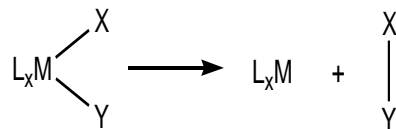# Reductive Elimination

- Reductive Elimination (RE) is the reverse of Oxidative Addition (OA). It is a very important process that is often the last step in catalytic cycles involving joining two carbon fragments together.

- The formal oxidation state of the metal is reduced by 2 units.

$$L_xM \underset{Y}{\overset{X}{\diagup}} \longrightarrow L_xM + \underset{Y}{\overset{X}{|}}$$

- RE favoured for complexes that are:
    - sterically hindered (*i.e.* bulky ligands).
    - electron poor (*i.e.* high oxidation state metal, poor donor ligands, overall +ve charge on complex).

- RE less well studied than OA because complexes that undergo RE are generally less stable.

- RE is particularly facile for: d^6 → Pd^{IV}, Pt^{IV}, Rh^{III}, Ir^{III}
                                                        d^8 → Ni^{II}, Pd^{II}, Au^{III}

- Reductive Elimination of H–H, R–H, R–R, R–SiMe$_3$, R–COR, H–COR is often favoured for thermodynamic reasons. Elimination of the above fragments always proceeds by a *concerted* mechanism (elimination of relatively non-polar X–Y).

- Eliminations that involve H (*e.g.* H$_2$, H-R, HCOR) are particularly fast. This is probably due to a lower kinetic barrier due to a relatively stable σ-complex ($L_xM \overset{H}{\underset{X}{\diagdown}}$) along the reaction pathway.

Reductive Elimination

- As there are several mechanisms for OA, the principle of microscopic reversibility (which states that a reversible reaction proceeds by the same mechanism in the forward and reverse directions) suggests that RE should show the same variety. However, **most RE goes by a concerted mechanism.**

- Concerted RE (as with concerted OA) occurs with retention of configuration:

RE in Octahedral d^6 Complexes (Pt^{IV}, Pd^{IV}, Ir^{III}, Rh^{III})
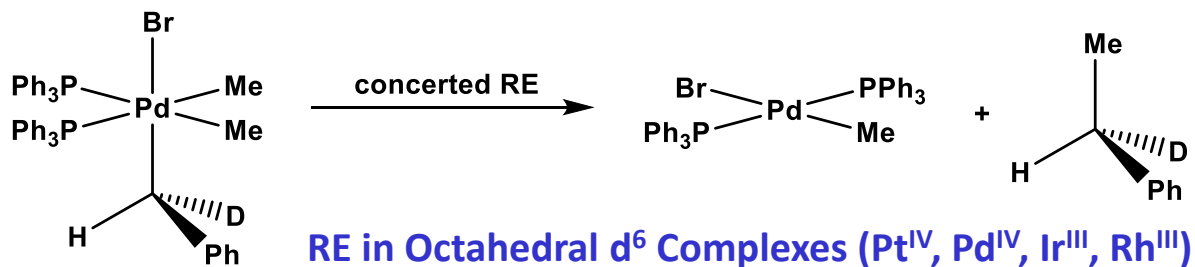
- Octahedral d^6 complexes tend to undergo RE readily. Usually this occurs after initial loss of a ligand to form a more reactive 5-coordinate complex:

R = CH$_2$COMe

Y-type distorted TBP

~70°

T-shaped geometry
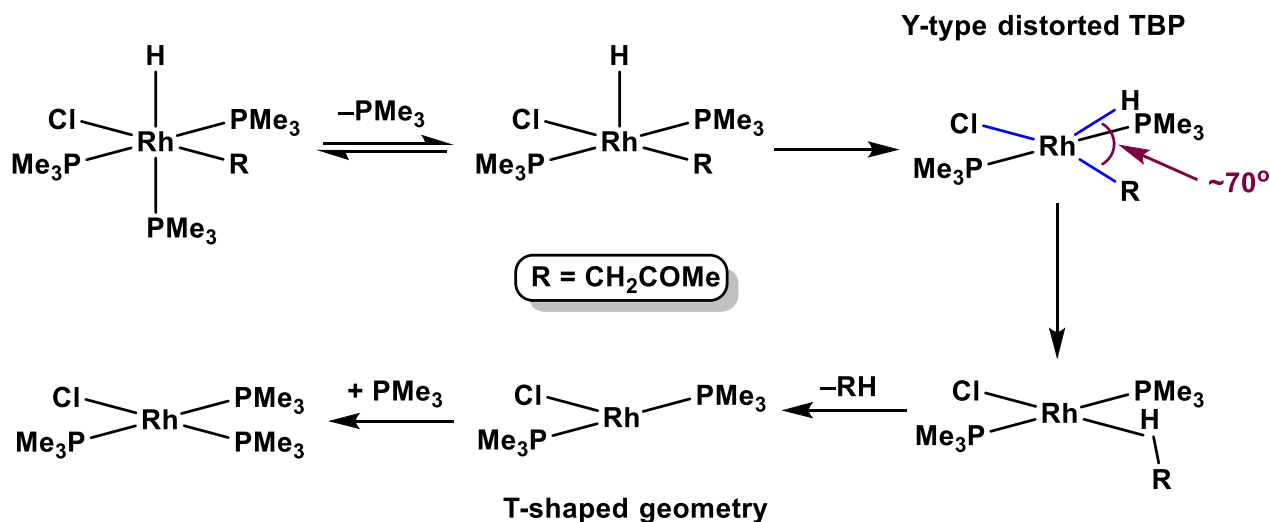
Reductive Elimination

▪ For d^6 5-coordinate complexes, square pyramidal or Y-type distorted TBP geometry is preferred over regular trigonal bipyramidal geometry.

▪ The small angle (~70°) between the two leaving groups in Y-type distorted TBP geometry is thought to facilitate formation of the transition state for reductive elimination.

▪ After reductive elimination, a T-shaped 3-coordinate species is formed. If the above mechanism is correct, then oxidative addition at 3-coordinate $RhCl(PR_3)_2$ should also be facile. Indeed, $RhCl(PPh_3)_2$ formed by dissociation of one PPh_3 from $RhCl(PPh_3)_3$ undergoes oxidative addition with H_2 at a rate at least 104 times faster than 4-coordinate $RhCl(PPh_3)_3$.

▪ The same reversibility argument also applies to RE of alkyl halides for which an S_N2 pathway is operative in the oxidative addition direction:
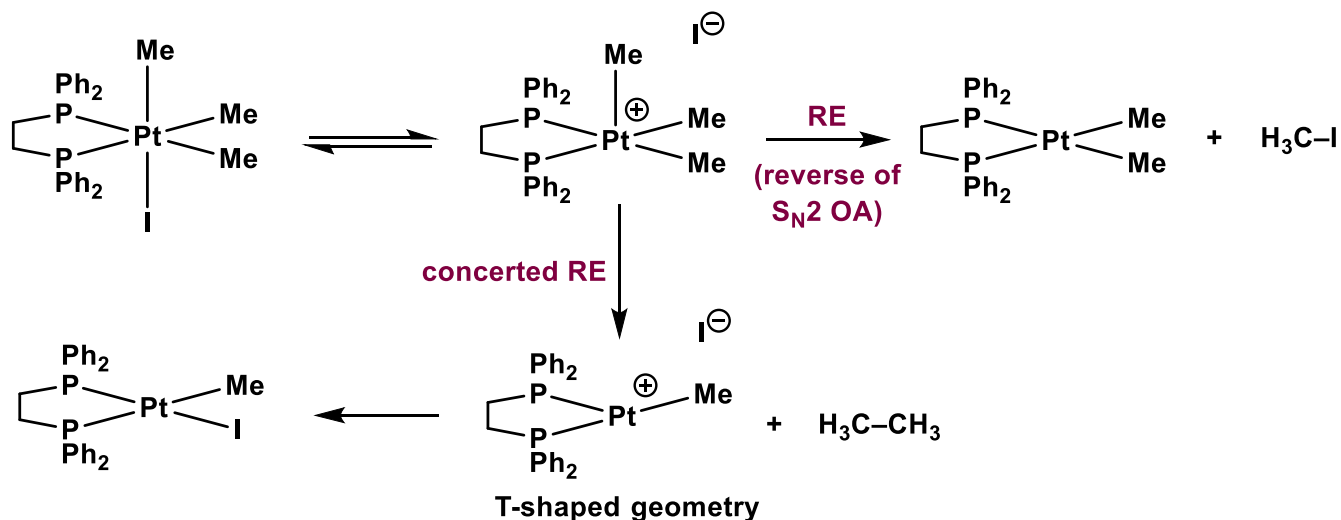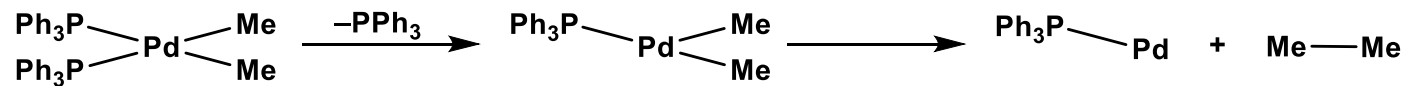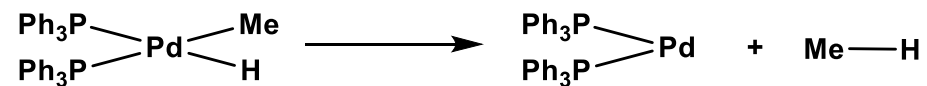
RE in Square Planar d^8 Complexes

