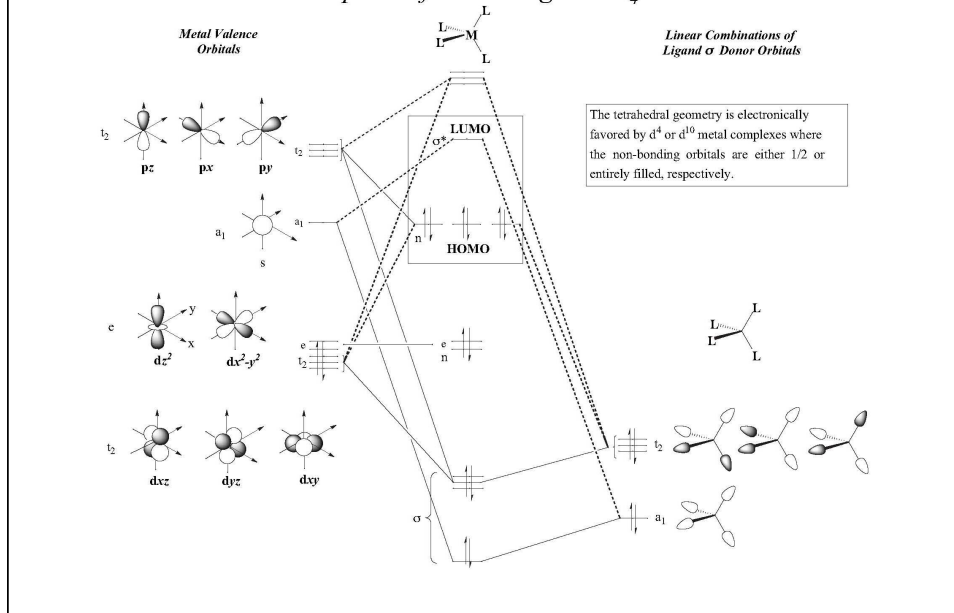
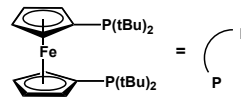
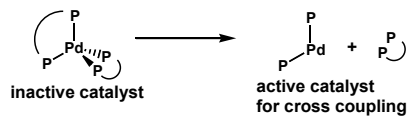
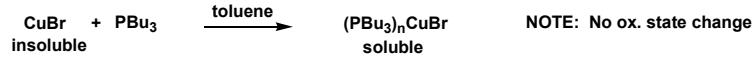


MO Description of σ bonding in ML_4 tetrahedral

Organometallic Reaction Mechanisms

Ligand association/dissociation

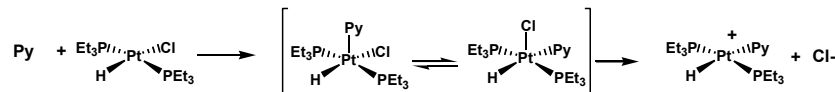


Ligand Exchange:

Associative - common for 16e- complexes

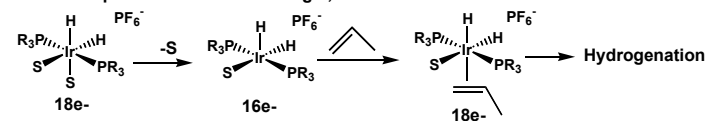
rate = $k[\text{py}][\text{Pt}]$

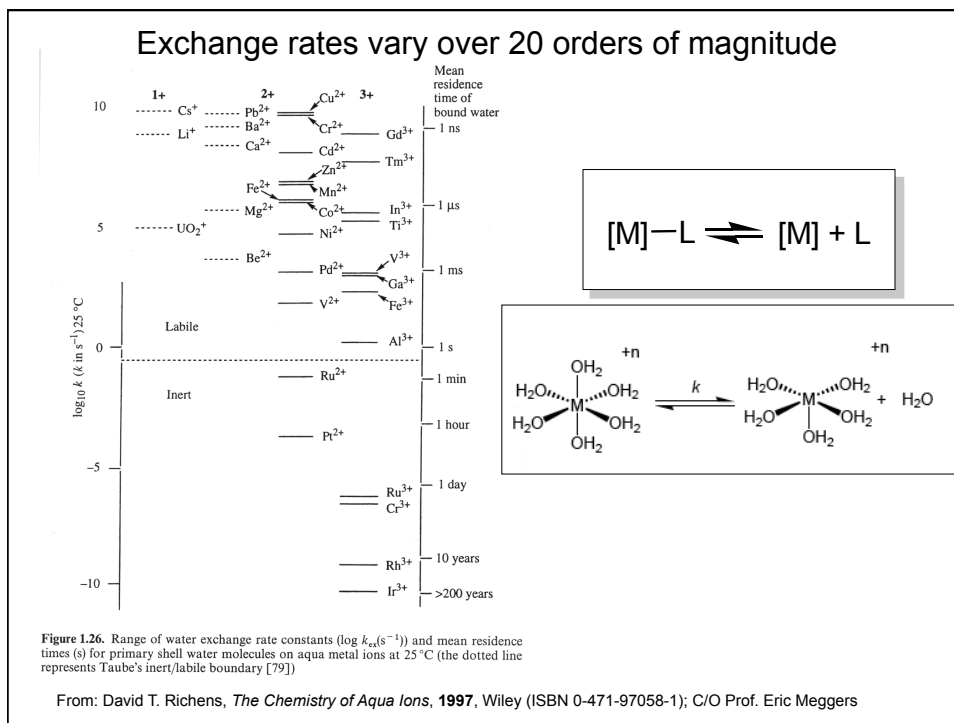
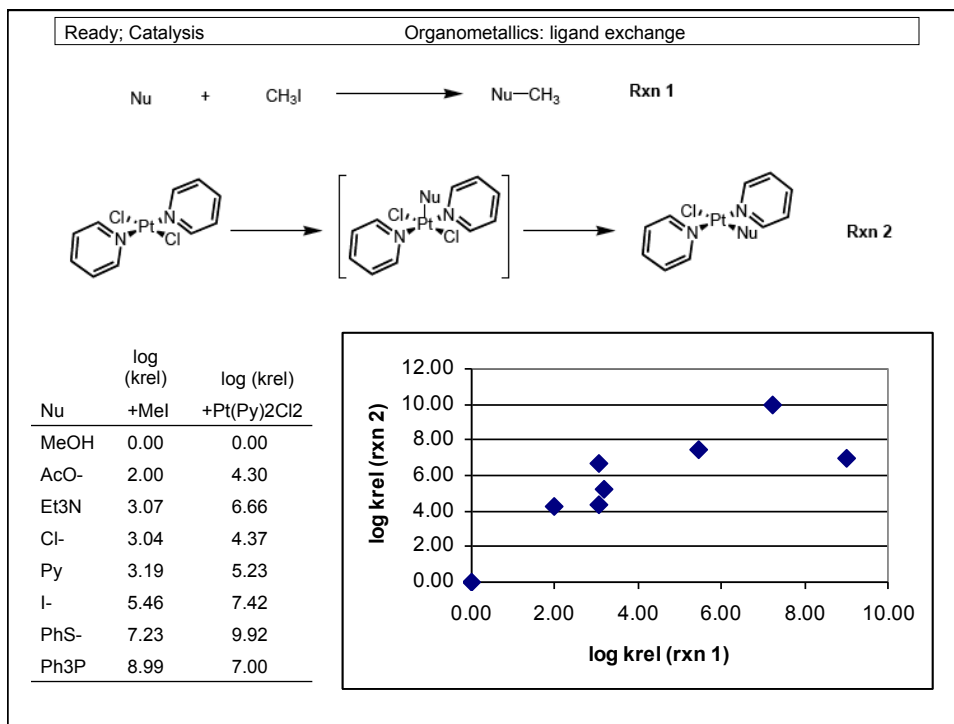
rate will depend on nature (sterics, electronics) of Nu and MLn



Dissociative - common for 18 e- complexes

Rate will depend on nature of leaving L, sometimes on new L'

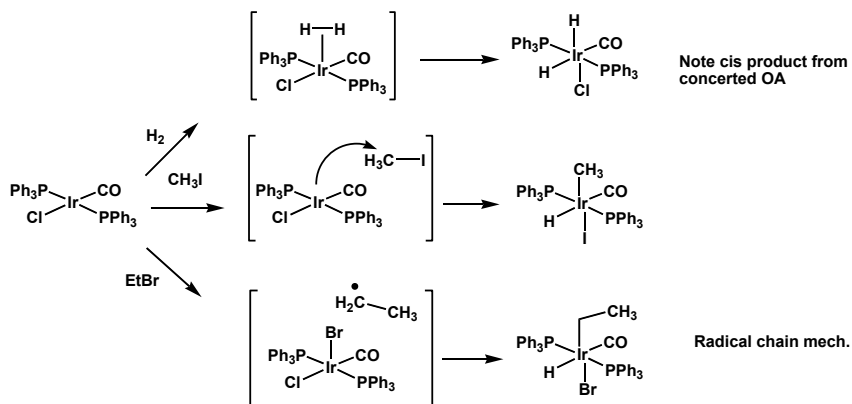
-L slow:
Rate = $k[\text{ML}]$ +L' slow:
Rate = $\frac{Kk_{+1}[\text{ML}][\text{L}']}{[\text{L}]}$



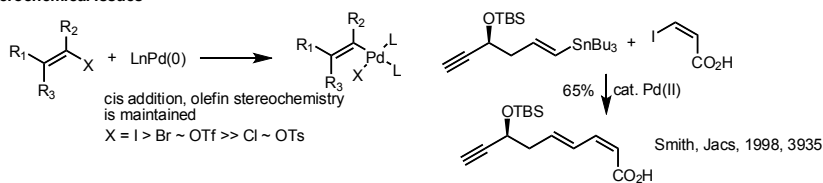
Oxidative Addition and Reductive Elimination



"O.A." and "R.E." give NO information on mechanism: can be concerted 3-centered, SN2-like or radical



