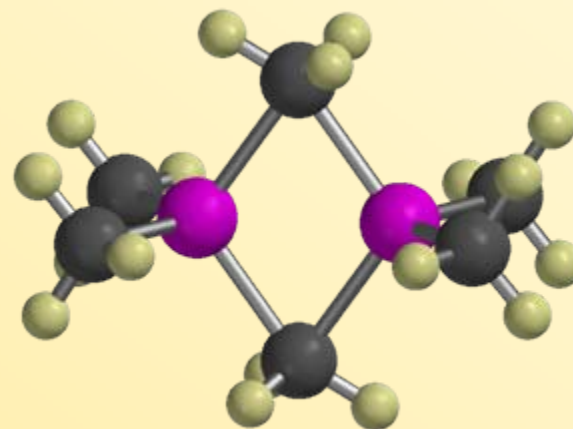
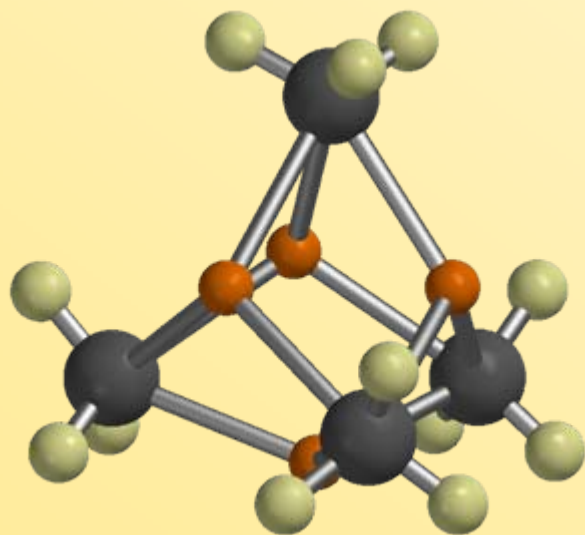


# *Main-group Organometallics*



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# Main group organometallics at a glance

- Structures
  - $\sigma$  bonds and 3c-2e (or even 4c-2e) bonds
- Synthesis
  - the first M-C bond
- Reactivity
  - nucleophilic and basic
  - auxiliaries in organic synthesis
  - source of organic groups for transition metals



# Structures

- Not always 8/18 e
- "Too many" electrons if:
  - large atomic radius
  - electropositive elements
  - small ligands
  - chelate structures
- "Too few" electrons for:
  - small atomic radius
  - less electropositive elements
- 8/18 e "preference" rather than "rule"



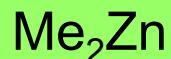
# Comparing coordination abilities



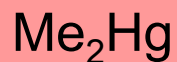
Mg much more electropositive  
strong acceptor  
polymeric



Cl are withdrawing!  
stronger acceptor  
polymeric



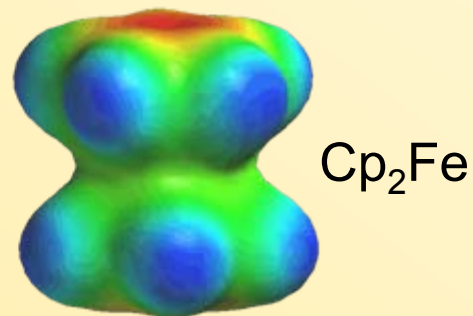
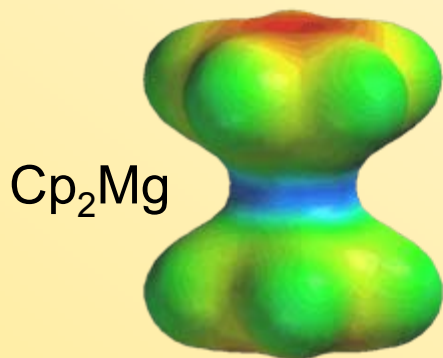
moderately strong acceptor  
monomeric, but exchanges Me groups



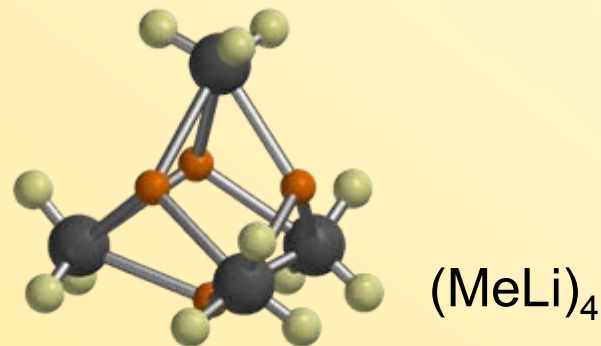
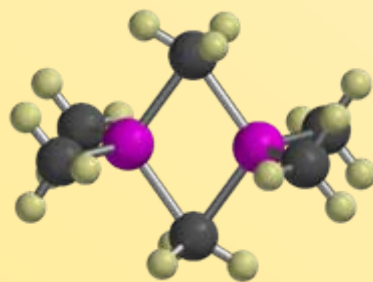
Hg much less electropositive  
very weak acceptor  
monomeric

