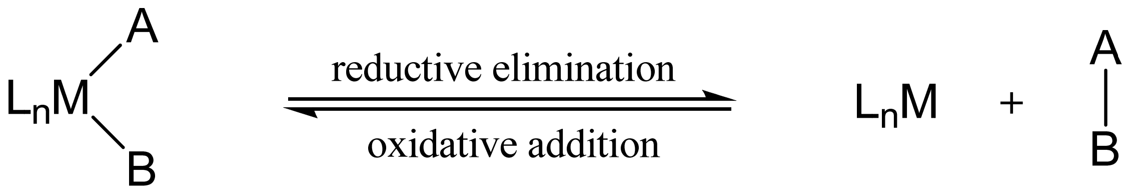
Reductive Elimination

- 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.



Δ OS = +2 Δ OS = -2

Δ EC = +2 Δ EC = -2

Δ CN = +2 Δ CN = -2

- 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***.

Change in d^n Configuration	Change in Coordination Geometry	Examples	Group	Remarks
$d^{10} \rightarrow d^8$	Lin. $\xrightarrow{X_2}$ Sq. Pl.	Au(I) → (III)	11	
	Tet. $\xrightarrow{-2L, X_2}$ Sq. Pl.	Pt, Pd(0) → (II)	10	
$d^8 \rightarrow d^6$	Sq. Pl. $\xrightarrow{X_2}$ Oct.	M(II) → (IV)	10	M = Pd, Pt
		Rh, Ir(I) → (III)	9	Very common
		M(0) → (II)	8	Rare
	TBP. $\xrightarrow{-L, X_2}$ Oct.	M(I) → (III)	9	
		M(0) → (II)	8	
$d^7 \rightarrow d^6$	2Sq. Pyr. $\xrightarrow{X_2}$ 2Oct.	2Co(II) → (III)	8	Binuclear
	2Oct. $\xrightarrow{-L, X_2}$ 2Oct.	2Co(II) → (III)	8	Binuclear
$d^6 \rightarrow d^4$	Oct. $\xrightarrow{-L, X_2}$ 7-c	Re(I) → (III)	7	
		M(0) → (II)	6	
		V(−I) → (I)	5	
$d^4 \rightarrow d^3$	2Sq. Pyr. $\xrightarrow{X_2}$ 2Oct.	2Cr(II) → (III)	6	Binuclear
	2Oct. $\xrightarrow{-L, X_2}$ 2Oct.	2Cr(II) → (III)	6	Binuclear
$d^4 \rightarrow d^2$	Oct. $\xrightarrow{X_2}$ 8-c	Mo, W(II) → (IV)	6	
$d^2 \rightarrow d^0$	Various	M(III) → (V)	5	
		M(II) → (IV)	4	

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

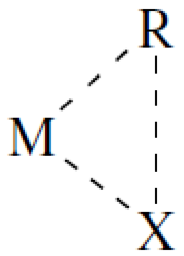
$$\begin{aligned}
L_nMRH &\longrightarrow L_nM + R{-}H\\
L_nMR_2 &\longrightarrow L_nM + R{-}R\\
L_nMH(COR) &\longrightarrow L_nM + RCHO\\
L_nMR(COR) &\longrightarrow L_nM + R_2CO\\
L_nMR(SiR_3) &\longrightarrow L_nM + R{-}SiR_3
\end{aligned}$$

- ***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 LnM(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.

