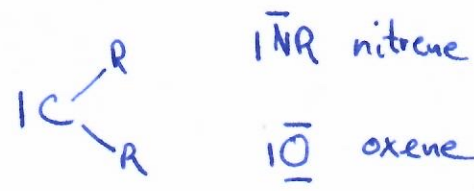


M≡C Multiple Bonds

Carbenes (carbynes)

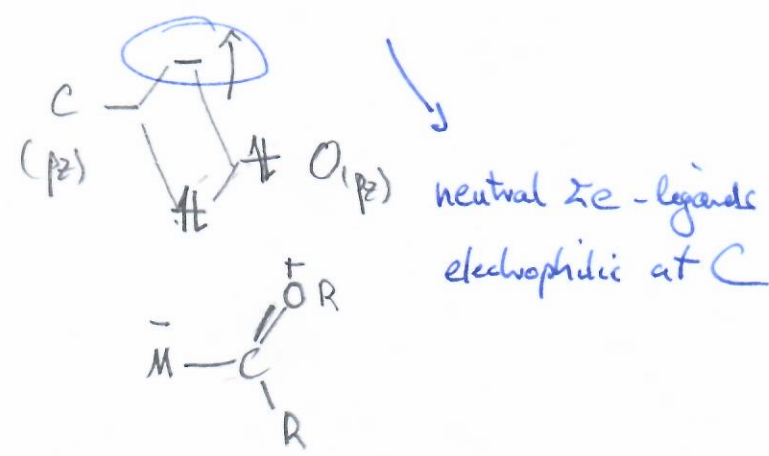
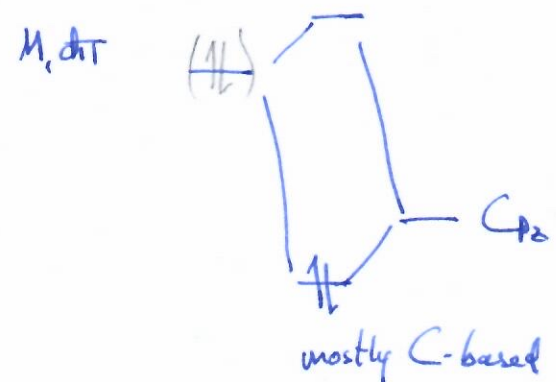
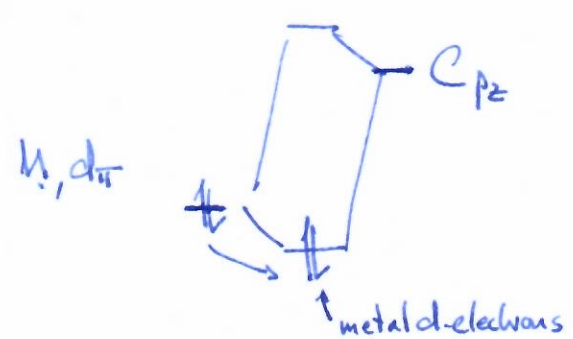


ICH_2
triplet ground state
vary M, L, R... → two extremes

a) Fischer carbenes (ZMC's)
mid to late TMs, rel electronegative
ancillary π -acceptors (CO!)
heteroatom substituents (R = OR, NR₂)

b) Schrock carbenes ('alkylidenes')
early to mid TMs, 2nd, 3rd row
(rel electropositive)
strong donor ligands ($\sigma > \pi$)
alkyl as H on carbene C