# Structures

- Strong preference for  $\sigma$ -donor groups
  - but Cp is often  $\pi$ -bound (deceptively like with transition metals)

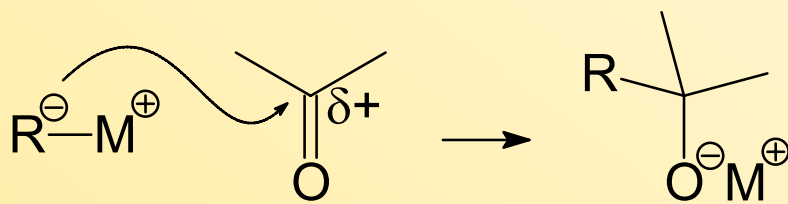


- Electropositive metals: often  $3c-2e$  or  $4c-2e$  hydrides/alkyls
  - as "stopgap"

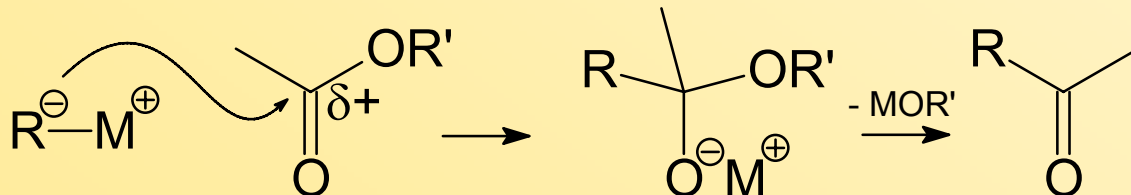


# Reactivity as Nucleophile

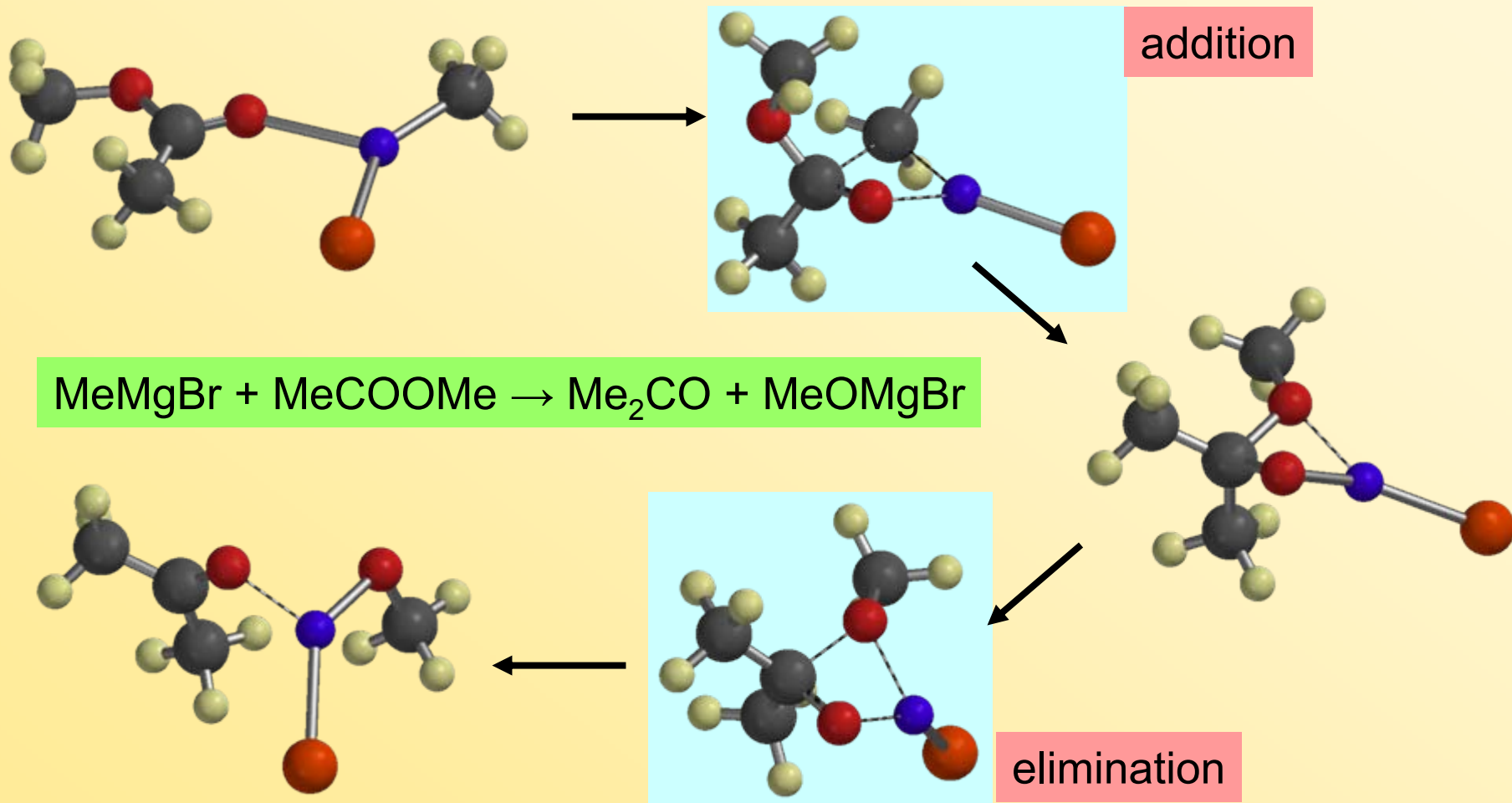
- Addition to polar C=X bonds  
(C=O, C=N, C≡N)



