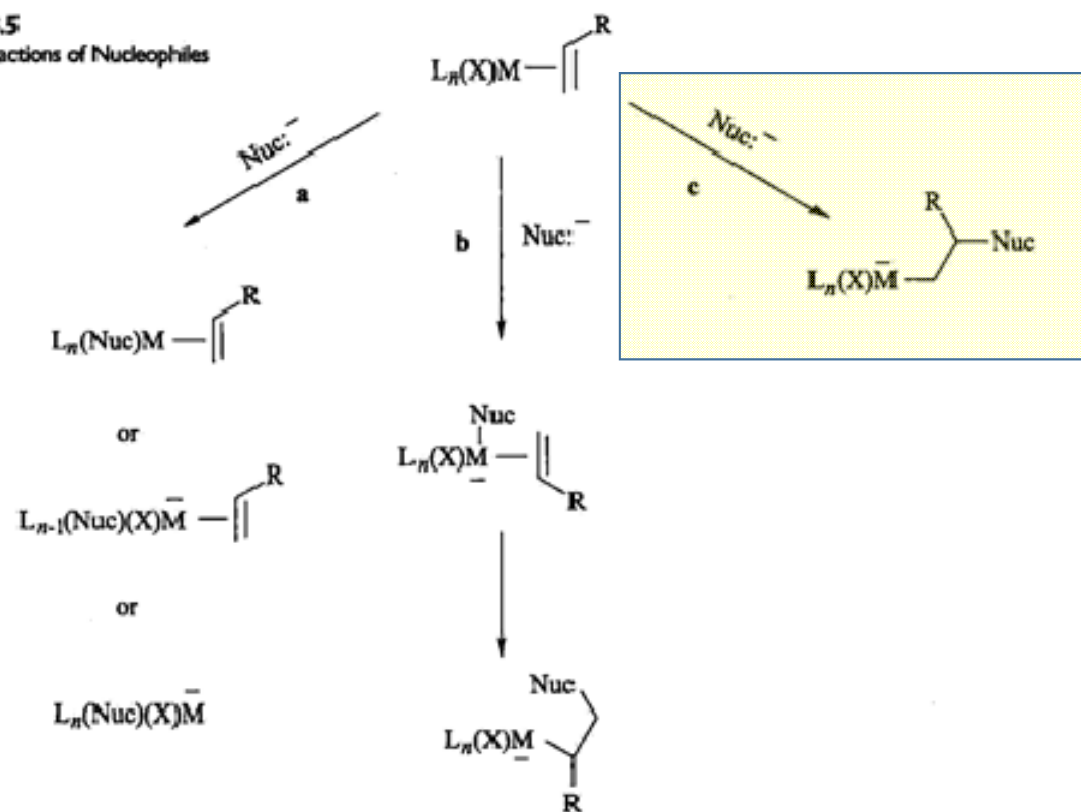


2. Nucleophilic attack on coordinated ligands

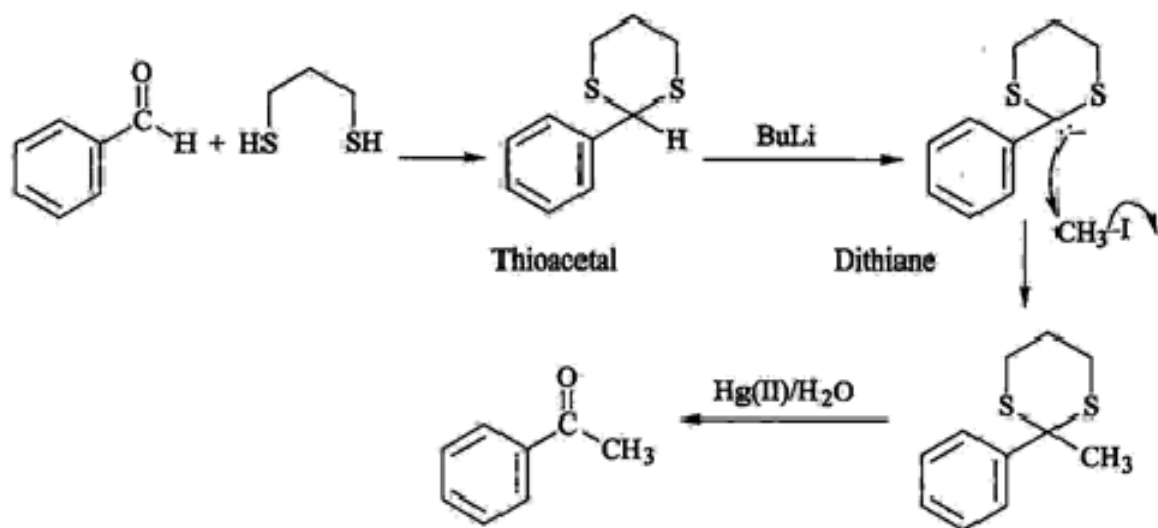
Scheme 8.5

Possible Reactions of Nucleophiles



- **direct attack can occur at any unsaturated ligand** such as CO, alkenes, alkynes, arenes
- free π -ligands such as alkenes normally react with electrophiles **NOT** nucleophiles so this is an example of **'umpolung'**: polarity reversal due to coordination.

An organic example:

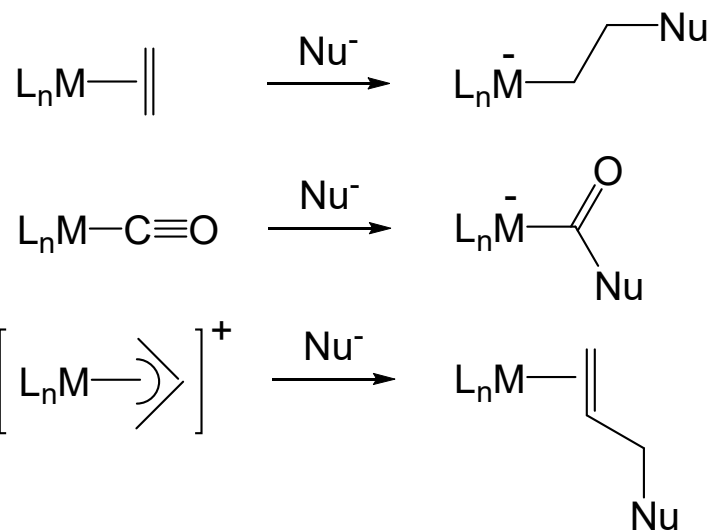


Factors favouring Nu⁻ attack at coordinated ligands:

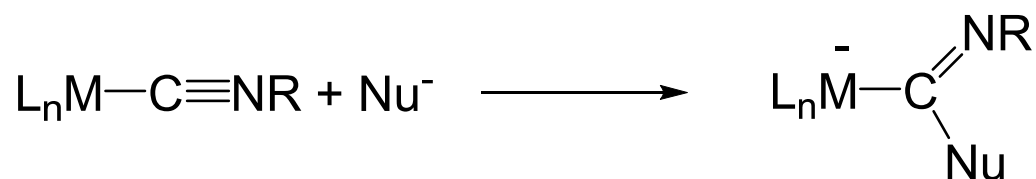
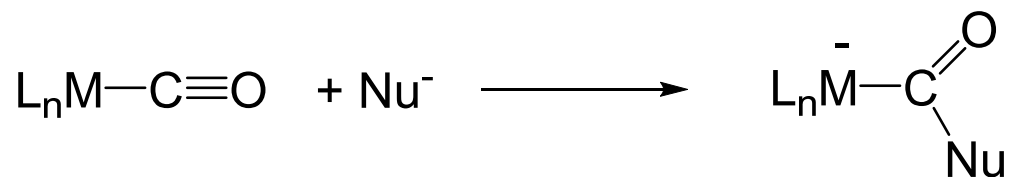
- Coordinatively saturated metal center
- Pi accepting ancillary ligands (eg. CO)
- Electron poor metal centers / cationic metal centers
- Soft nucleophiles (hard nucleophiles usually attack the metal first)

Example: **free CO** and all but the most activated **alkenes only react with very strong nucleophiles**; free alkenes react with electrophiles

BUT ALL react readily with mild nucleophiles when complexed to electron poor metals



