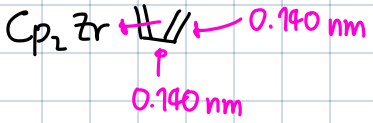
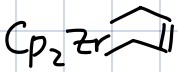
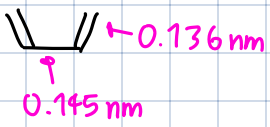
22.11.

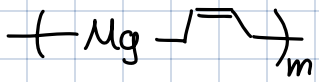
Dienes

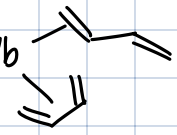


because ⟷  resonance str.

whereas 

⇝ Also seen in $(CO)_3Fe$ 

or 

or $Cp\,NbCl_4 \rightarrow Cp\,Nb$ 

Diene complexes

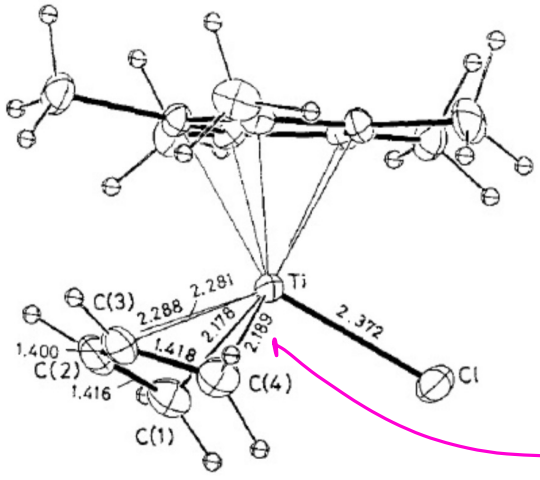
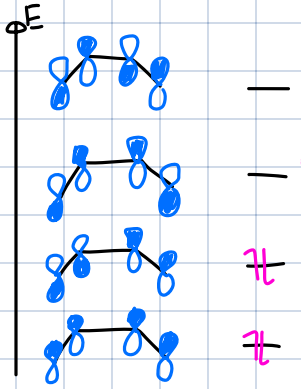


Fig. 1. Molecular structure of a typical s-*cis*-diene complex of type **2**, [TiCp*Cl(butadiene)] (cf. **11b**).

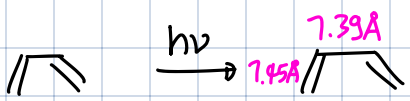
all of them are actually bonding

Angew. Chem. Int. Ed. 1987, 26, 723-742.

⇝ To describe can always draw the MO diag. of butadiene:



e⁻ back donation from the metal

↳ Can excite e^-: 

Also in alkynes the π-backodon. is observed:

Alkyne complexes

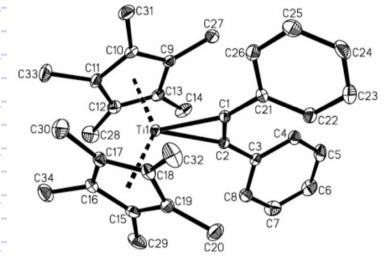
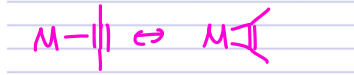


Fig. 1. ORTEP plot of 2. The thermal ellipsoids correspond to 30% probability. For clarity the hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Ti–C_1 2.103(3), Ti–C_2 2.099(3), C_1–C_2 1.306(4), Ti–C_1–C_2 71.7(2).



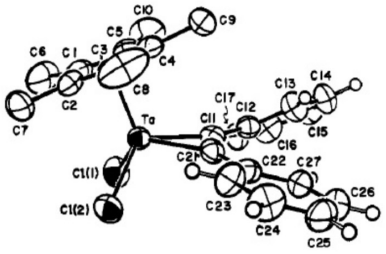


Figure 4. The $Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}PhC{\equiv}CPh)Cl_2$ molecule, viewed from the side and showing the stereochemistry about the tantalum atom.

