Labile or inert?

Labile – a compound that undergoes reactions with a relatively high rate of substitution

Inert – a compound that undergoes reactions with a slow rate of substitution

Inert is a relative term, $t_{1/2}$ > 1 min at 25 ^{o}C

<u>3 main factors that affect the whether a complex is labile or inert:</u>

1. Size: Smaller metal ions tend to be more inert as ligands are held more tightly.
2. Charge on Metal: The greater the charge on a metal ion in a complex, the greater the tendency towards the complex being inert
3. Number of d electrons and configuration

Octahedral geometry d-electron configuration: labile or inert?

# of d-electrons / configuration	Reactivity	Notes
d^1	Labile	N/A
d^2	Labile	N/A
d^3	Inert	N/A
d^4 Low Spin	Inert	N/A
d^4 High Spin	Labile	Especially labile as it is structurally distorted by the Jahn-Teller effect.
d^5 Low Spin	Inert	N/A
d^5 High Spin	Labile	N/A
d^6 Low Spin	Inert	N/A
d^6 High Spin	Labile	N/A
d^7 High Spin	Labile	N/A
d^8 Square Planar	Inert	For d^8 and above low spin is the same as high spin.
d^8	Intermediate	This configuration is intermediate, especially with weak field ligands.
d^9	Labile	Like d^4 H.S. this configuration is especially labile as it is distorted by Jahn-Teller effect.
d^{10}	Labile	N/A

Trans-effect vs Trans-influence

Trans-influence – If “A” forms a very strong sigma-bond to the metal, it competes for the metal orbitals with the leaving group, “X,” thus weakening the M–X bond

Trans-influence determined by sigma-donor strength (basicity):

$$R_3Si^- > H^- > H_3C^- , NC^- > \text{olefin}, CO > R_3P > NO_2^- > I^- > Br^- > Cl^- > H_3N > HO^- > H_2O$$

Trans-effect – A strongly sigma-donating and/or pi-accepting group “A” will greatly increase the reaction rate relative to a weak sigma-donor/poor pi-acid “A.” Factors that dominate the trans-effect include:

1. Ground state weakening of M–X bond (trans-influence)
2. Stabilization of the presumed 5-coordinate intermediate

Taking into account BOTH trans-influence and pi- effects:

$$NO^+ > CO > CN^- > PR_3, H^- > H_3C^- > Ph^- > NO_2^-, I^- > Br^- > Cl^- > \text{py}, H_2O, HO^-, NH_3$$

Inner Sphere Reactivity

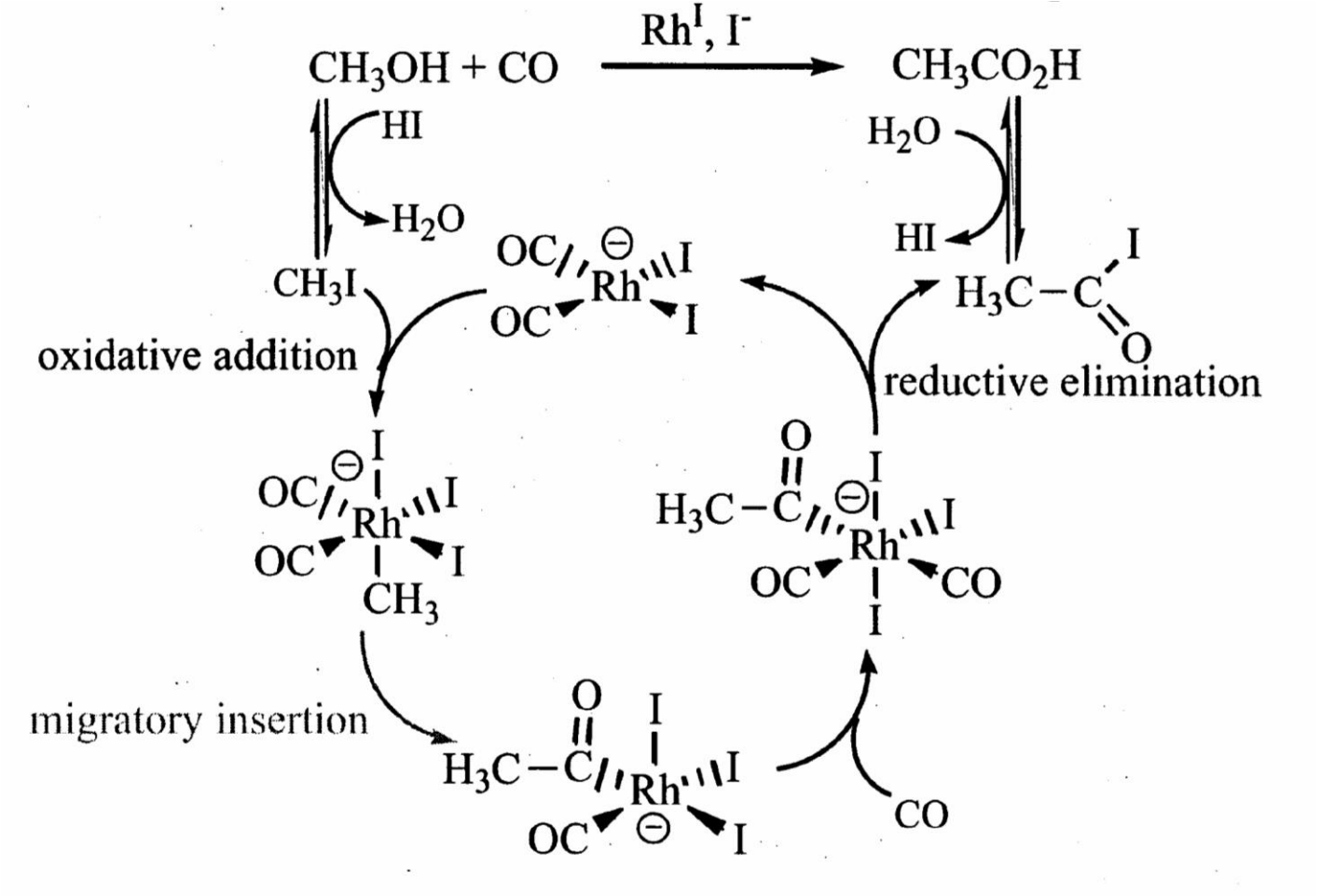
Metal Centered – gain or loss of ligands

