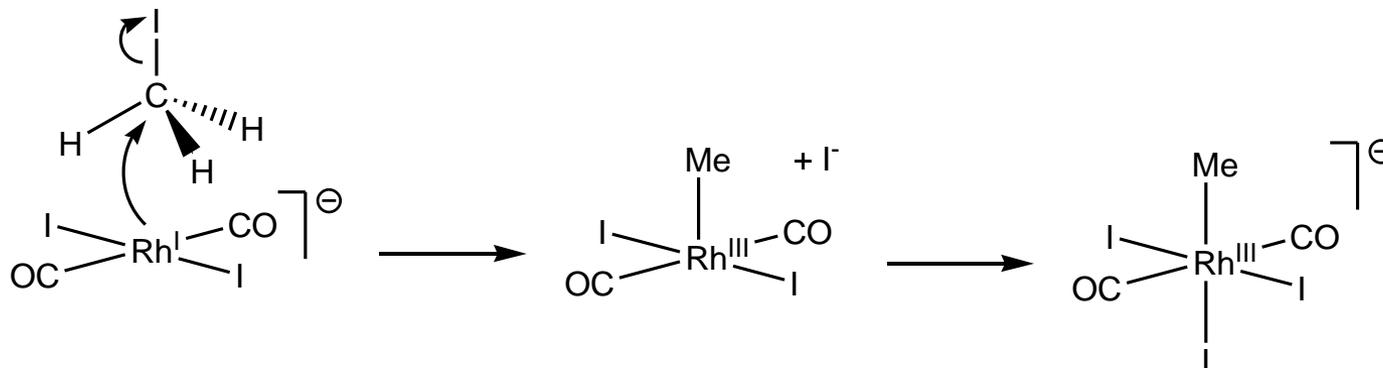
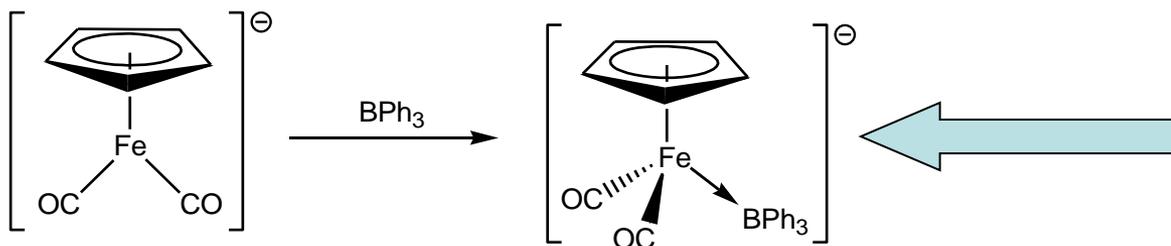
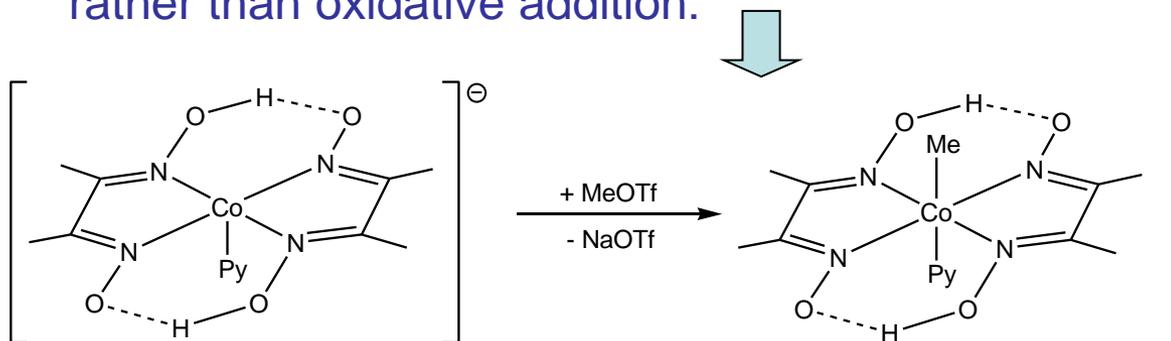


