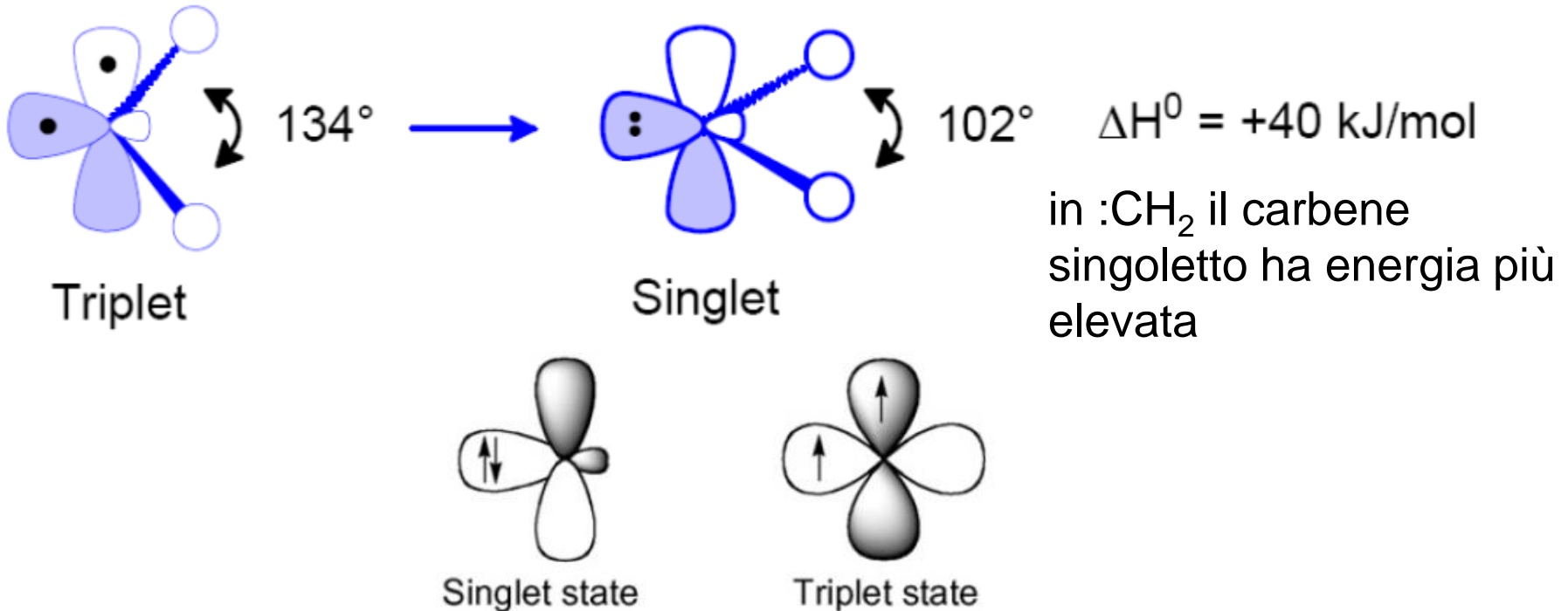
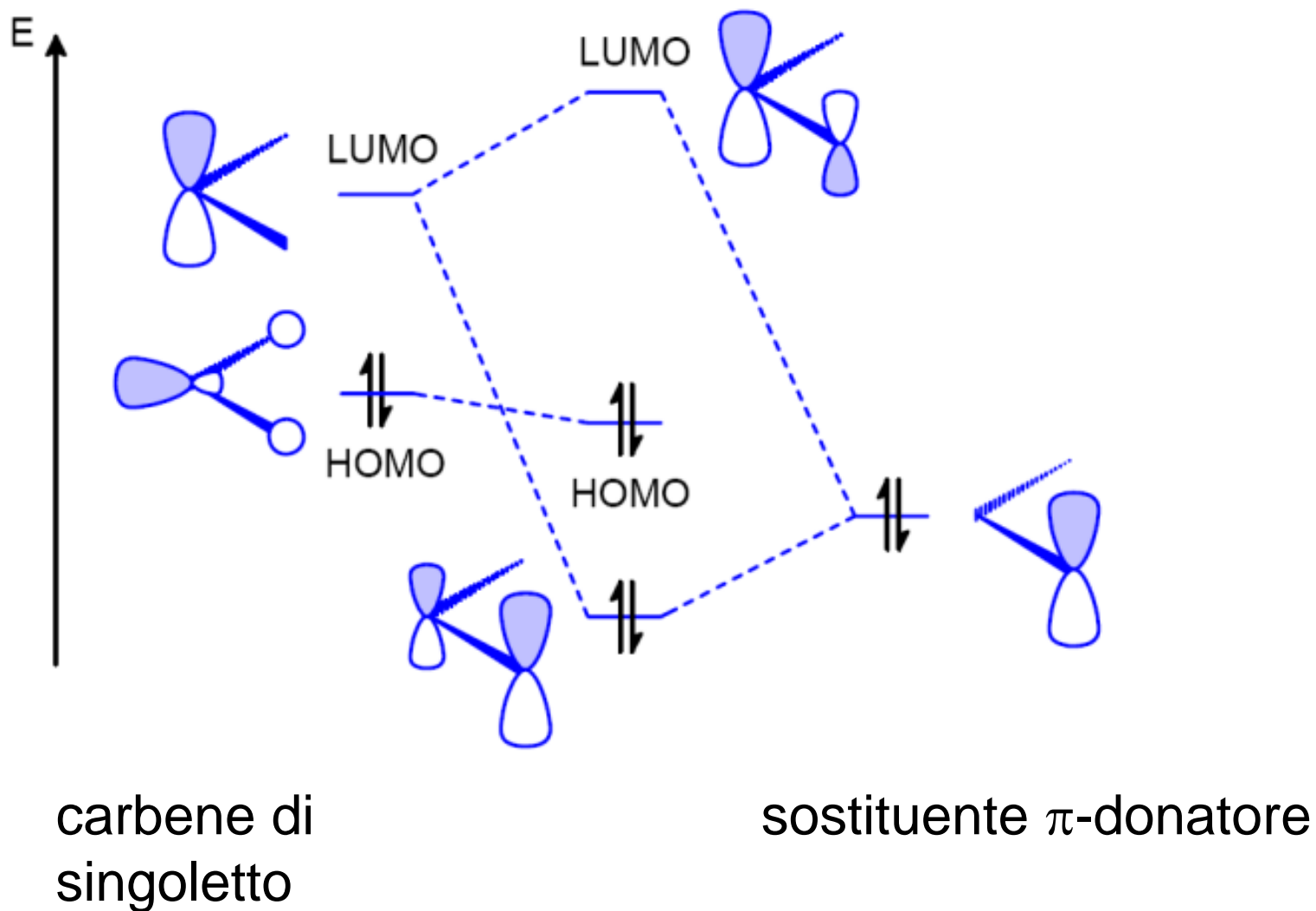