a) Nucleophilic attack at coordinated **CO** and **RNC**



Relative rates on insertion: $CO \ll L_nM-CO < L_nM-CO < [L_nM-CO]^+$

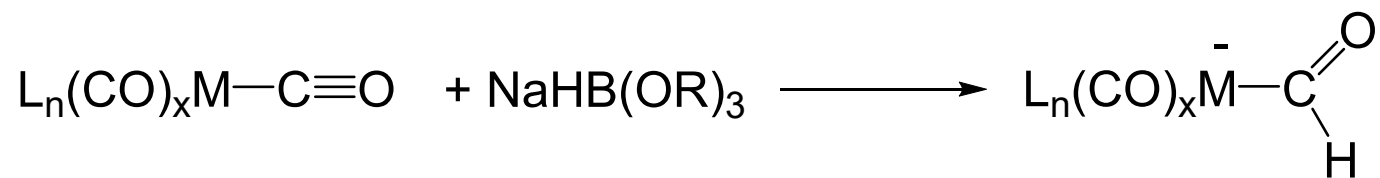
Strong donor L,
Strong backbonding

Weak donor L,
Weak backbonding

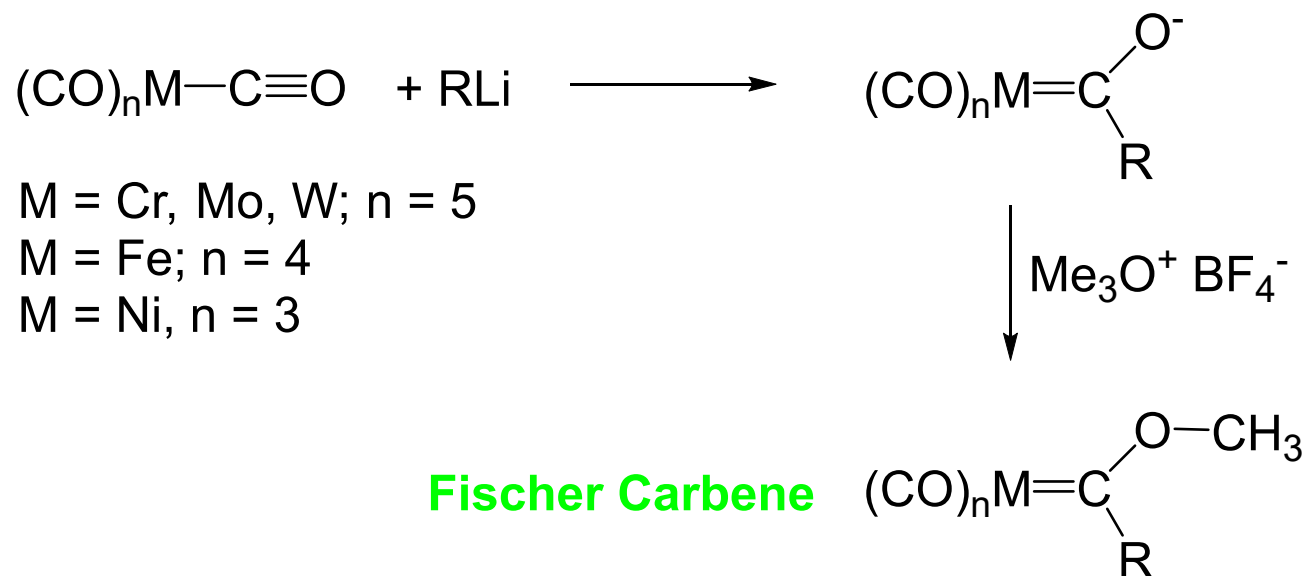
Reacts with strong Nu-
like RLi



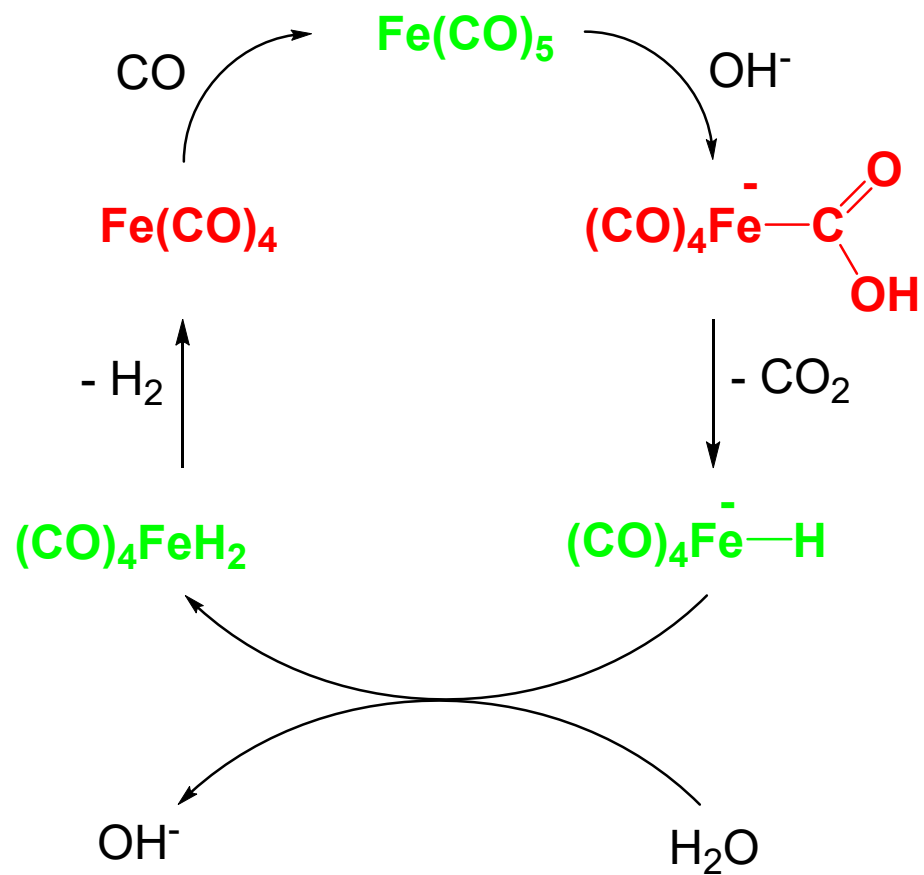
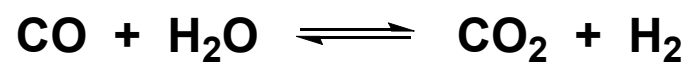
Reacts with weak Nu-
like H₂O



M = Cr, W, Fe; L = CO or PR₃

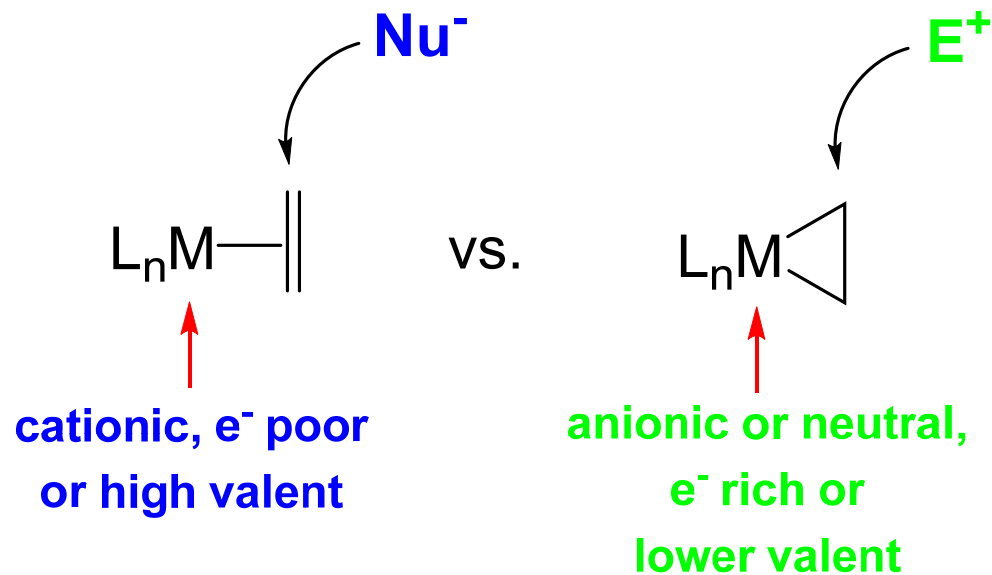


Water-gas shift reaction:



b) Nucleophilic attack at **coordinated π -ligands**

Generally speaking, free π -systems are susceptible to electrophilic attack but their coordinated counterparts, nucleophilic attack; it does depend on the metal and ligand set some:



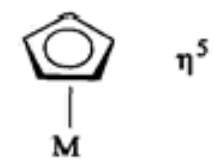
Davies-Green-Mingos (DGM) rules: predict **which** unsaturated ligand will be attacked AND the **regiochemistry of attack**.

Rule 1 Even before odd

Rule 2 Open before closed

Rule 3 Regiochemistry: *open, even polyenes are attacked at the terminal position; open, odd polyenes are not normally attacked at a terminal C unless the metal fragment is strongly electron withdrawing*

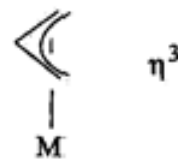
- **Even** and **odd** refer to the **number of C** in the π -system
- **Open** and **closed** refer to whether the π -system is a **closed loop** or **open-ended**



