Basic Organometallic Reactions

There are several additional fundamental types of reactions in organometallic chemistry

The more complex reactions are normally some combination of these fundamental ones

1) Lewis Acid Dissociation

- many transition metal compounds, especially hydrides, can lose as Lewis acid (i.e., deprotonate)

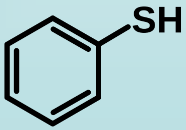
$$H{-}Co(CO)_4 \rightleftharpoons H^+ \quad + \quad {}^-Co(CO)_4$$

change in number of metal valence e$^-$'s	**0**
change in formal metal oxidation state	**-2**
change in coordination number at the metal	**-1**

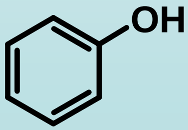
This may be a surprise, but many transition metal hydrides are quite acidic
-notice that making the metal more electron rich decreases acidity

$HCo(CO)_4$ **(pK_a = 8.3, CH_3CN)** $H_2Fe(CO)_4$ **(11.4)** $HCo(CO)_3PPh_3$ **(15.4)**

Winkler, J. R. et al (Gray, H. B.) *J. Am. Chem Soc.* **1986**, *108*, 2263.

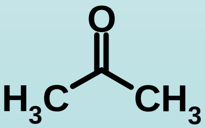


(pK_a = 10.3, $CH_3S(O)CH_3$)



(18.0)

H_2O **(32.0)**



(24.4)

2) Lewis Base Dissociation

Very, very, very..........common process

$$\overset{18e}{Fe(CO)_5} \rightleftharpoons \overset{16e}{Fe(CO)_4} + CO$$

$$\overset{16e}{Pd(PPh_3)_4} \rightleftharpoons \overset{14e}{Pd(PPh_3)_3} + PPh_3$$

change in number of metal valence e^-'s	**-2**
change in formal metal oxidation state	**0**
change in coordination number at the metal	**-1**

-Reverse reaction: Lewis base Association

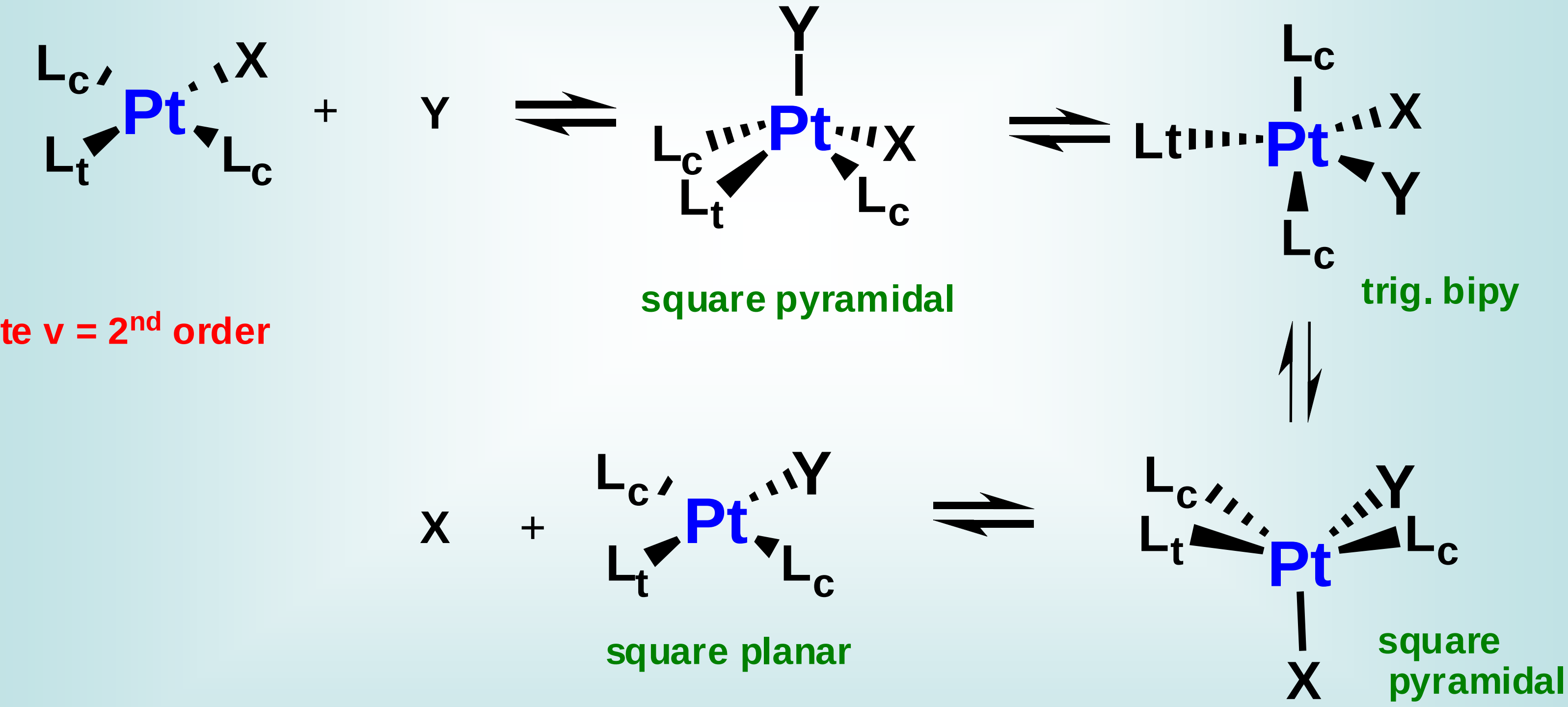
Obvious application are in ligand substitution processes, which may be <u>dissociative</u> ('S_N1 like')

