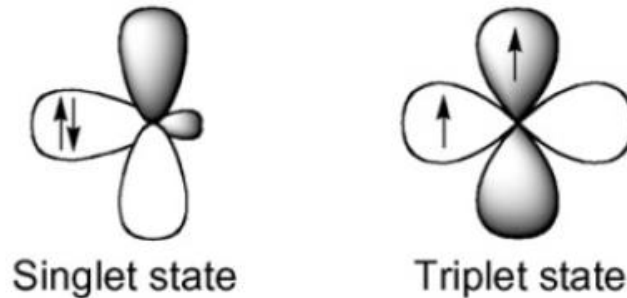
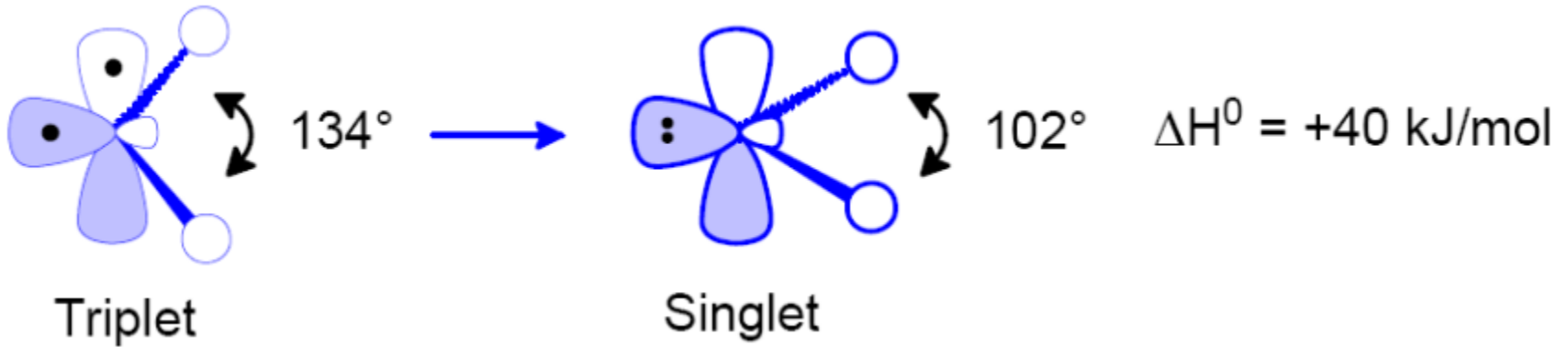
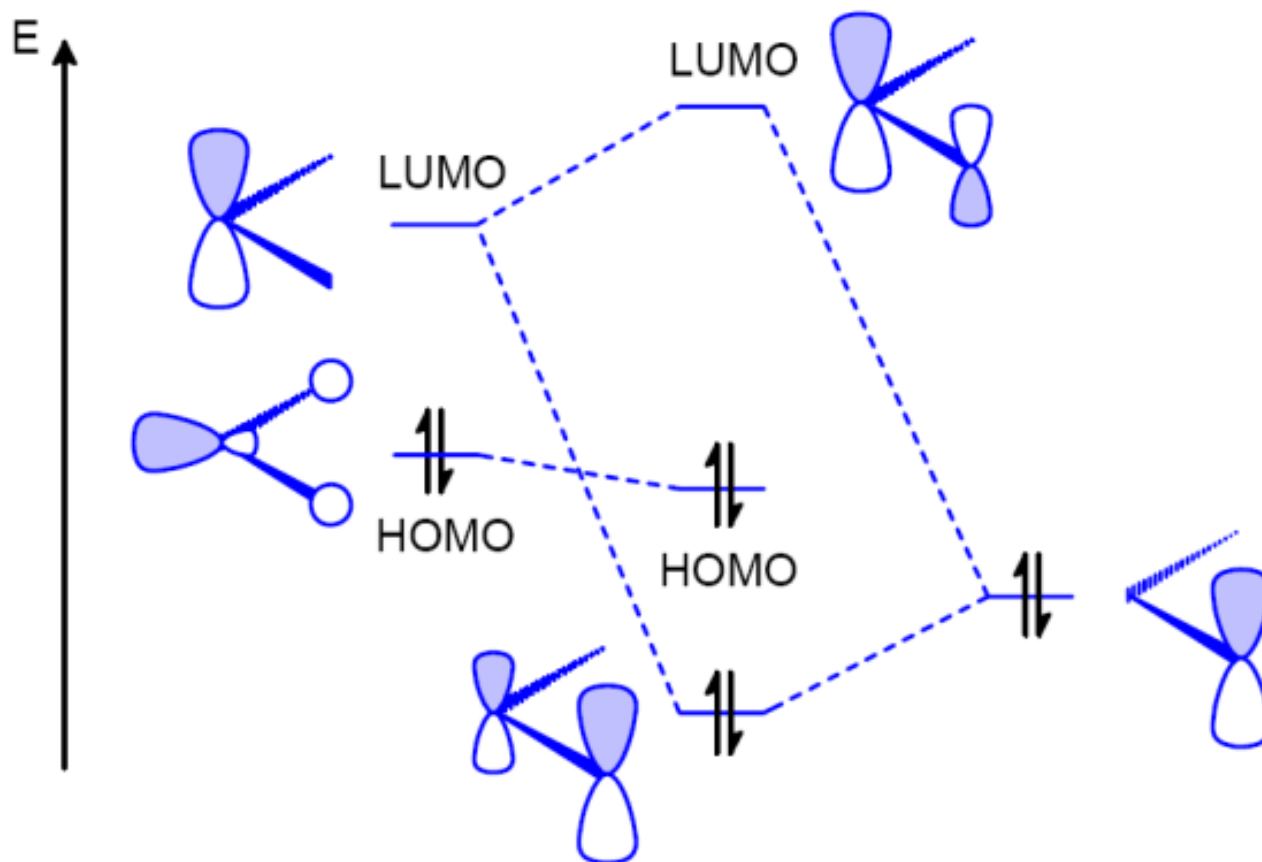