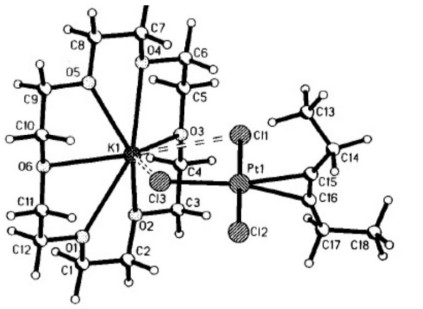
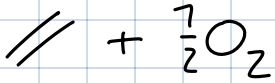


Fig. 2. Molecular structure of [K(18-cr-6)][$PtCl_3$(EtC≡CEt)] (4b).

Angew. Chem. Int. Ed. 1987, *26*, 723-742.
Inorg. Chem. 1981, *20*, 387-393.

7. Wacker Process

 $+ \frac{1}{2}O_2 \xrightarrow[Cu^{2+},H_2O]{PdCl_4^{2-}} CH_3CHO$ (Acetaldehyde)

↑ in form of some salt

 $+ H_2O + PdCl_4^{2-} \longrightarrow CH_3CHO + Pd^0 + 2HCl + 2Cl^-$

$8Cl^- + Pd^0 + 2Cu^{2+} \longrightarrow PdCl_4^{2-} + 2[Cu^{I}Cl_2]^-$

↑ d^{10}, happy in linear geom.

$2[CuCl_2]^- + 2H^+ + \frac{1}{2}O_2 \longrightarrow 2Cu^{2+} + 4Cl^- + H_2O$

⇒ Cu^{2+} is the co-catalyst that is oxidized by O_2

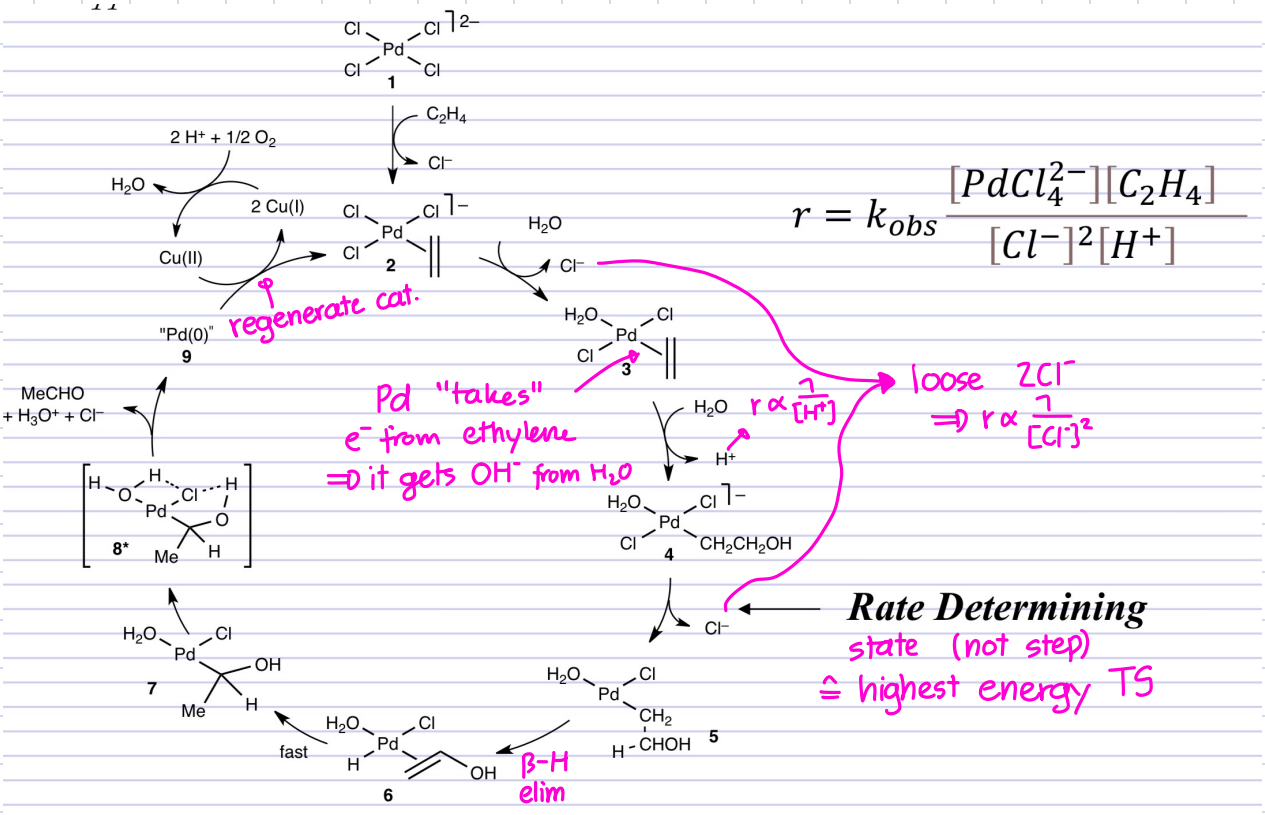
↝ But where do the H^+ come from?
⇒ Try the rxn in heavy water (D_2O):