$$Ni(CO)_4 \overset{slow}{\rightleftharpoons} Ni(CO)_3 + CO \xrightarrow[fast]{L} LNi(CO)_3$$

$v = k\,[\,Ni(CO)_4]$ 1st order

Most common for 18 e^- systems

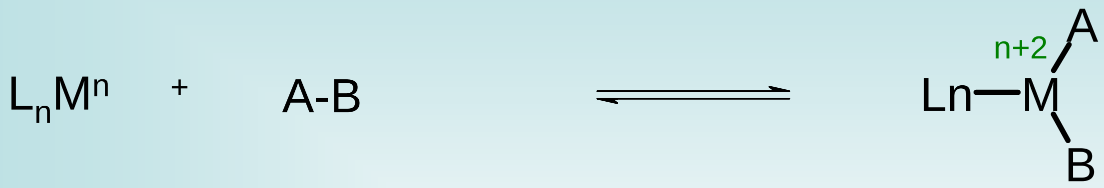
- Alternatively, this can be associative, i.e., "S_N2 like"
  - -more common fo 16 e^-, d^8 square planar complexes (i.e., Ni^{II}, Pd^{II}, Pt^{II}, Rh^I, Ir^I)



rate v = 2nd order

3) Oxidative Addition

- represented by

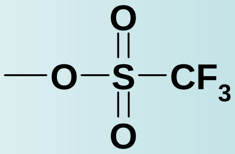


change in number of metal valence e^-'s	**+2**	**(14 - 16 e)**
change in formal metal oxidation state	**-+2**	**(0 - +2)**
change in coordination number at the metal	**+2**	

for more details, see: R Yamamoto pp. 222-239
R Collman & Hegedus pp. 279-321

-Overall reaction is cleavage of the A-B bond with bonding to the metal

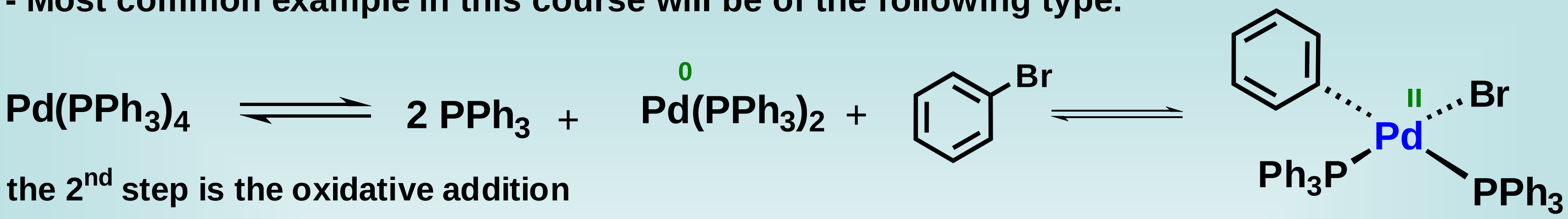
- Most common A-B is R_3C-X X = halogen or pseudohalogen



triflate

-Classic 'organic' example is Grignard reagent formation

- Most common example in this course will be of the following type:



- the 2nd step is the oxidative addition

Therefore, system needs: a) 2 available oxidation states i.e., Pd^{o}/Pd^{II} , Fe^{o}/Fe^{II}, Ir^{I}/Ir^{III}
b) open coordination site

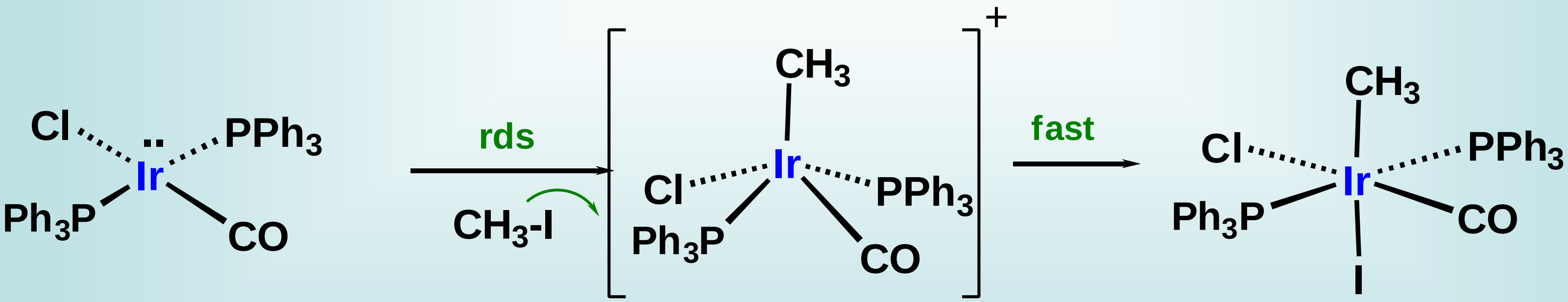
Note: v. hindered ligands (P*t*-Bu$_3$) may encourage monocoordination, which then adds <u>rapidly</u>

- Reverse reaction: Reductive Elimination

<u>Mechanism</u>

- Most is known about late transition metals (such as Ir, Ni groups)

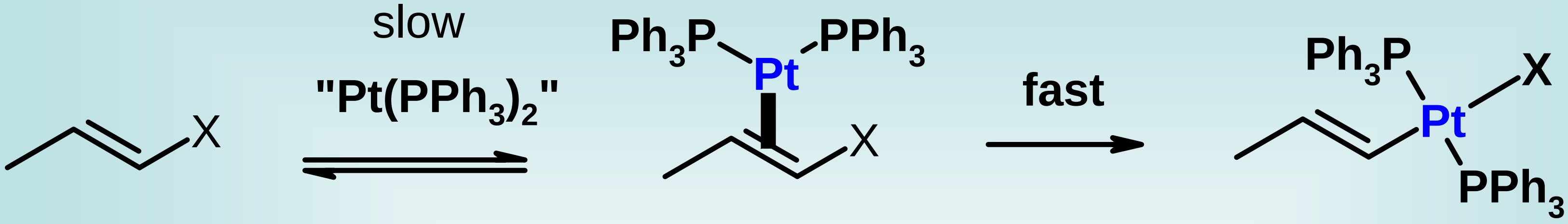
A) If the R of R-X is <u>alkyl</u> (especially 1^{o} or 2^{o}), the reaction is believed to (often) occur via an <u>S$_N$2</u> substitution



- *Inversion* at alkyl carbon *has* been observed

- Kinetics are overall 2nd order $v = k\,[Ir^{I}]\,[CH_3I]$

B) Vinyl (and perhaps aryl) halides go via π - complex formation, with ultimate direct insertion