REACTIONS WITH ELECTROPHILES: ELECTROPHILIC ADDITION

- Oxidative addition by S_N2 or Ionic mechanisms involves electrophilic attack on the metal as the first step (see below):



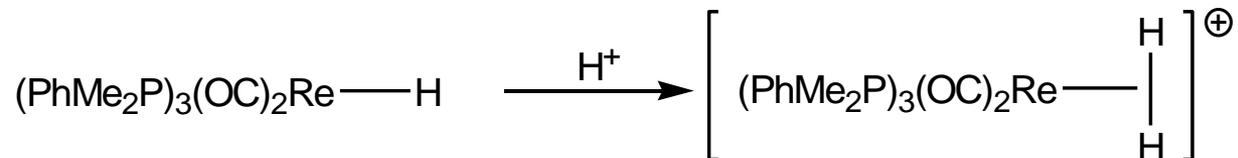
- If the 2nd step doesn't take place, this process is called electrophilic addition rather than oxidative addition:



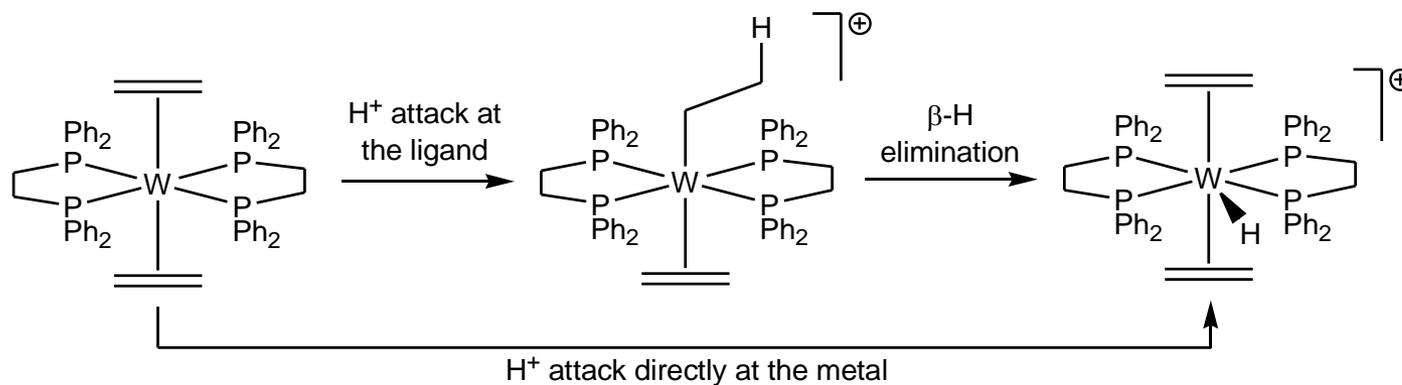
- Electrophilic addition of other zero-electron donor ligands (e.g. AlR_3 or BR_3) at the metal can also occur. However, the formation of stable complexes such as that shown below is extremely rare.

REACTIONS WITH ELECTROPHILES: ELECTROPHILIC ADDITION

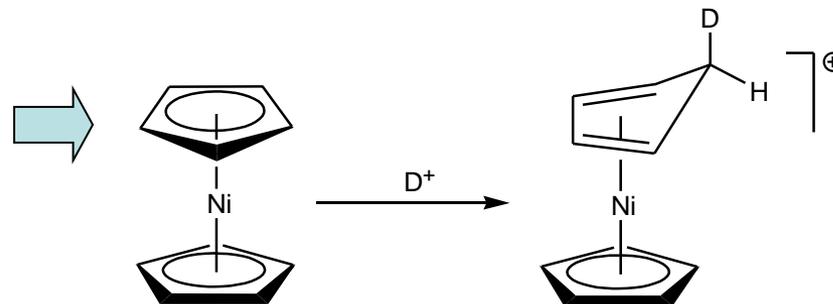
- Protonation of a metal-hydride to give a dihydrogen complex:



- Protonation of an alkene complex. For the example shown below, initial protonation occurs at the ligand *and* at the metal (2 competing pathways).