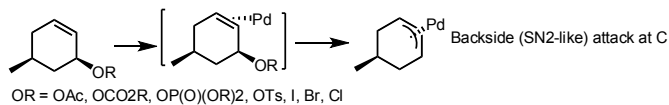
Stereochemical Issues



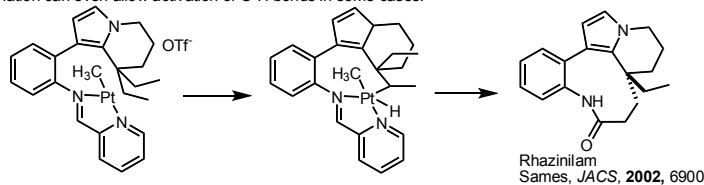
Vinyl and Aryl C-X much more reactive than alkyl C-X despite more e- rich alkyl C-X
 Why? precoordination



Precoordination with allylic substrates allows O.A. to moderately activated bonds:

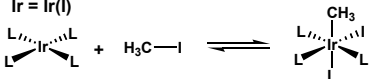
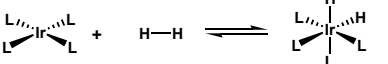
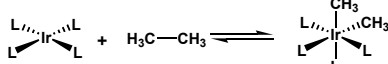
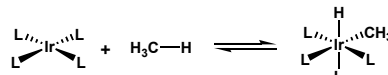


Precoordination can even allow activation of C-H bonds in some cases:



Oxidative Addition: Thermodynamics

Bond strength is reflected in ease of O.A., with exceptions

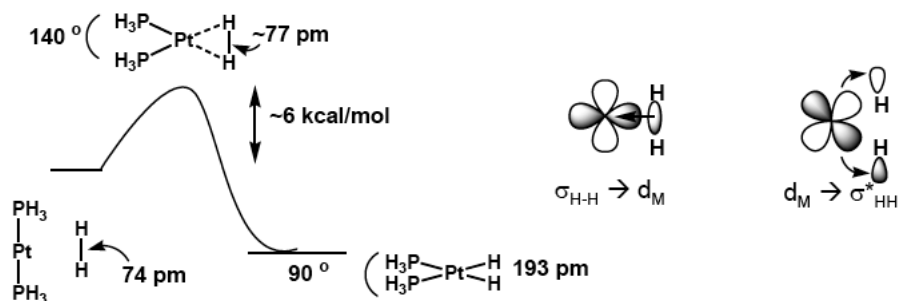
| Rxn | BDE (kcal/mol) of Cleaved Bond | est ΔG for O.A. |
|--|-----------------------------------|-------------------------|
| $\text{Ir} = \text{Ir(I)}$  | 56 | -25 |
|  | 104 | -6 |
|  | 88 | +6 |
|  | 104 | +8 |

M-H bonds are stronger than we might predict

O.A. to C-H and C-C remain very challenging, but could be valuable (more on this later in the course)

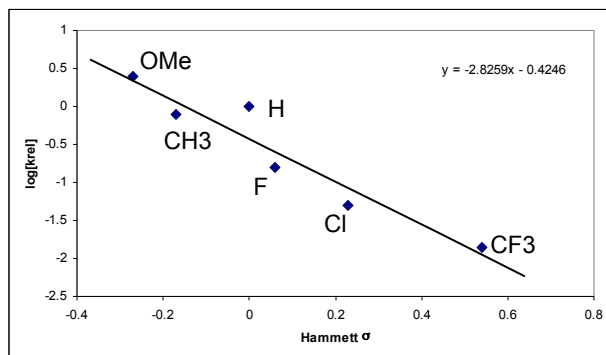
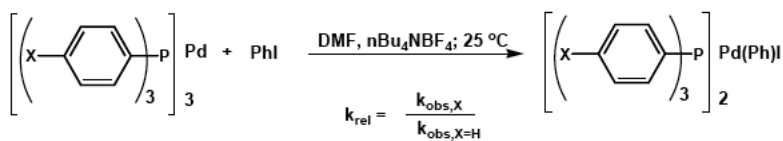
A picture of oxidative addition from calculations.

From CHNF, figure 5.2



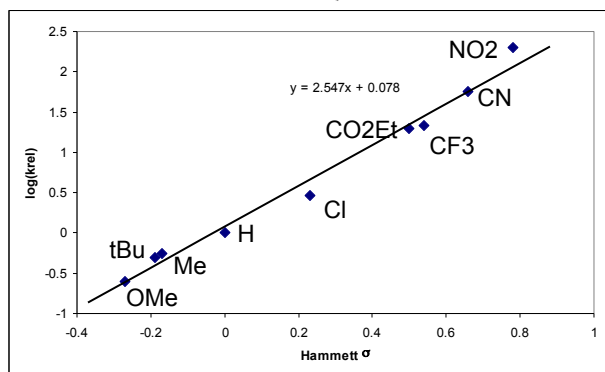
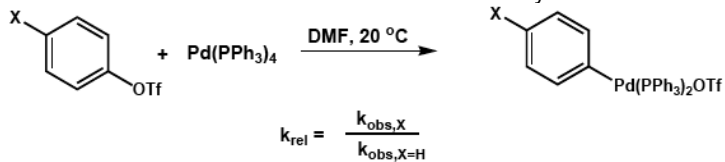
Oxidative addition: reactivity trends