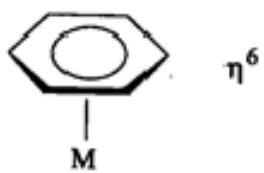
Odd closed



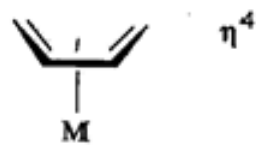
Odd open



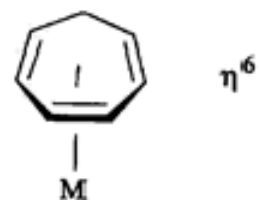
Odd open



Even closed



Even open



Even open

Figure 8-4
Classification of π Ligands

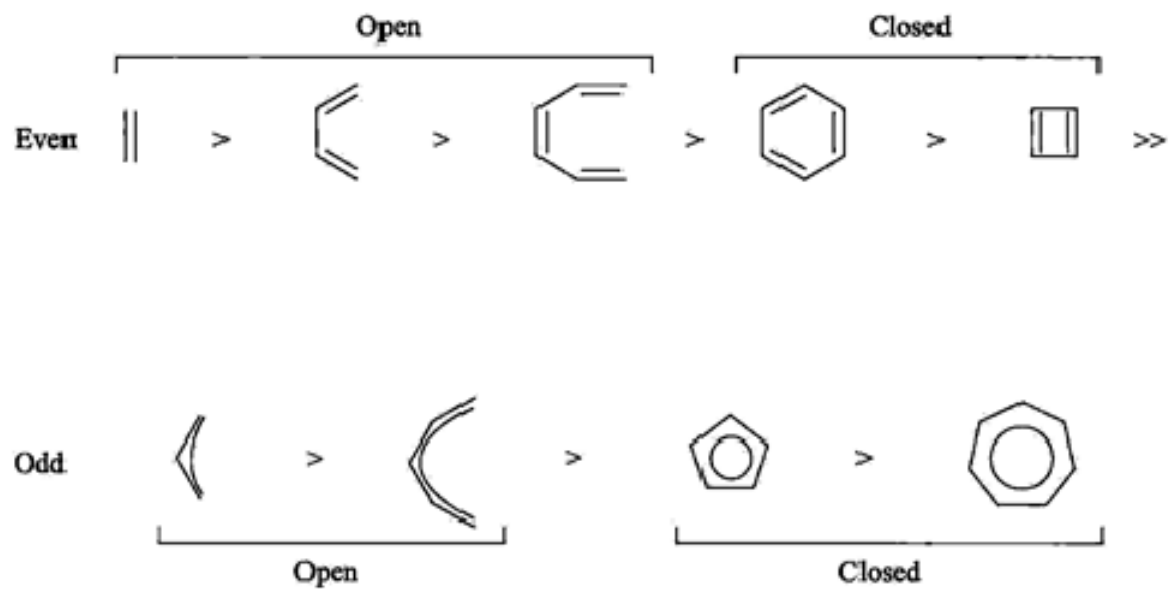


Figure 8-5
 Relative Reactivity of Pi Ligands

Rationale for the DGM rules

Rule 1 Even before odd:

- HOMO of even is doubly occupied while HOMO of odd is singly occupied
- more charge can be transferred from an even polyene resulting in a more positive centre for enhanced Nu-attack

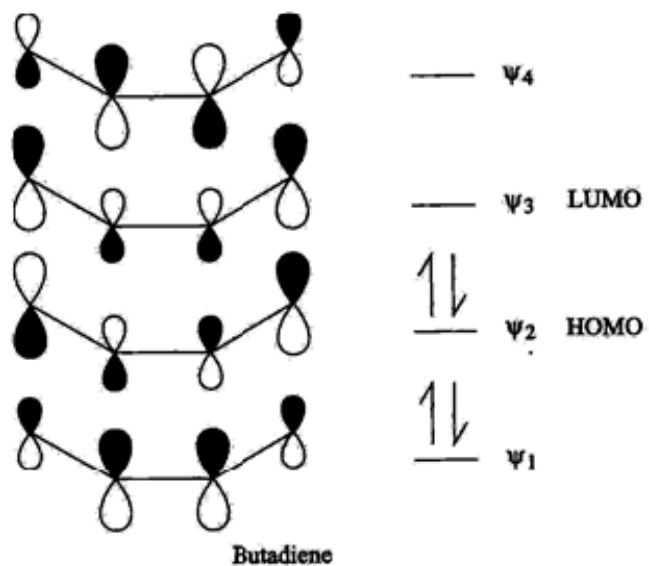
Rule 2 Open before closed:

- closed rings have more even charge distribution than open polyenes
- some sites on open polyenes will therefore bear more positive charge than in closed ring systems

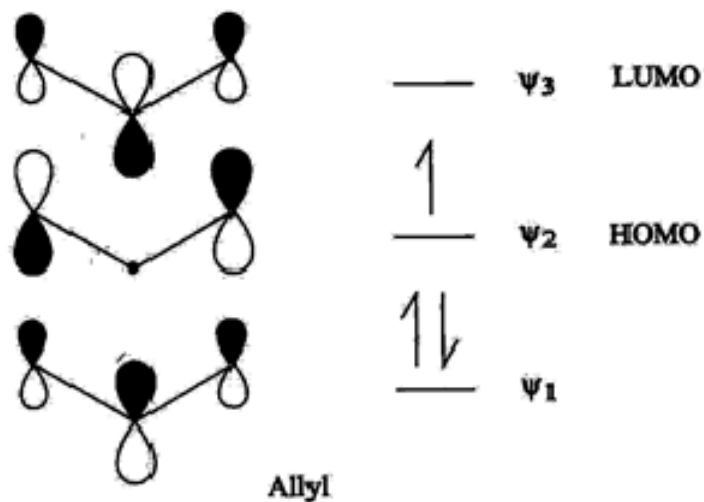
Rule 3 Regiochemistry of attack:

- consider the nature of the Nu⁻ / ligand interaction: Nu⁻ is a donor and donates electron density into an empty M.O. on the ligand (usually the LUMO).

for an even polyene like butadiene this will be Ψ_3 . Since Ψ_3 has larger lobes at the terminal C, the best overlap will occur if the Nu⁻ attacks at this site.

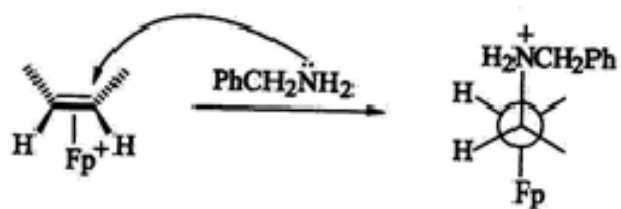


- for **odd** polyenes (eg. allyl) the **LUMO** could be either Ψ_3 (if the ene has anionic character) or Ψ_2 (if the metal is a very good acceptor).
- if the **LUMO is Ψ_3** , attack occurs at the central C because this has the biggest lobe and also no formal negative charge.
- if the **LUMO is Ψ_2** , attack occurs at the terminal C because this has the largest lobe (there is a node at the central C in the allyl case)