- Square planar complexes show a variety of mechanisms for reductive elimination:

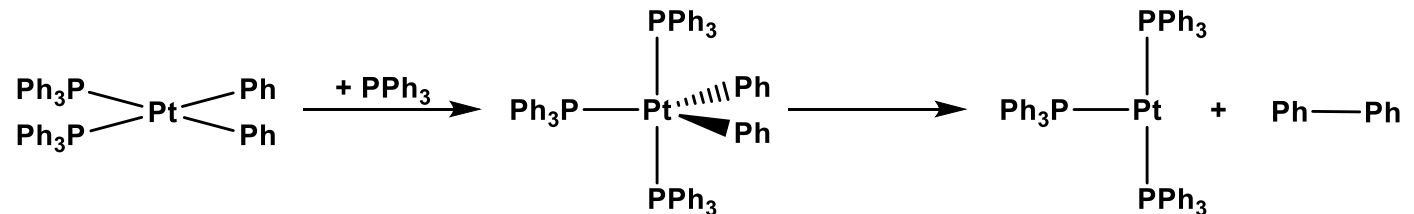 1) Dissociative; 2) Non-dissociative; 3) Associative:

1)

2)

Note: low coordinate metal complexes may be stabilized by coordination of solvent.

3)

- Irrespective of whether RE is dissociative, non-dissociative or associative, in order for *concerted* RE to occur, **the two leaving groups must be *cis* to one another.**

Investigations of Reductive Elimination

RE Mechanisms can be probed by kinetics:

- For the dissociative RE of ethane from *cis*-[PdMe$_2$(PPh$_3$)$_2$], addition of PPh$_3$ retards the rate of reaction (rate ∝ 1/[PPh$_3$]). This indicates that PPh$_3$ dissociation takes place before RE. It is not due to the conversion of [PdMe$_2$(PPh$_3$)$_2$] to [PdMe$_2$(PPh$_3$)$_3$] as this is not observed by NMR spectroscopy.

- The rates of RE differ hugely for the complexes shown below:

	A	B	C	D
k (s^{-1})	1.0 x 10^{-3}	9.6 x 10^{-5}	4.8 x 10^{-7}	No reductive elimination, even at 100 °C
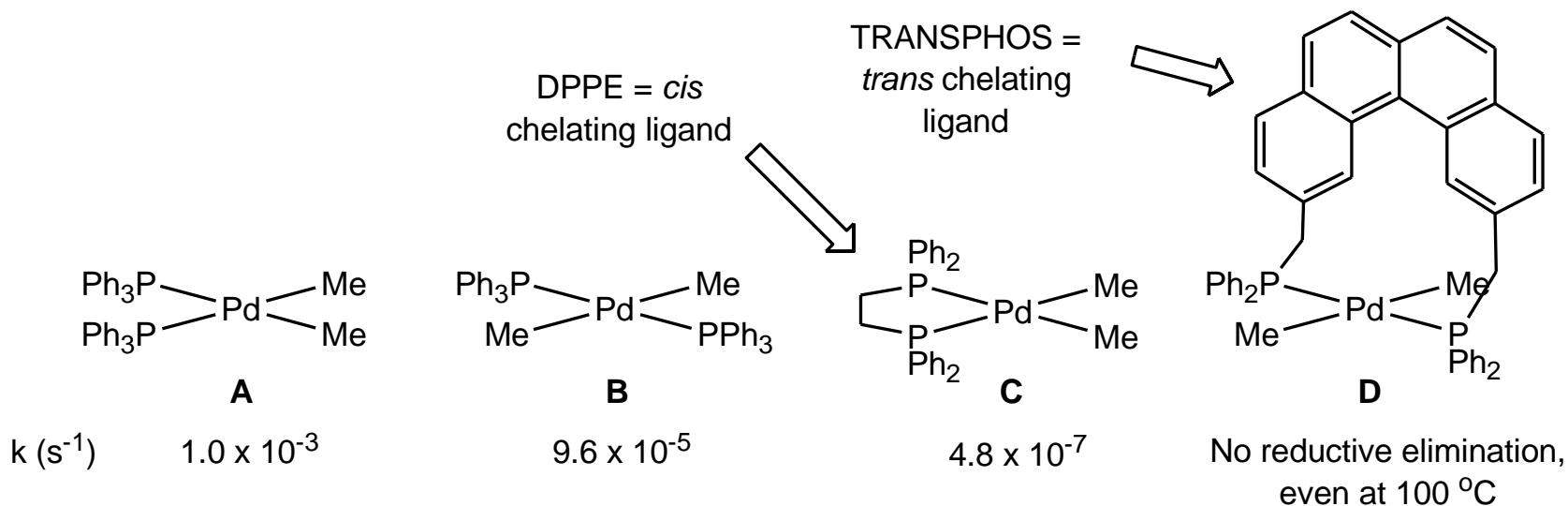
- Rate of RE lower for **B** than **A** because *cis* to *trans* isomerization must occur before RE can occur.
- Although the two methyl groups in **A** and **C** are *cis*, reductive elimination is much slower for **C** because phosphine dissociation is so much slower with a chelating phosphine.
- For complex **D**, the TRANSPHOS ligand does not allow the methyl groups to adopt a *cis*-conformation, so reductive elimination is prevented.

Investigations of Reductive Elimination

Mechanisms can also be probed by crossover experiments:

- When a solution containing a 1:1 mixture of *cis*-[Pd(CH$_3$)$_2$(PPh$_3$)$_2$] and *cis*-[Pd(CD$_3$)$_2$(PPh$_3$)$_2$] is heated, reductive elimination occurs to give only C$_2$H$_6$ and C$_2$D$_6$. No CH$_3$CD$_3$ is formed. This rules out coupling between R groups of different molecules of the complex (an intermolecular mechanism) or free methyl radicals which would be sufficiently long-lived to migrate in solution from one molecule to the next.

Binuclear Reductive Elimination:

- Binuclear oxidative addition/reductive elimination is important for metals that prefer to change their oxidation state by one, rather than two units.

- 2 [H–Co(CO)$_4$] → [Co$_2$(CO)$_8$] + H$_2$
        (radical mechanism involving H atom transfer)

- [H–Mn(CO)$_5$] + [PhCO–Mn(CO)$_5$] → [Mn$_2$(CO)$_{10}$] + PhCHO