Reaction rate increases with electron density on Pd

Amatore, *Organometallics*, 1995, 1818

Oxidative addition: reactivity trends

Reaction rate decreases with electron density on ArX

Jutand, *OM*, 1995, 1810

Oxidative addition: reactivity trends

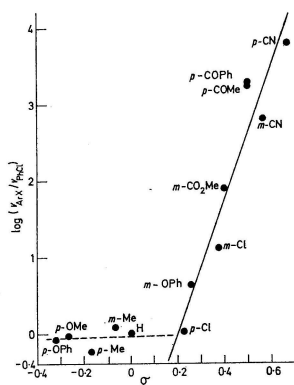
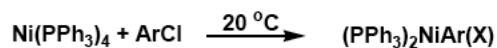
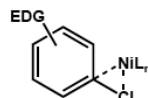
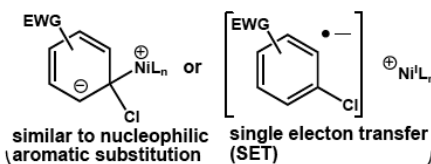


FIGURE 1 Correlation of relative rates of oxidative addition of substituted aryl halides with σ (D. M. McDaniel and H. C. Brown, *J. Org. Chem.*, 1968, 28, 420) at 0.02M- PPh_3 .

Kink indicates change in mechanism



3 centered T.S.
minimal charge build up

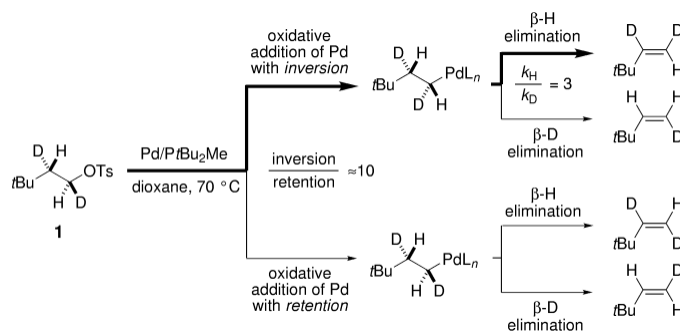


significant charge build up

Oxidative addition: reactivity trends

With sp^3 electrophiles, $\text{S}_{\text{N}}2$ pathway dominates with $\text{Pd}(0)$

Rxns show other traits of $\text{S}_{\text{N}}2$ (solvent effects, leaving group trends)

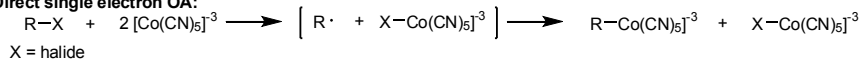


From Fu, *ACIEE*, 2002, 3910

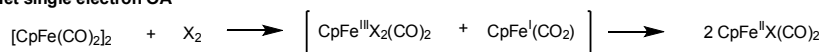
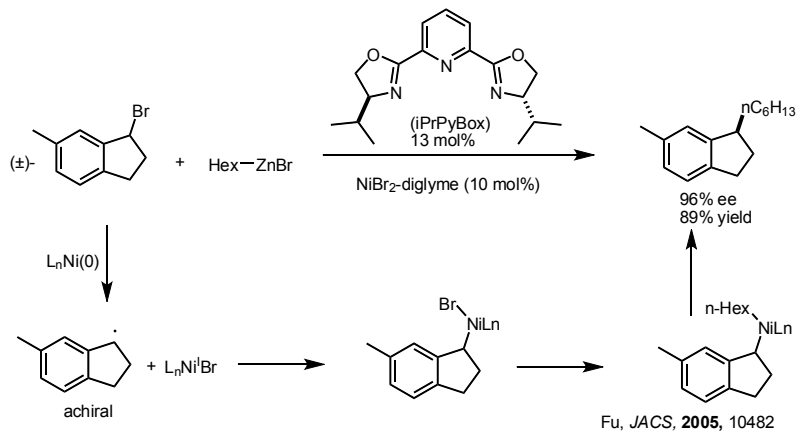
See also Fu, *ACIEE*, 2003, 5749

Ready; Catalysis

Organometallics: Oxidative addition

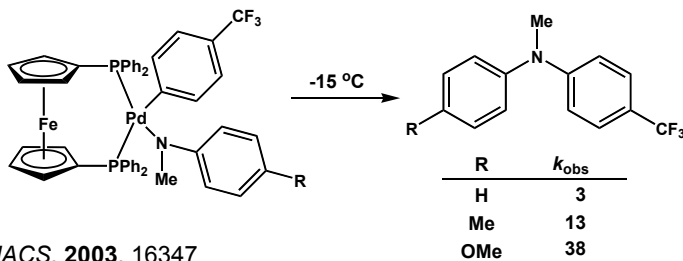
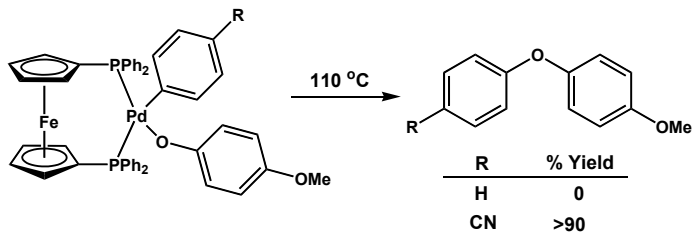
Direct single electron OA:

X = halide

Net single electron OA**Single electron OA in catalysis**

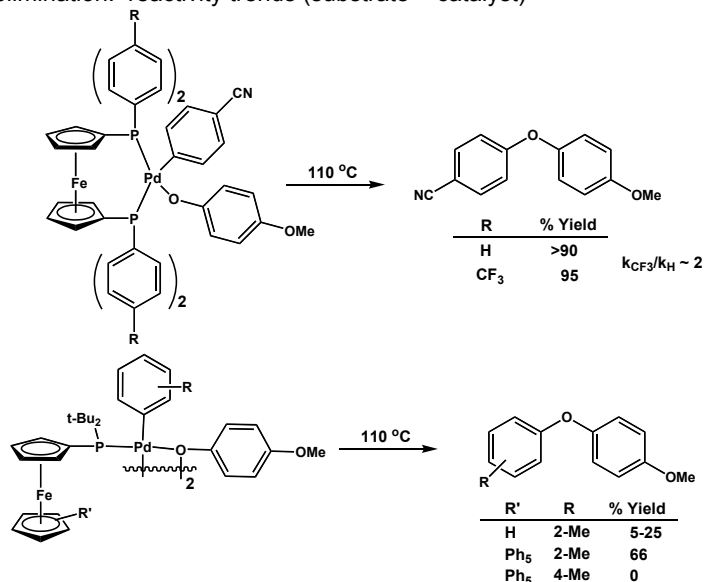
Ready; Catalysis

Organometallics

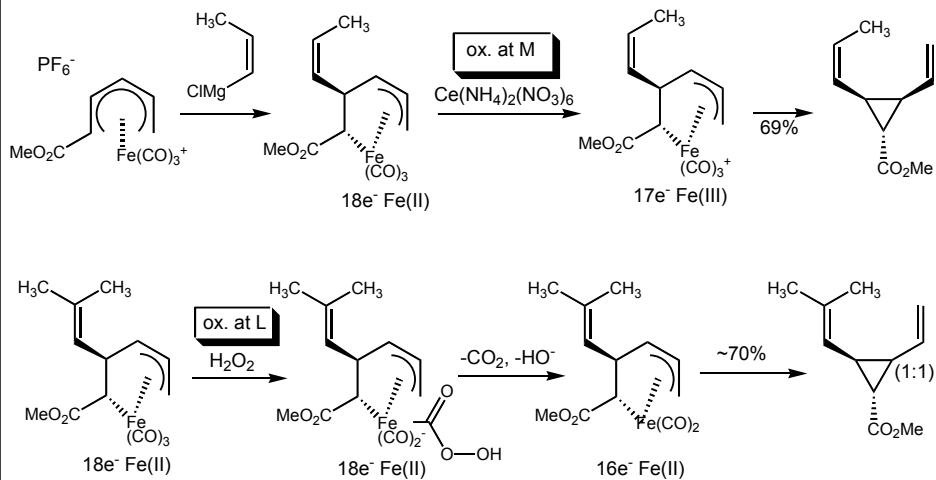
Reductive elimination: reactivity trends (substrate)