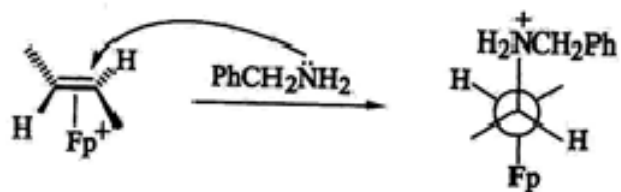


(i) alkenes

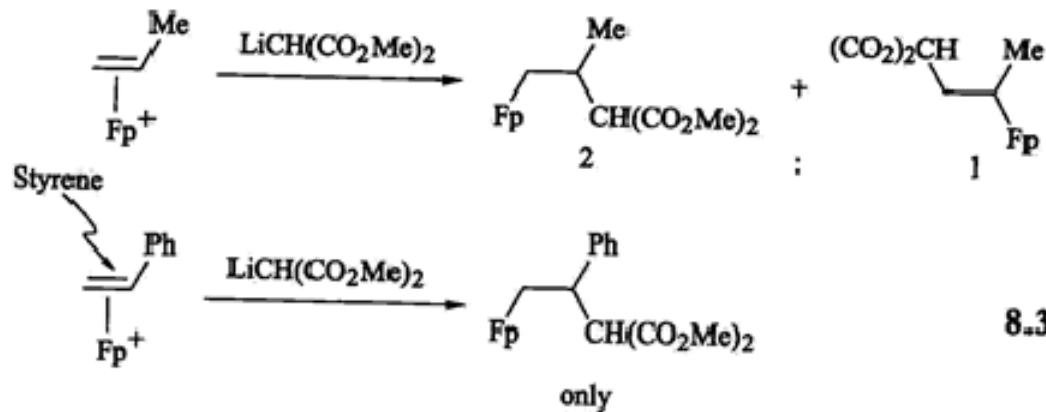
Fp⁺ complexes most widely used examples



Fp = Cp(CO)₂Fe



Attack is *anti*



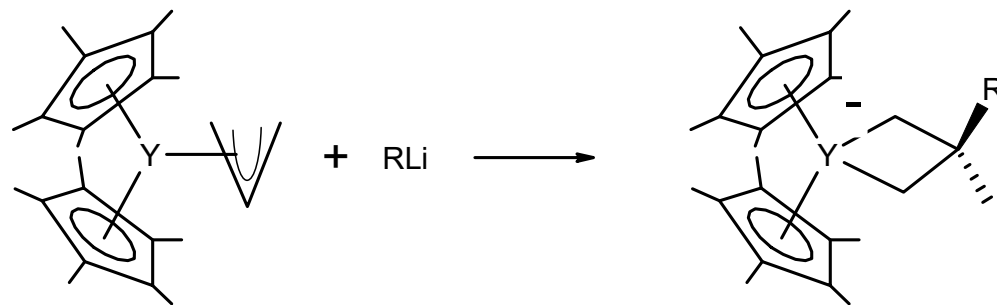
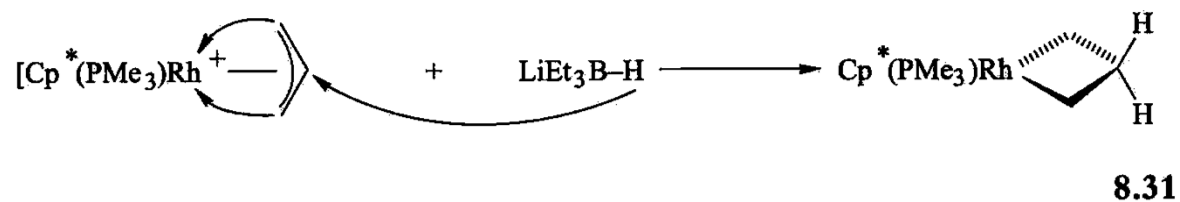
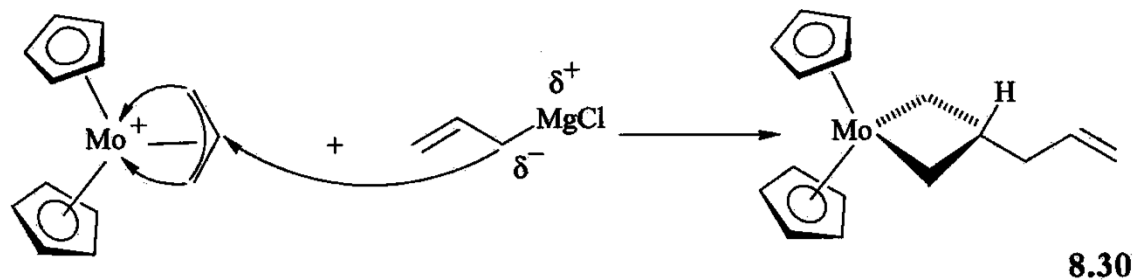
8.33

Preference is for the *most substituted alkene C*

(ii) η^3 -allyls

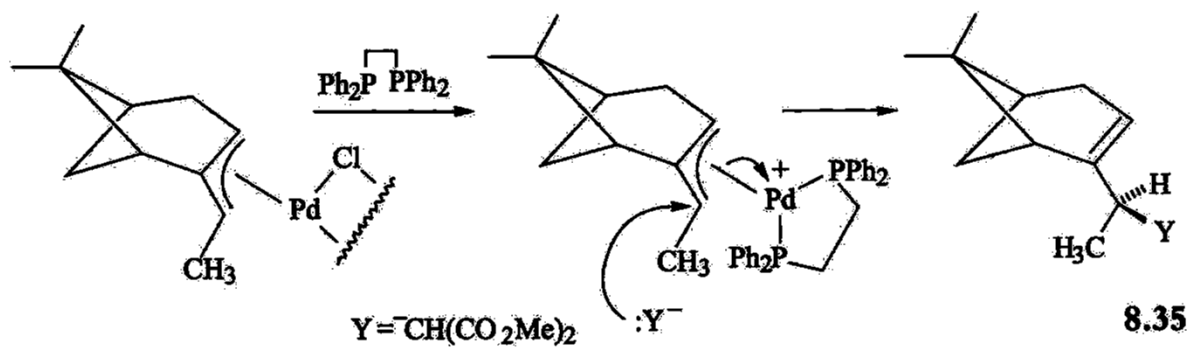
If the allyl is relatively *electron rich*:

Attack at central C

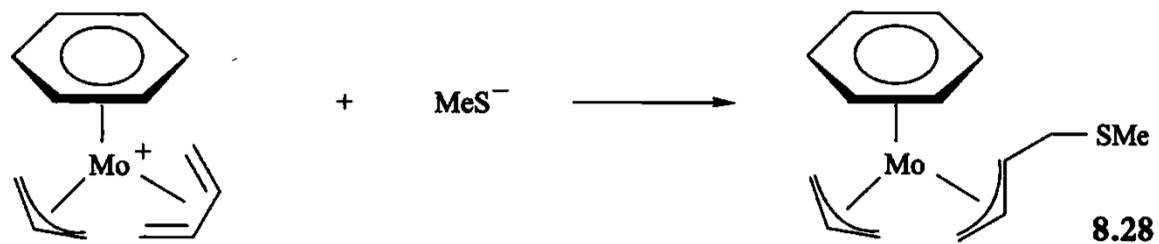


If the allyl is relatively *electron poor*:

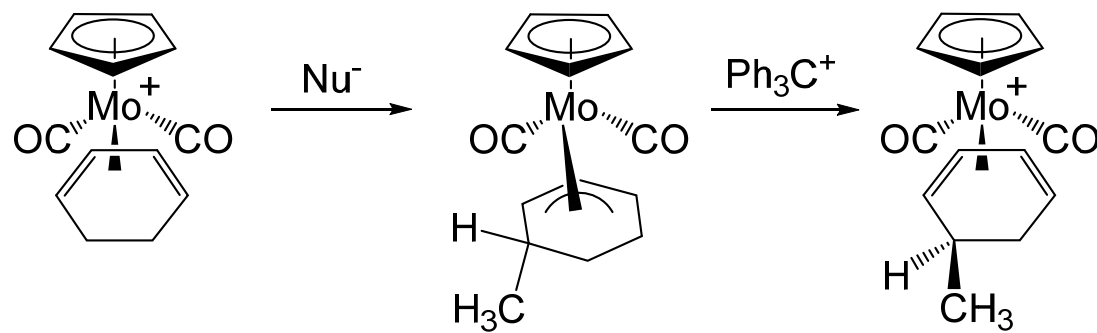
Attack at terminal C



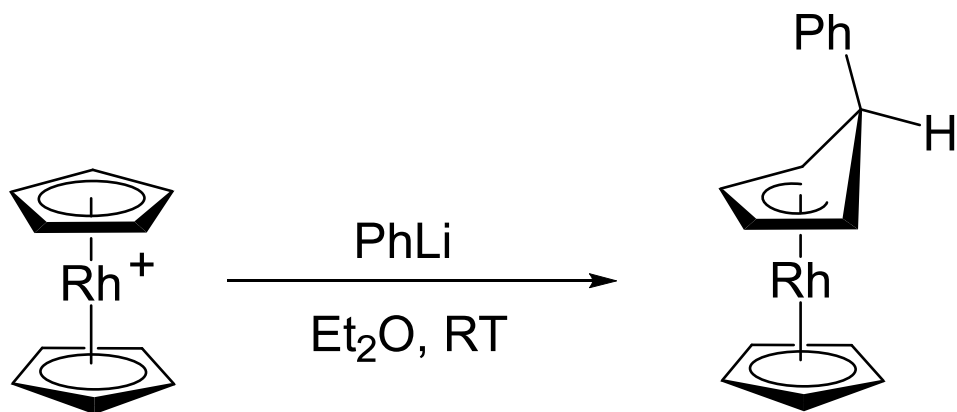
(iii) η^4 -dienes



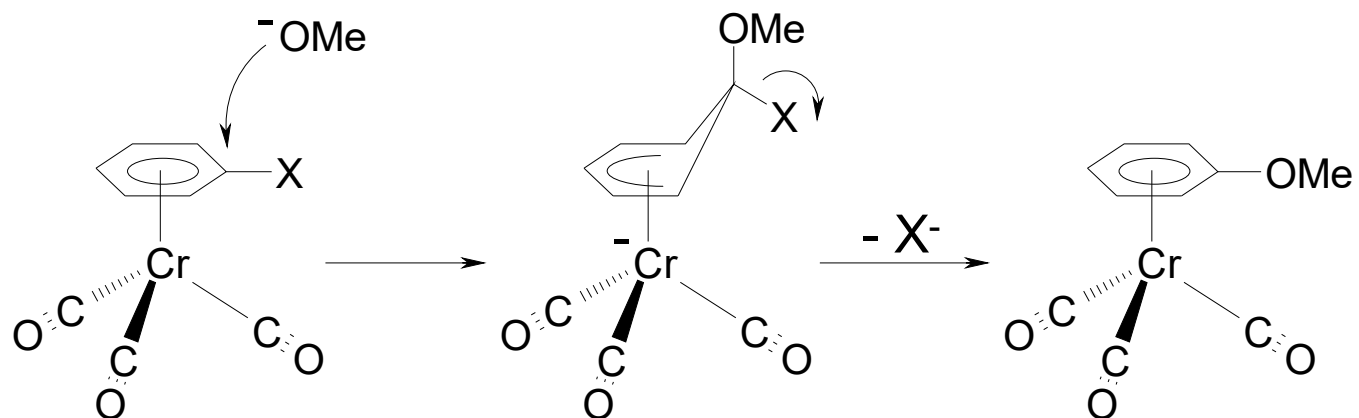
Note: Even before odd; open before closed