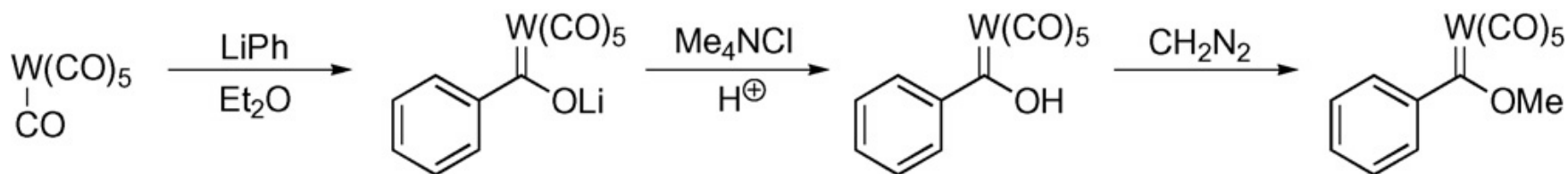
# Carbeni



# Sostituenti $\pi$ -donatori stabilizzano lo stato di singoletto

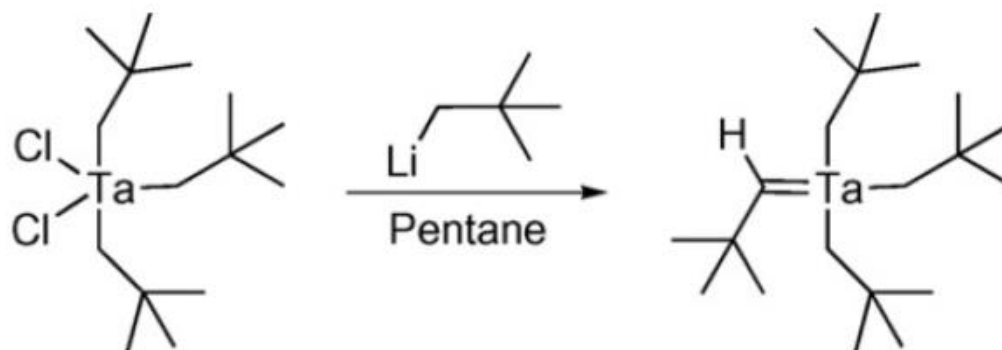


# 1964: primo complesso metallo-carbene (*Fischer*)

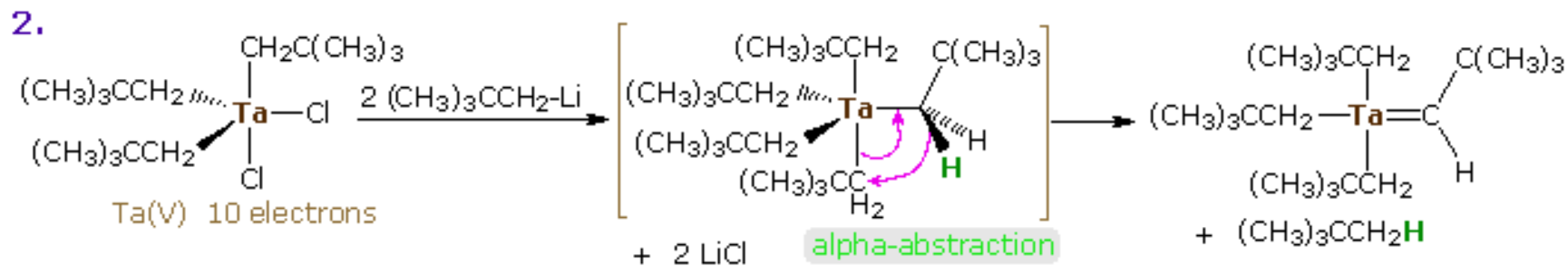


*metossifenilmetilene tungsteno(0) pentacarbonile*

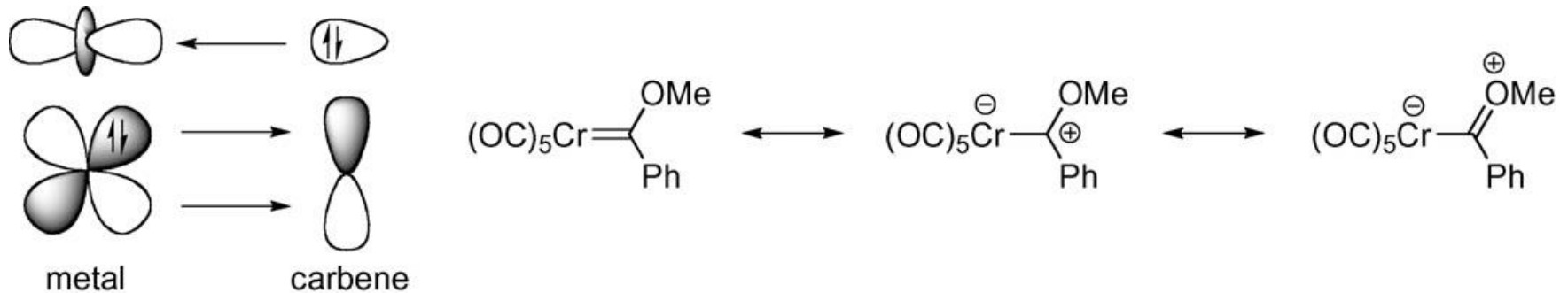
# 1974: primo complesso metallo-alchilidene (Schrock)



$\alpha$ -hydrogen abstraction

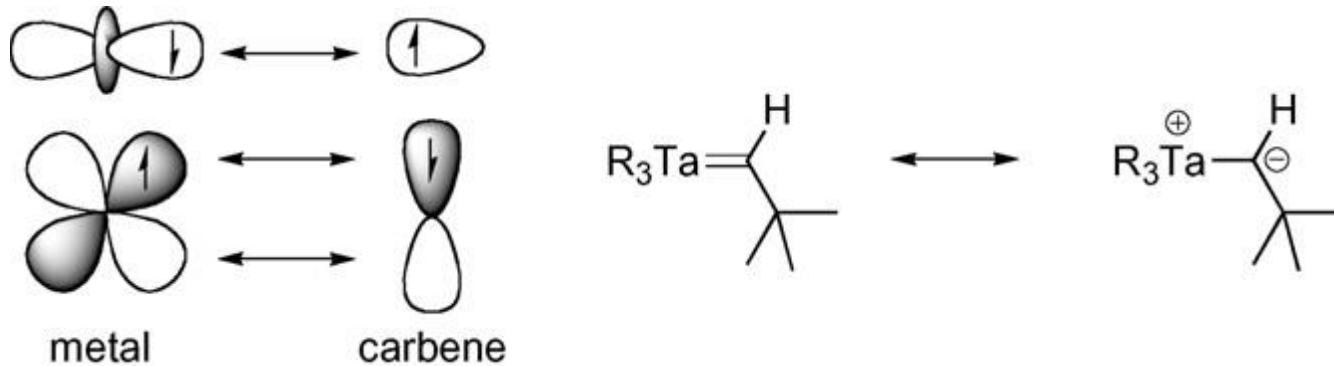


# Carbeni di Fischer

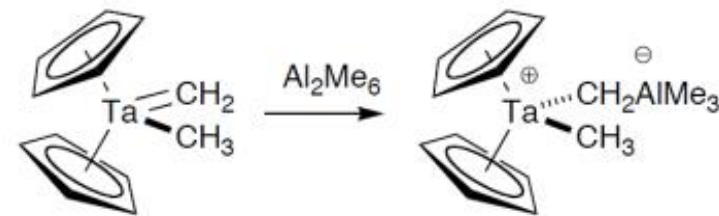
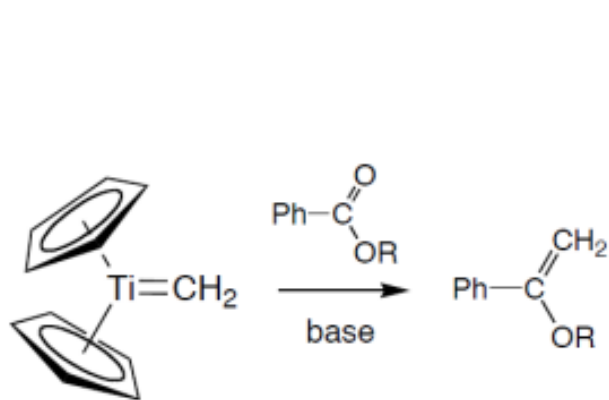


1. Carbeni singoletto, ben stabilizzati da eteroatomi (e.g. aminocarbeni e alcossicarbeni)
2. Metallo in basso stato di ossidazione, con leganti ancillari  $\pi$ -accettori
3. Elettroni  $\pi$  polarizzati verso il metallo (vedi forme di risonanza)
4. Elettrofili al legame carbonio–metallo (C elettron-povero) (*Fisher* = *Electrophilic Reagent*)

# Carbeni di Schrock



1. Carbeni debolmente stabilizzati (alchilideni)
2. *Early transition metals* in alto stato di ossidazione, con leganti ancillari  $\sigma$ - e  $\pi$ -donatori
3. È un vero doppio legame, polarizzato verso il carbonio
4. Nucleofili al legame carbonio–metallo (C elettrone-ricco)
5. Si comportano come metallo-ilidi (reazione di Wittig)

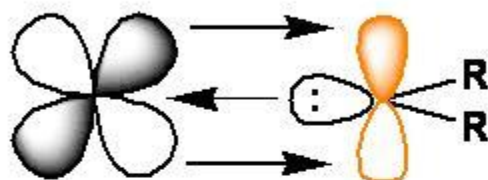


Reagente di Tebbe (reazione tipo Wittig)

# Typical Ligands – Transition Metal Carbene Complexes

## FISCHER

- Electrophilic Carbon



neutral  $CR_2$  (L-type ligand)  
(similarities to  $PR_3$ )

strong  $\sigma$ -donor  
poor or OK  $\pi$ -acceptor

2-electron donor

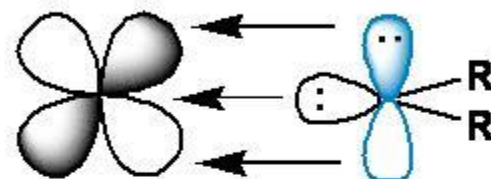
R =  $\pi$ -donor  
(OR,  $NR_2$ , Ph)

Late TMs, Low oxidation  
states ( $Mo^0$ ,  $Fe^0$  etc.)