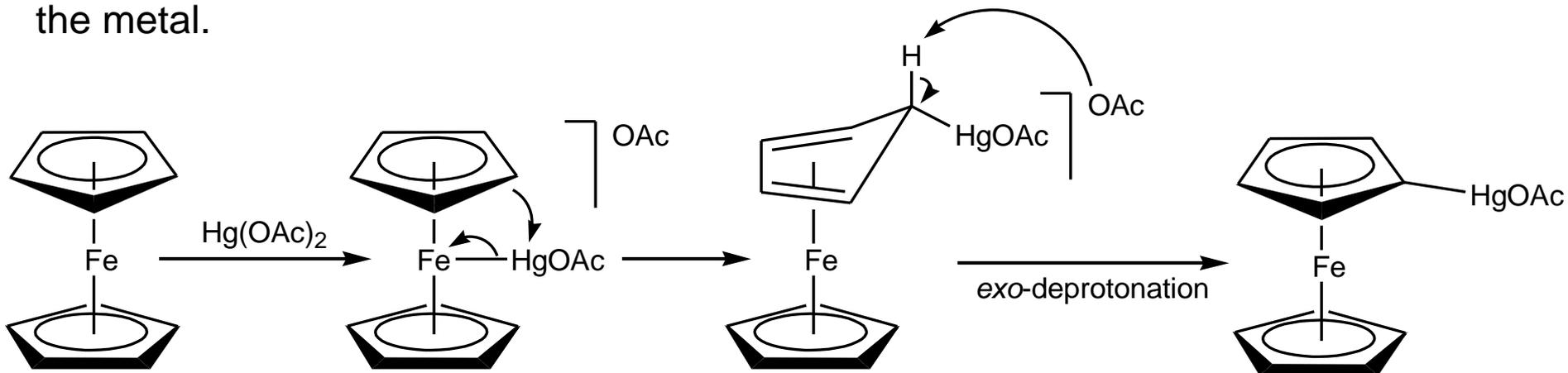


- Direct electrophilic attack by D⁺ on a cyclopentadienyl ring → *exo* attack (on the least hindered face).