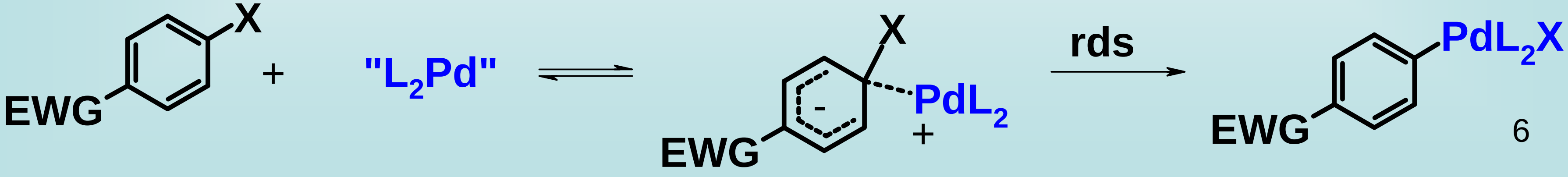
- **Goes with retention of configuration of C=C configuration**
- **Also believed to be mechanism for addition of H_2**

B') Aryl halides go via direct insertion into C-X bond (*clearly related to B*)

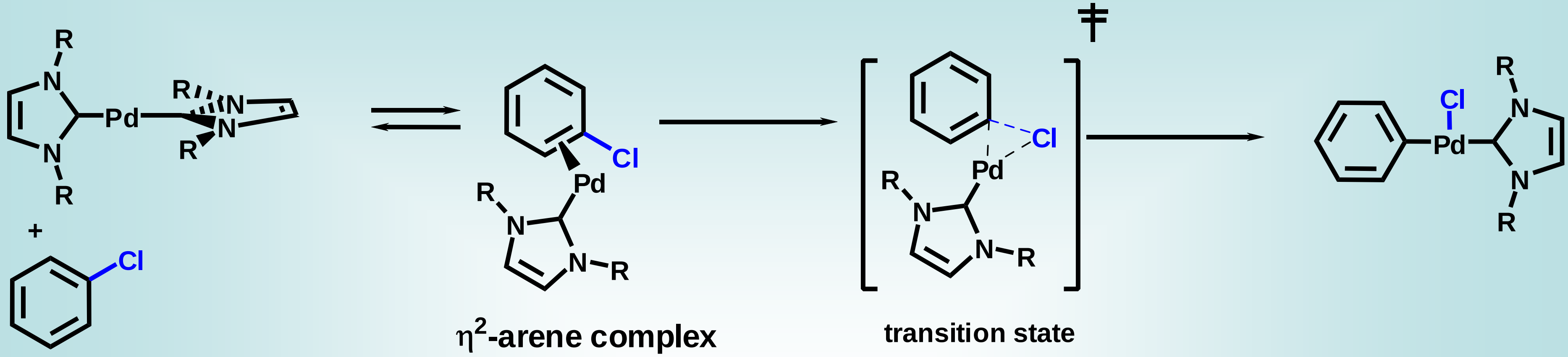
i.e.,

Could result in retention of configuration in some cases

C) - Now defrocked - Nucleophilic Aromatic Substiution - was an old proposal for aryl cases, to rationalized that cases with electron withdrawing groups "always" go *faster*



C)' - much more likely and often detected in calculations is initial formation of an η^2-benzene complex



Green, J. C. J. Organomet. Chem. **2005**, *690*, 6054.

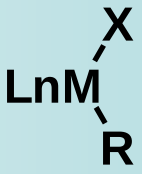
- comment - I think oxidative additions to aryl halides/pseudo halides 'always' go this was

Update: very recent kinetic support for this Hartwig, J. F. et al *J. Am. Chem. Soc.* 2009, *131*, 8141.

D) - Electron transfer, radical mechanisms of competitive for alkyl-X cases (Ni, Mg)

i.e. $L_nM + RX \xrightarrow{\text{rds}} [\,L_nM^+ \quad RX^{-\bullet}]$

$[\,L_nM^+ \quad RX^{\cdot-}] \longrightarrow [L_nM\text{-}X + R\bullet] \longrightarrow$

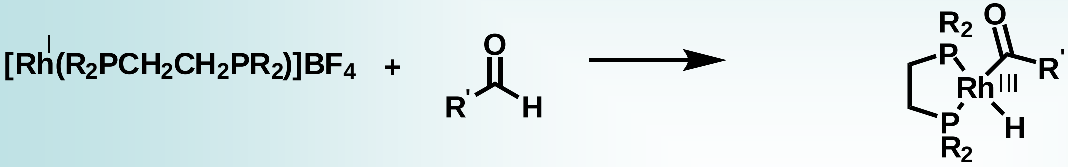


$LnM(X)(R)$

-this is likely the Grignard oxidative addition mechanism
-means racemization during the process for alkyl R

Note: C-H Activation - one of the major mechanisms is an oxidative addition

Bi, S. *Chem. Phys. Lett.* ***2006,*** *431*, 385.