$$C_2H_4 + D_2O \xrightarrow{O_2,\ cat.} CH_3CHO$$

$$C_2D_4 + H_2O \xrightarrow{O_2,\ cat.} CD_3CDO$$

⇒ All the protons come from the ethylene !

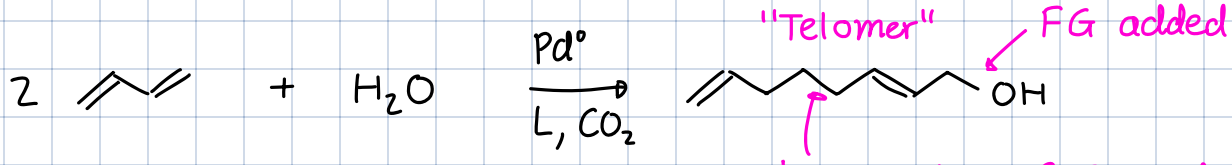
Mechanism:

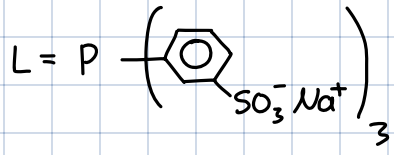


$$r = k_{obs}\frac{[PdCl_4^{2-}][C_2H_4]}{[Cl^-]^2[H^+]}$$

Chem. Eur. J. 2002, 16, 8738.

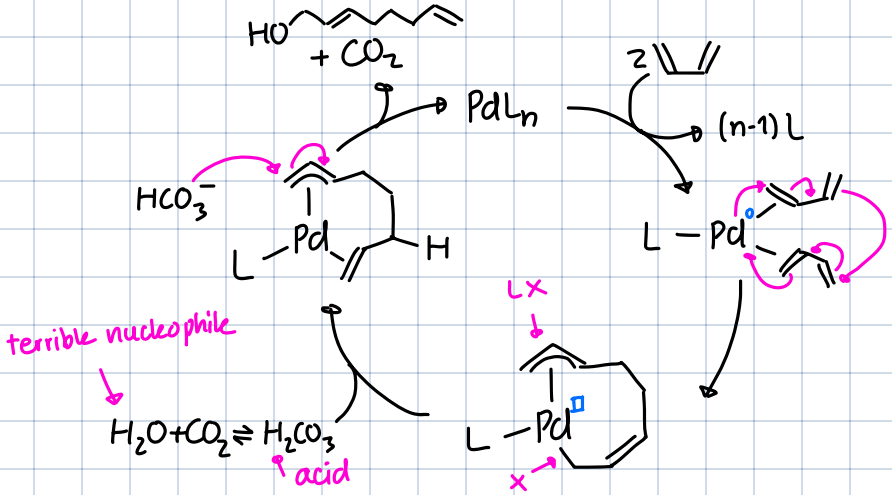
"The beauty of the chemistry of dienes"