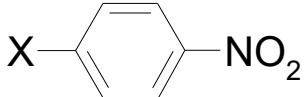
(iv) η^5 -cyclopentadienes



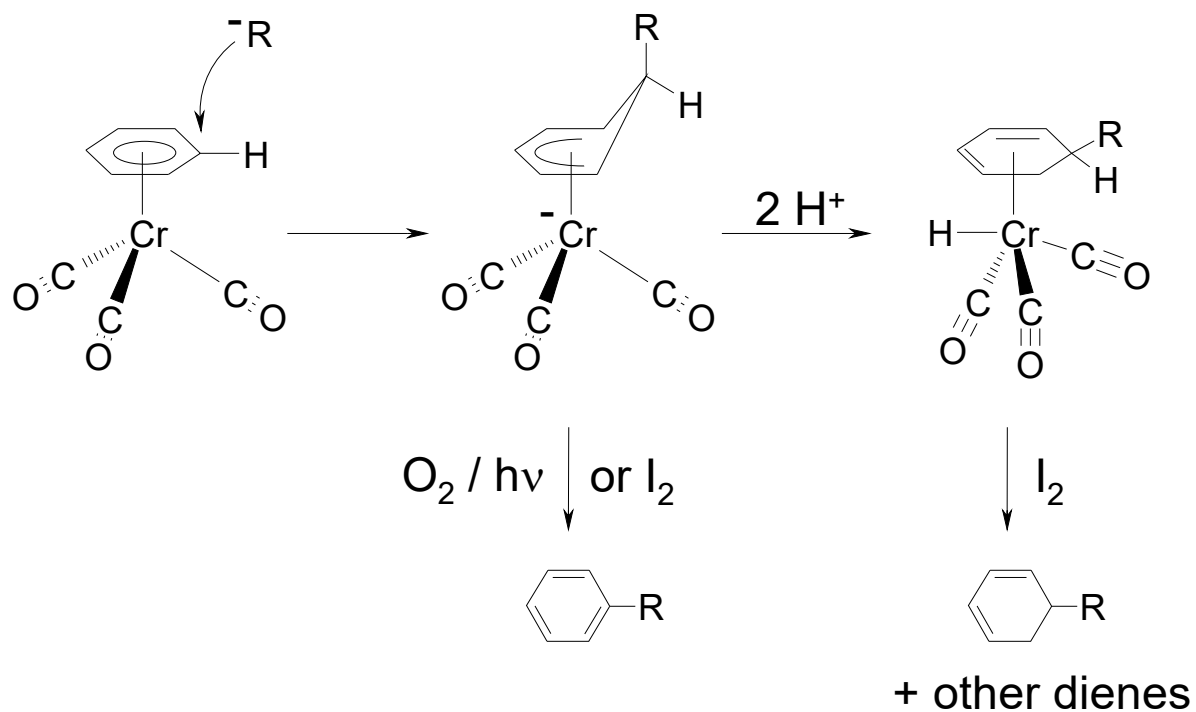
(v) η^6 -arenes



rate: $X = F > Cl > Br > I$

rate is comparable to free 

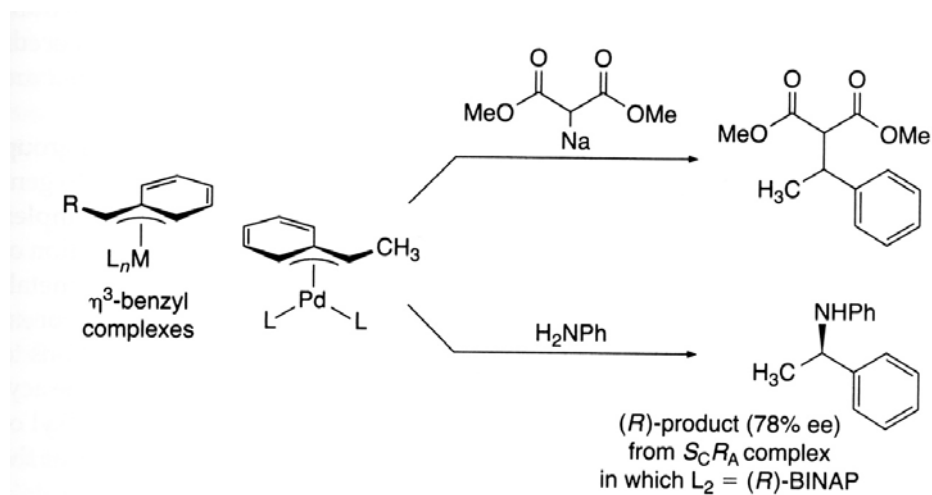
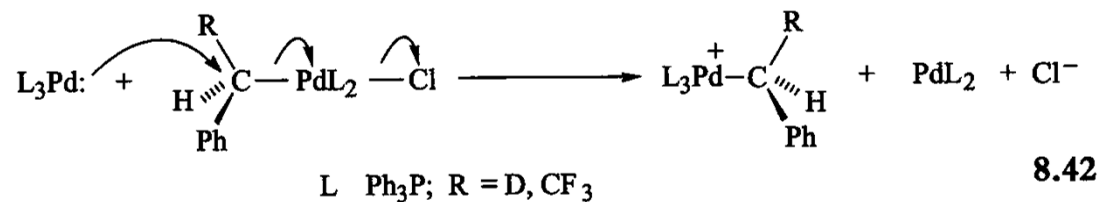
Semmelhack (Princeton): carbanion attack by 'soft' nucleophiles

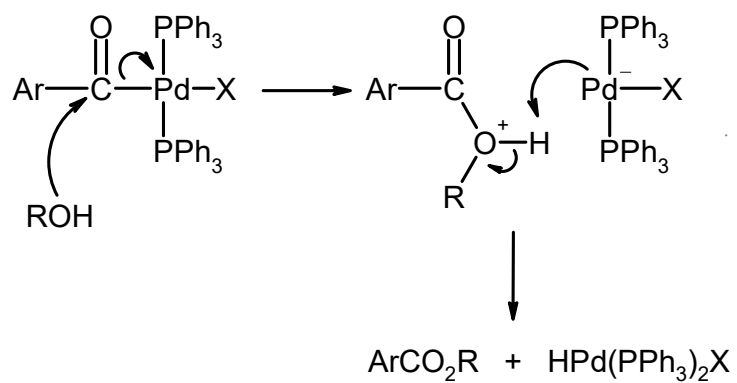


Works for $\text{R} = \text{CMe}_2\text{CN}$, CH_2CN , $\text{CH}(\text{CO}_2\text{Me})_2$ and other stabilized carbanions

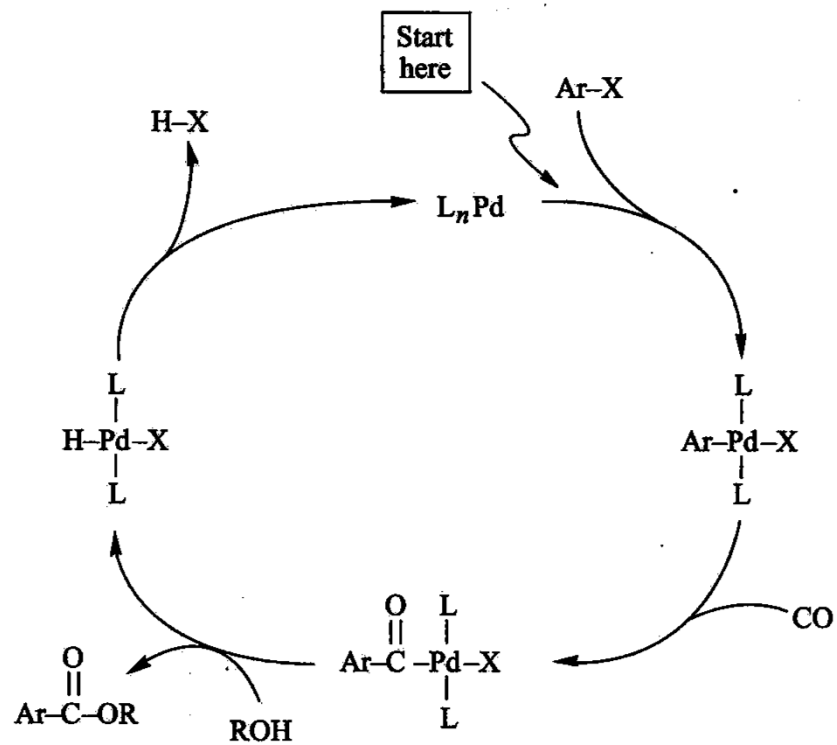
3. Nucleophilic abstraction: part or all of the ligand is removed from the metal during nucleophilic attack