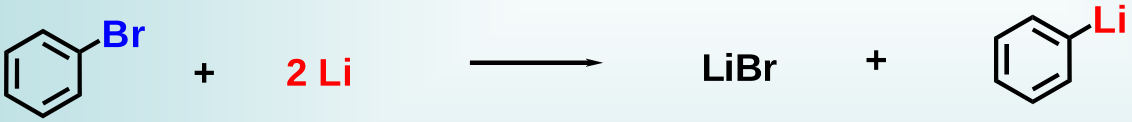


Dong, V. *Chem. Commun.* **2014**, *50*, 13645.

Aside: One electron oxidative additions also exist

$$2\ L_nM^o \ + \ A\text{-}B \longrightarrow L_n\overset{I}{M}\text{-}A \ + \ L_n\overset{I}{M}\text{-}B$$

Conventional organic example - Lithium-Halogen exchange

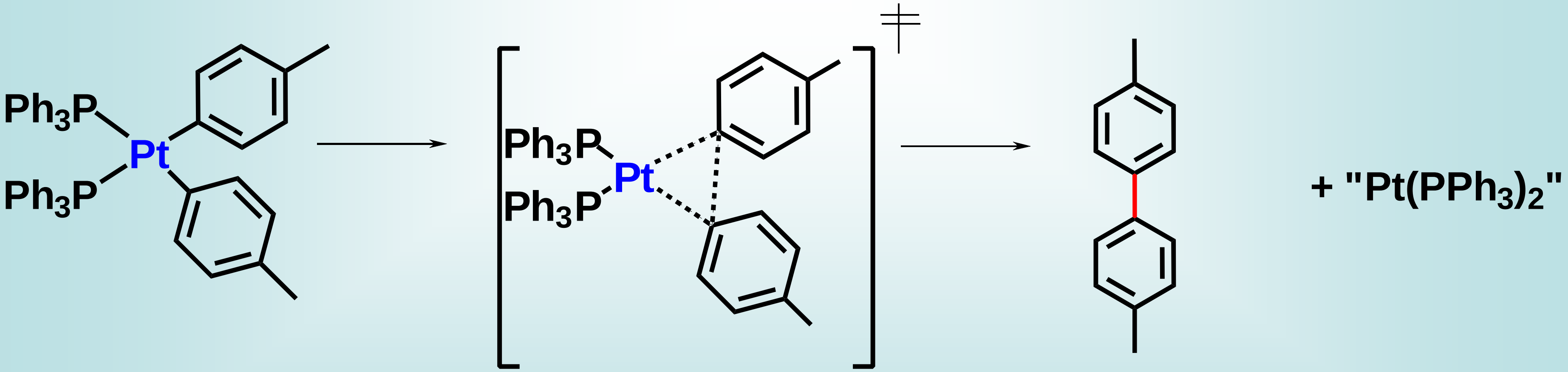


Many new opinions on these matters:

R Hartwig, J. F. Synlett **2006**, 1283.
R Espinet, P.; Echavarren, A. M. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 4704.
R Jutand, A. *Eur. J. Inorg. Chem.* **2003**, 2017.
Alcazar-Roman, L. M.; Luis, M.; Hartwig, J.F.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *J. Am. Chem. Soc.* **2000**, *122*, 4618. (chelate PR_3)
Hartwig, J. F.; Paul, P. *J. Am. Chem. Soc.* **1995**, *117*, 5373 (monodentate PR_3)
R Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314.
Lersh,M.; Tilset, M. *J. Am. Chem. Soc.* **2005**, *127*, 2471 (C-H activation).