$\pi$ -acceptors  
(CO, CNR,  $P(OR)_3$ )

## SCHROCK

- Nucleophilic Carbon



$CR_2^{2-}$  ( $X_2$ -type ligand)  
(similarities to  $M=O$  or  $M=NR$ )

strong  $\sigma$ -donor  
strong  $\pi$ -donor

4-electron donor

R = H, Alkyl

Early TMs (often  $d_0$ ), High  
oxidation states ( $Ta^V$ ,  $W^VI$ )

$Cl^-$ ,  $Cp^-$ , Alkyl,  
Imido, Amido

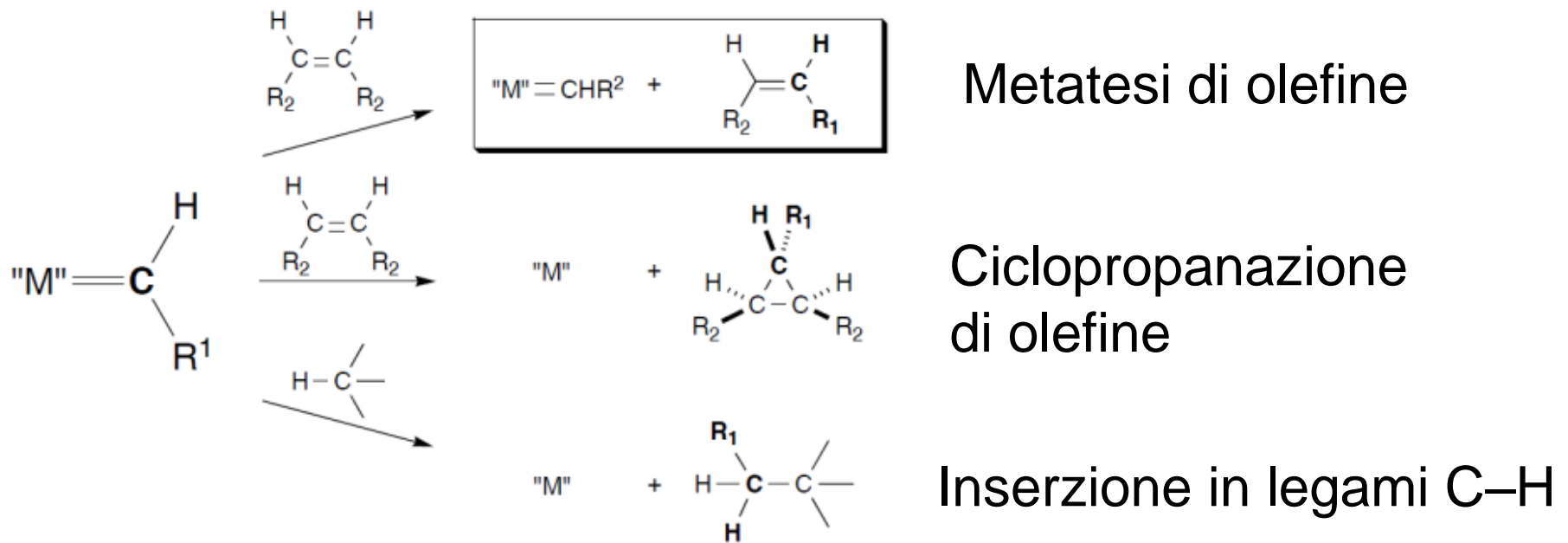
properties

typical R groups in  $CR_2$

typical metals

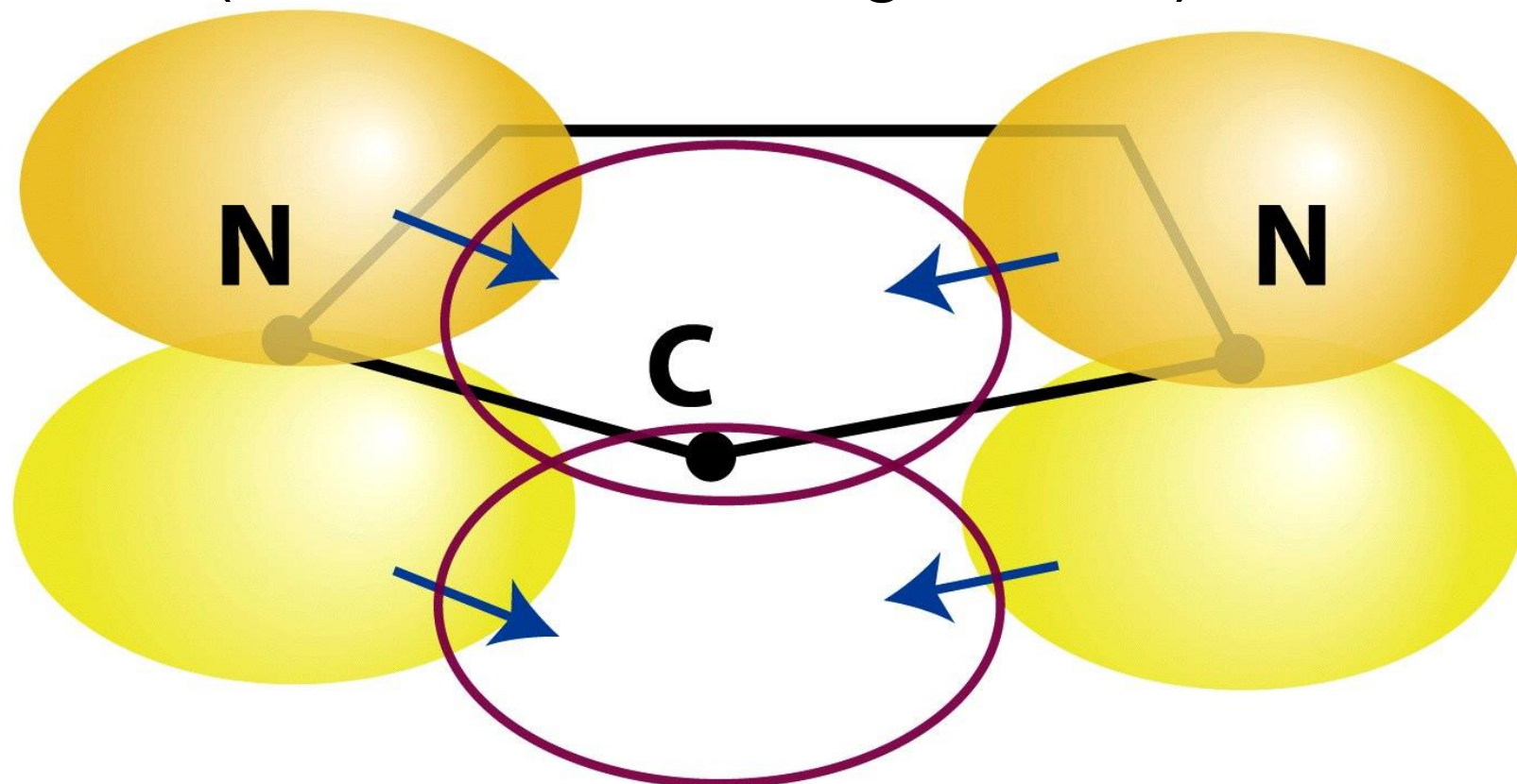
typical co-ligands

# Applicazioni in catalisi dei carbeni di Schrock e carbeni di Fischer

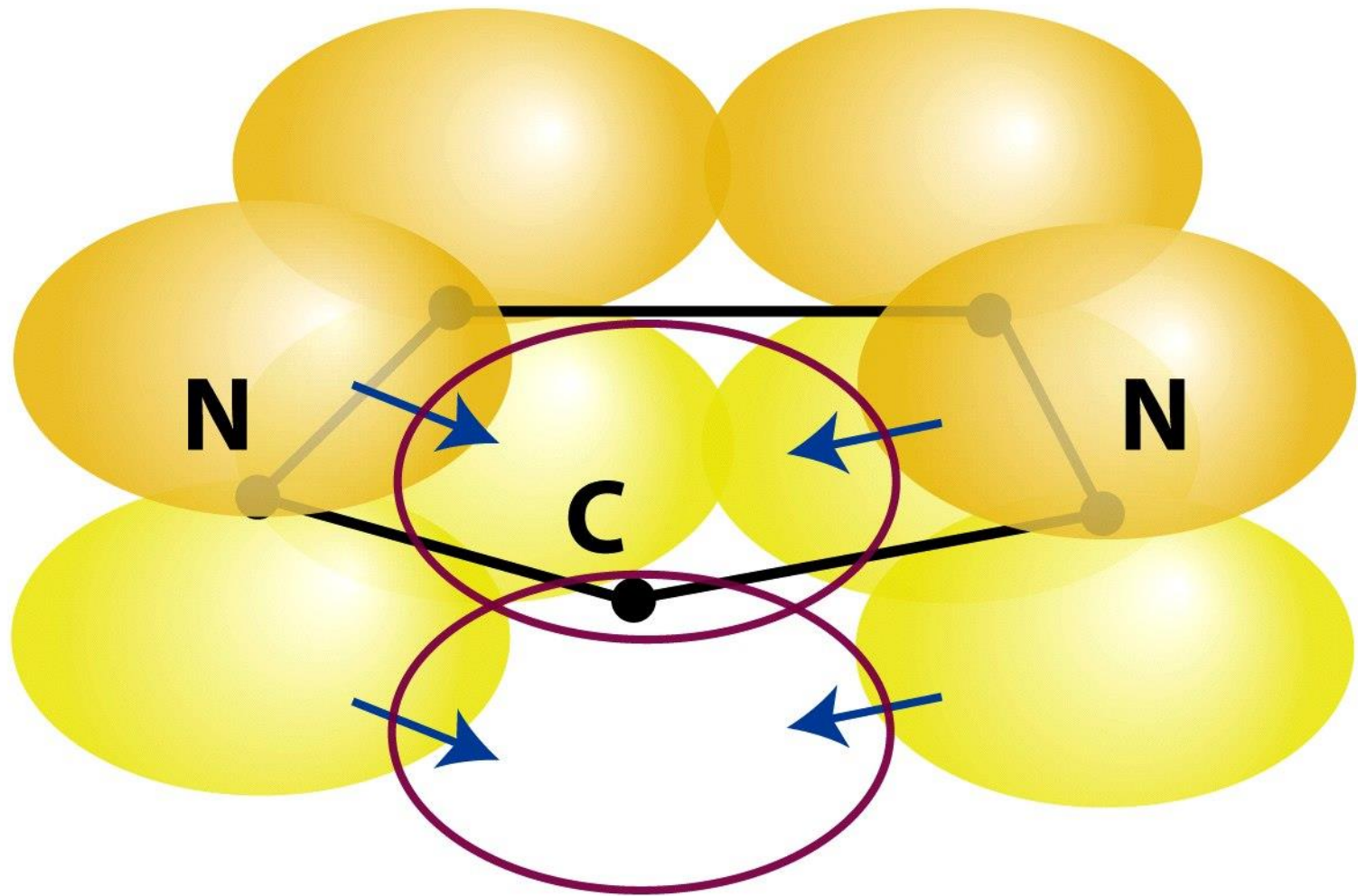




Carbeni N-Eterociclici  
(*N-Heterocyclic Carbenes*, NHC)  
(carbeni di Arduengo, 1991)

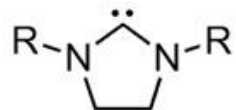


Carbeni tipo Fischer