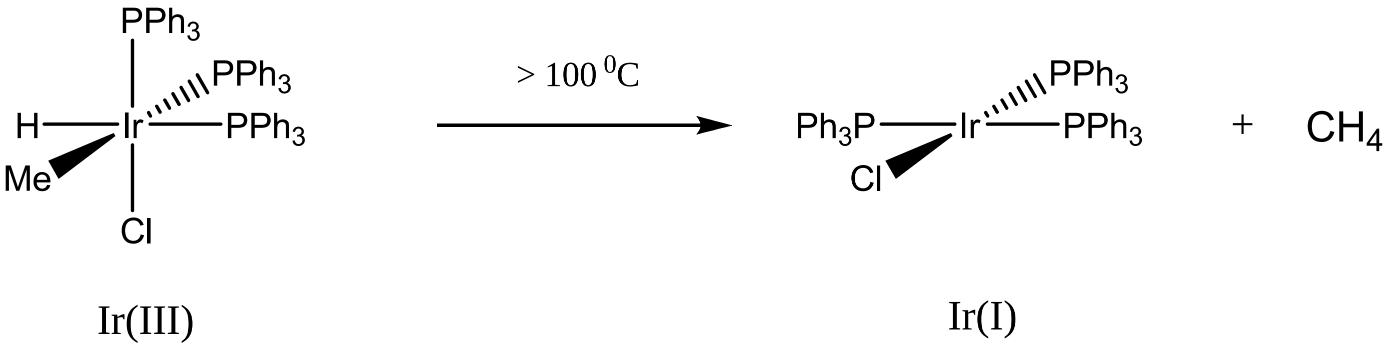
Reductive Elimination – O_h complexes

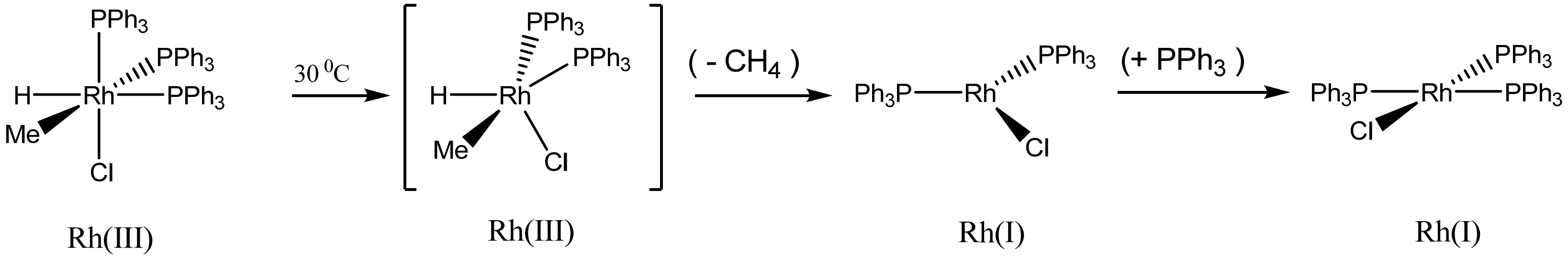
- Octahedral d^6 complexes of Pt(IV), Pd(IV), Ir(III), and Rh(III) tend to undergo reductive elimination readily but often with ***initial loss of a ligand to generate a 5-coordinate intermediate***, a much more reactive species than the starting 6-coordinate complex.

- When ligand dissociation does not occur, reductive elimination can be slow, even when it would otherwise be expected to be very favorable.

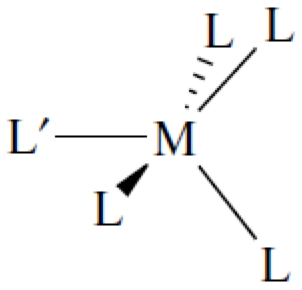
- For example, complexes with an alkyl group *cis* to a hydride are rare because reductive elimination of an alkane is usually very thermodynamically favorable.

- A stable example of this type is *mer*-$[IrH(Me)Cl(PMe_3)_3]$, with H and Me *cis*, which survives heating to 100°C.