4) Reductive Elimination - reverse of oxidative addition

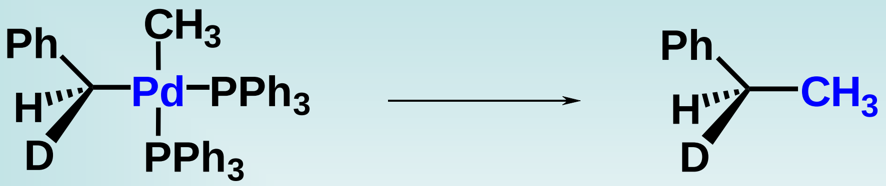
change in number of metal valence e⁻'s	-2	(16e - 14e)
change in formal metal oxidation state	-2	(+2 - 0) (or +3 - +1)
change in coordination number at the metal	-2	



transition state
-not an intermediate

In 'normal' cases, the reaction goes by a concerted mechanism

-and, importantly for organic chemists.......



retention of configuration at carbon

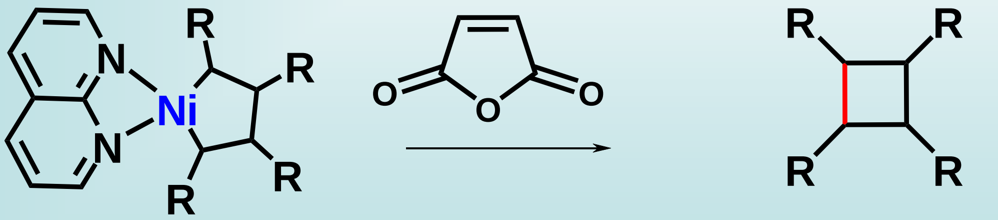
Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981

Note: Whether the precursor is square planar or trigonal bipyramidal, it's the *cis* groups which reductively eliminate

Other notes on reductive elimination:

- **Again, need two accessible oxidation states**
- **Non 18 e^- situations must be accessible**
- **Ni group (Ni, Pd, Pt) are the usual synthetic choices; Co group (Rh, Ir) are also common**

Since metal becomes more electron rich during the reaction, the reaction is sometimes accelerated by addition of a ligand which is electron withdrawing



Reaction assisted by

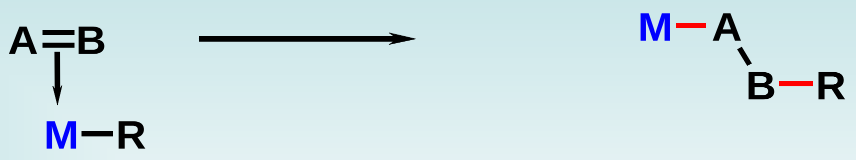
-electron poor ligands
-sterically bulky ligands ($P(t\text{-Bu})_3$)
-1st row > 2nd row > 3rd row
- hydride doing red. elim.
- ligands with wide bite angles
-$L_nM(A)(B)$ with n = 1 or 3 over n = 2 or 4

More details in general:

Yamamoto, pp. 240-5
Collman, Hegedus pp 322-33

5) Insertion (Migration)

-There is more than one type possible

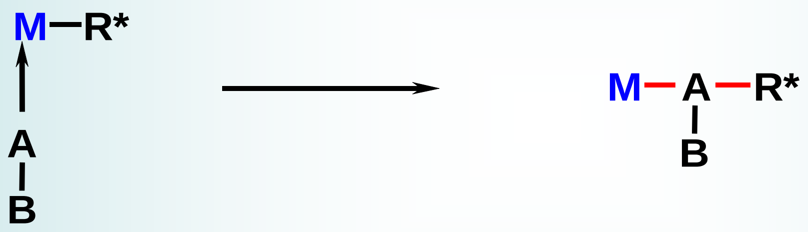


M-R is a

Metal-C or
Metal-H bond

Best examples - Heck reaction carbopalladtion
- β- hydride elimination (reverse)
- [2+2] step of alkene metathesis

or



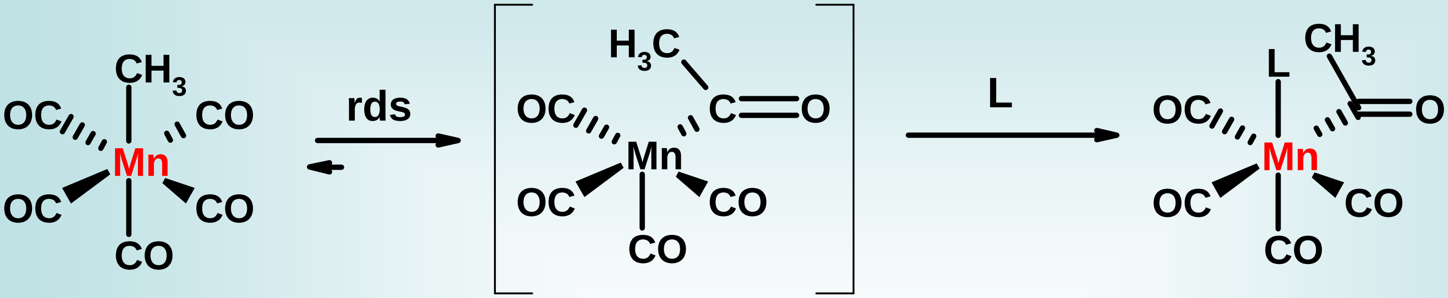
$A{=}B$ is $R'_2C{=}CR'_2$ $R'_2C{=}O$ $R'_2C{=}NR'$