Hartwig, JACS, 2003, 16347
OM, 2003, 2775

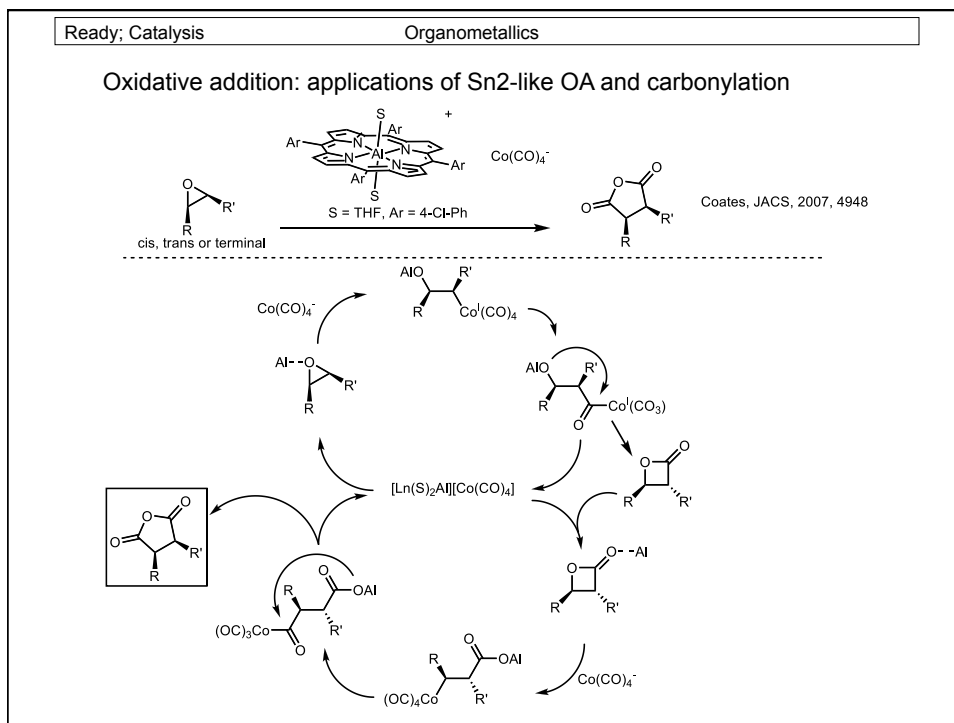
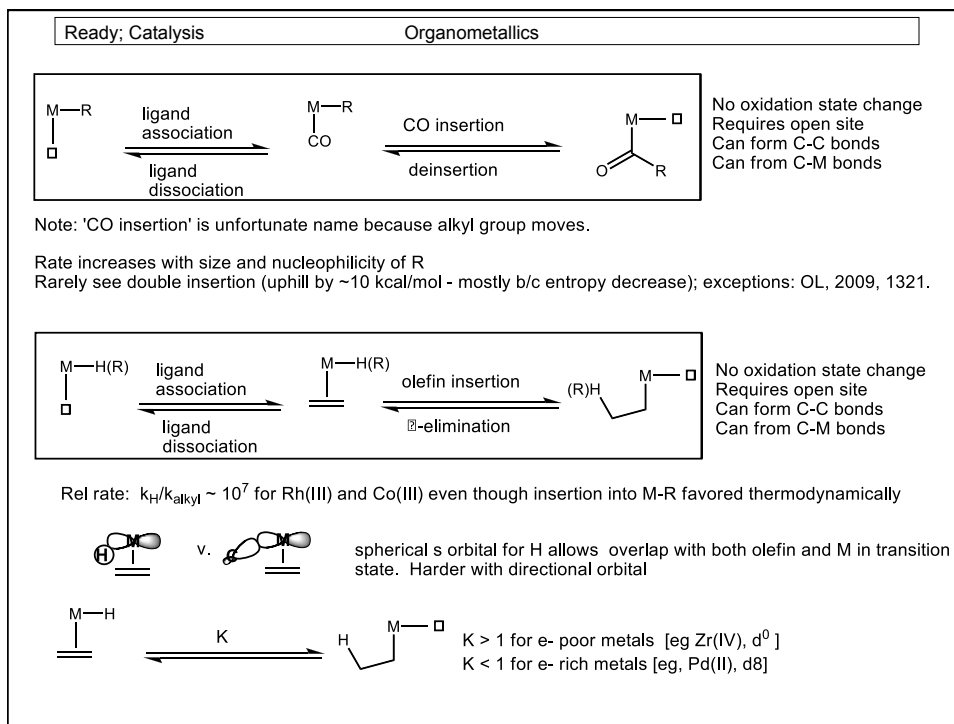
Reductive elimination: reactivity trends (substrate + catalyst)



Oxidation-induced reductive elimination



Donaldson, OL, 2005, 2047



agostic interactions: stable intermediates on the way to α - or β -hydride elimination

- Stable interactions often found with electron-poor metals
- Especially common with d^0 metals
- Computation with Ti(carbene) and W(carbyne) estimates BDE ≤ 10 kcal/mol (OM, 2006, 118)

Schrock, et al

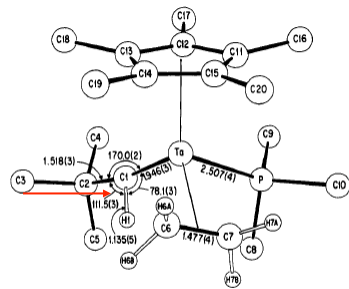
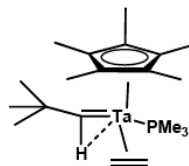
172 *J. Am. Chem. Soc.*, Vol. 103, No. 1, 1981

Figure 4. A perspective view of the molecular structure of Ta(η^5 -C₅Me₅)(CHCMe₃)(η^2 -C₂H₄)(PMe₃) (2). Except for H(1) and the four ethylene hydrogen atoms, all hydrogen atoms have been omitted for clarity. The thermal ellipsoids do not represent the experimental values (see Figure 3).

Things to noteTa(III) carbene (d^2)Small Ta-C-H angle (78°)

Long C-H bond (1.14Å, average here is 1.085Å)

i.e. weakening of C-H bond

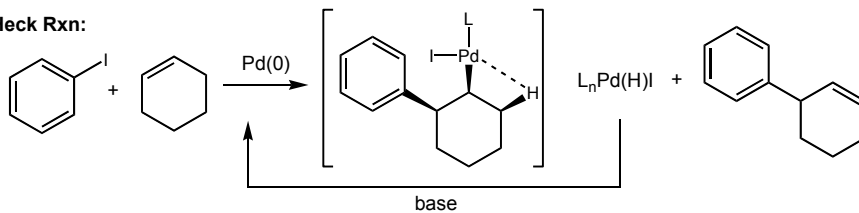
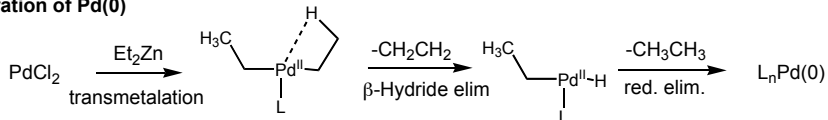
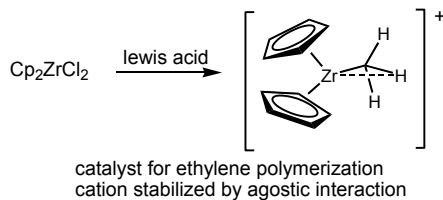
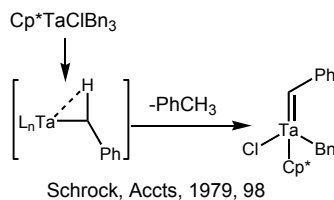
Big Ta-C-C angle (170°)