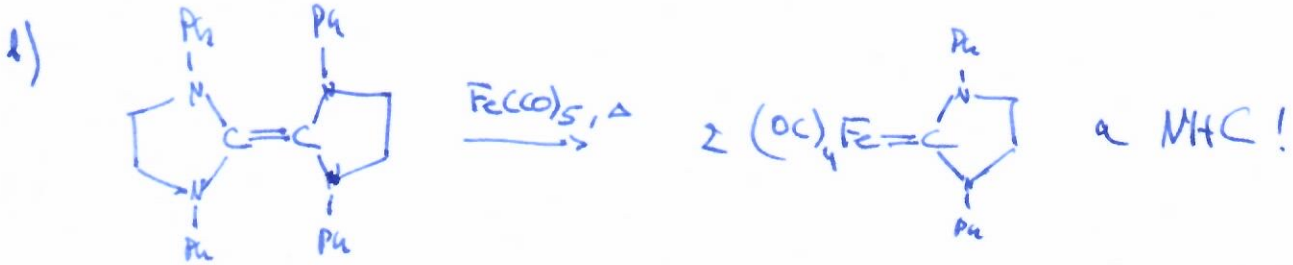
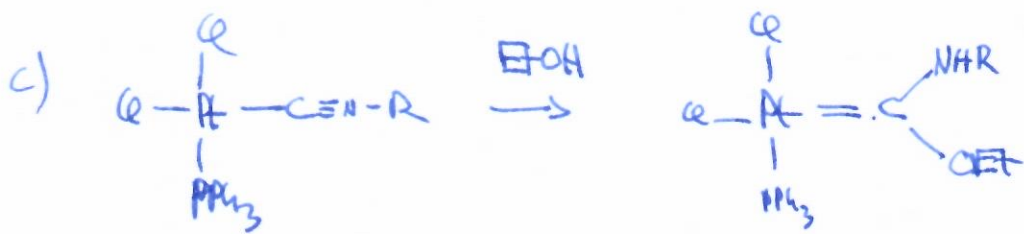
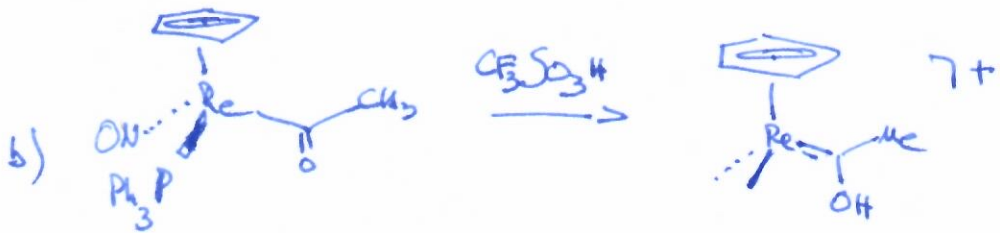
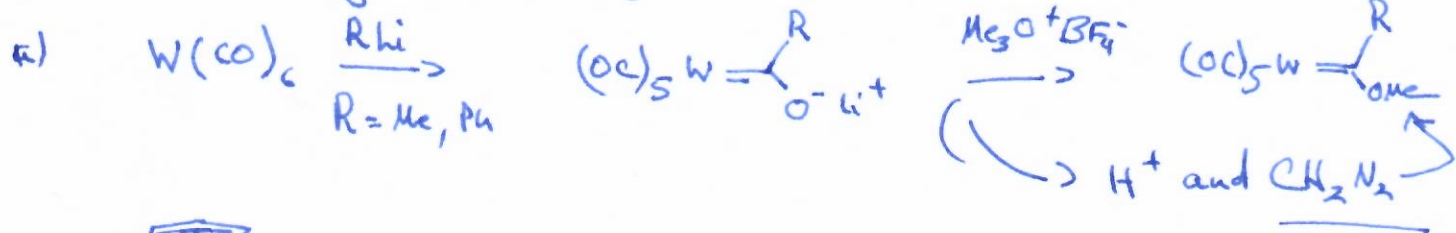
focus on M to C_{p_z} interaction:



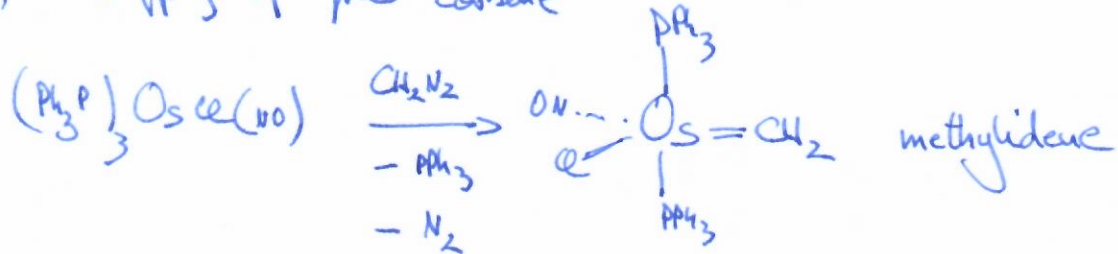
mostly C-based
↓ CR_2^{2-}
formally dianionic
nucleophilic at C
2/4 e^- donor

Synthesis of carbenes

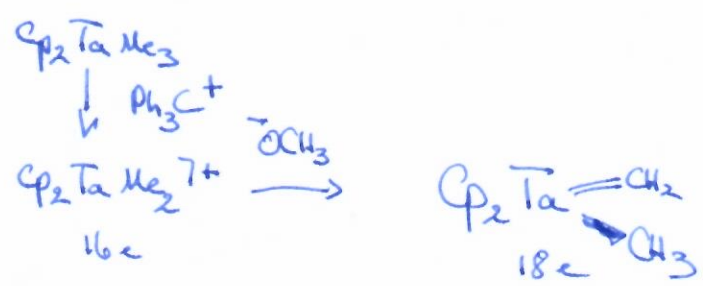
Fischer synthesis (Angew. Chem. IEE 1964, 3, 580 - first carbene!)



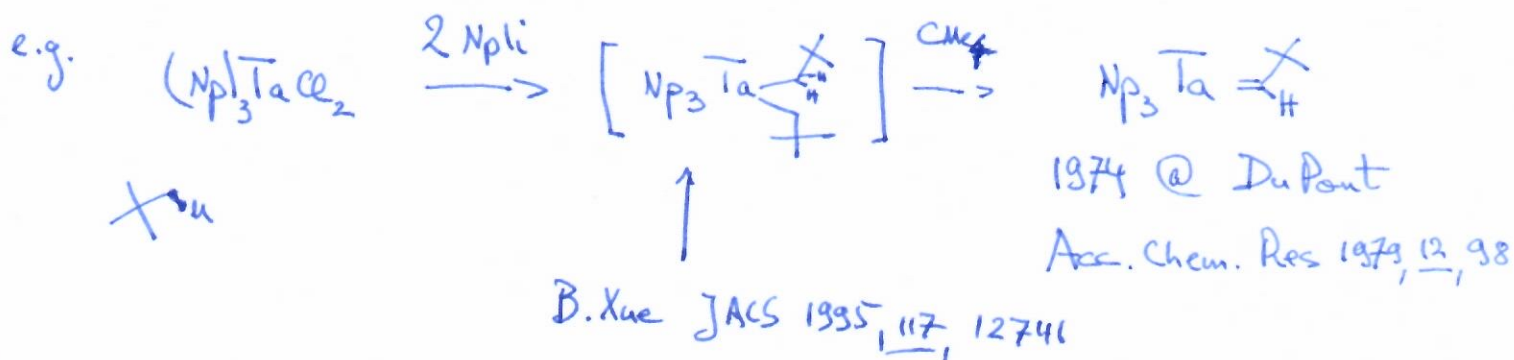
e) trapping of 'free' carbene



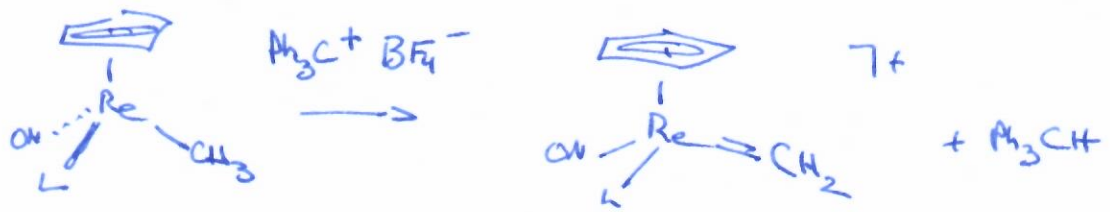
f) deprotonation external base:



g) internal base - α -abstraction



h) hydride abstraction

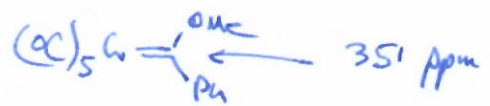
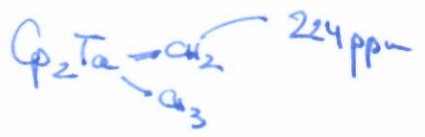


Spectroscopy:

ν_{CO} in $Cr(CO)_6$: 2000 cm^{-1} $M=C=O$
 $(OC)_5Cr = \begin{matrix} \text{OR} \\ | \\ \text{C} \\ | \\ \text{OR} \end{matrix}$: 1953 cm^{-1}

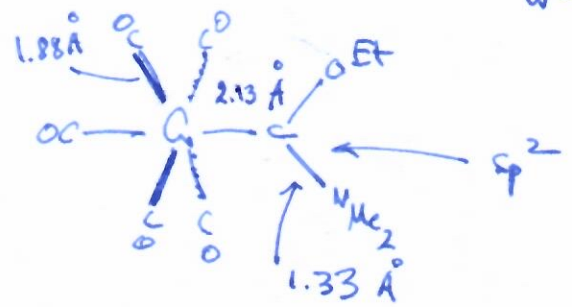
carbene is stronger donor and weaker acceptor than CO

$^{13}C-NMR$: $200 \sim 400 \text{ ppm}$



^1H-NMR : $+20 \rightarrow -10 \text{ ppm}$

$C-C$: $2.04 - 2.17 \text{ \AA}$



$C_{sp^2} - N$: 1.36

$C_{sp^2} = N$: 1.28