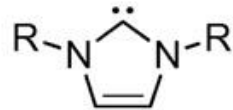


struttura di risonanza aromatica  
sei elettroni (M-C)

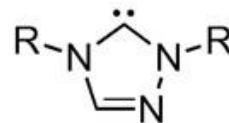
# Principali NHC



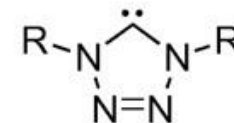
Imidazolidin-



Imidazol-

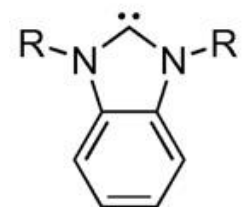


Triazol-

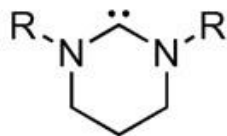


Tetrazol-

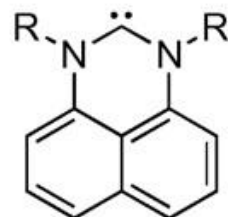
R = Alkyl, aryl



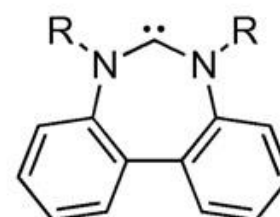
Benzimidazol-



Hexahydropyrimidin-



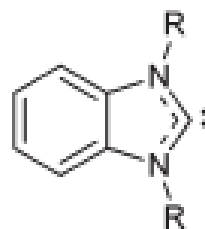
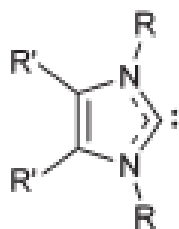
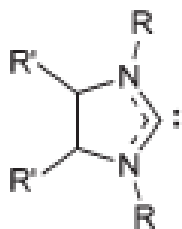
Dihydroperimidin-



Dihydro-dibenzo-diazepin-

-ylidene

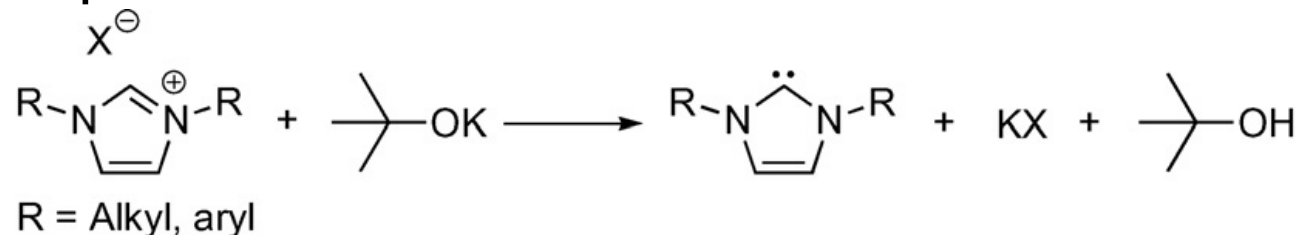
**imidazolidinylieni, imidazolylieni, benzimidazolylieni**