- Substitution at  $sp^2$  carbon  
(often *via* addition)



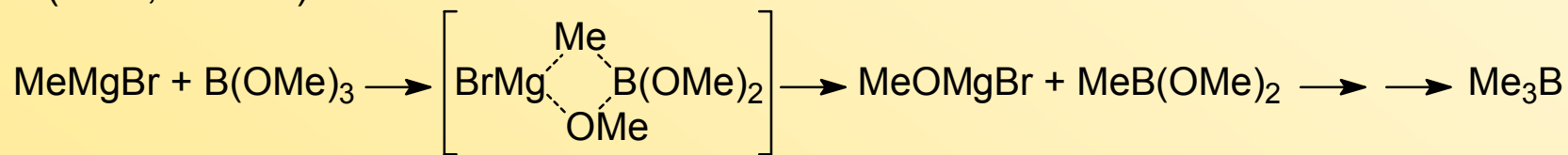
# Reactivity as Nucleophile



# Reactivity as Nucleophile

- Substitution at  $sp^3$  carbon does occur  
but is far less easy  
and often has a multistep mechanism

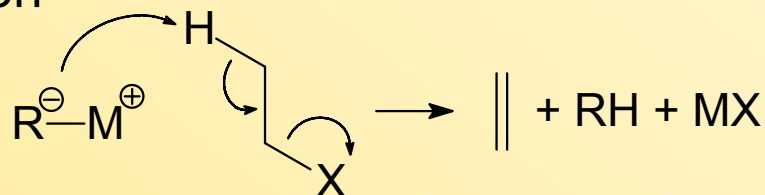
- Substitution at other elements:  
often easy for polar M-X bonds  
(Si-Cl, B-OMe)



# Reactivity as Base

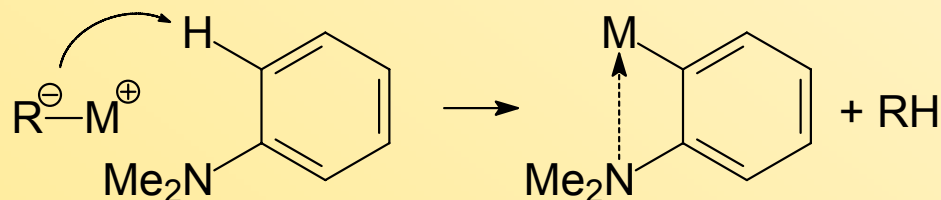
- More prominent in polar solvents
  - think of free  $R^-$  acting as base

- Elimination



- mechanism can be more complex than this

- Metallation



- chelate effect more important than inductive effect!