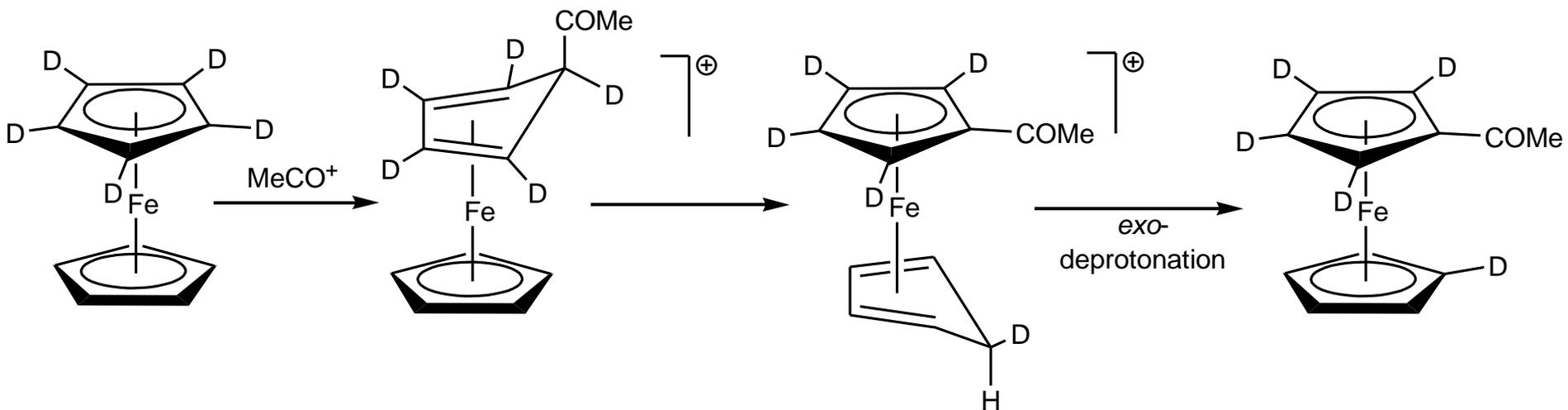


REACTIONS WITH ELECTROPHILES: ELECTROPHILIC ADDITION

- Electrophilic attack {by soft $\text{Hg}(\text{OAc})_2$ } on a cyclopentadienyl ring \rightarrow initial attack at the metal.