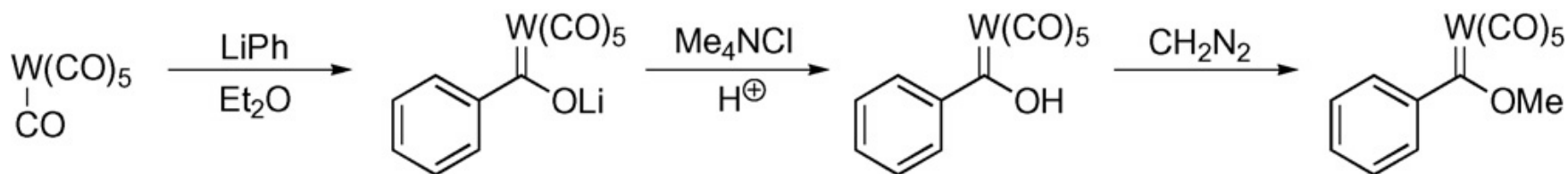
# Carbeni



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

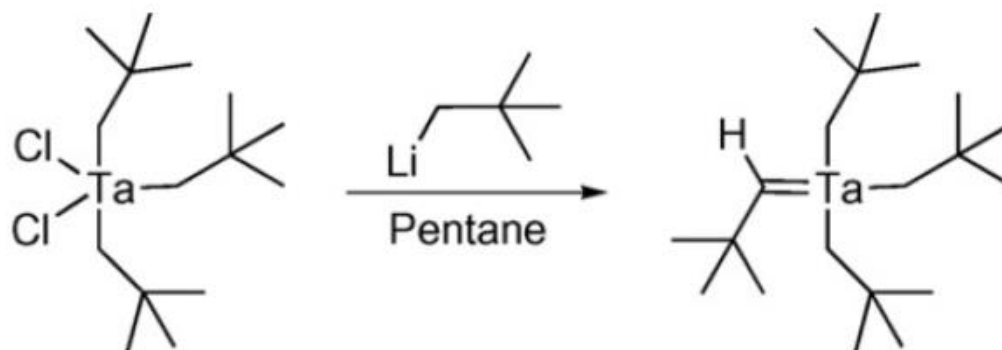


# 1964: primo complesso metallo-carbene (*Fischer*)

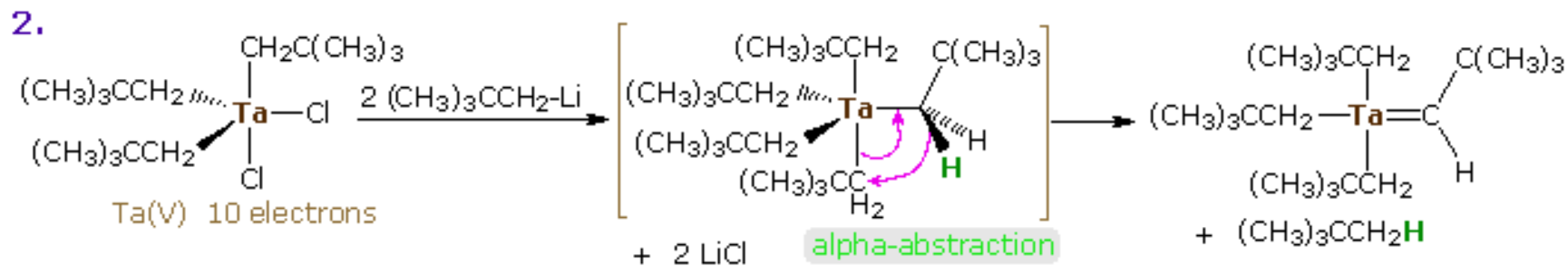


*metossifenilmetilene tungsteno(0) pentacarbonile*

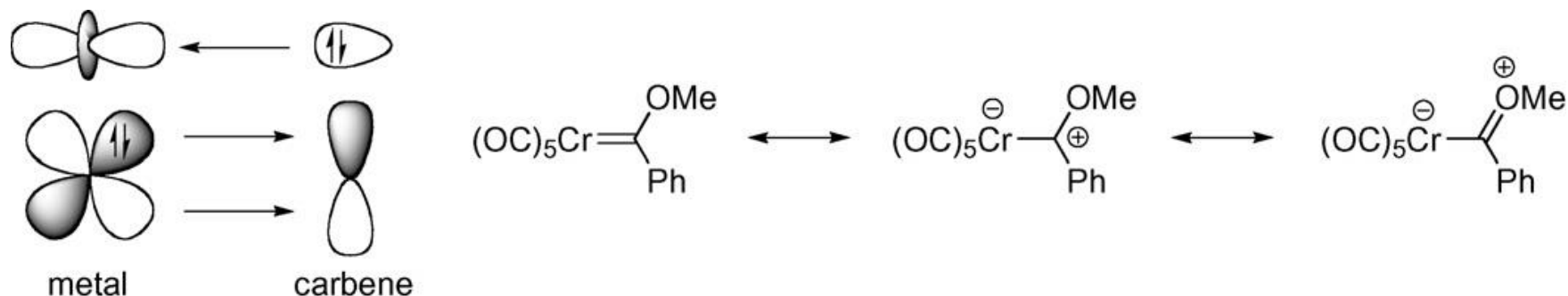
# 1974: primo complesso metallo-alchilidene (Schrock)



$\alpha$ -hydrogen abstraction

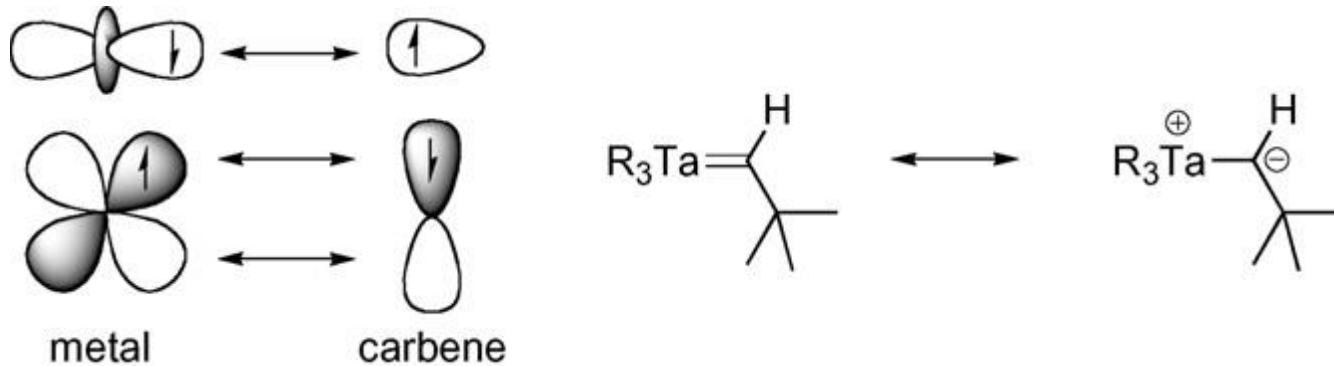


# Carbeni di Fischer

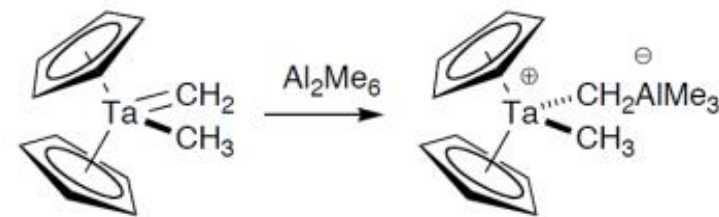
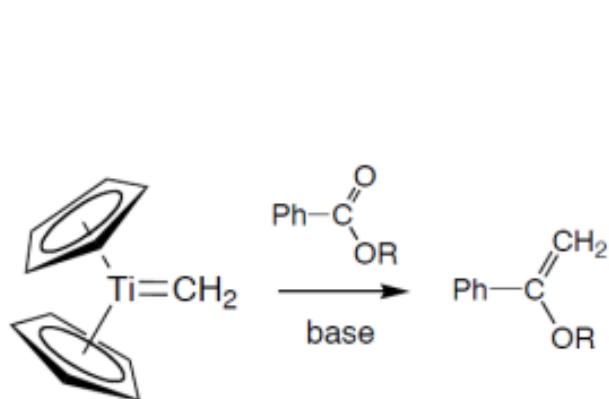


1. Carbeni singoletto, ben stabilizzati da eteroatomi (e.g. aminocarbeni e alcossicarbeni)
2. Metallo in basso stato di ossidazione, con leganti ancillari  $\pi$ -accettori
3. Elettroni  $\pi$  polarizzati verso il metallo (vedi forme di risonanza)
4. Elettrofili al legame carbonio–metallo (C elettron-povero)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

# Carbeni di Schrock

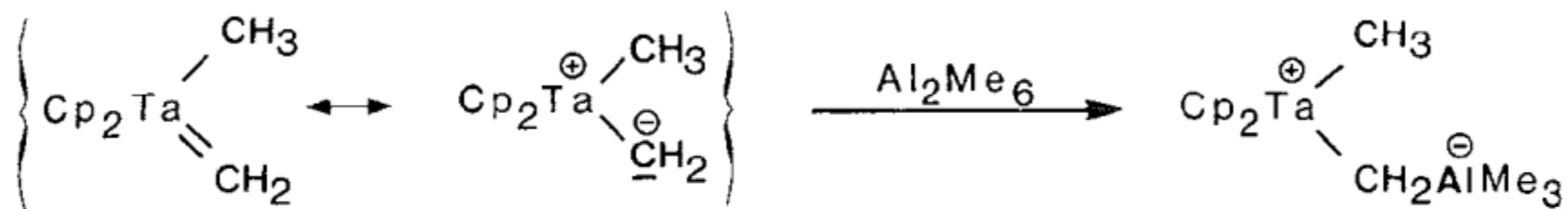


1. Carbeni debolmente stabilizzati (alchilideni)
2. *Early transition metals* in alto stato di ossidazione, con leganti ancillari  $\sigma$ - e  $\pi$ -donatori
3. È un vero doppio legame, polarizzato verso il carbonio
4. Nucleofili al legame carbonio–metallico (C elettrone-ricco)
5. Si comportano come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