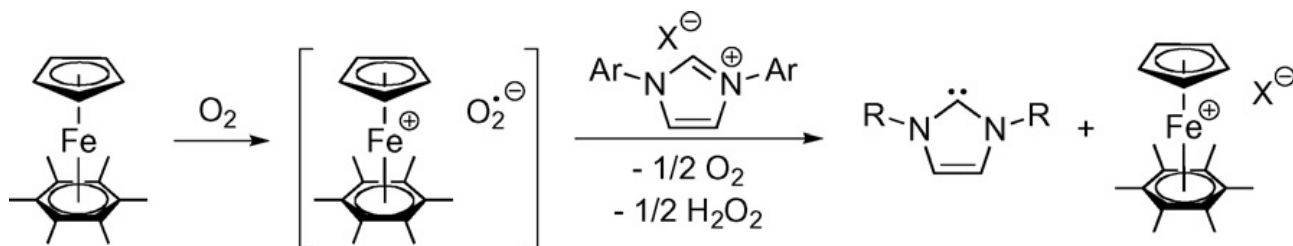
R,R' =  
e.g. alkyl, aryl, halogen

# Metodi per ottenere NHC stabili

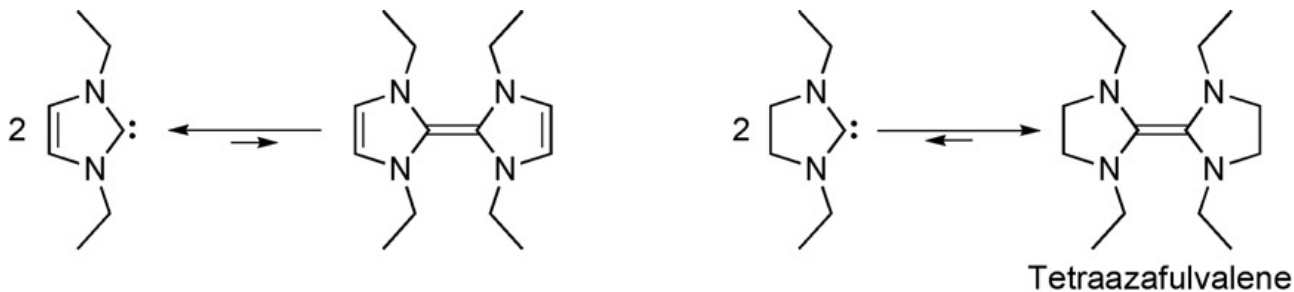
Deprotonazione di sali di imidazolio con basi forti



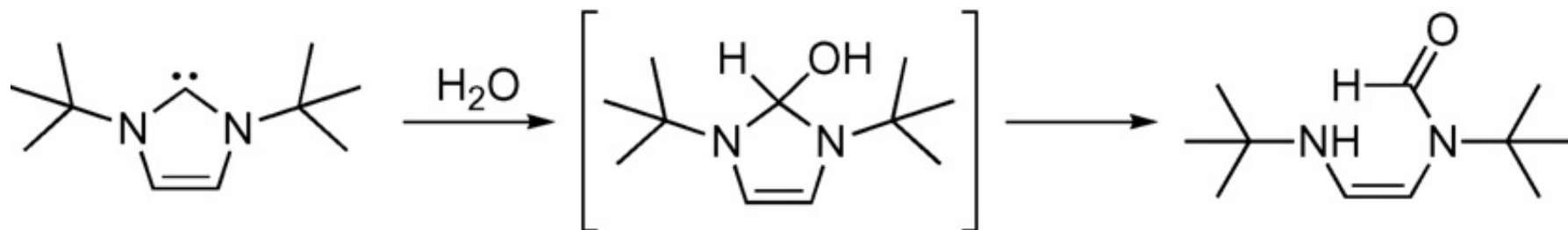
Deprotonazione radicalica di sali di imidazolio con  $\text{O}_2^-$



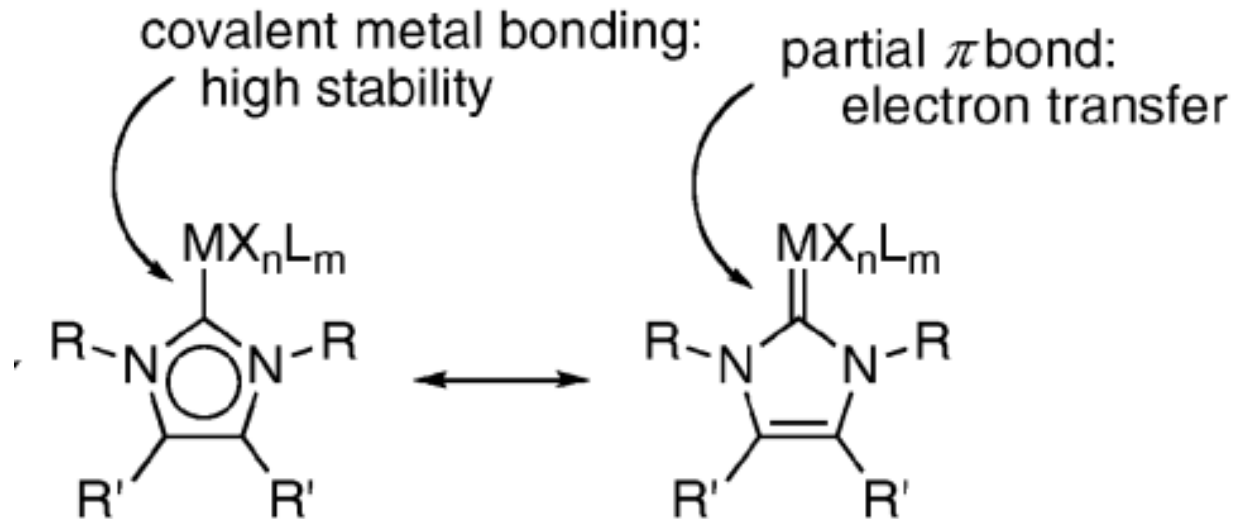
Possibile dimerizzazione



*Gli NHC sono estremamente sensibili all'umidità , ma sono cineticamente stabili verso l'ossigeno di tripletto*



# Legame M-C nei carbeni NHC



1. Forti  $\sigma$ -donatori
2. Contributi  $\pi$  modesti
3. TEP inferiori a quelli delle fosfine
4. Flessibilità sintetica (variazioni dei gruppi R ed R')

*I leganti NHC sono generalmente dei leganti  $\sigma$ -donatori più forti della maggior parte dei leganti fosfinici più comuni e anche delle fosfine più basiche.*

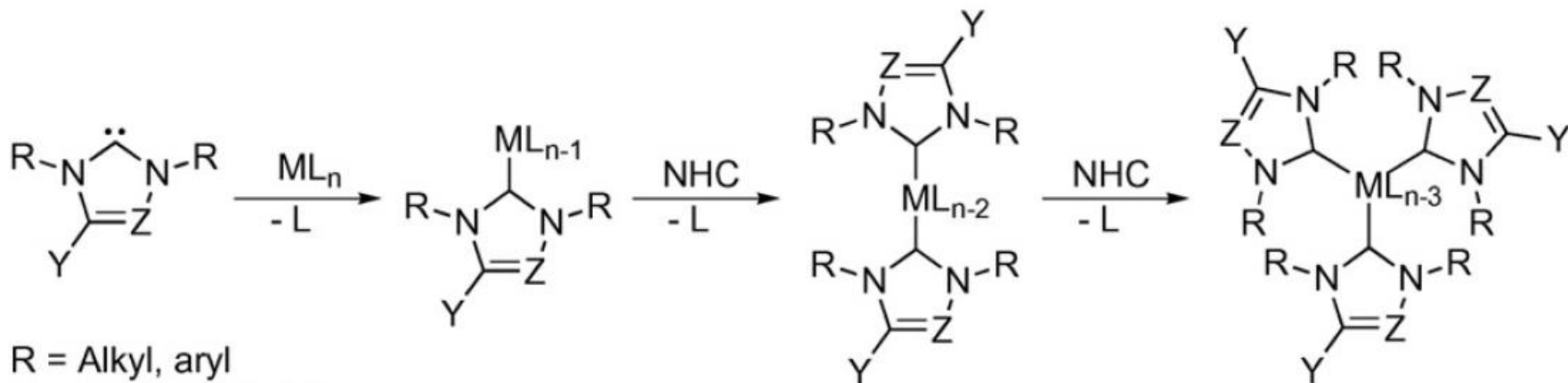
# Legame M–C nei carbeni

*In generale, la capacità  $\pi$ -accettrice dei carbeni legati a centri metallici diminuisce passando dai carbeni di Schrock a quelli di Fischer (non-diamminocarbeni) agli NHC.*

*Gli NHC si legano fortemente ai metalli via  $\sigma$ , mentre il contributo di  $\pi$ -retrodonazione è quasi sempre trascurabile. La componente  $\pi$  diventa significativa con i metalli del Gruppo 11, cioè rame, argento e oro.*

*Esistono esempi con tutti i metalli dal Gruppo 4 al 12*

# Sintesi di composti M-NHC a partire da NHC stabili per sostituzione

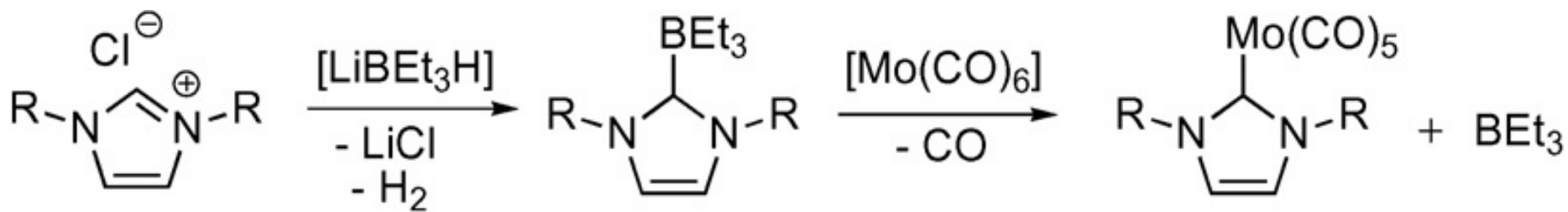


R = Alkyl, aryl  
 Y = H, Cl, alkyl, aryl  
 Z = CY, N

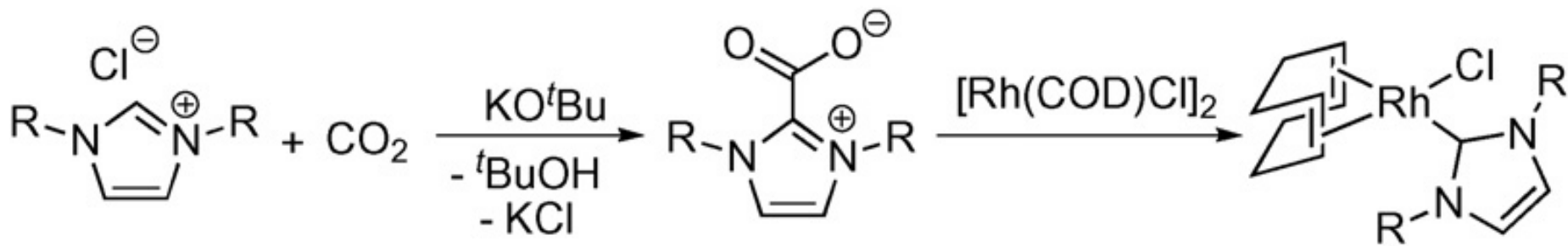
L = RCN,  $PR_3$ , THF, CO, THT, pyr, DMS...



# Sintesi di composti M-NHC a partire da “carbeni mascherati”



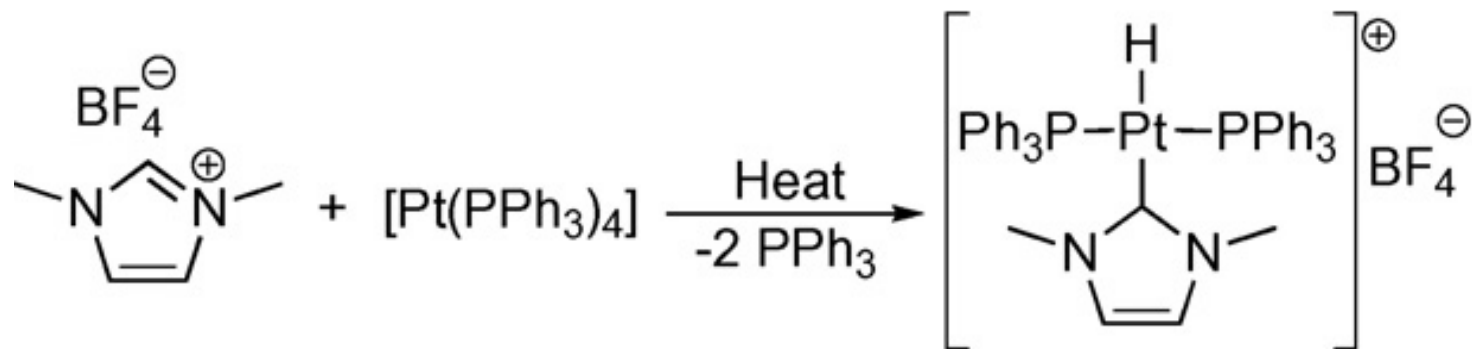
*trialchilborano-2-imidazolo*



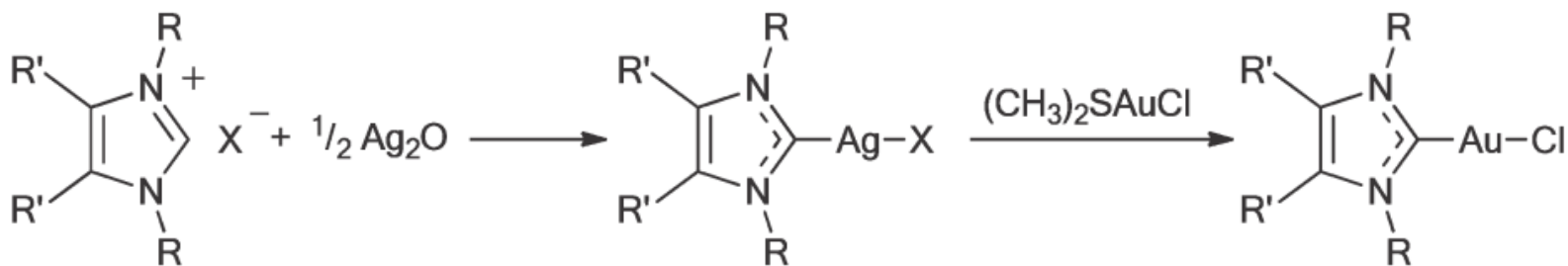
*carbossilato-2-imidazolo*

# Sintesi di composti M-NHC

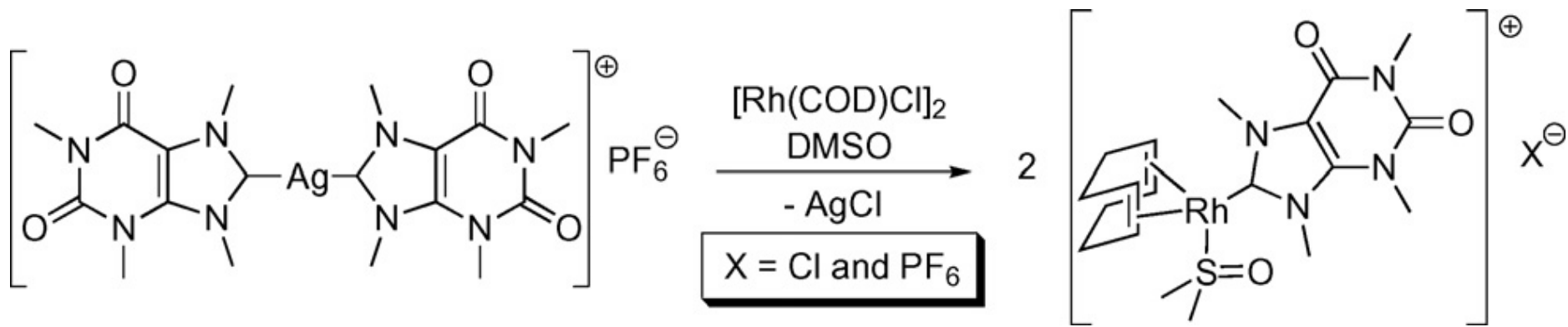
*addizione ossidativa di sali di imidazolio su precursori zerovalenti*

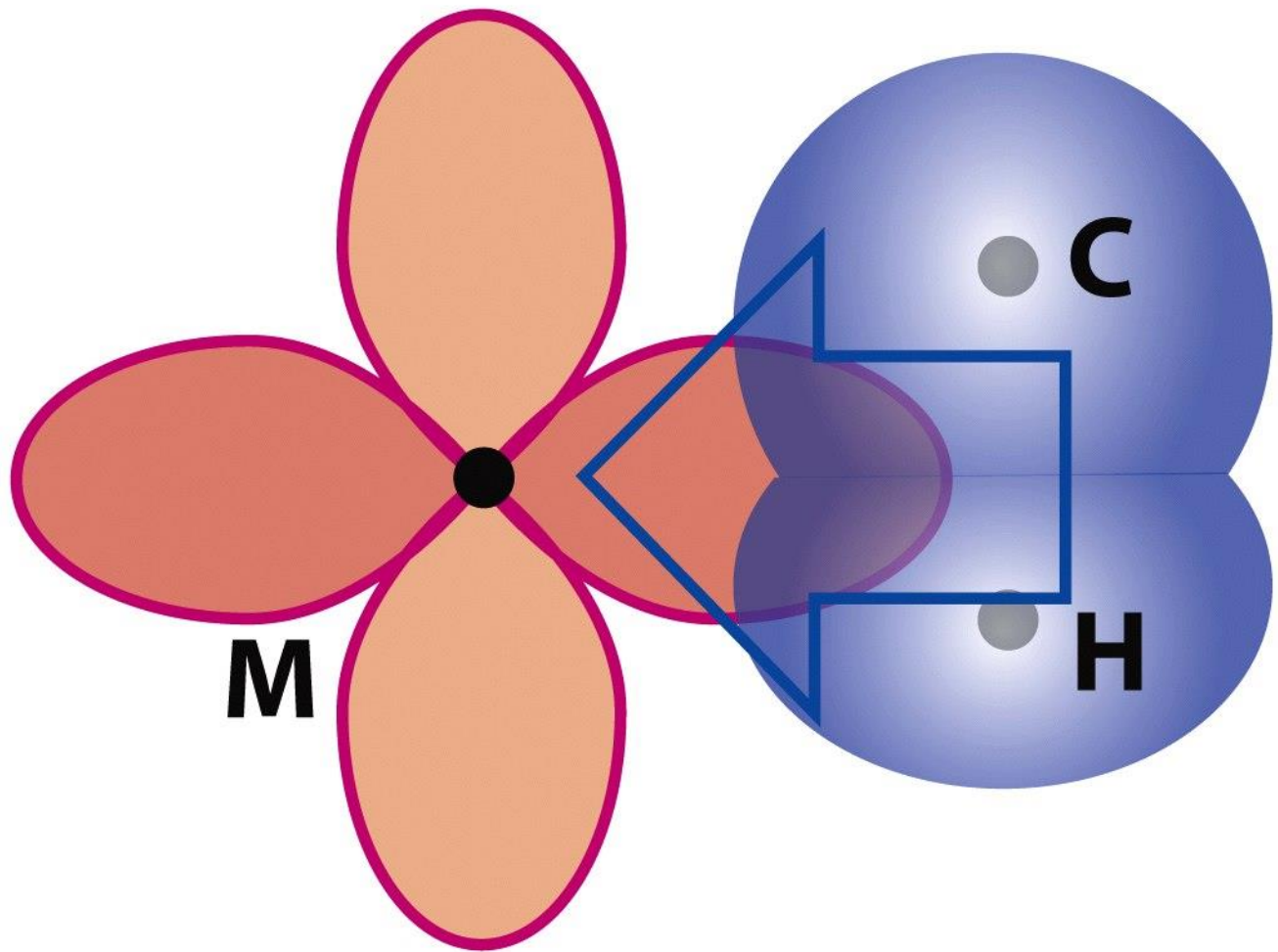


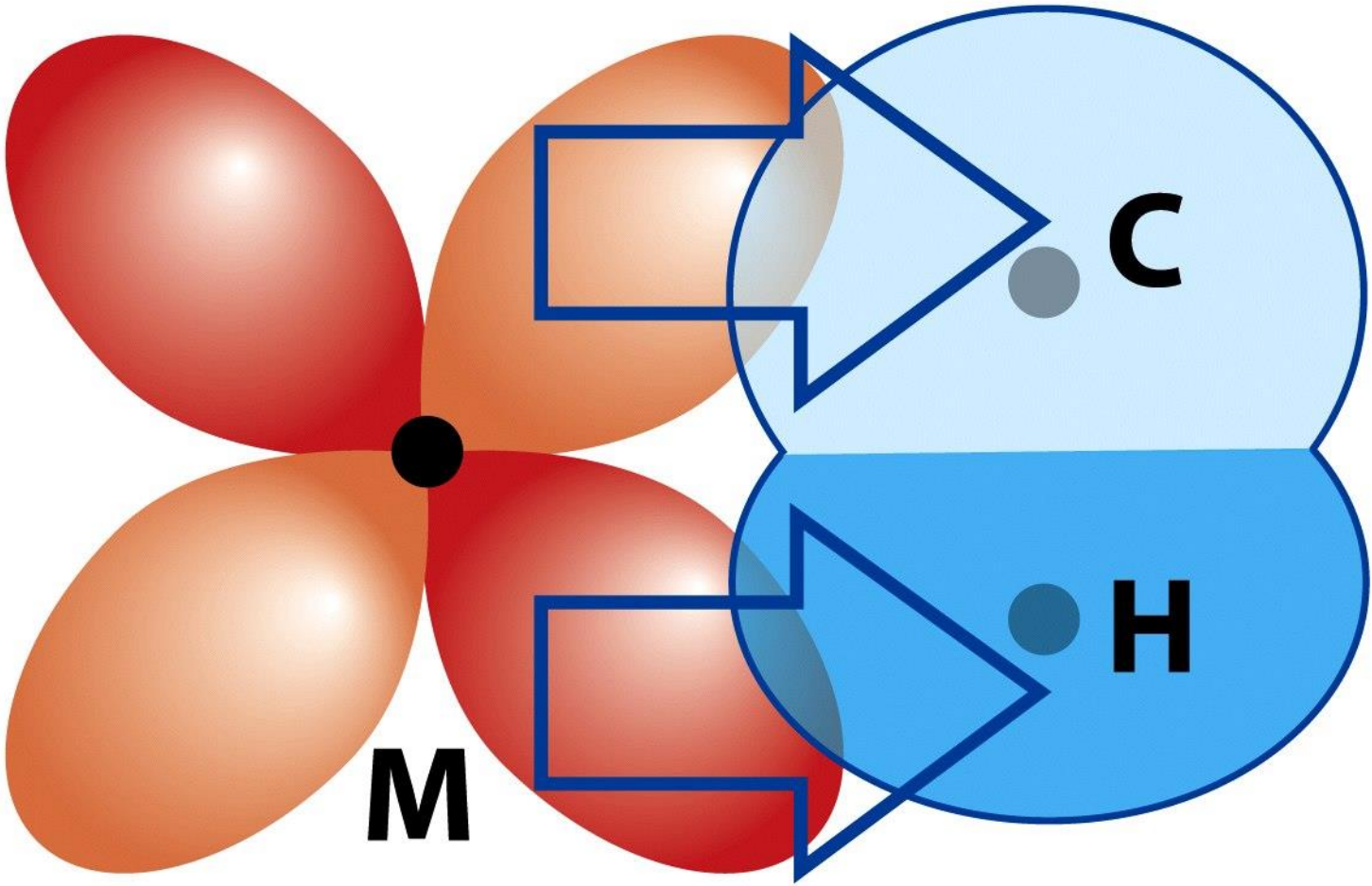
*trans-metallazione a partire da alogenuri di Ag-NHC*