Unrelated to agostic interactions:

Ethylene C's out of plane (average 0.33Å out of 4H plane)

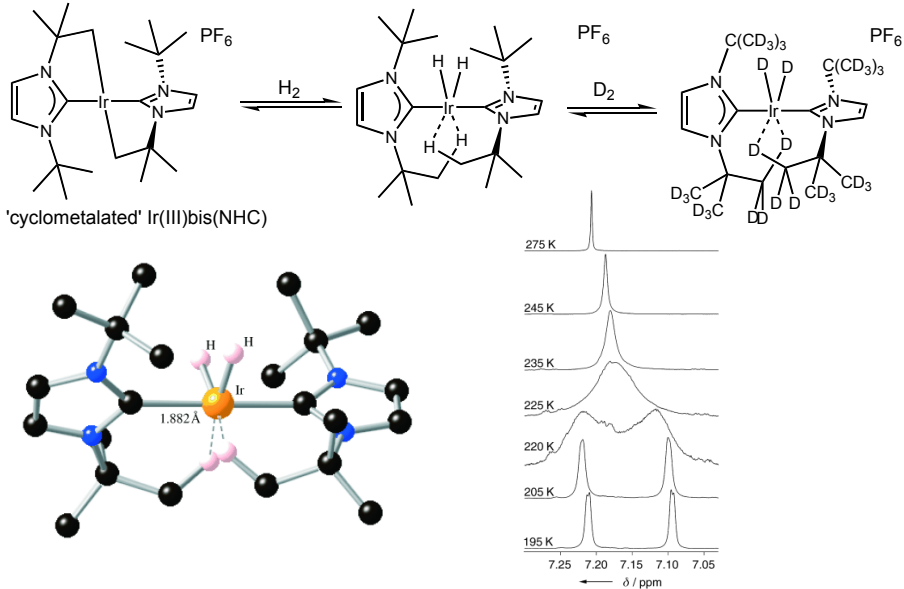
Long ethylene C-C distance (1.48 v. 1.34 when free)

Agostic interactions are likely unobserved intermediates in normal transition metal-catalyzed reactions:

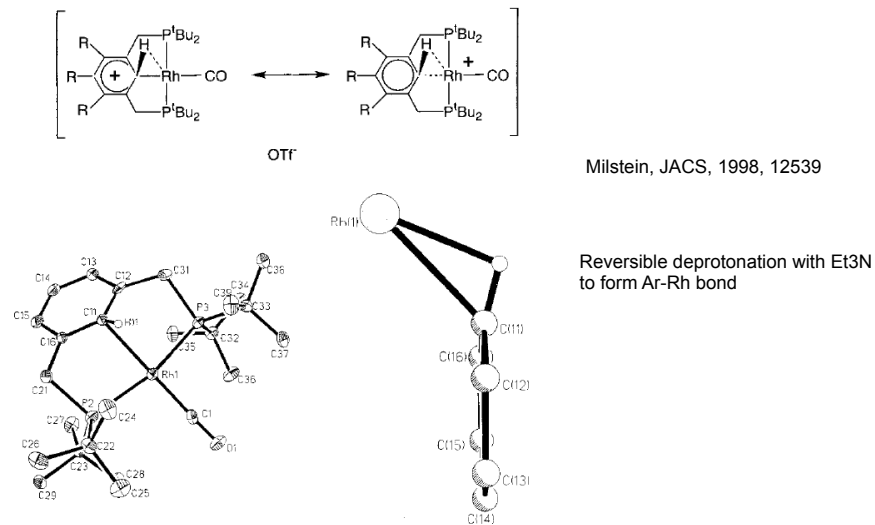
Heck Rxn:**Generation of Pd(0)** **α -agostic interactions can happen, too**likely intermediate in α -elimination:

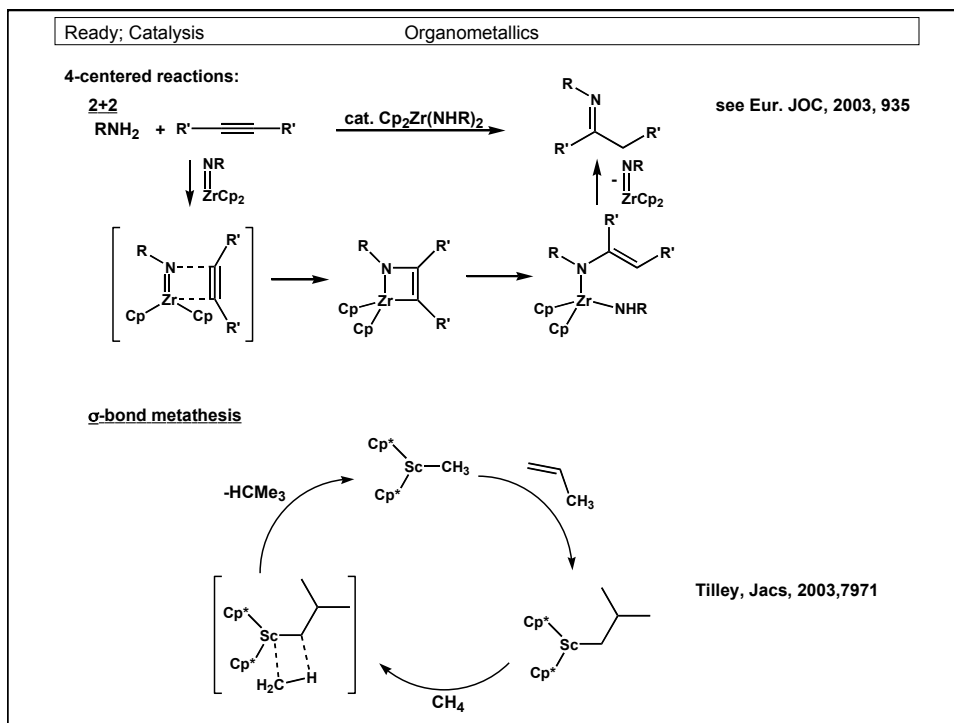
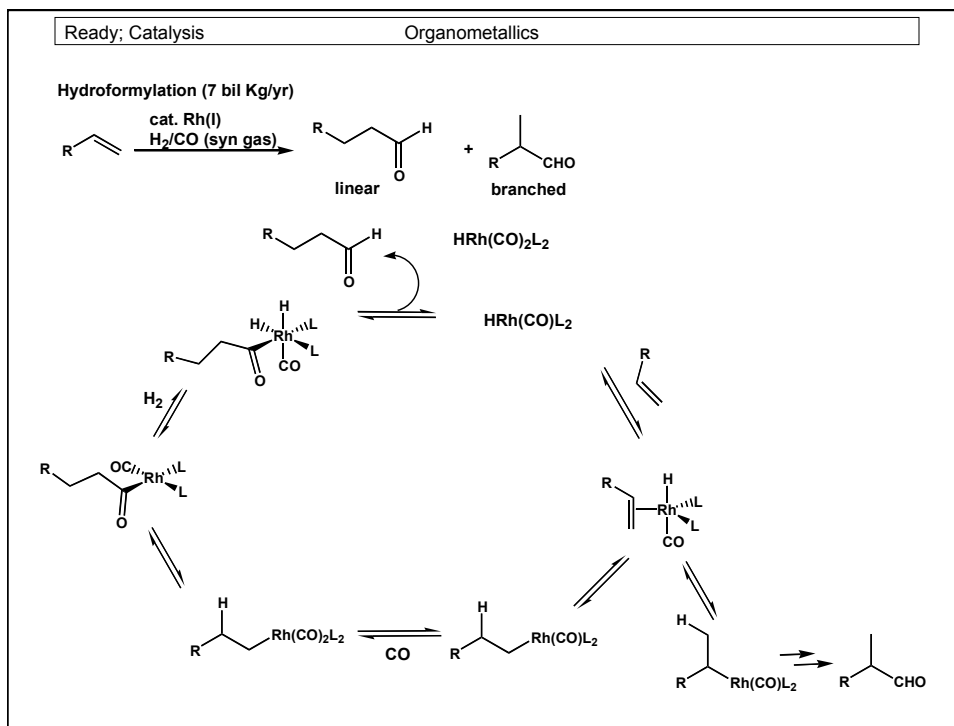
Agostic interaction can be dynamic

Nolan, ACIEE, 2005, 2512

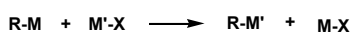


A C-H complex observed crystallographically :



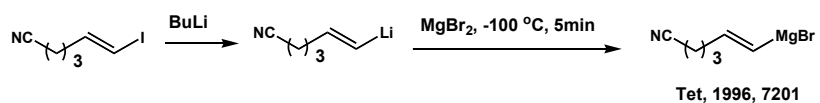


Transmetalation

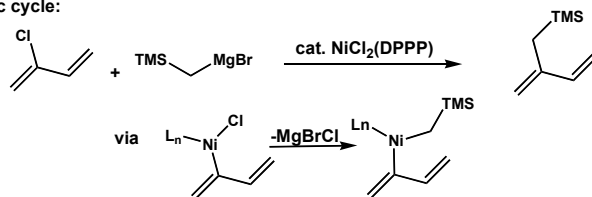


Stoichiometric Use:

Great way to make Grignards, alkyl zincs, cuprates, stannanes etc. Esp useful on small scale where O.A. to R-X not possible



In catalytic cycle:



- T.M. usually from more eletropositive M to more electronegative M
- Endothermic T.M.'s can be part of catalytic cycle if R-M' subsequently reacts
- Likely by associative mech for coordinatively unsaturated M
- Likely metathesis for coordinatively saturated