# Reactivity as Base

- Metallation (2)
  - sometimes an unwanted side reaction of nucleophilic addition/substitution

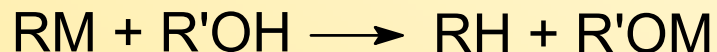


(the enolate is now "protected" from further nucleophilic attack)

- only acidic C-H bonds (acetylenes, cyclopentadiene)  
react without "assistance" by coordinating groups

# Reactivity as Base

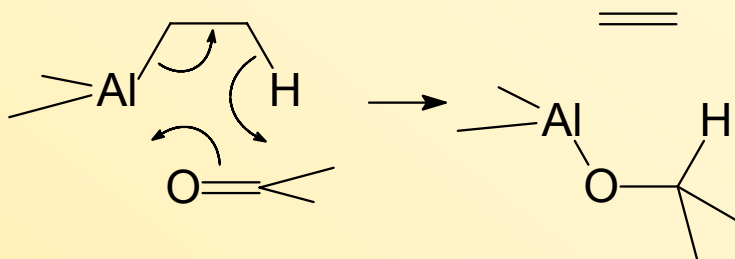
- Reaction with acidic X-H bonds



- also with amines, amides etc (LDA!)
- generally very fast ("complete on mixing")
- important issue when handling polar organometallics
  
- deprotonating X-H bonds is kinetically much easier than C-H bonds

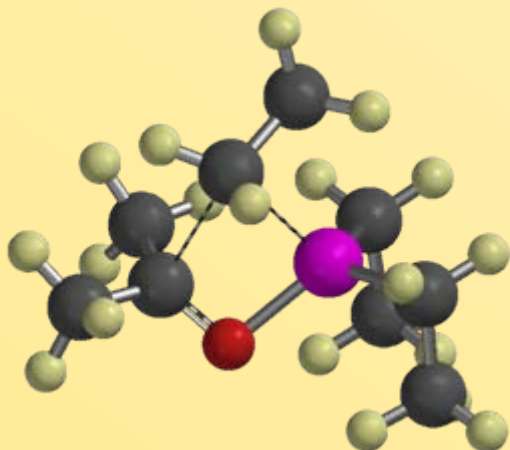
# Reactivity as Reductor

- $\beta$ -hydrogen transfer

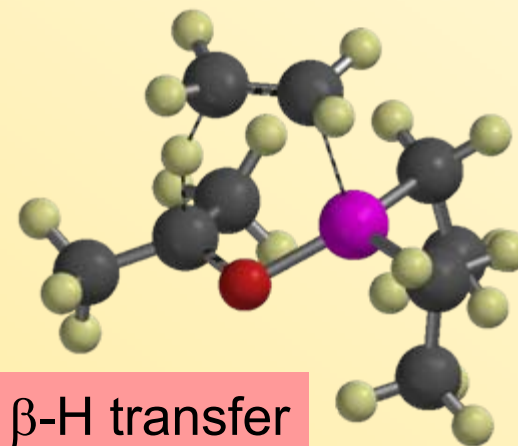
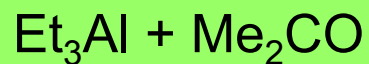


mainly for Al:

- for more electropositive elements, deprotonation and nucleophilic attack are faster
- for less electropositive elements, often no reaction



addition



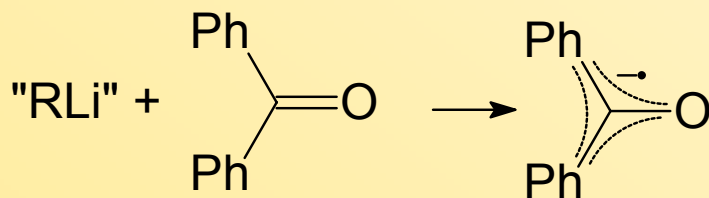
$\beta$ -H transfer

# Reactivity as Reductor

- Single-electron transfer (SET)

For electropositive elements:

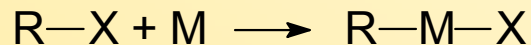
- M has a low electron affinity
- the M-C bonding orbital is high in energy
- SET from there to another molecule is easy



- SET often leads to the same final products as simple addition (via "radical recombination")

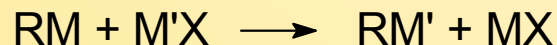
# Synthesis

- Direct synthesis



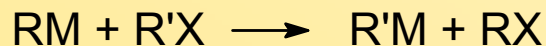
- only for electropositive metals (Li, Mg, ...)

- Transmetallation



- M more electropositive than M'
- reason why organoLi and organoMg compounds are so popular

- Metal-halogen exchange



- mainly for M = Li, X = Br or I, R = alkyl, R' = aryl
- mechanism not completely clear



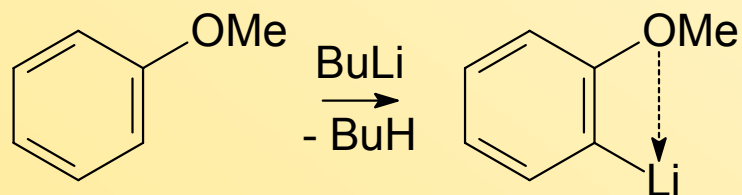
# Synthesis

- Addition of hydrides to olefins



mainly for B, Al

- Metallation of C-H bonds



often assisted/directed by chelate effect