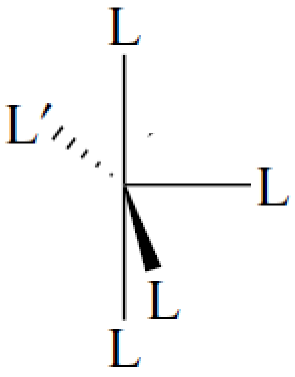




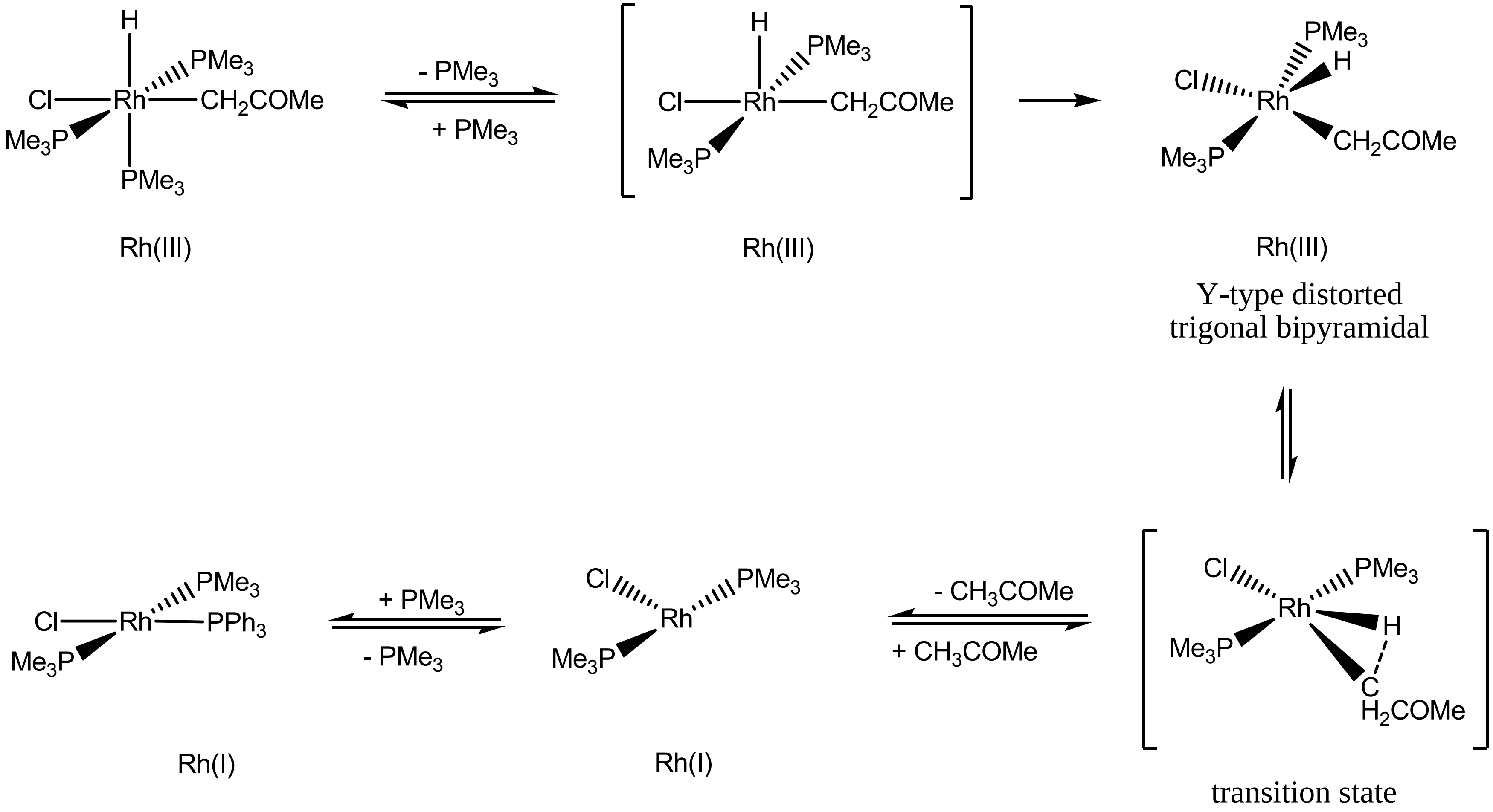
- The Rh analog with its weaker M−PMe$_3$ bonds, gives reductive elimination even at 30°C.
- It is the PMe$_3$ *trans* to the *high-trans-effect* hydride ligand that is lost.
- The 5-coordinate intermediate may be more reactive because it can more readily distort to reach the transition state for reductive elimination.
- It might be expected to be able to gain access to the **Y-type distorted trigonal bipyramidal** structure.



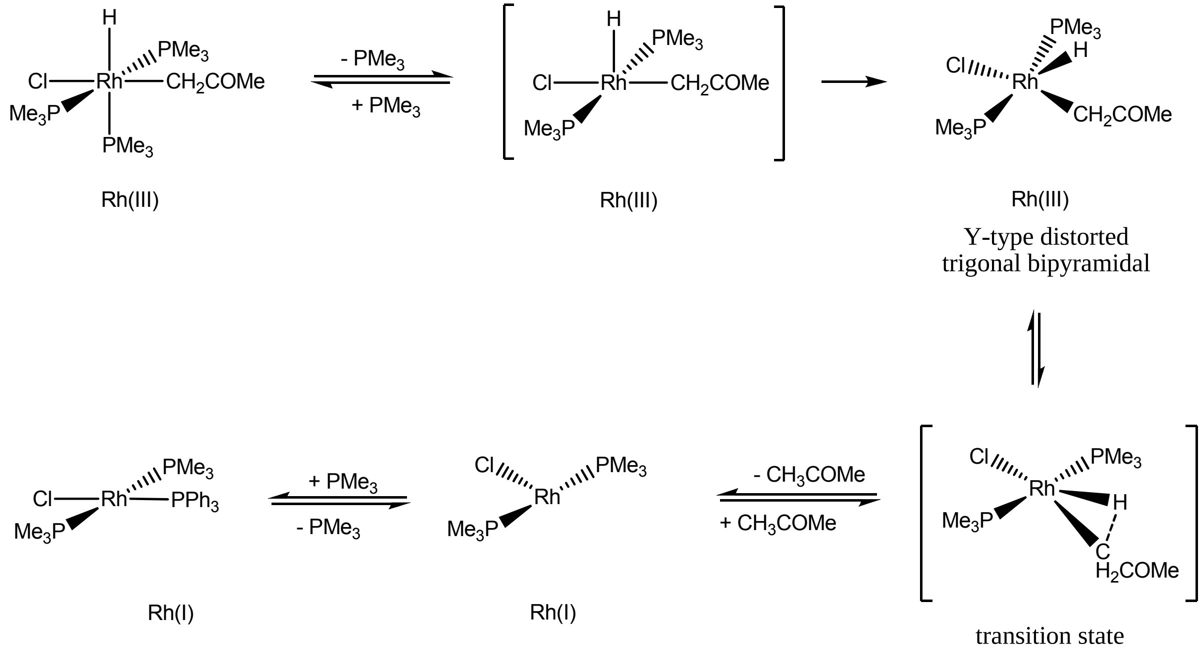
TBP

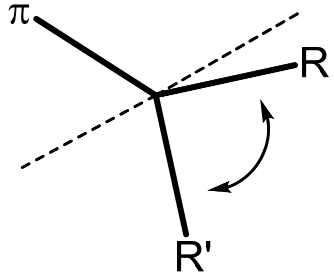


distorted
trigonal pyramidal
or Y geometry



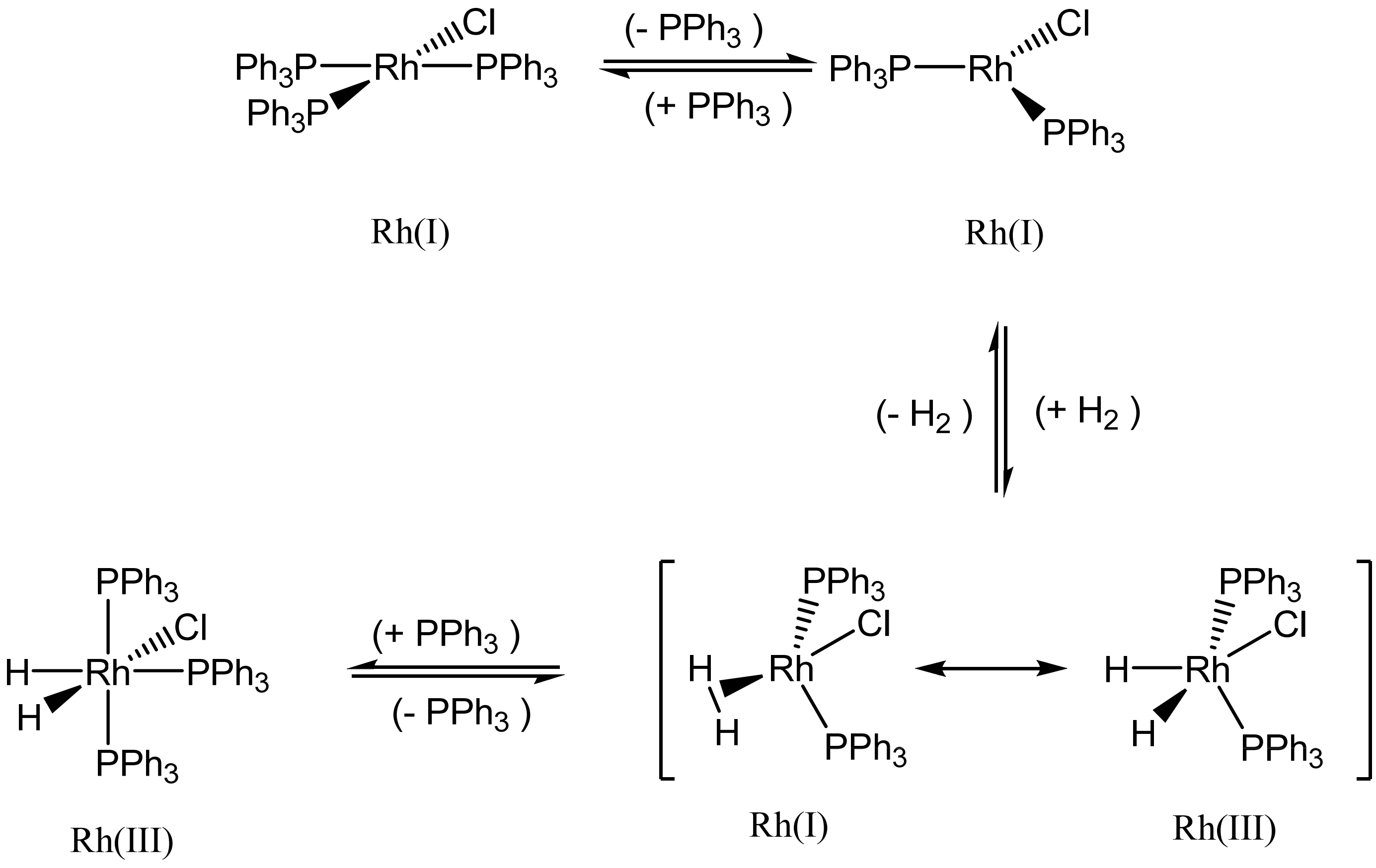
- Example of a common general mechanism for reductive elimination is Milstein's octahedral d^6 species (L = PMe_3; R = CH_2COMe).
- The reverse mechanism (dotted arrows) often holds for oxidative addition to square planar d^8 species (e.g., R = H).



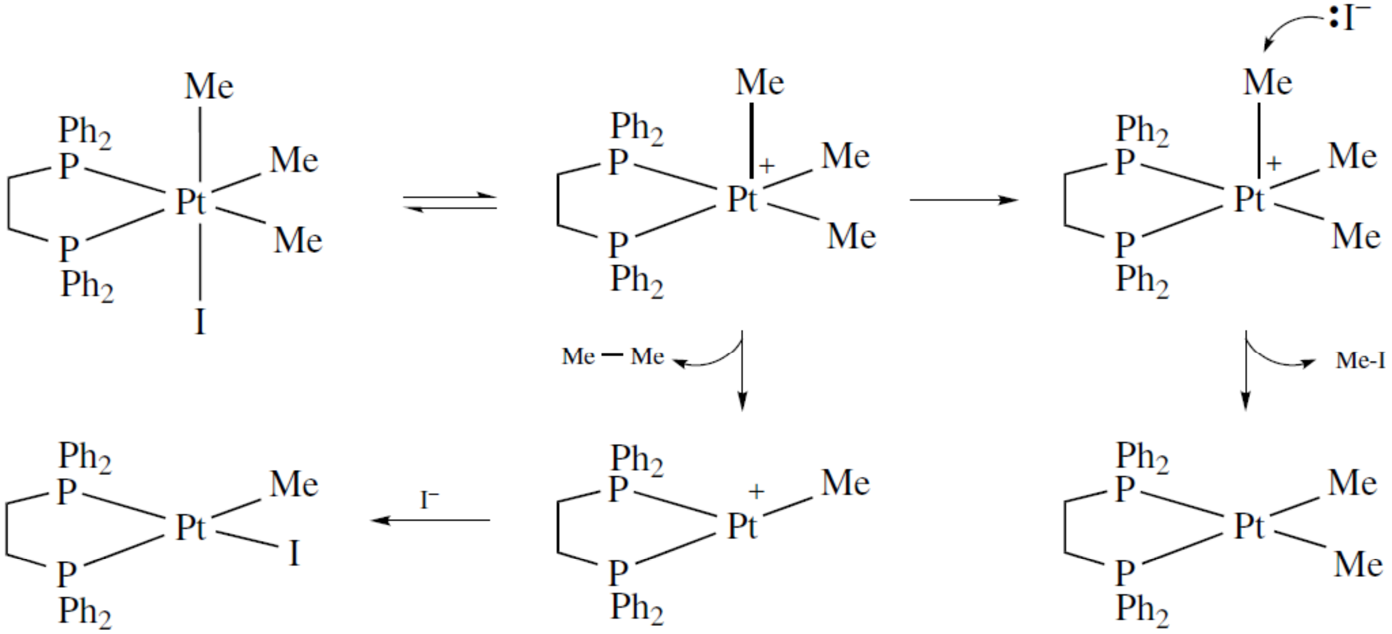


- A Y structure is favored where one π-donor ligand, Cl in this case, is located at the basal position of the Y.
- This structure brings the two groups to be eliminated, R and H, very close together.
- The typical small R−M−H angle for these groups, 70°, may facilitate achievement of the proposed transition 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 *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 $RhCl(PPh_3)_2$, formed by loss of a PPh_3 group from $RhCl(PPh_3)_3$, 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 ***S_N2 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.

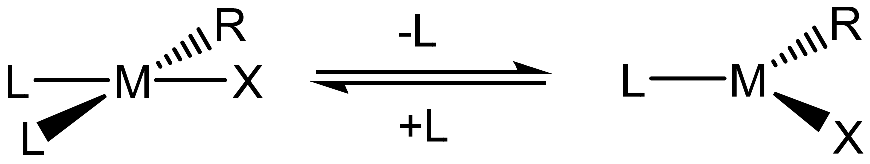


The mechanism for reductive elimination to form C−C and C−Hal bonds in octahedral d^6 species in Goldberg's complex. The reverse mechanism holds for oxidative addition to square planar d^8 species.

Reductive Elimination – Square Planar complexes

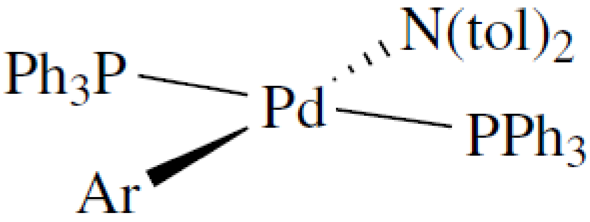
- Square planar d^8 complexes show a variety of reductive elimination mechanisms:

  - dissociative
  - Non-dissociative
  - associative



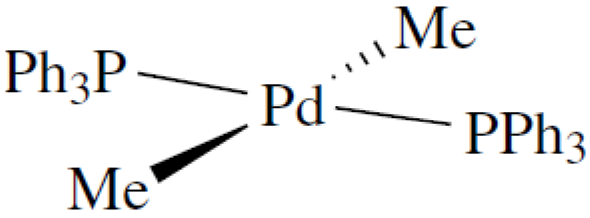
- Sometimes a ligand dissociates from $MRXL_2$, and the elimination occurs from the 3-coordinate MRXL intermediate, resulting in initial formation of a 1-coordinate ML metal fragment; this is the case for PdR_2L_2 and several Au(III) species.
- In some cases, the 4-coordinate trans-$MRXL_2$ species can 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 trans-[PdAr(N{tolyl}$_2$)(PPh$_3$)$_2$] where reductive elimination of Ar–N{tolyl}$_2$ takes place via competing dissociative and non-dissociative pathways.



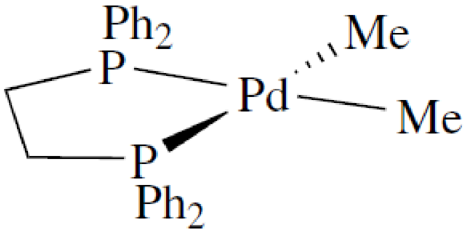
- ***Pt(II) is often slow to eliminate***, perhaps because ligand dissociation is harder, but oxidative addition of RX to give a Pt(IV) intermediate can promote reductive elimination.
- Some progress has been made in understanding these mechanistic differences in MO terms.

- Mechanisms are probed via the kinetics.
- For example, in the dissociative reductive elimination of Me−Me from trans-[$PdMe_2(PPh_3)_2$], added PPh_3 retards the reaction in an inverse first-order way (the rate is proportional to 1/[PPh3]).

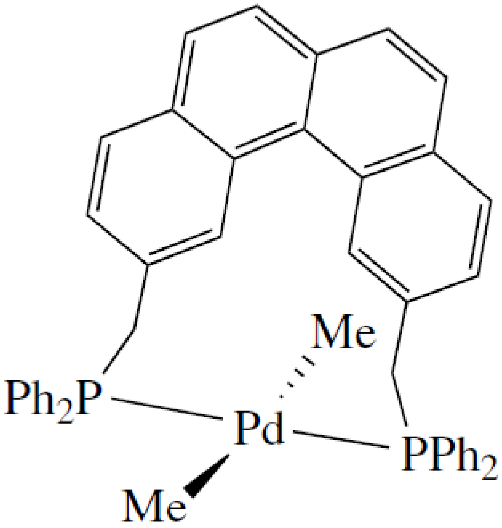


- This suggests that loss of phosphine takes place to give the 3-coordinate intermediate PdR_2L.
- The retardation might alternatively have been due to formation of PdR_2L_3, which would have to be less reactive than PdR_2L_2 itself.
- It can be shown by NMR that this does not happen, however.

- 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.

- In an important general mechanistic experiment that is useful for this problem, the crossover experiment, a mixture of *cis*-$Pd(CH_3)_2L_2$ and *cis*-$Pd(CD_3)_2L_2$, is thermolyzed.

- We find that only C_2H_6 and C_2D_6 are formed, showing that the ***reaction is intramolecular***; that is, R groups can couple only within the same molecule of starting complex.

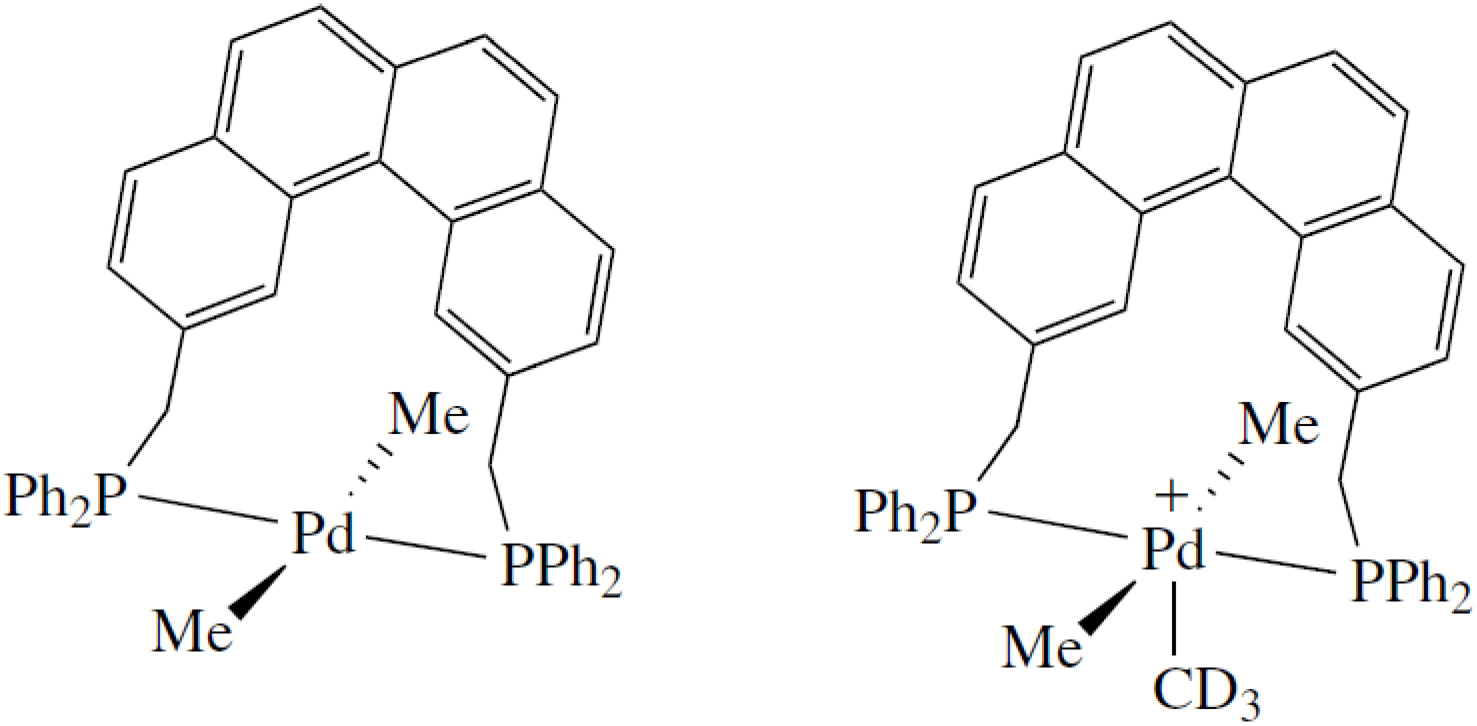
- This experiment rules out coupling between R groups originating in different molecules of the complex (the intermolecular route).

- The crossover product, CH_3CD_3, would have been formed if alkyl groups eliminated in a binuclear way, or free methyl radicals had been involved because they are sufficiently long-lived to migrate through the solution from one molecule of palladium complex to the next.

- We always need to do proper control experiments; for example, even if CH_3CD_3 is formed, we need to check whether scrambling happens in the reaction or whether the CH_3 and CD_3 groups exchange between the starting materials before reductive elimination takes place or in the analytical method used to detect crossover.

- This can be done by isolating the starting materials after partial conversion to products to make sure that no $Pd(CH_3)(CD_3)L_2$ is present.

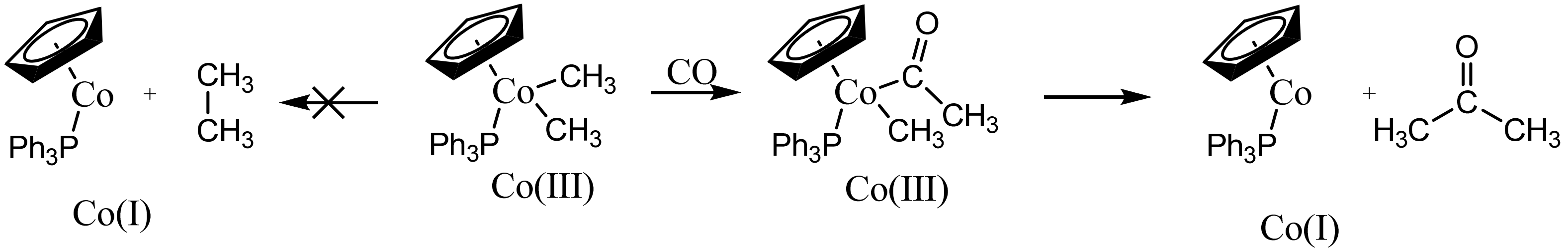
- Pd(IV) is not a very stable oxidation state
- It often acts as a transient intermediate in reactions however.
- The transphos complex reacts with CD_3I to give CD_3CH_3.
- This probably goes via the unstable Pd(IV) intermediate below.



Other complexes

- Dialkyls containing β hydrogens often β-eliminate to give an alkyl hydride and alkene before they reductively eliminate R−H.
- In $PdEt_2(PR_3)_2$, the *cis* isomer reductively eliminates butane.
- The trans isomer, in which the two R groups are not properly oriented for reductive elimination, the β-elimination–reductive elimination path is followed to give ethylene and ethane.

- Reductive elimination involving acyl groups is easier than for alkyls.
- For example, the cobalt dimethyl shown does not lose ethane but undergoes migratory insertion with added CO to give an acyl alkyl complex, which subsequently loses acetone; a crossover experiment with the protonated d^0 and deuterated d^6 dialkyls showed that this reaction is also intramolecular:



- Formation of new carbon–heteroatom (O,N,S) bonds is also possible by reductive elimination.
- Goldberg et al. found a methyl platinum(IV) acetate that forms methyl acetate in this way,36
- Hartwig discovered a series of carbon heteroatom reductive eliminations as well as catalytic reactions that involve these steps.
- These are of great use in organic synthesis (e.g., Buchwald–Hartwig reaction).