$:A{-}B$ is $:C{=}O$ $:C{=}NR'$ $:CR'_2$

Best example - carbonylation of metal carbonyl complexes

Most common :A-B is CO

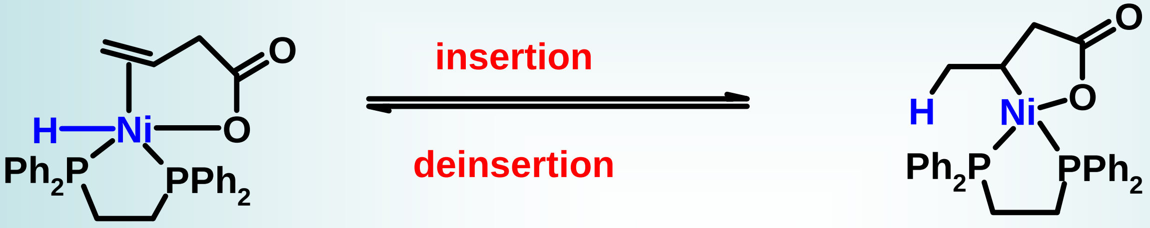
-The reaction is a concerted migration of R*, with retention of configuration at R* and the metal, if they are chiral



Change in # of valence electron at the metal	-2	(18 to 16e)
Change in metal oxidation state	0	(+1 to +1)
Change in coordination number	-1	(6 to 5)

Note: Reverse reaction is deinsertion

Most common A=B in this case are alkenes or alkynes
-for example, the intermediate step in hydrogenation



- The reverse reaction in this case (β-elimination) is one of the most common reactions of alkylmetals - main mode of decomposition

-again, if inserting group is alkyl, generally there is retention of configuration at R*

see R Cross, R. J., in "Chemistry of the Metal-Carbon Bond", Hartley and Patai, 1982, V.2

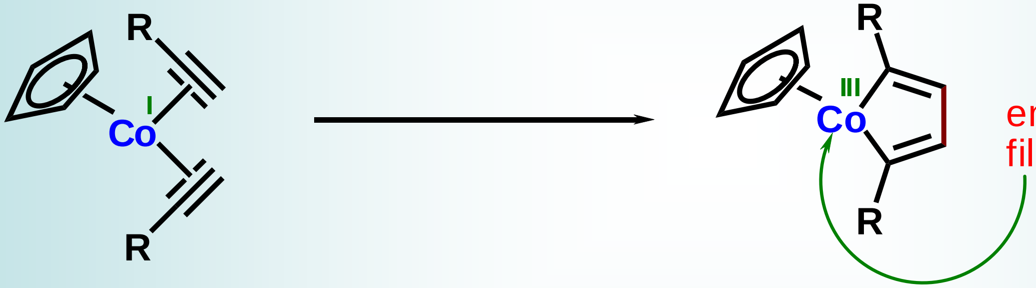
R Yamamoto, p. 246-272

6) Oxidative Coupling

(sometimes being called reductive coupling, since the *alkene/alkyne* is reduced)

Oxidative coupling occurs when two 'π-bound' ligands on the metal react with each other to form (usually) a C-C σ bond

One of the best known examples is....



empty coordination site ultimately filled by a ligand

-This has become increasingly important with a variety of metals and transformations

- The 2+2 cycloadditions of metal carbene/alkylidenes could be considered this process, or it could be considered an insertion

Change in number of valence electrons at metal	-2 (18 to 16e)
Change in metal oxidation state	+2 (+1 to +3)
Change in metal coordination number	0 ('3' to '3')

Note: There are several other fundamental mechanisms, but they have a close 'organic' analogy