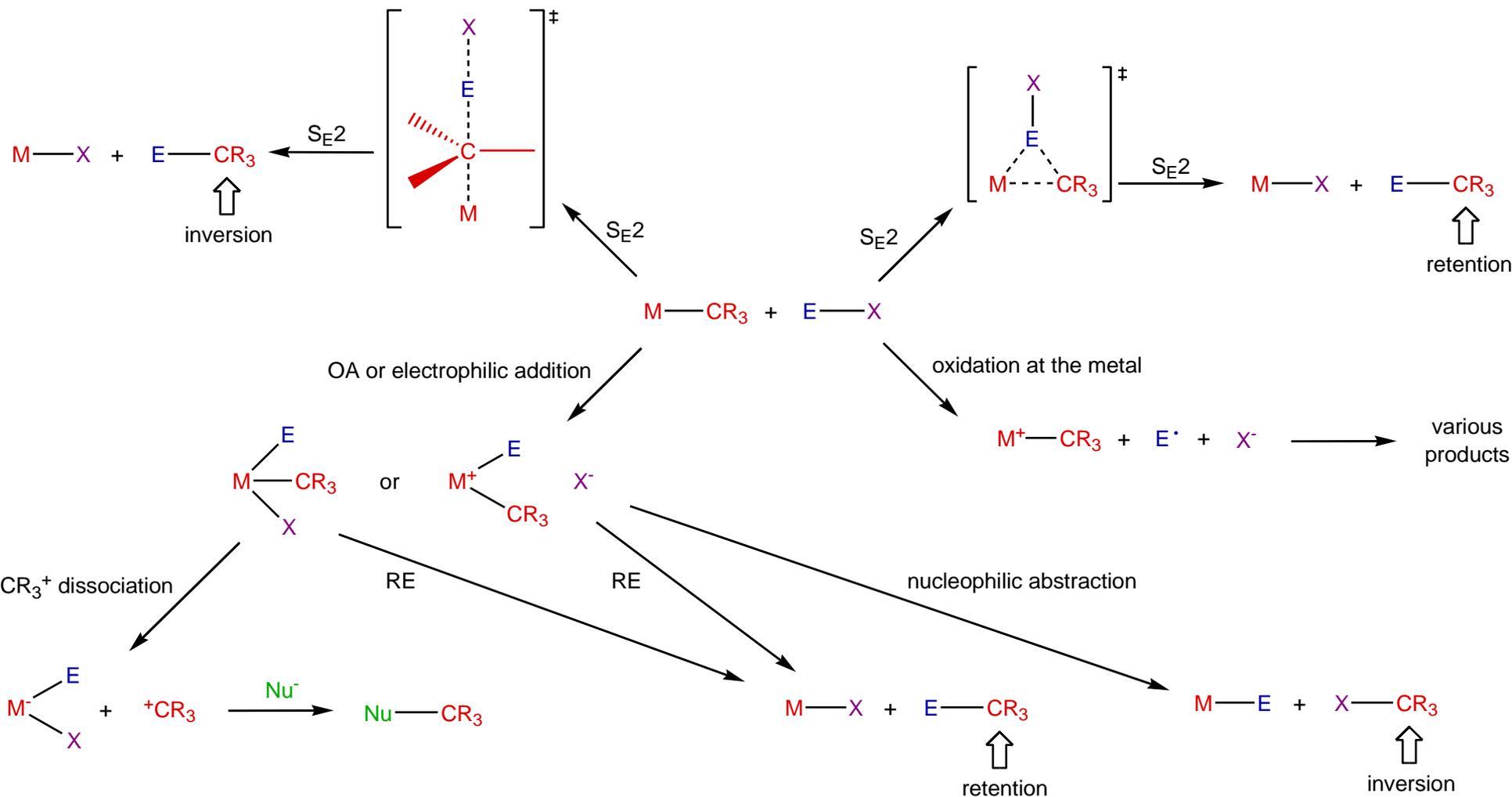


- Electrophilic attack {by hard " COMe^+ " } on a cyclopentadienyl ring \rightarrow initial attack at the ligand (the acetyl cation attacks both the C_5D_5^- and