclopropane (X_2) form of the alkene hydride product, and for α elimination if we consider the X_2 form for the product carbene hydride.
- Both γ and δ elimination are more obvious examples of oxidative addition.



Homework

- Browse through the ACS journal "*Organometallics*" and identify both an oxidative addition reaction as well as a reductive elimination reaction (it is ok if the reactions are part of a more complex catalytic cycle).
- **Assign oxidation states of metal centers, CN# , electron counting, geometry, types of M-L bonding interactions and suggest a mechanism for the reactions chosen.**