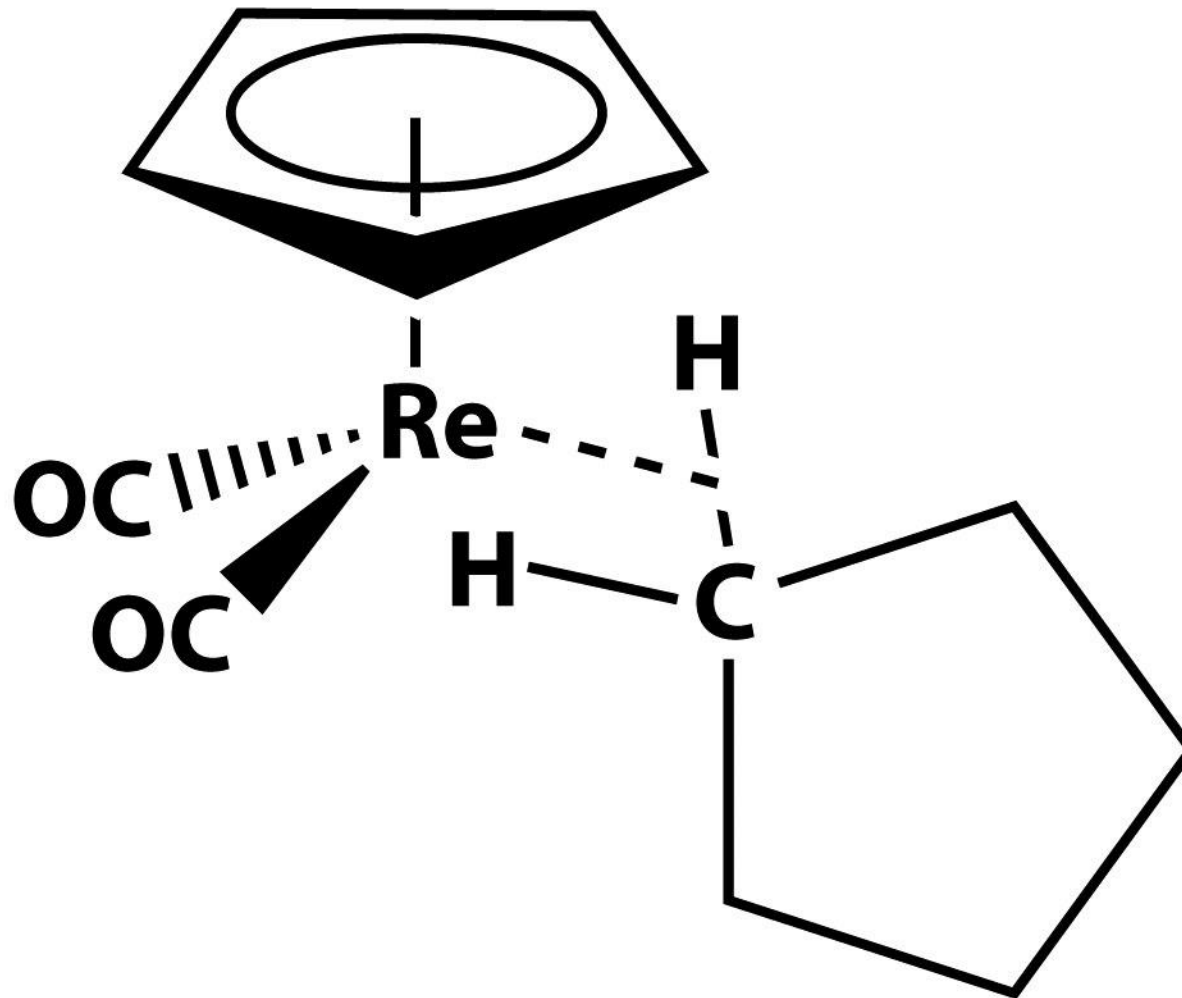


# Sintesi di composti M-NHC per *trans*-metallazione da NHC di Ag

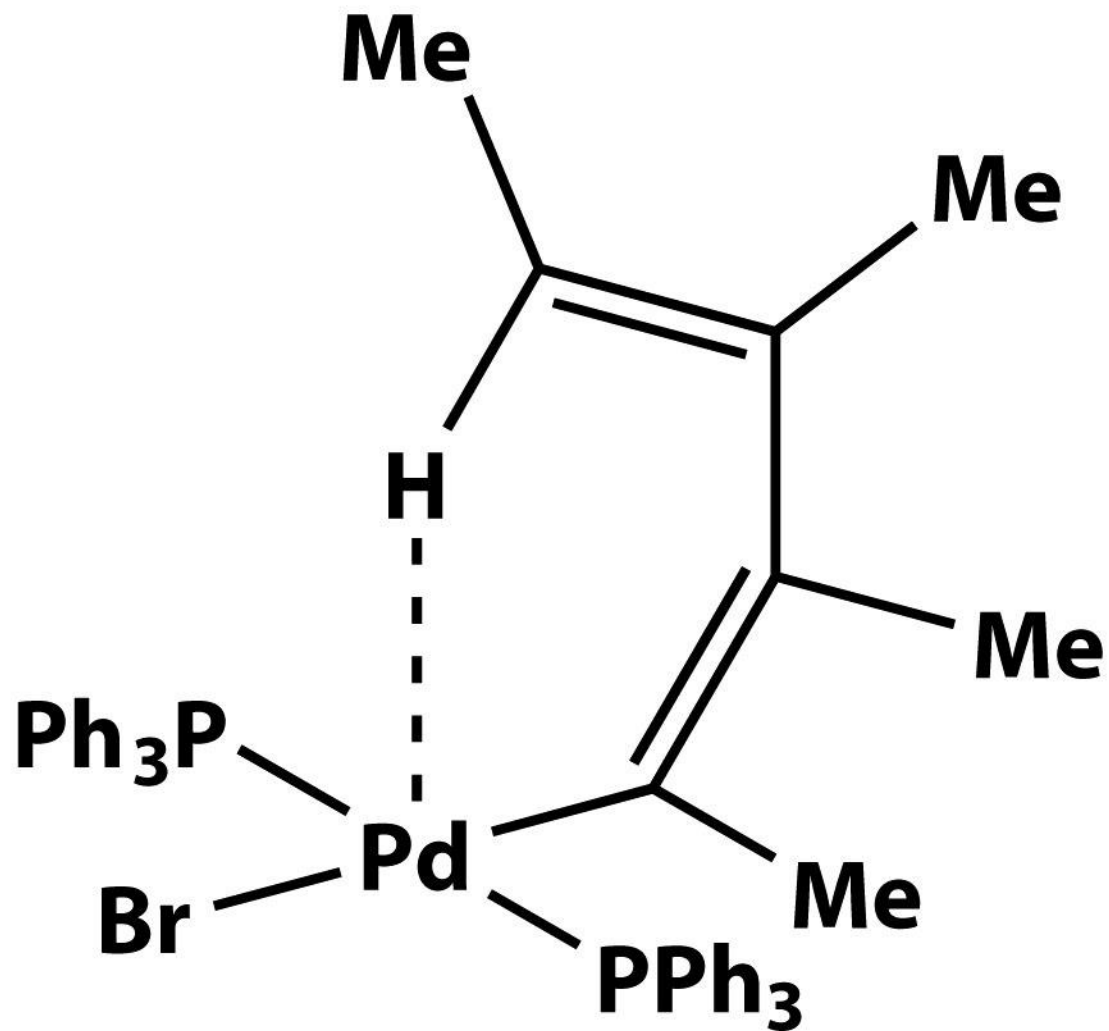








Identificato nel 1988 tramite spettroscopia NMR in soluzione



Interazioni C-H *agostiche*