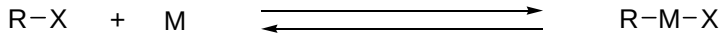
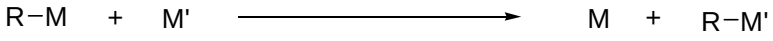
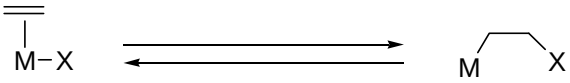
Oxidative addition, reductive elimination



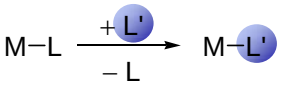
Transmetallation



Migratory insertion, β-elimination



Ligand exchange



A **reaction mechanism** ...

... is a **theorie** deduced from available experimental **data**.

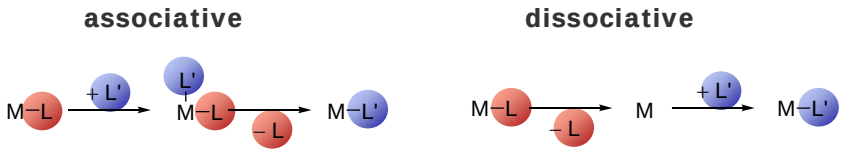
... can only be disproved

... cannot be proved to be true

... explains the available experimental data **and...**

... allows predictions that can be **tested** experimentally.

Ligand exchange: Trends



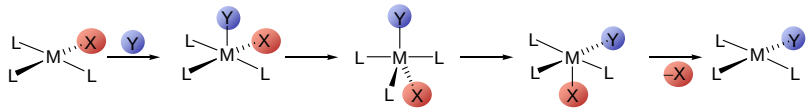
Type of complex	16-e⁻ and 17-e⁻ complexes	18-e⁻ complexes
Rate law	First order in entering ligand	Zero order in entering ligand
Activation parameters	$\Delta S^{\ddagger} < 0$	$\Delta S^{\ddagger} > 0$
Electronic effects	basic entering ligand electrophilic metal	
Effect of departing ligand	small	large
Steric effects	more accessible metal	more hindered metal

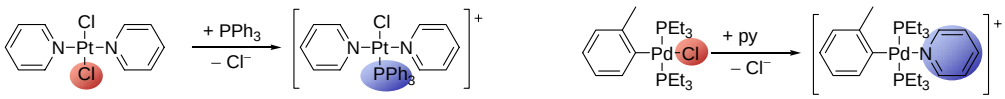
Ligand exchange: 16-e⁻ Complexes

d^8 complexes, square-planar: Ni(II), Pd(II), Pt(II), Rh(I), Ir(I), Au(III)

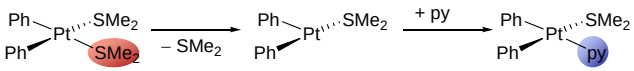
very common in catalysis

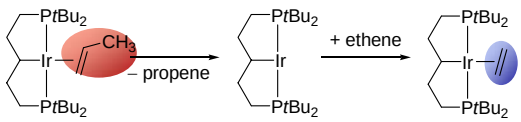
usually associative:





sometimes dissociative:



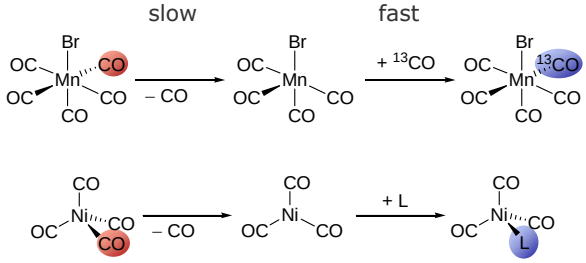


Ligand exchange: 18-e⁻ Complexes

d^6 complexes, octahedral: Cr(0), Fe(II), Ru(II), Rh(III), Ir(III), Pt(IV), ... many more

d^{10} complexes, tetrahedral: Ni(0), Pd(0), Pt(0), Cu(I)

usually dissociative:

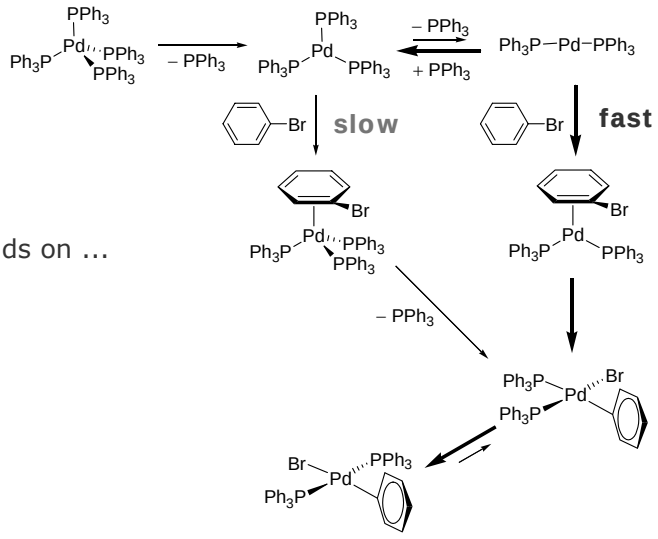


$$M{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M + X \xrightarrow[+\,Y]{k_2} M{-}Y$$

rate law: $$-\frac{d[MX]}{dt} = \frac{k_1 k_2 [MX][Y]}{k_{-1}[X] + k_2[Y]} \approx k_1[MX] \quad \text{if } k_{-1}[X] \ll k_2[Y]$$

Oxidative Addition

Concerted mechanism: Addition of aryl halides, vinyl halides

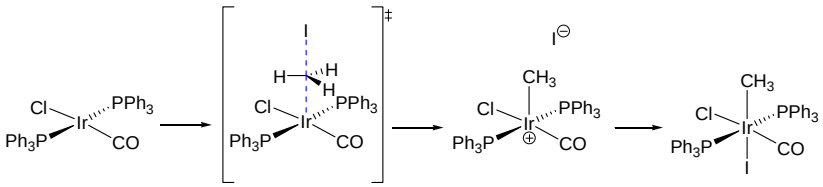


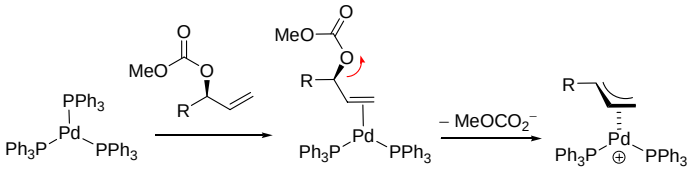
Rate depends on ...
... halide
... ligand
... aryl
... metal

Similar mechanisms: Addition of H_2, C-H-Bonds, disilanes, ...

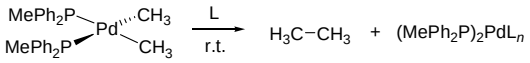
Oxidative Addition

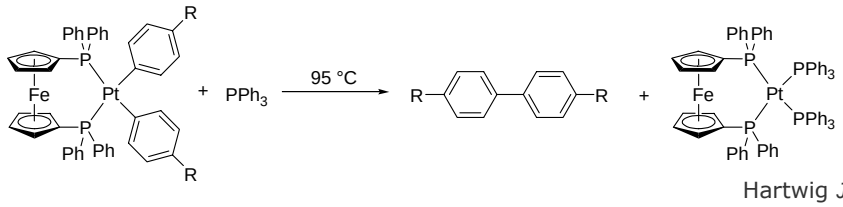
S_N2 mechanism: Addition of alkyl halides, allyl carbonates





Reductive Elimination





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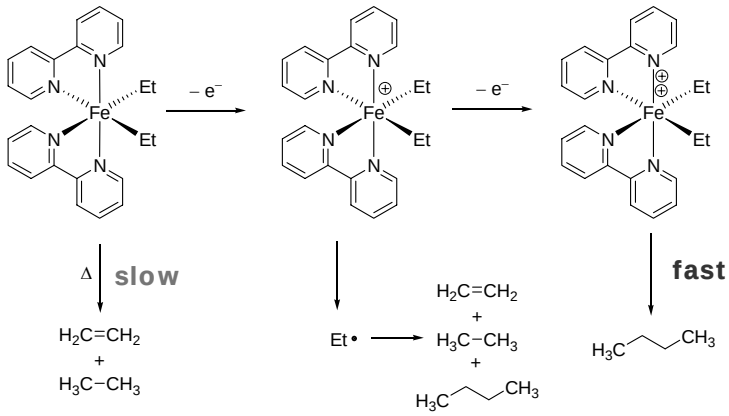
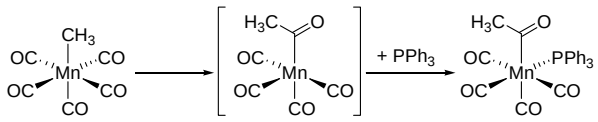


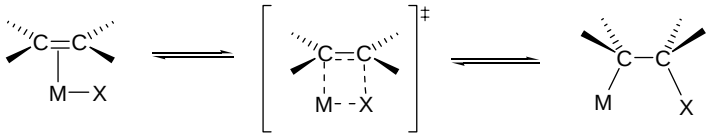
Migratory Insertion, β-Elimination

Carbonyl Insertion



e.g. Monsanto Process, carbonylation, decarbonylation

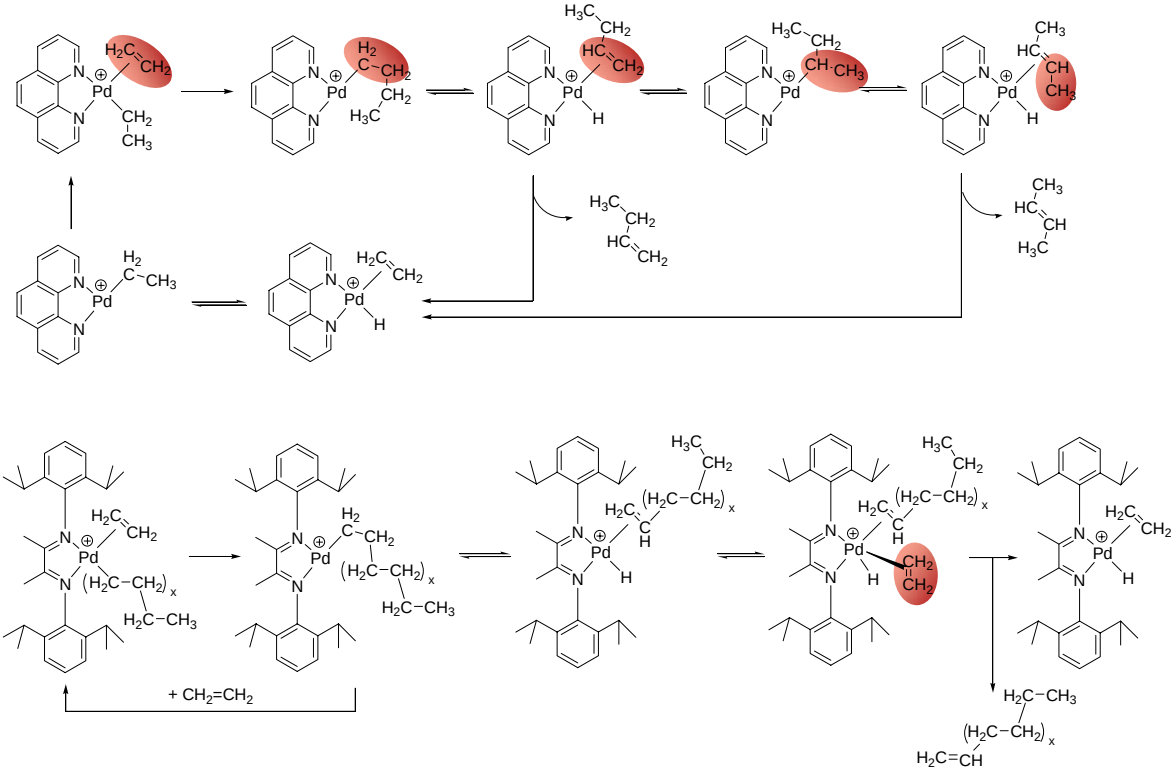
Olefin Insertion



X = H, alkyl, aryl

e.g. Heck reaction, hydrogenation, olefin polymerization

Dimerization vs. Polymerization



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