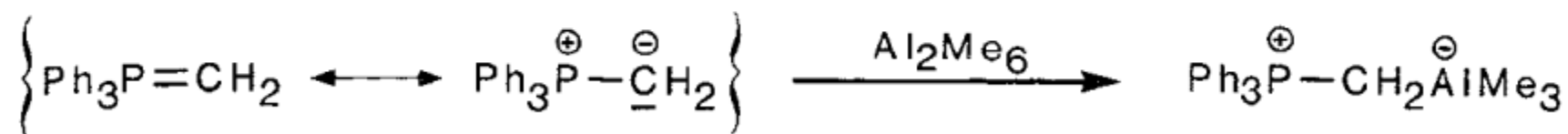


Reagente di Tebbe (reazione tipo Wittig)

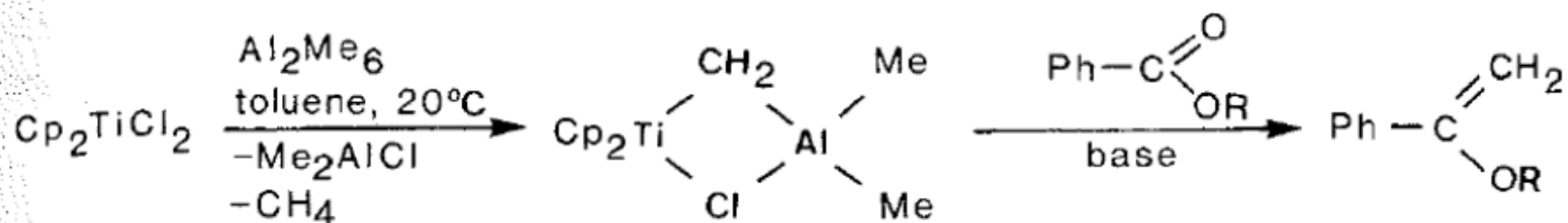
TM-alkylidene complexes therefore react like metal ylides:



compare:

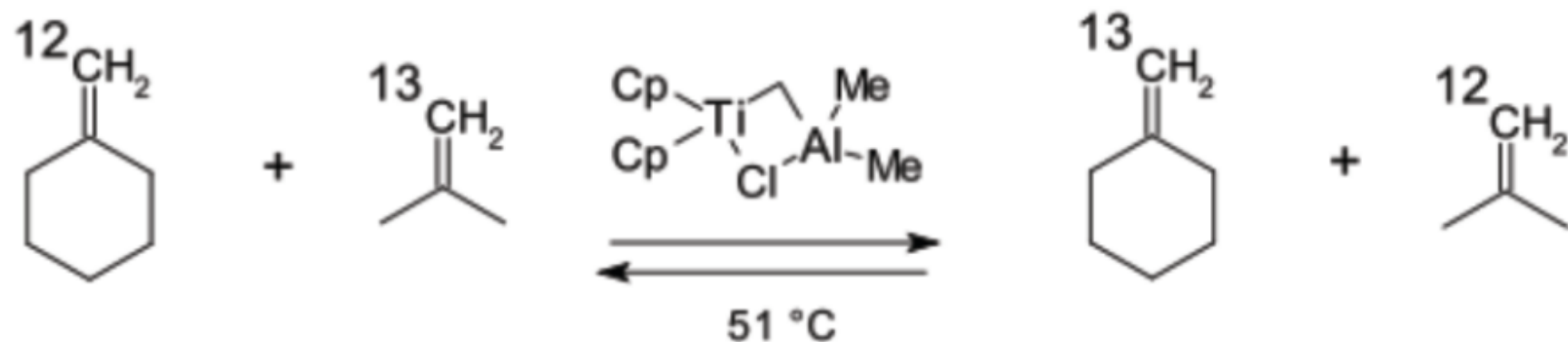


A preparative application of this analogy is found in the **Tebbe reagent**, an alternative to the Wittig reagents (*Grubbs, 1980*):



The actual **methylene-transfer reagent** in this reaction is the alkylidene complex  $\text{Cp}_2\text{Ti}=\text{CH}_2$ , formed from the Tebbe reagent by loss of  $\text{Me}_2\text{AlCl}$ . Conventional Wittig reagents are not suitable for this conversion of esters into vinyl ethers.

### Tebbe chemistry – Tebbe reagent

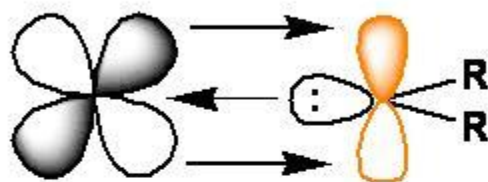




# Typical Ligands – Transition Metal Carbene Complexes

## FISCHER

- Electrophilic Carbon



neutral  $\text{CR}_2$  (L-type ligand)  
(similarities to  $\text{PR}_3$ )

properties

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

2-electron donor

typical R groups in  $\text{CR}_2$

R =  $\pi$ -donor  
(OR,  $\text{NR}_2$ , Ph)

typical metals

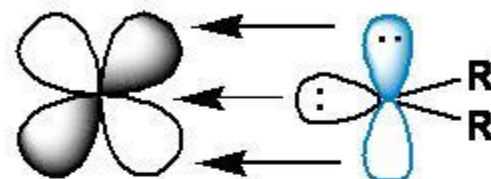
Late TMs, Low oxidation  
states ( $\text{Mo}^0$ ,  $\text{Fe}^0$  etc.)

typical co-ligands

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

## SCHROCK

- Nucleophilic Carbon



$\text{CR}_2^{2-}$  ( $\text{X}_2$ -type ligand)  
(similarities to  $\text{M}=\text{O}$  or  $\text{M}=\text{NR}$ )

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

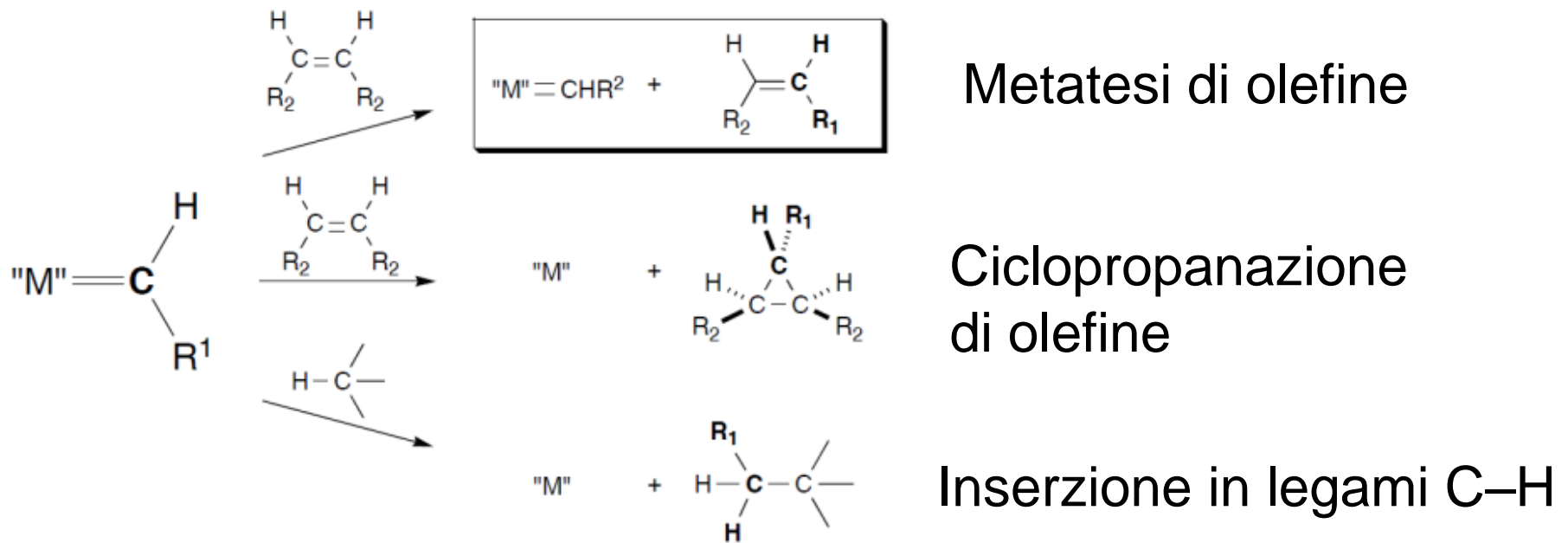
4-electron donor

R = H, Alkyl

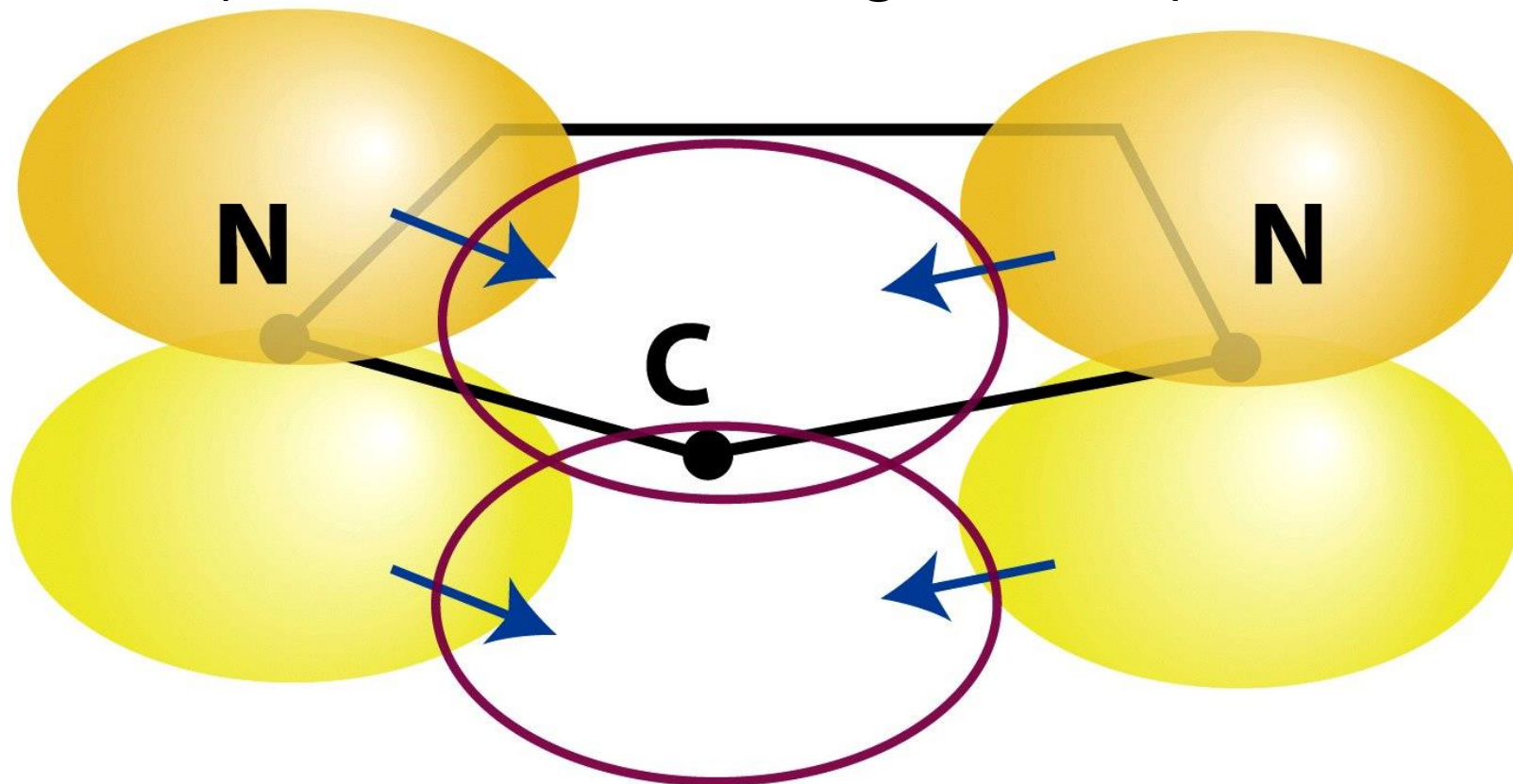
Early TMs (often  $d_0$ ), High  
oxidation states ( $\text{Ta}^V$ ,  $\text{W}^VI$ )

$\text{Cl}^-$ ,  $\text{Cp}^-$ , Alkyl,  
Imido, Amido

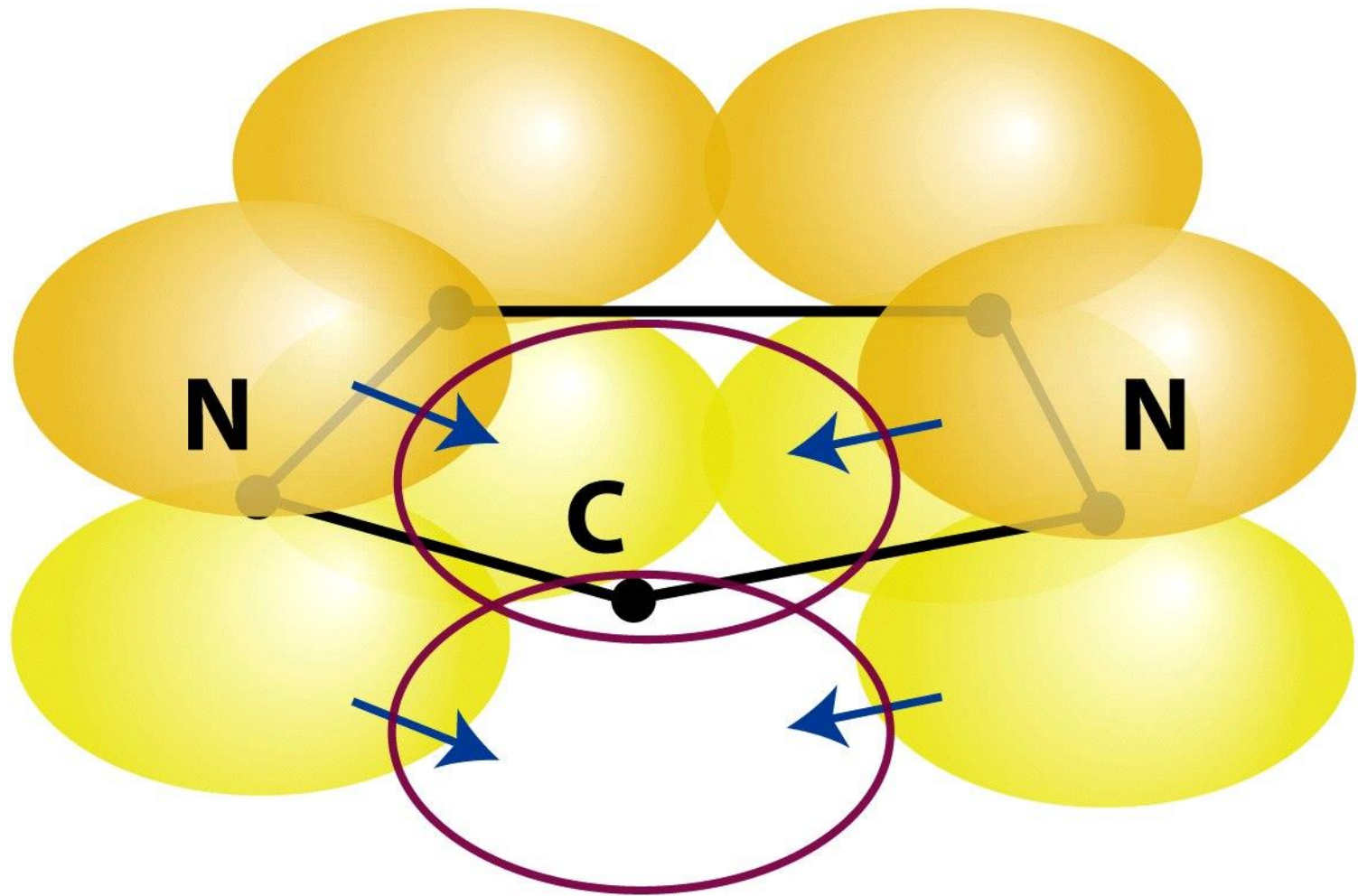
# Applicazioni in catalisi dei carbeni di Schrock e carbeni di Fischer



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

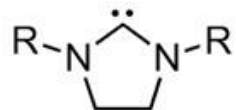


Carbeni tipo Fischer

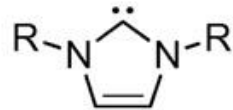


struttura di risonanza aromatica  
sei elettroni (M-C)

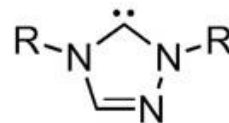
# Principali NHC



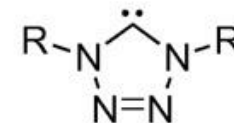
Imidazolidin-



Imidazol-

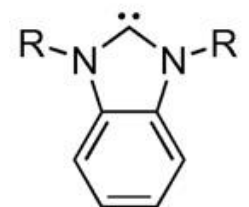


Triazol-

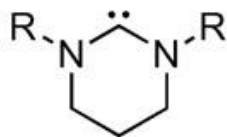


Tetrazol-

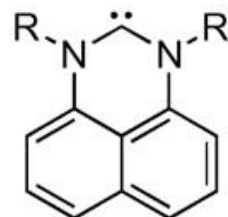
R = Alkyl, aryl



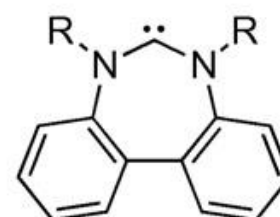
Benzimidazol-



Hexahydropyrimidin-



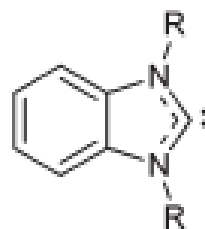
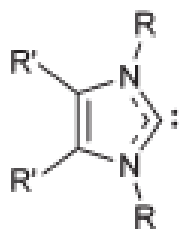
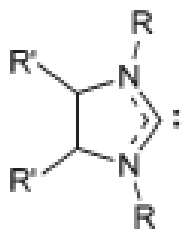
Dihydroperimidin-



Dihydro-dibenzo-diazepin-

-ylidene

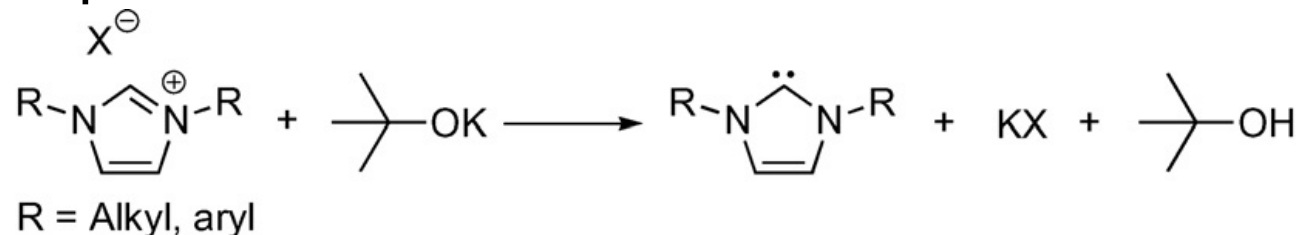
**imidazolidinylieni, imidazolylidene, benzimidazolylidene**



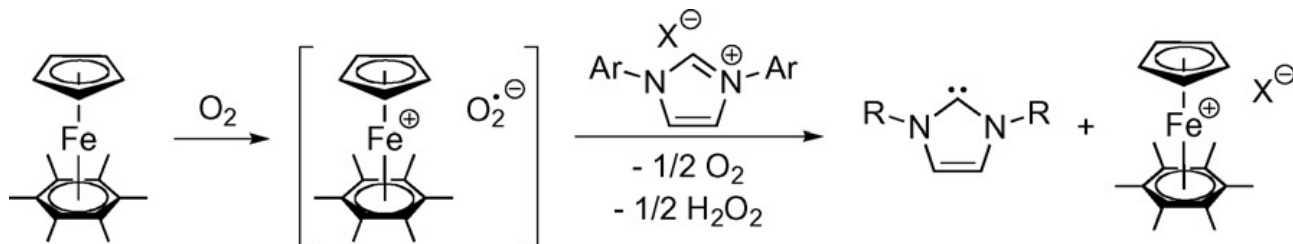
R,R' =  
e.g. alkyl, aryl, halogen

# Metodi per ottenere NHC stabili

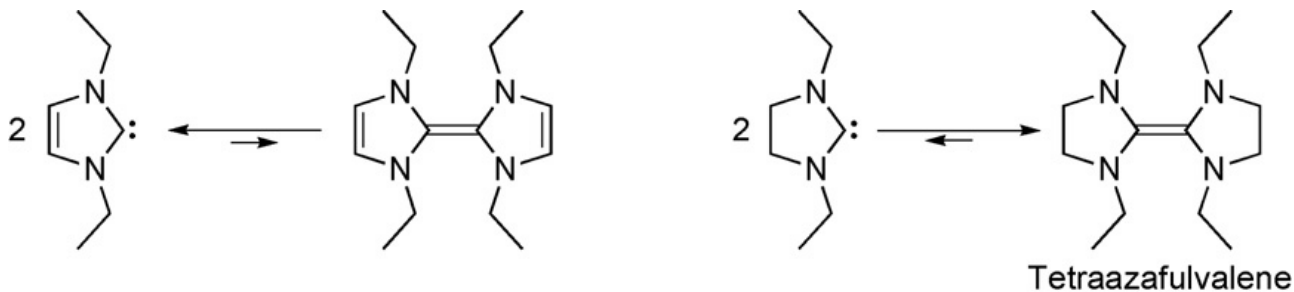
Deprotonazione di sali di imidazolio con basi forti



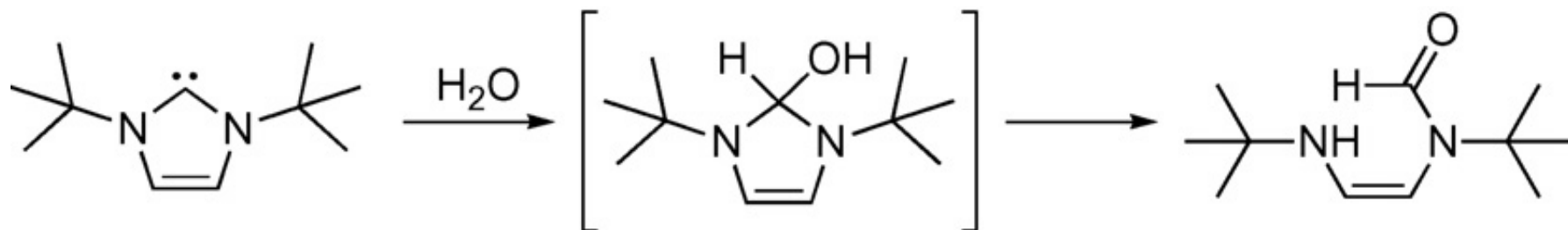
Deprotonazione radicalica di sali di imidazolio con  $\text{O}_2^-$



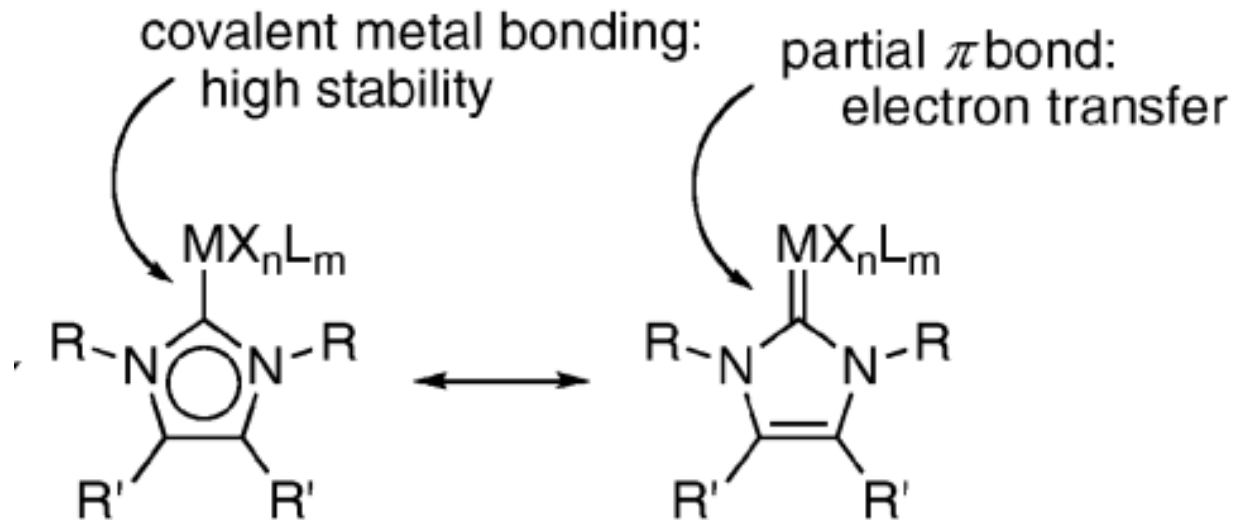
Possibile dimerizzazione



*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.*



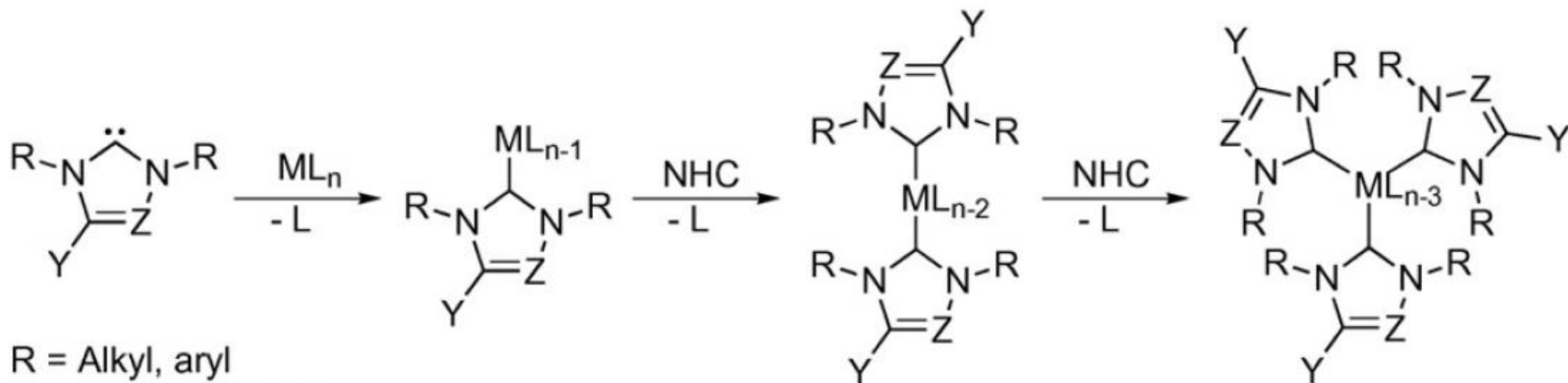
# Legame M–C nei carbeni

*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*

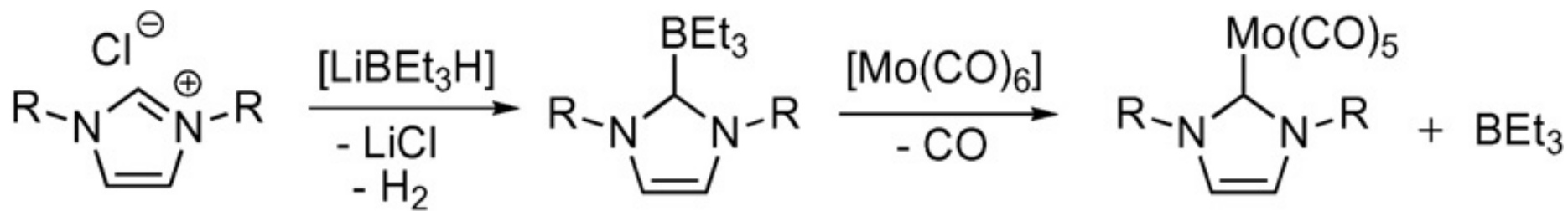
# Sintesi di composti M-NHC a partire da NHC stabili per sostituzione



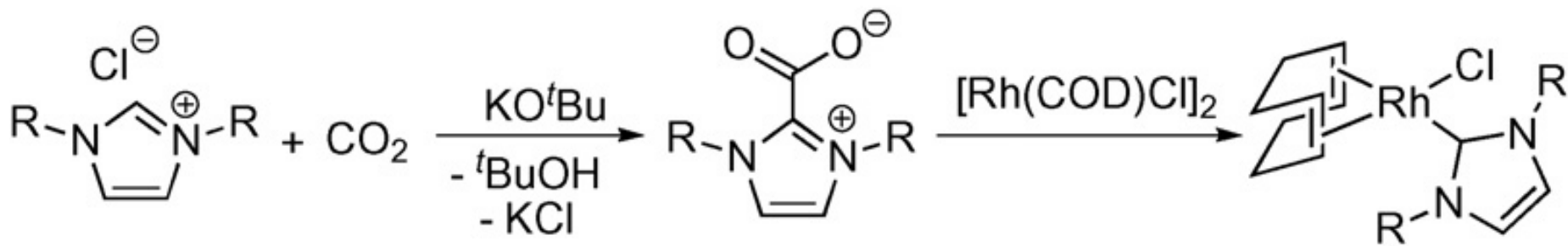
R = Alkyl, aryl  
Y = H, Cl, alkyl, aryl  
Z = CY, N

L = RCN, PR<sub>3</sub>, THF, CO, THT, pyr, DMS...

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



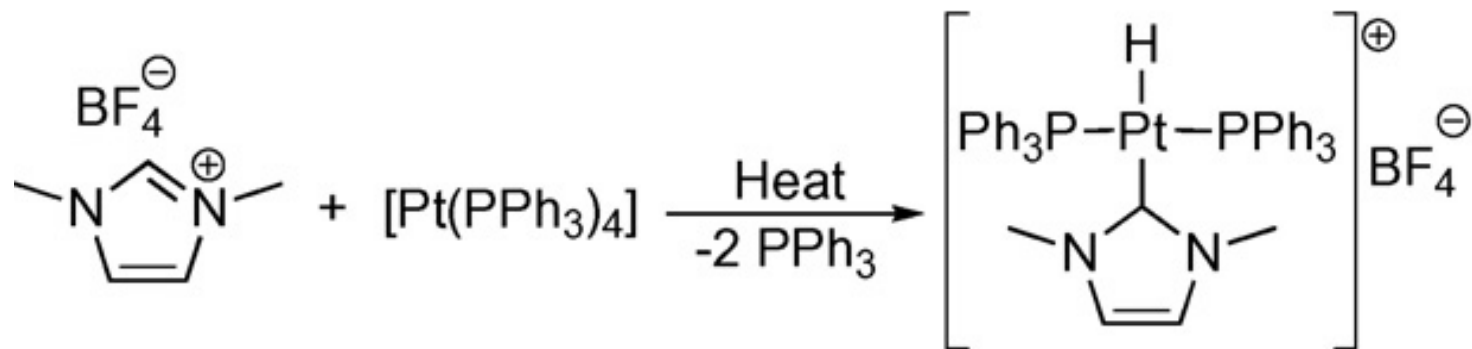
*trialchilborano-2-imidazolo*



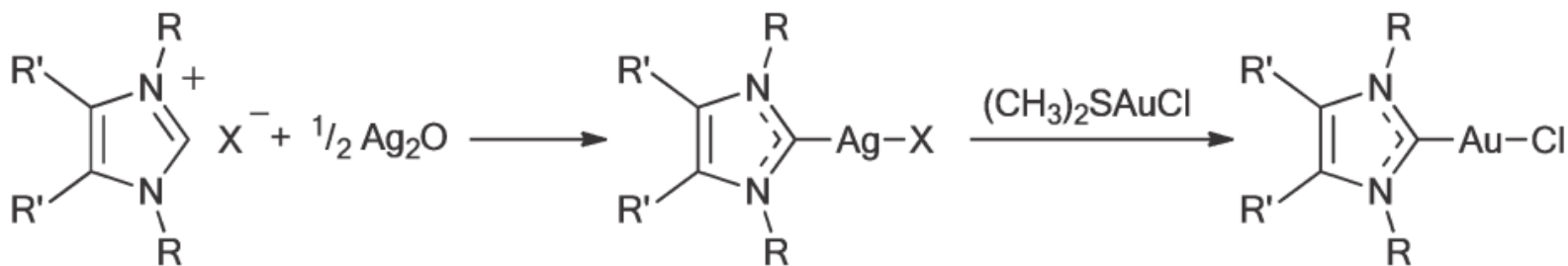
*carbossilato-2-imidazolo*

# Sintesi di composti M-NHC

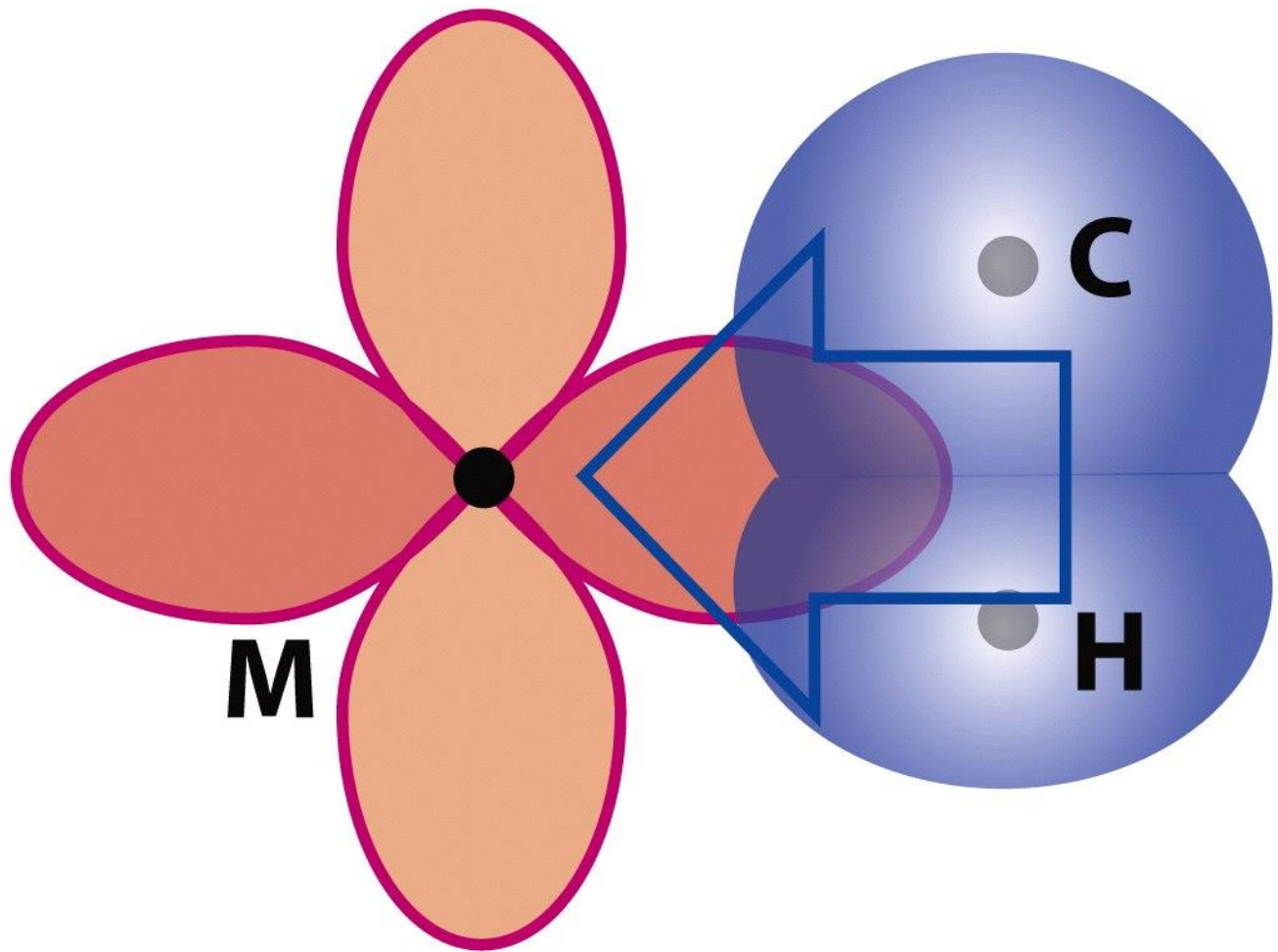
*addizione ossidativa di sali di imidazolio su precursori zerovalenti*

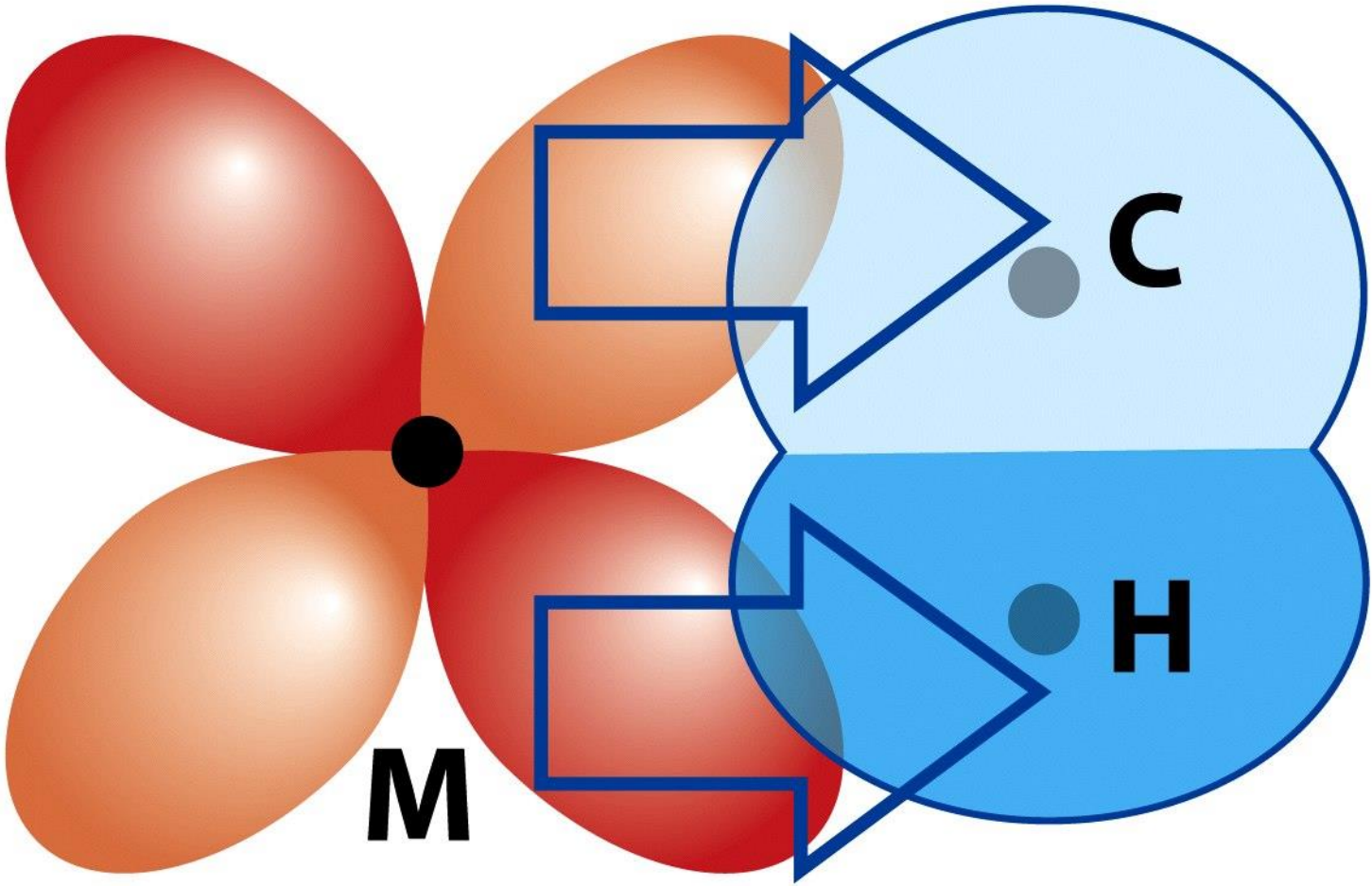


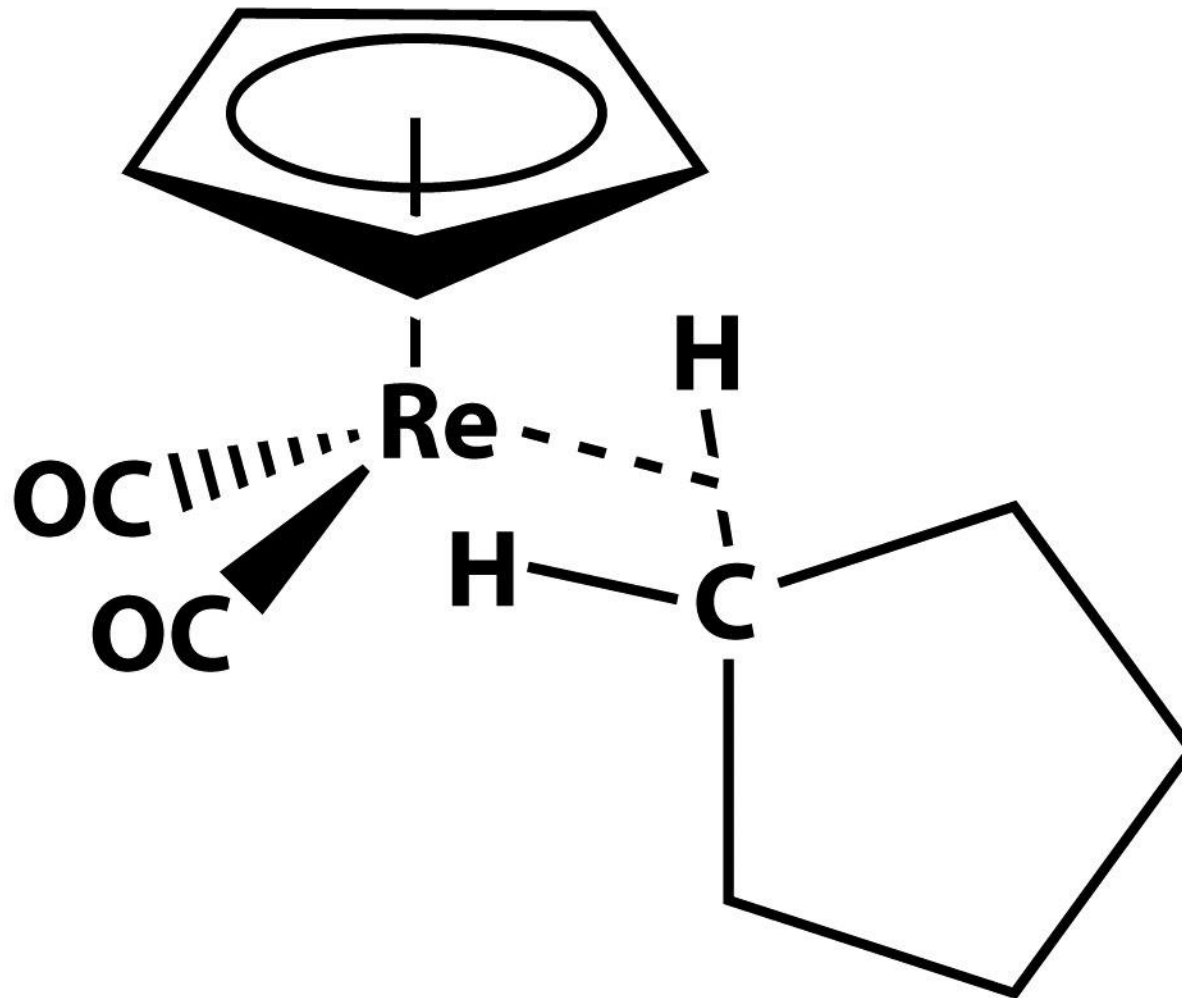
*trans-metallazione a partire da alogenuri di Ag-NHC*





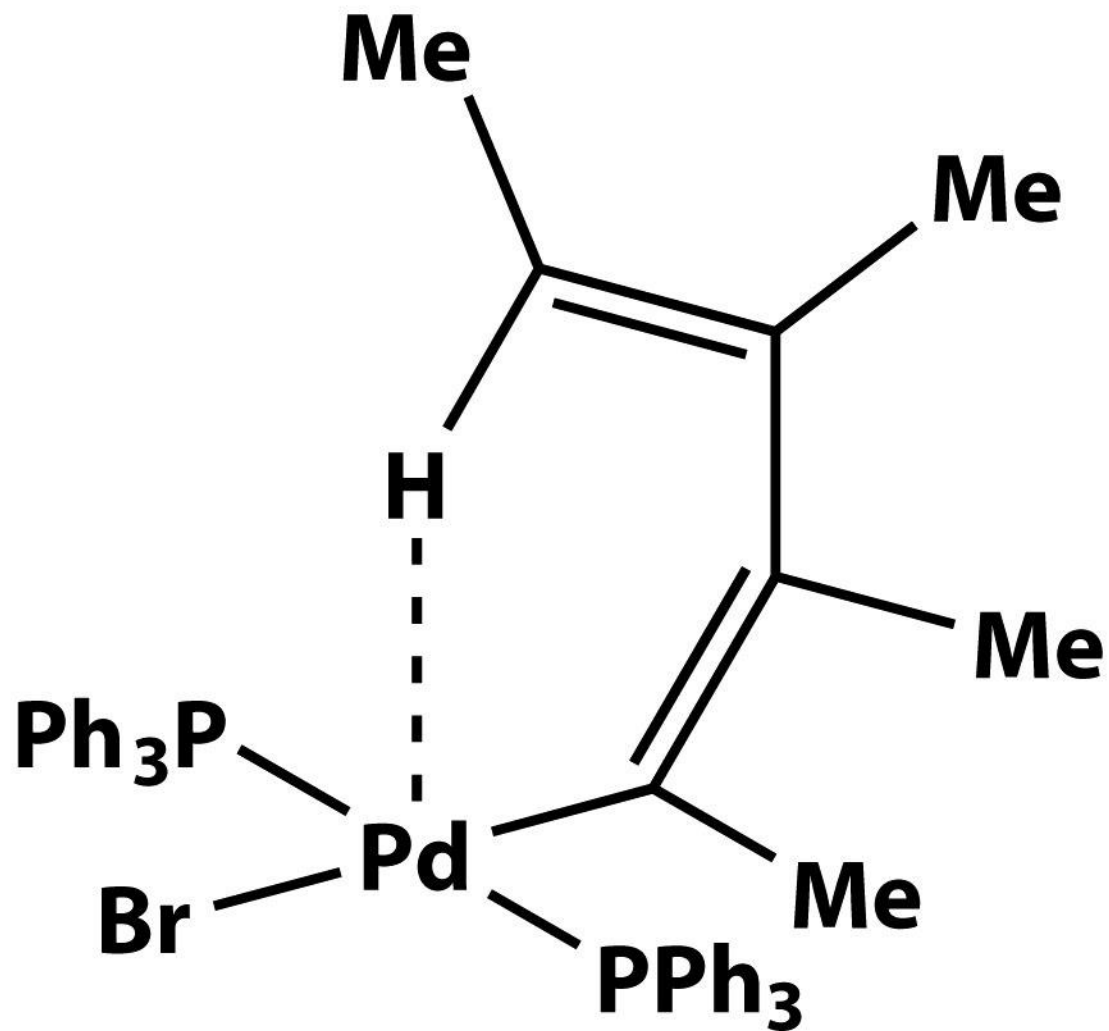






Identificato nel 1988 tramite spettroscopia NMR in soluzione





Interazioni C-H *agostiche*