the C_5H_5^- rings, but only attack on the former is shown).



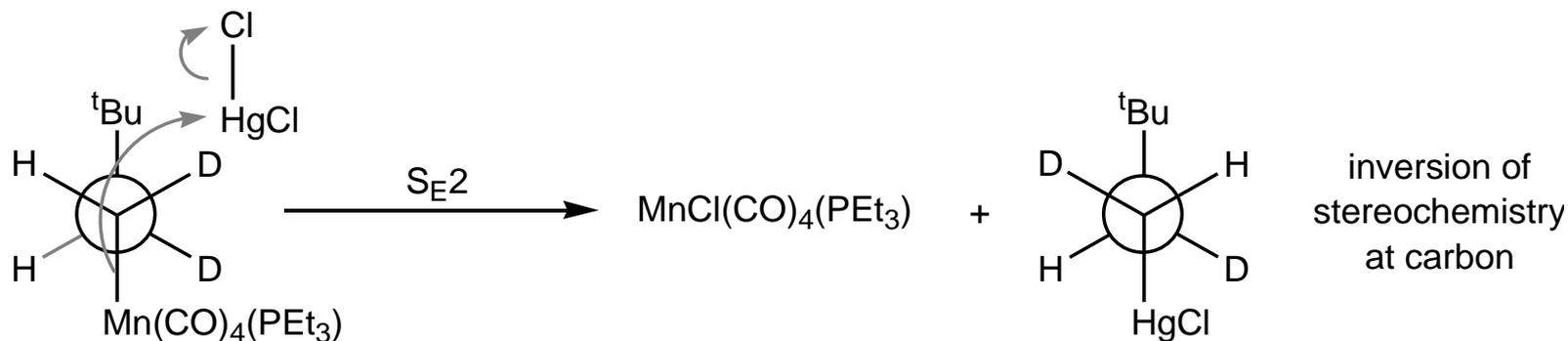
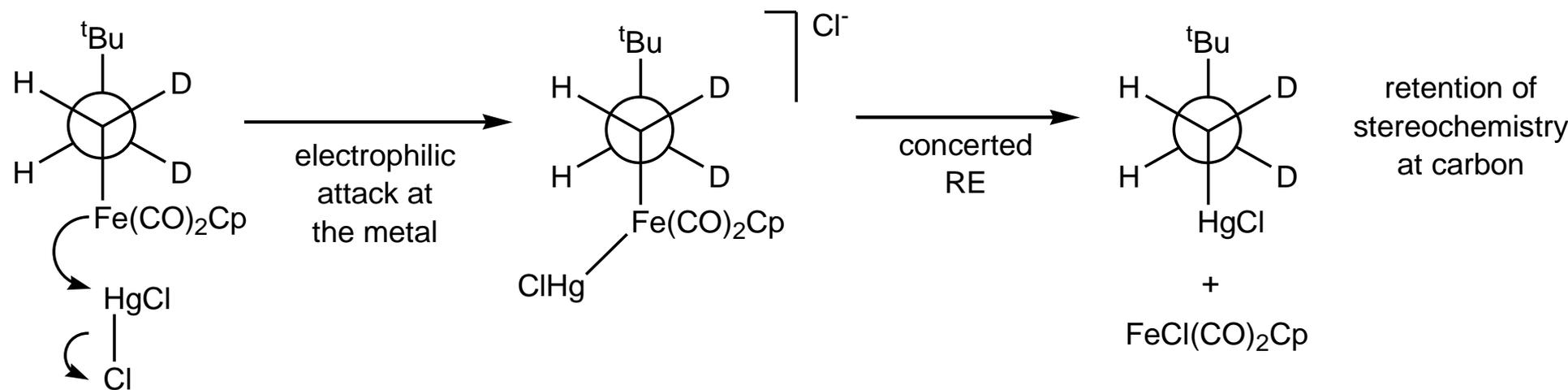
REACTIONS WITH ELECTROPHILES: ELECTROPHILIC ABSTRACTION

