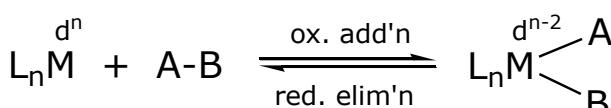


Reminder: Oxidative Addition (O.A.) and Reductive Elimination (ER):

$$\begin{array}{l}
 \Delta \text{ O.S.} = \mathbf{-2} \\
 \Delta \text{ C.N.} = \mathbf{-2} \\
 \Delta \text{ V.E.} = \\
 \Delta \text{ } d^n = \mathbf{-2} \\
 \\ \mathbf{+2}
 \end{array}$$



$$\begin{array}{l}
 \Delta \text{ O.S.} = \mathbf{+2} \\
 \Delta \text{ C.N.} = \mathbf{+2} \\
 \Delta \text{ V.E.} = \mathbf{+2} \\
 \Delta \text{ } d^n = \mathbf{-2}
 \end{array}$$

ER favoured for electron-deficient metal requires:

- Saturated 18 e- complexes.
- Two ligands that can eliminate *cis* to one another.
- M with accessible lower OS separated by 2 units.
- **Mostly concerted pathway with non-polar three center transition state ((H₂, Si-H, C-C))**

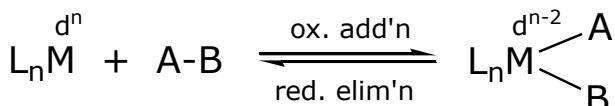
O.A, common for d⁸ and d¹⁰ metals, requires:

- Non-bonding electron density at the metal.
- A vacant coordination site.
- M with accessible higher OS separated by 2 units.

4 types of mechanism: concerted ,S_N2, ionic radical.

Reminder: Oxidative Addition (O.A.) and Reductive Elimination (ER):

$$\begin{array}{l}
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$$\begin{array}{l}
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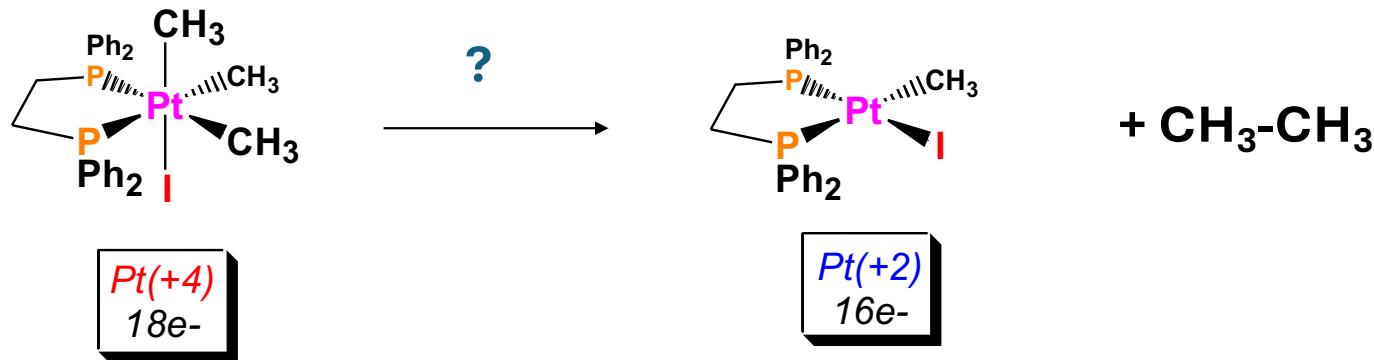
ER favoured :

- Electron-poor metal center
- Π -acid ligands ligands with electron-withdrawing groups
- Bulky ancillary ligands
- Smaller metals
- Electron rich A and B ligands

O.A. favoured:

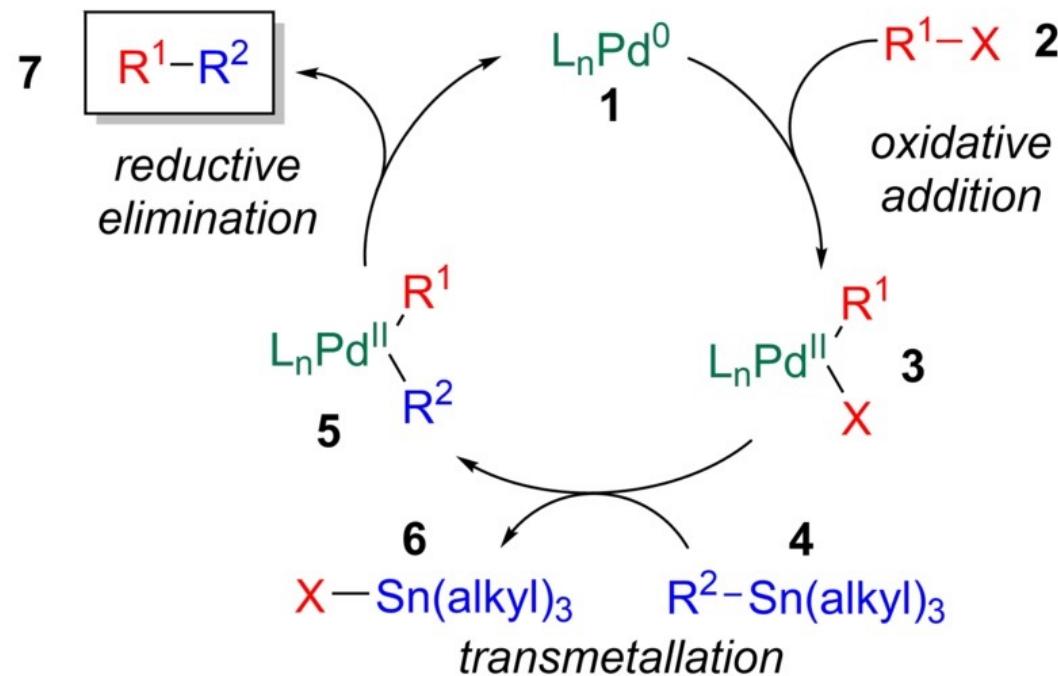
- When the metal is electron rich (π -basic).
- With hard or strong σ -donor ancillary ligands.
- Small ligands are present.
- The metal is large.
- For strong M-A and M-B and weak A-B bonds.

Reminder : Reductive Elimination



But ... mechanism involves loss of I^- in the first step to create a electron-deficient species
Then iodide binds again to give square planar 16 e complex

Reminder: Application: Pd-catalyzed cross-coupling cycle
(Stille, Sonogashira, Susuki)



R^1, R^2 = allyl, alkenyl, aryl; X = Cl, Br, I, OTf, etc.

L = phosphine; alkyl = Me, Bu