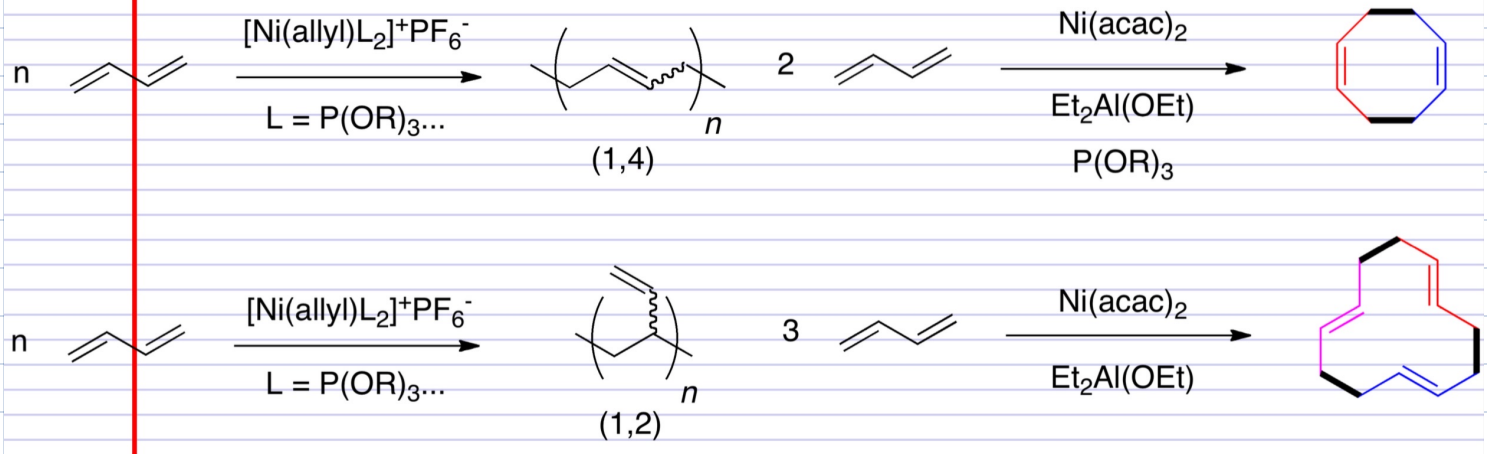
~ Phosphine complex that will stabilize Pd

Mechanism:



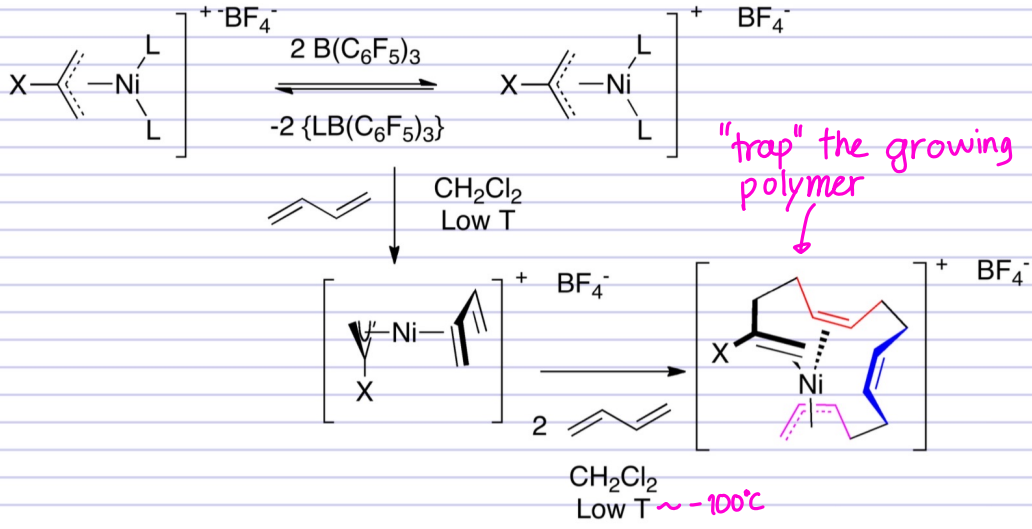
Polymerized telomers are used in tire industry for highly durable rubber

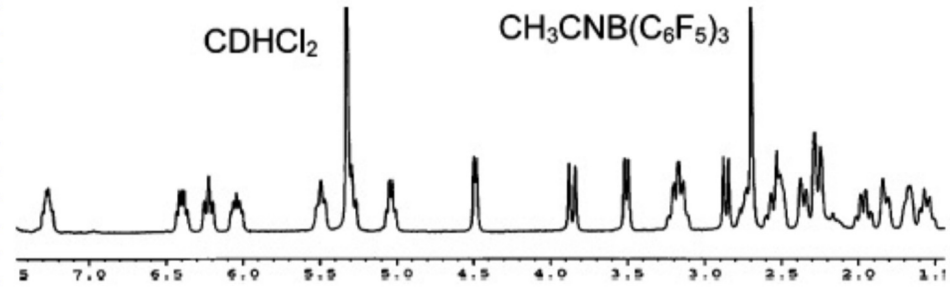
3.2. *Applications: Telomerization vs. Polymerization of Butadienes*



Porri et al.
J. Polym. Sci. C 1967, 16, 2525.
Tobisch, S.
Acc. Chem. Res. 2002, 35, 96.