Nu⁻ can be metal or organic based:





Scheme 8.7
Nucleophilic Abstraction of
Sigma-Acyl-Pd Complexes

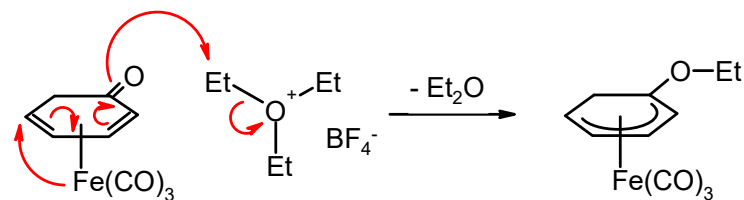
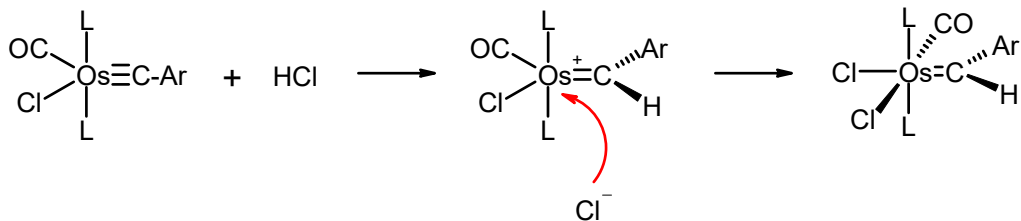
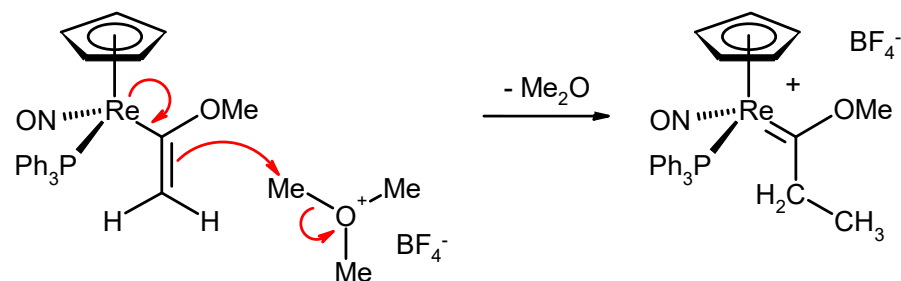
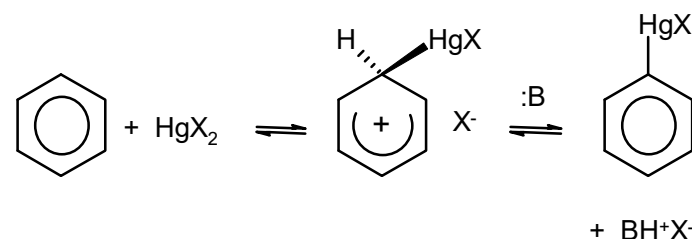


R = Alkyl X = Cl, Br, I

4. Electrophilic Reactions

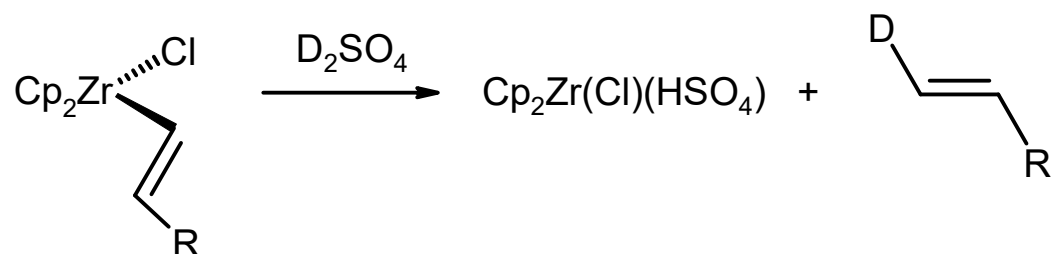
i) Electrophilic addition

- attacking E^+ can include metallic ions or complexes (eg. HgX^+), organic electrophiles (egs. R_3O^+ , δ^+ C of CH_3I) or non-metallic electrophiles (egs. H^+ , NO_2^+ , CO_2 , X_2 , etc.)

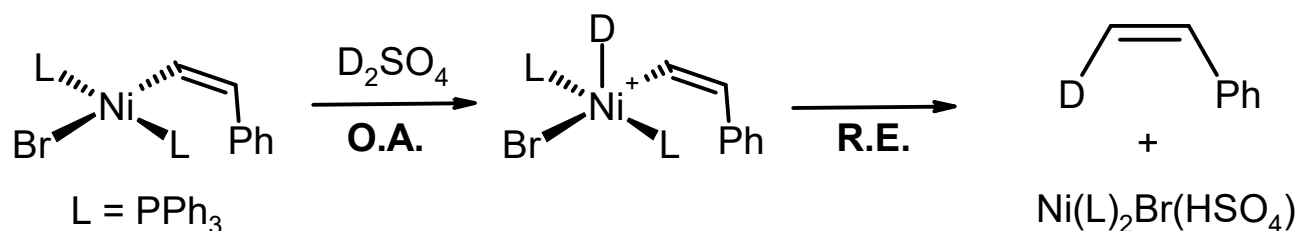


ii) Electrophilic abstraction

Most common example: cleavage of M-C bonds by acid



direct attack at C (carbanion character; HOMO has a large coefficient at C)



initial protonation at metal \equiv oxidative addition (HOMO has largest coefficient at M; i.e., electron rich metal)
retention of configuration during elimination

Hydride abstraction by electrophilic carbocations (usually Ph_3C^+) is another well-known example:

