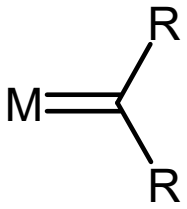
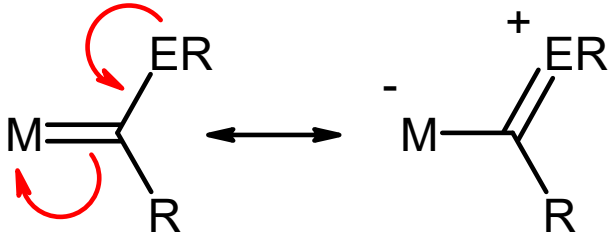
G Alkylidenes (Carbenes)



R = H, alkyl, aryl

Schrock alkylidene

True M=C, hindered rotation



E = O, S, N, P

Fischer carbene

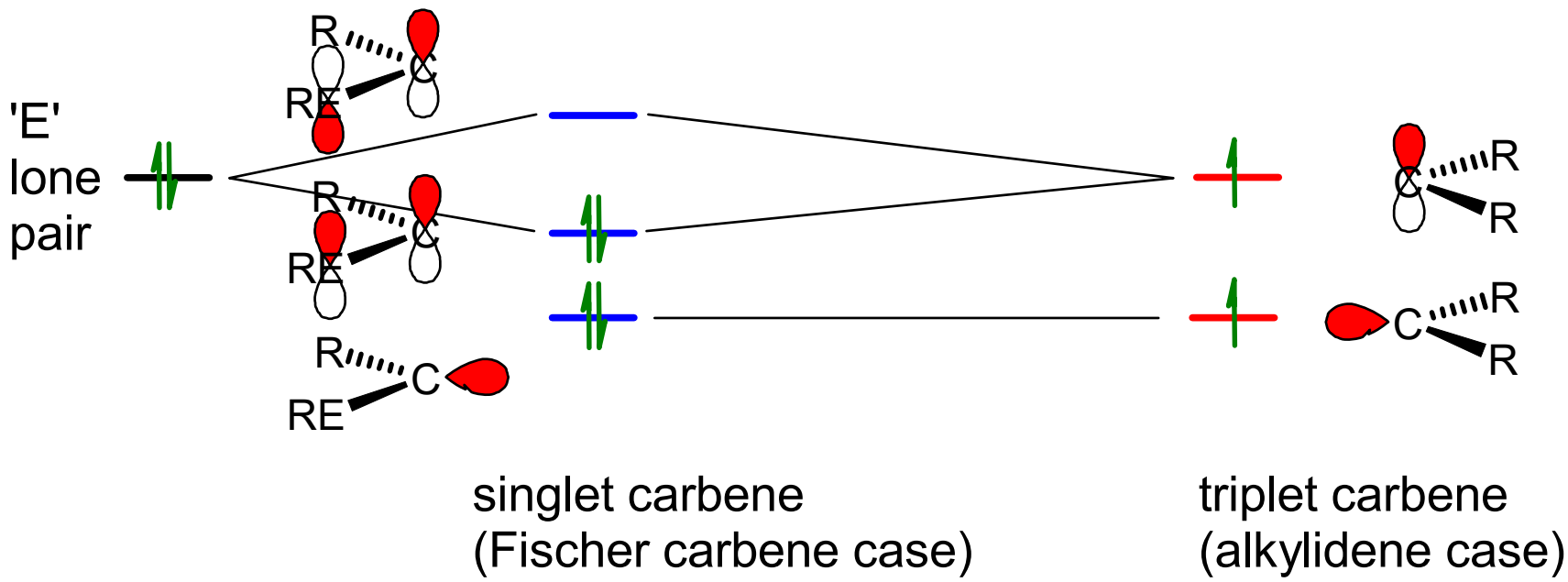
Partial M=C, low barrier to rotation

Table 10-1 Fischer- and Schrock-Type Carbene Complexes

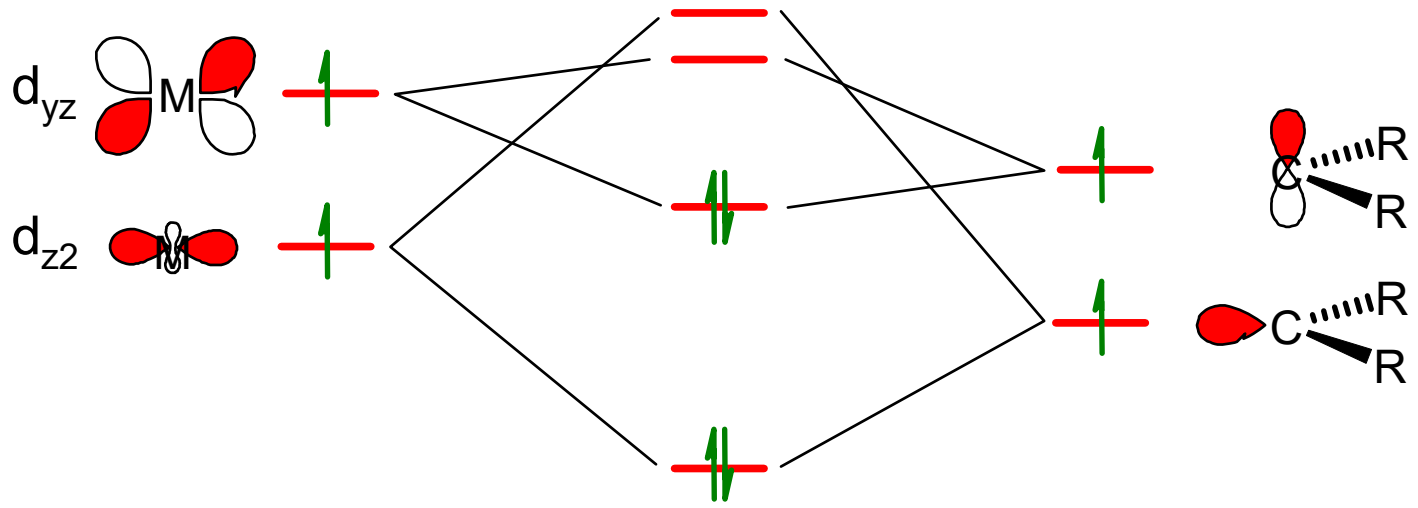
Characteristic	Fischer-Type	Schrock-Type (Alkylidenes)
Typical metal [ox. state]	Middle to late transition metal [Fe(0), Mo(0), Cr(0)]	Early transition metal [Ti(IV), Ta(V)]
Substituents attached to $C_{carbene}$	At least one electronegative heteroatom, e.g., O or N	H or alkyl
Typical ligands also attached to metal	Good π acceptor, e.g., CO	Good σ or π donor, e.g., Cp, Cl, alkyl
Electron count	18 e^-	10-18 e^-
Typical chemical behavior	Nucleophile attacks at $C_{carbene}$	Electrophile attacks at $C_{carbene}$
Ligand type	L	X_2

Bonding picture

the free carbene:



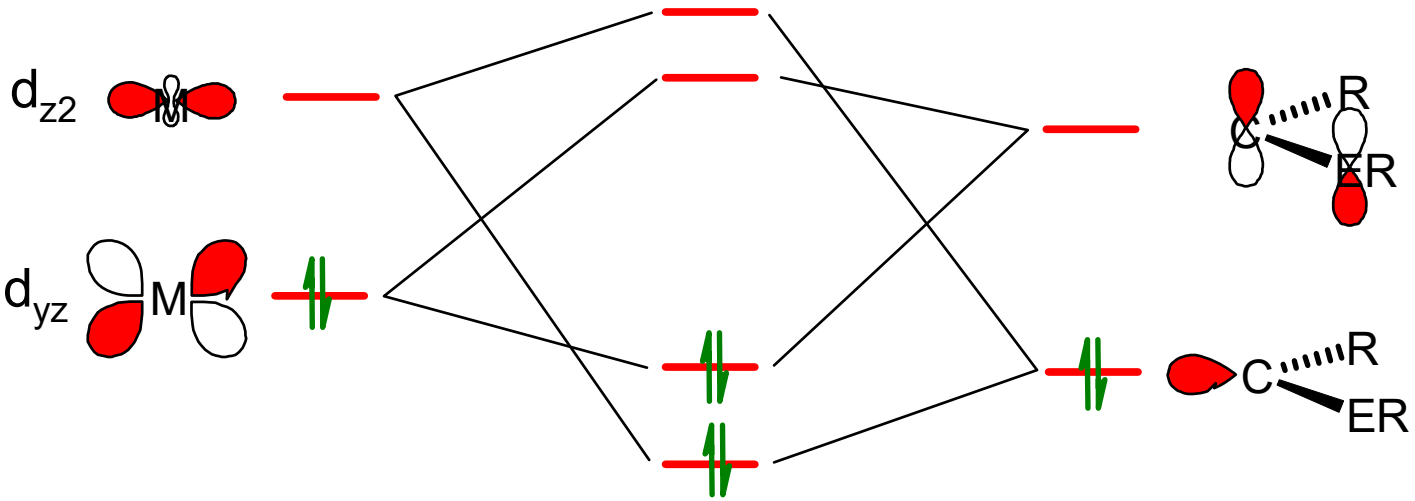
the metal complexes:



alkylidene case

HOMO has more C character so this is the site of electrophilic attack

LUMO has more M character so this is the site of nucleophilic attack



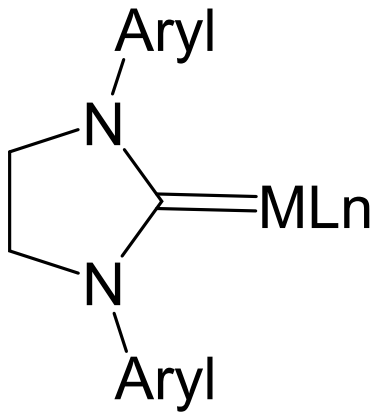
Fischer carbene case

HOMO is mainly metal in character so electrophiles attack the metal

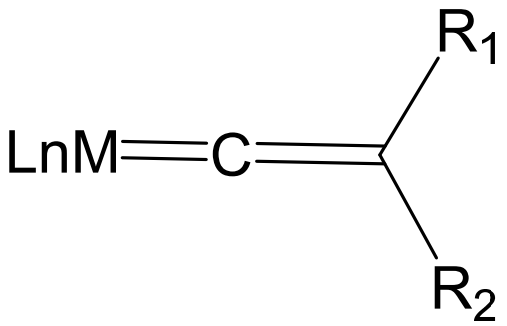
LUMO is mainly C in character so nucleophiles attack the C

Two related classes:

N-heterocyclic carbenes (NHC's)

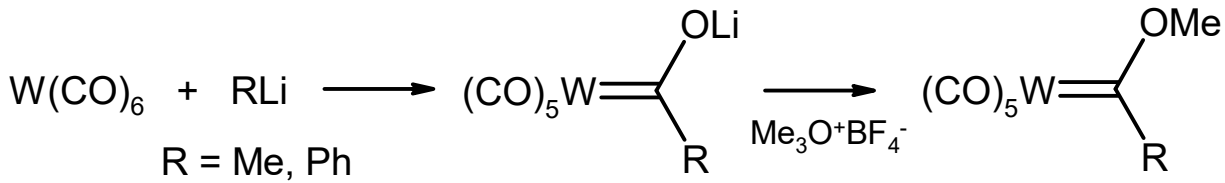


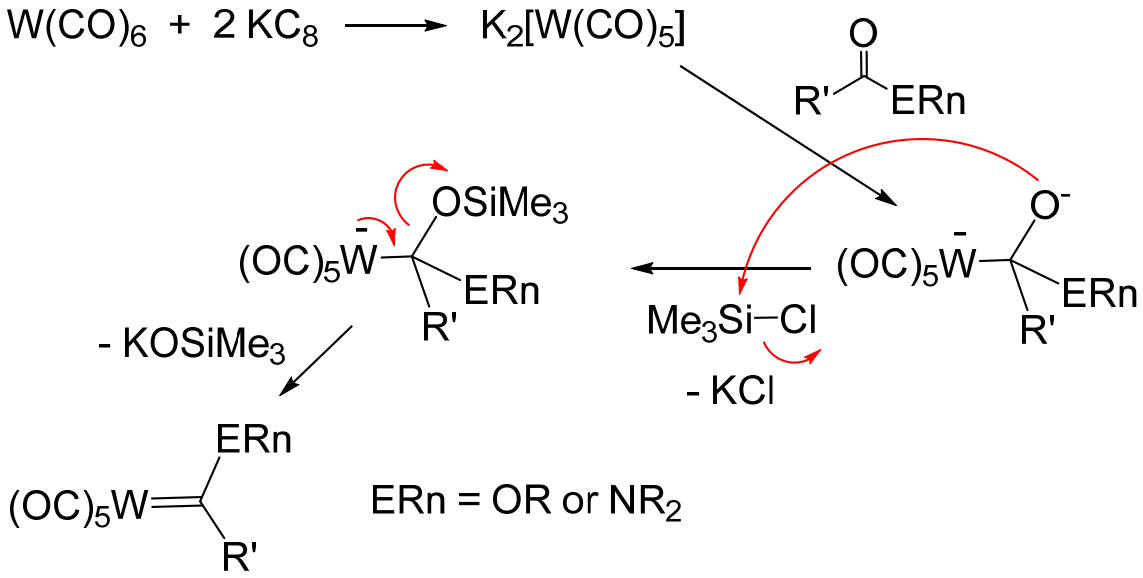
vinylidenes



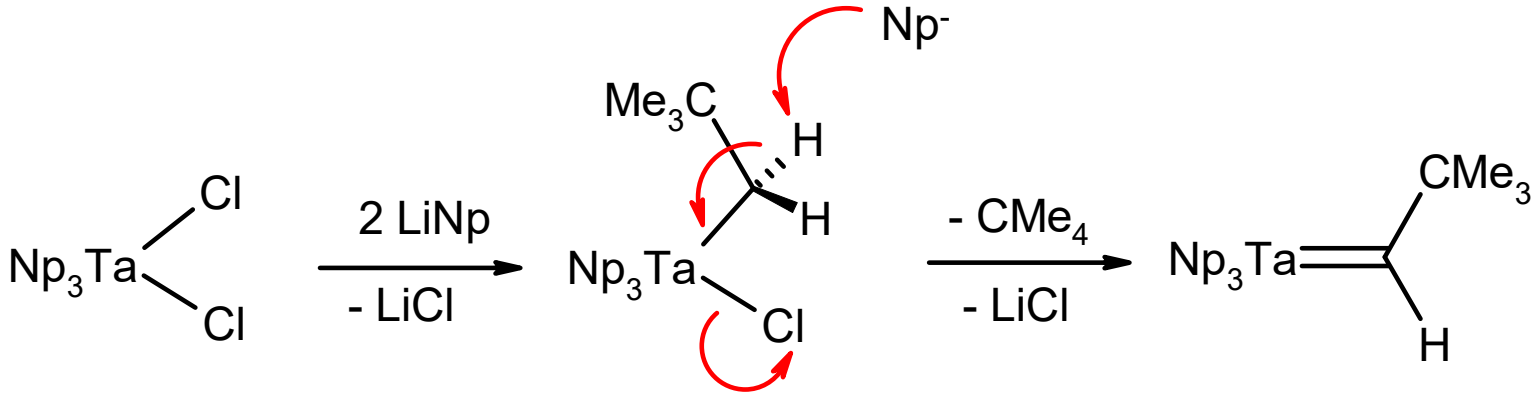
Synthesis

Fischer carbenes





Schrock alkylidenes

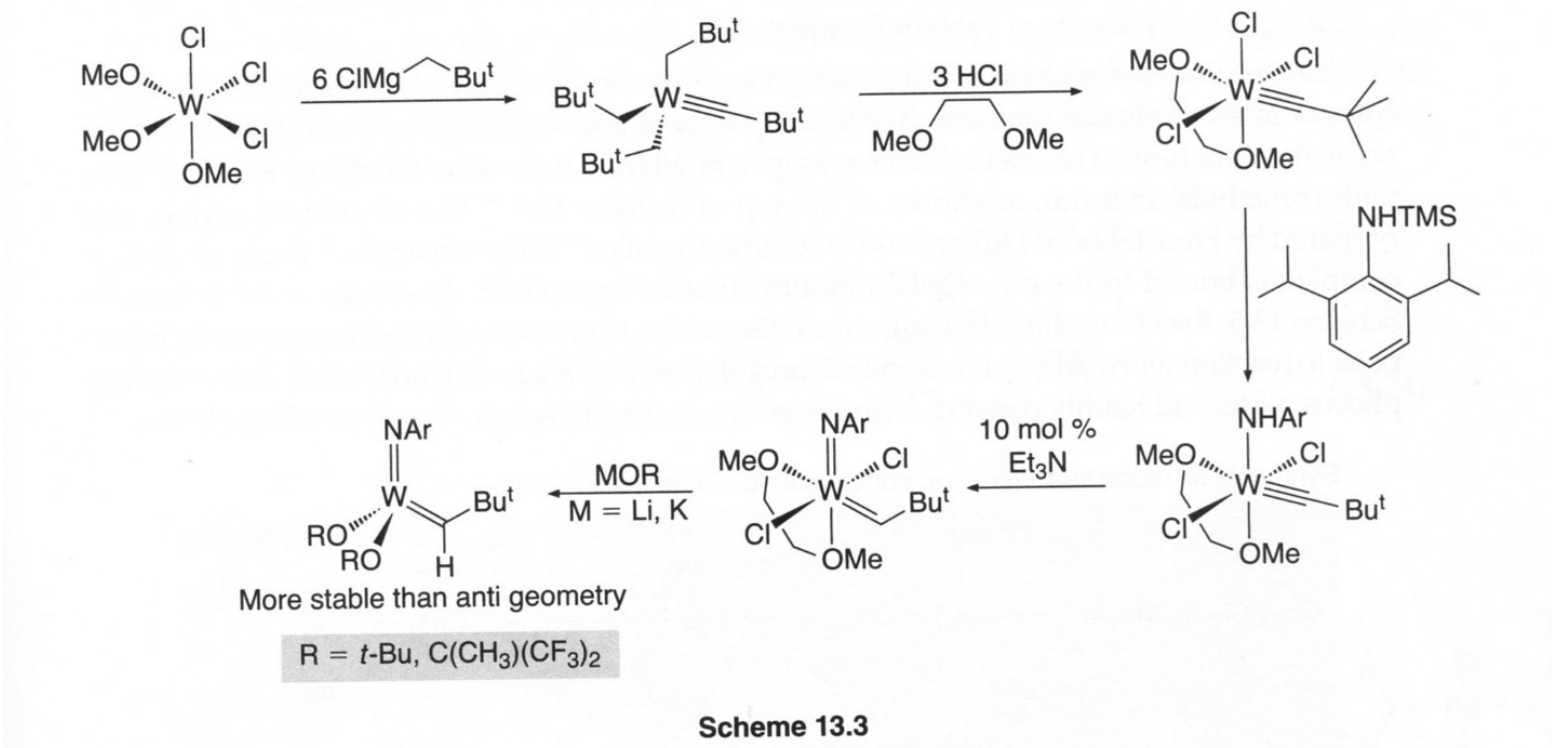


Np = Me_3CCH_2

$$OsCl(NO)(PPh_3)_3 + RCHN_2 \longrightarrow Cl(NO)(PPh_3)_2Os{=}CHR + PPh_3 + N_2$$

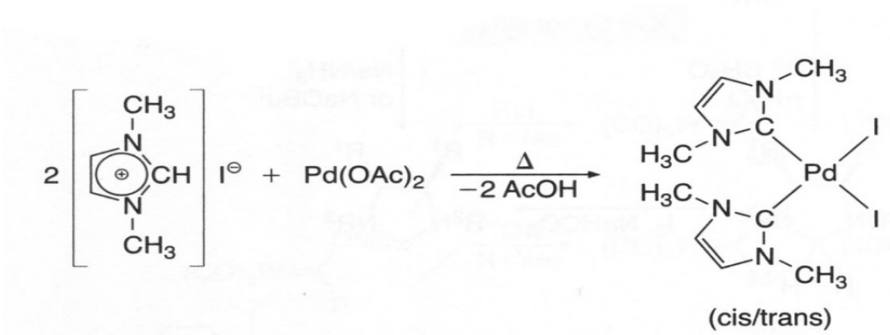
R = Me, Ph, H

Classic Schrock Alkylidene Catalyst

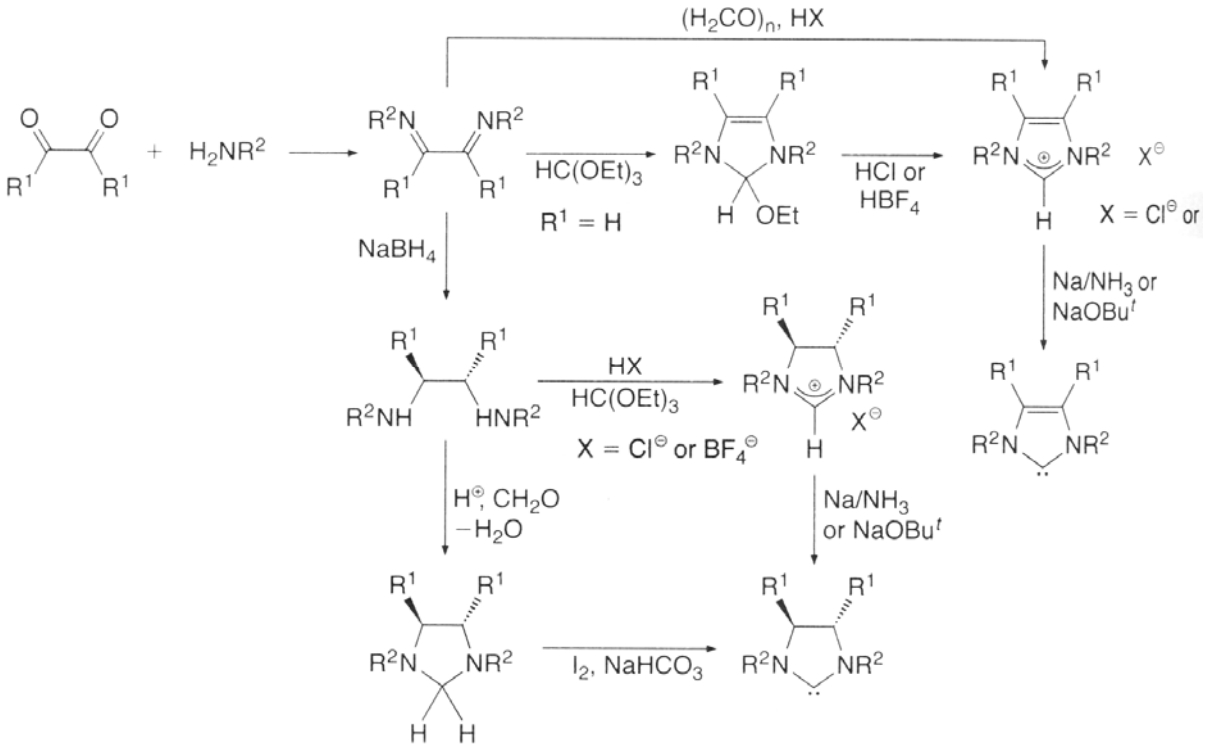


Scheme 13.3

NHC Synthesis: from carbene precursors



or the stable free carbene



Vinylidene synthesis: terminal alkyne rearrangement