- Abstraction of alkyl groups (alkides) is most common
- Can occur by a wide variety of different mechanisms:

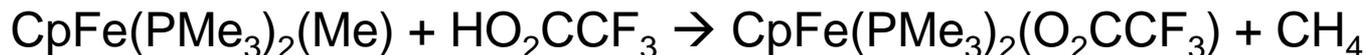


REACTIONS WITH ELECTROPHILES: ELECTROPHILIC ABSTRACTION

- TM alkyls are often cleaved from the metal using X_2 (Cl_2 , Br_2 , I_2), H_2O , HX or HgX_2 .

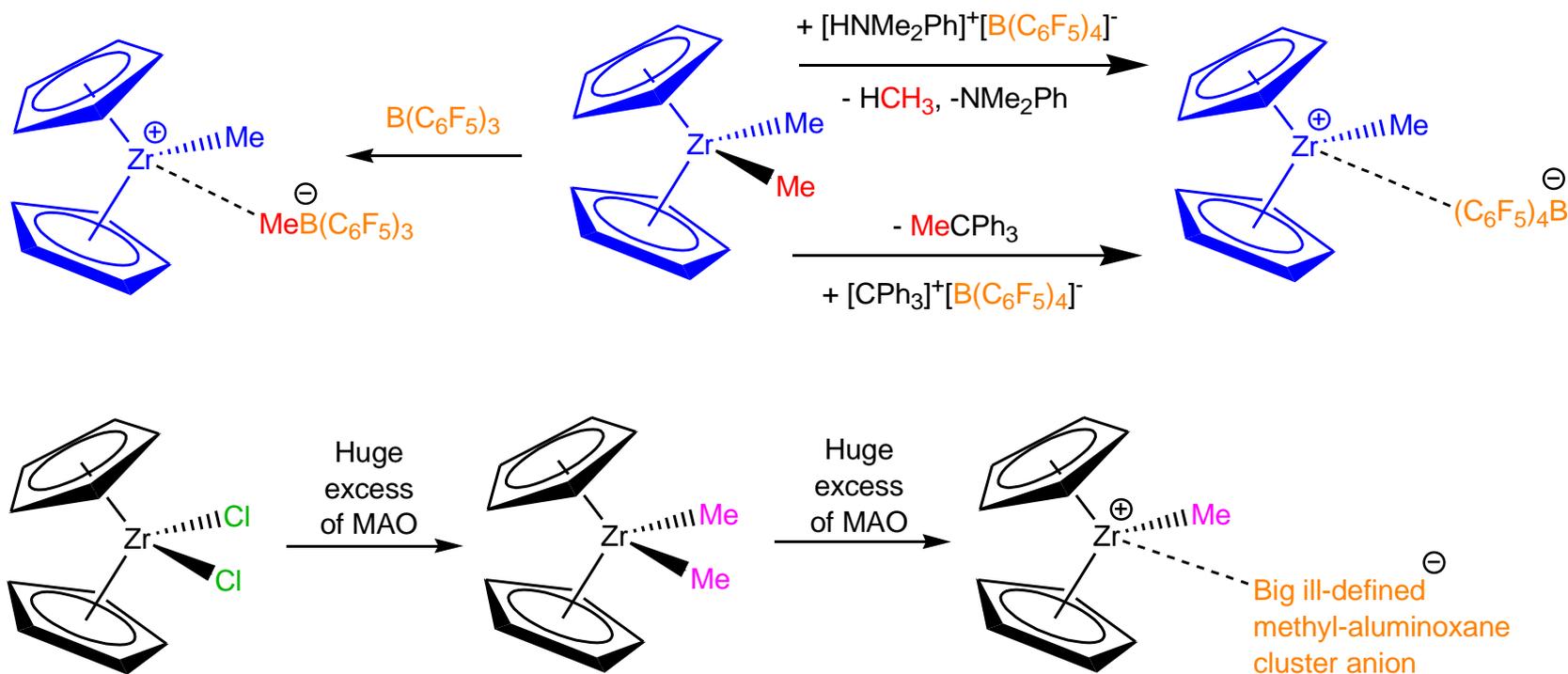


- As with $Li-R$ or $BrMg-R$, $M-R$ bonds in electropositive early TM complexes (e.g. Sc^{III} , Zr^{IV} , Ta^V) are readily cleaved by H_2O . By contrast, late transition metal alkyl complexes are often stable to water, so stronger acids and more vigorous conditions may be required.



REACTIONS WITH ELECTROPHILES: ELECTROPHILIC ABSTRACTION

- While X_2 , H_2O , HX or HgX_2 can be used to effect electrophilic abstraction, the alkyl group is always replaced by another nucleophile (X^- or OH^-).
- By contrast, the electrophiles $[CPh_3]^+[B(C_6F_5)_4]^-$, $B(C_6F_5)_3$ or $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ are often used to remove an alkylidene or hydride, leaving behind a coordinatively and electronically unsaturated, positively charged complex (generally highly reactive).



MAO = $(MeAlO)_n$ = partly hydrolyzed $AlMe_3$ = usually used in 1000x excess.

Thought to be composed of a range of large aluminoxane clusters as well as remaining $AlMe_3$.

WEAKLY-COORDINATING ANIONS (WCA)

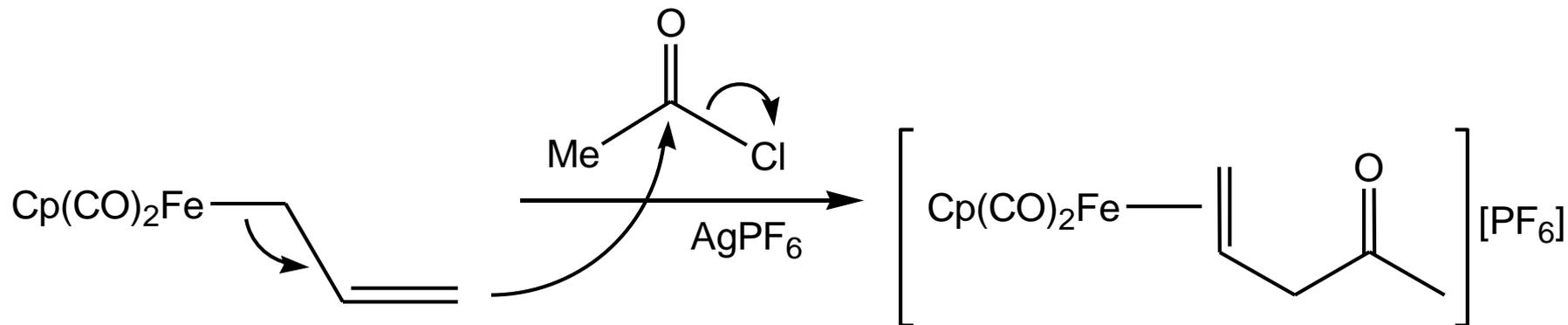
Weakly Coordinating Anions - for an excellent review see I. Krossing, Noncoordinating Anions - Fact or Fiction? - A Survey of Likely Candidates, *Angew. Chem. Int. Ed.*, **2004**, 43, 2066-2090.