Wilke G.
Angew. Chem. Int. Ed. 1963, 2, 105.
Henc et al.
J. Organometal. Chem. 1980, 191, 425.





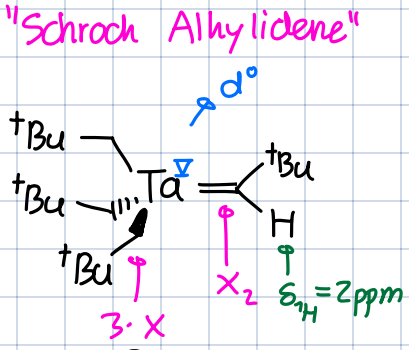
O'Connor et al. J. Am. Chem. Soc. 2007, 129, 4143.

MC double bonds, triple bonds and more

History:

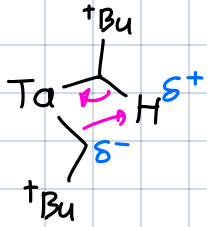
Schrock 1974 → Nobel prize 2005

$TaCl_5 + {}^tBuCH_2MgCl \rightarrow ({}^tBuCH_2)_3TaCl_2$



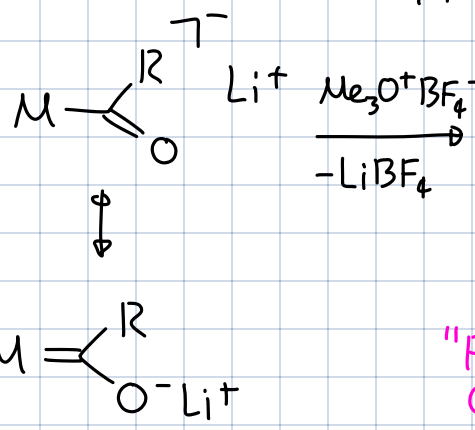
$({}^tBuCH_2)_3TaCl_2 \rightarrow {}^tBuCH_2-Ta(^tBu)_3$ (α-H abstraction)

Subclass of σ-BM



1964 Fischer in Munich discovered a different type of metal alkylidene

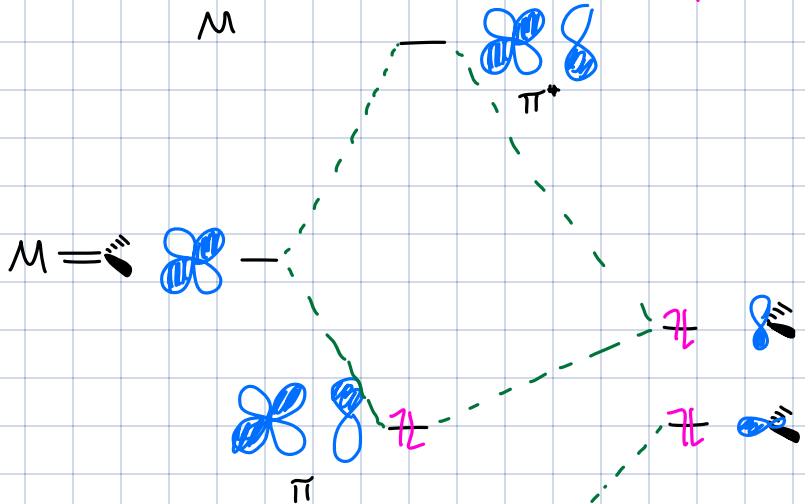
$M(CO)_6 + R-Li \rightarrow$



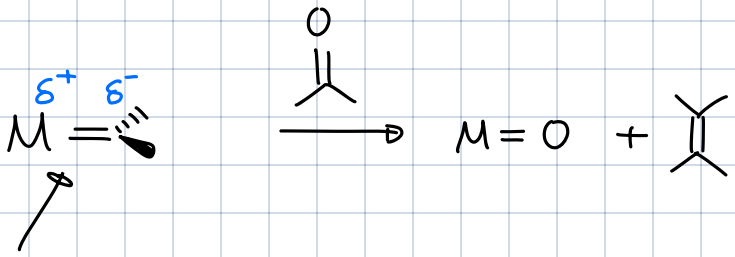
M = Cr, Mo, W

d⁶, 18 e⁻
"Fischer Carbene"

Electronic Structure 1. Schrock Alkylidene



⇒ The e^- are mainly carbon-based (as more electroneg. than M)

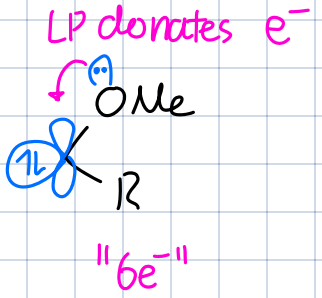
⇒ 

like the Wittig reagent!
"Pseudo-Wittig"

↳ Difference to get Fischer Carbene

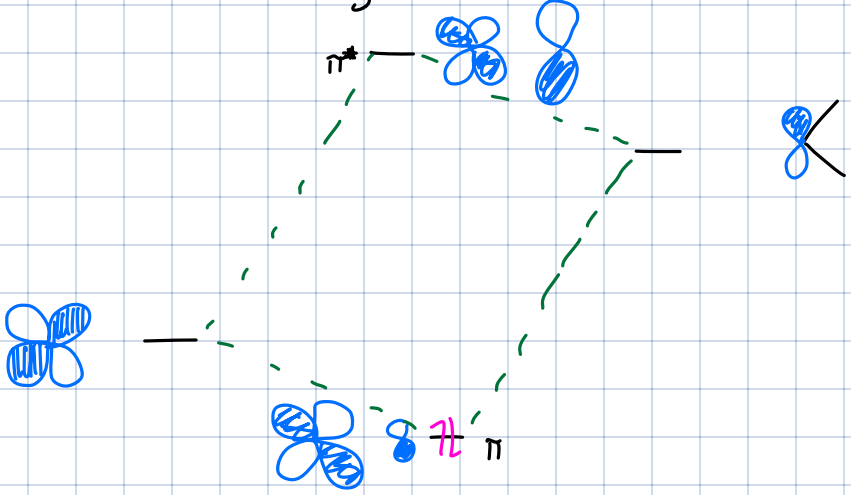
I have plenty of e^- on M, BUT have CO ligands ⇒ Strong π-acceptors that will lower the energy of the d-orbitals

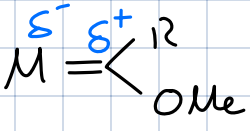
Also the alkyl ligand has OMe ⇒ donate e^-:



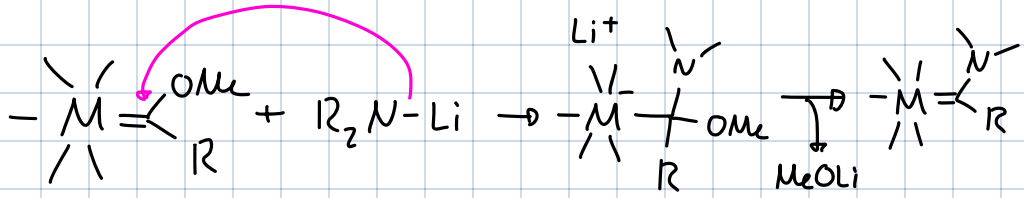
⇓

To get the MO diag.:



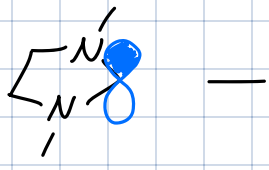
⇒ π-MO is metal-based, 

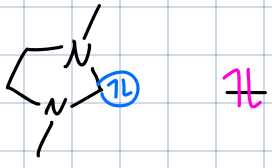
⇒ Reacts as nucleophile:



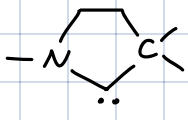
N-Heterocyclic Carbenes (NHCs)
(Arduengo, Bertrand)

→ strong σ-donor
weak π-acceptor

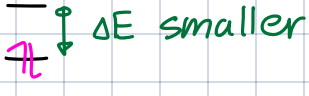




⇒ Can tune how strong σ-don./π-acc., e.g. by



⇒

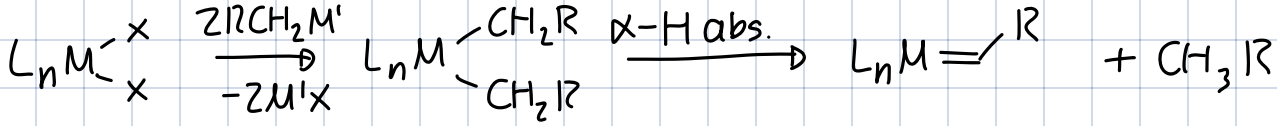


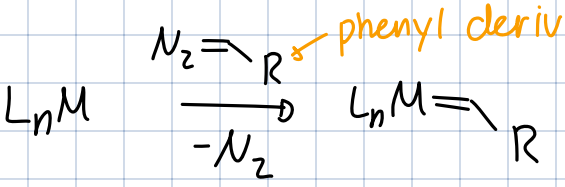
Can also stabilize H^+:

$NHC\cdots H-CNH^{+}$

(or a "soft proton" Au^+): $NHC-Au-CNH^{+}$

Synthesis of (Metal) carbenes

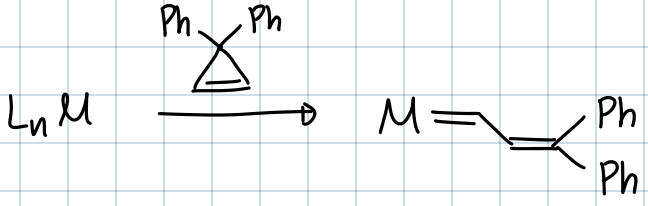




↝ done on multi-ton scale

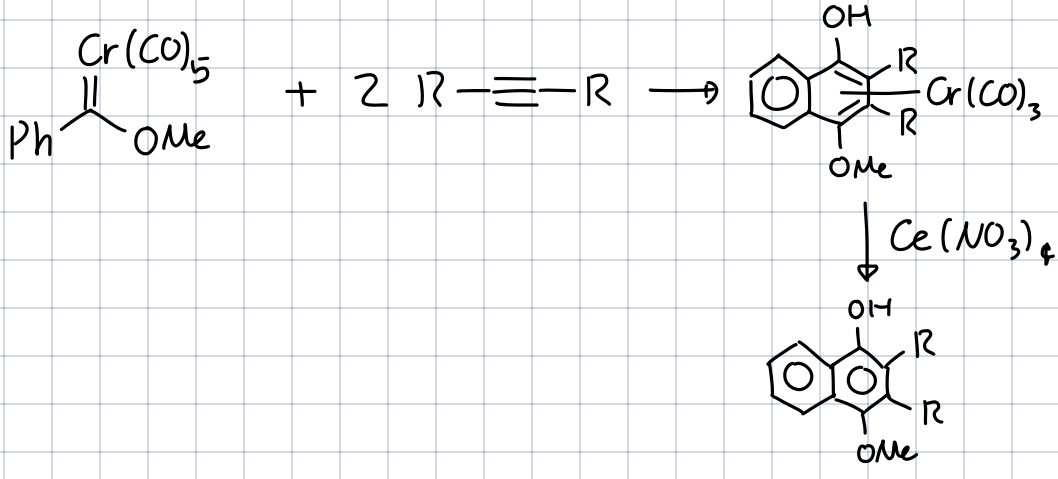
↓

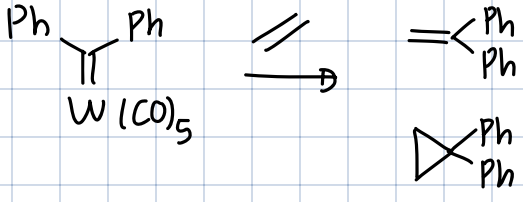
no accident (reported) so far



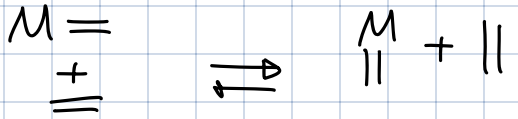
Reactivity:

Fisher Carbenes: Wulff Chemistry





Schroch alkylidene:



[2+2] Cycloaddn.

↝ next week