1. *Ligand substitution*
2. *Oxidative addition*
3. *Reductive elimination*
4. Nucleophilic displacement
5. Transmetallation

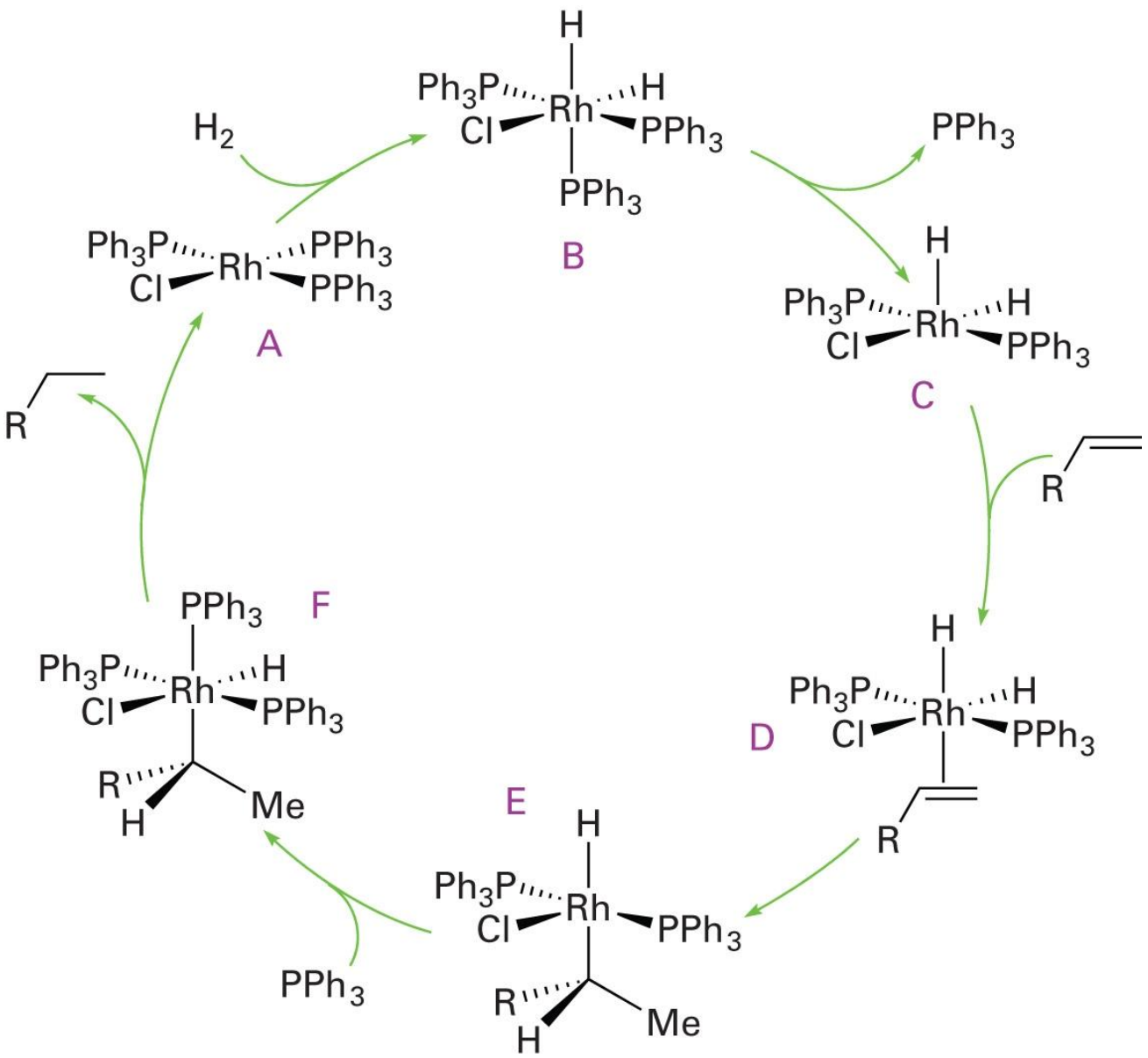
Ligand Centered – modification of ligands

1. *Migratory insertion*
   a) *Carbonyl insertion*
   b) *1,2–insertion*
2. *Hydride elimination*
3. *Abstraction*

Monsanto Acetic Acid Process



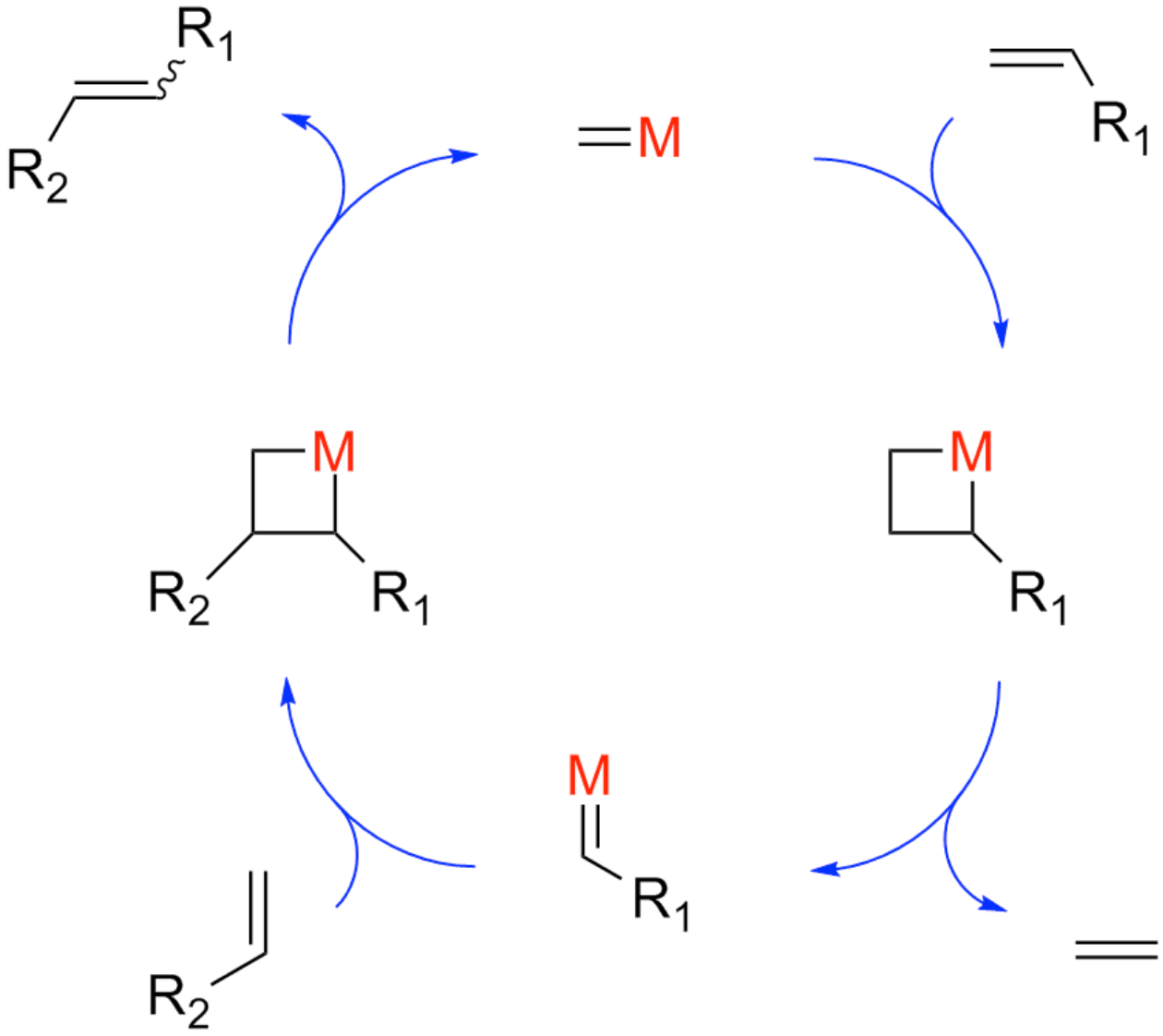
Olefin hydroformylation



At each step give:

1. Type of reaction
2. Oxidation state
3. d-electron count
4. Total electron count

Chauvin mechanism for olefin metathesis



At each step give type of reaction