Generation	Anions	Properties
G1	Picrate (<i>o</i> -C ₆ H ₂ (NO ₂) ₃ -2,4,6) Perchlorate (ClO ₄ ⁻) Triflate (OSO ₂ CF ₃ ⁻)	Not very “non-coordinating” by modern standards. Picrates and perchlorates are also explosive.
G2	BF ₄ ⁻ , PF ₆ ⁻ , AsF ₆ ⁻ , SbF ₆ ⁻ Sb ₂ F ₁₁ ⁻	Not bad, but often a bit too reactive (prone to giving up F ⁻)
G3	B(C ₆ F ₅) ₄ ⁻ B{C ₆ H ₃ (CF ₃) ₂ -3,5} ₄ ⁻ CRB ₁₁ H ₅ Br ₆ ⁻ (a <i>closo</i> carborane) Sb(OTeF ₅) ₆ ⁻ Al{OC(CF ₃) ₃ } ₄ ⁻ <i>etc.</i>	Excellent WCAs – very unreactive and non-coordinating. They have allowed the preparation of extremely reactive species such as: Cp ₂ ZrMe ⁺ , CH ₃ ⁺ , SiMes ₃ ⁺ , H(OEt) ₂ ⁺ , CCl ₃ ⁺ , ClF ₆ ⁺ , Xe(OTeF ₅) ⁺ , [Cu(CO) ₄] ⁺ , [Pt(CO) ₄] ²⁺ <i>etc.</i>

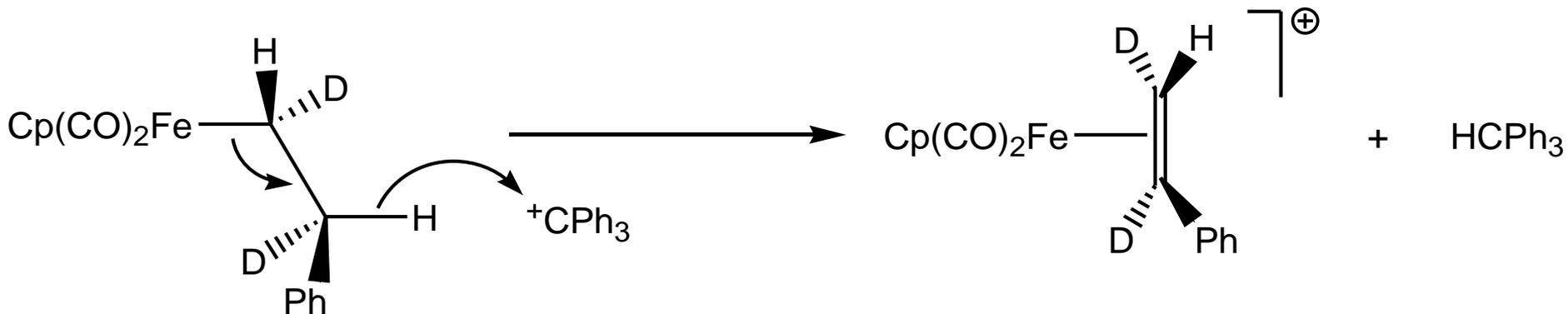
REACTIONS WITH ELECTROPHILES: ELECTROPHILIC ABSTRACTION

Other electrophilic abstraction reactions

- Conjugated substituents such as allyl groups can be removed by electrophilic attack at positions further away from the metal:



- Strong electrophiles can also abstract a substituent from the β-carbon:



REACTIONS WITH ELECTROPHILES: ELECTROPHILIC ABSTRACTION

Other electrophilic abstraction reactions

- Strong electrophiles can also abstract a substituent from the α -carbon:

