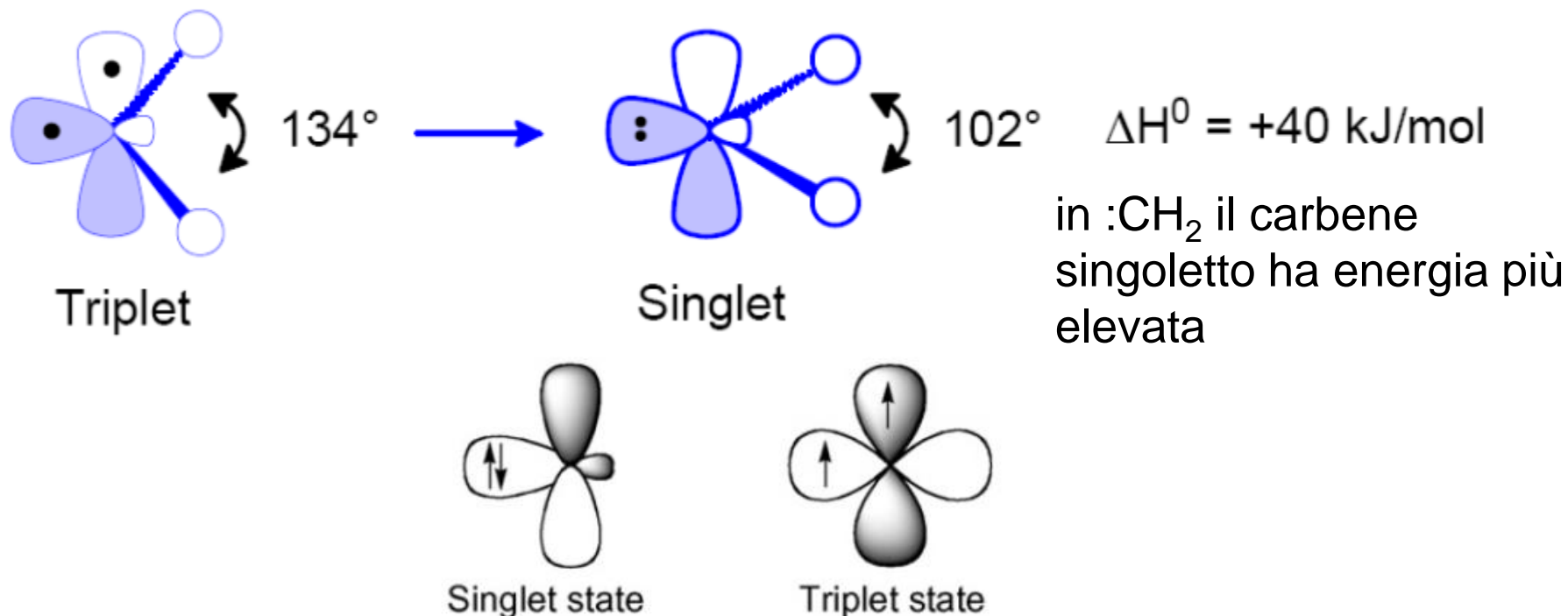
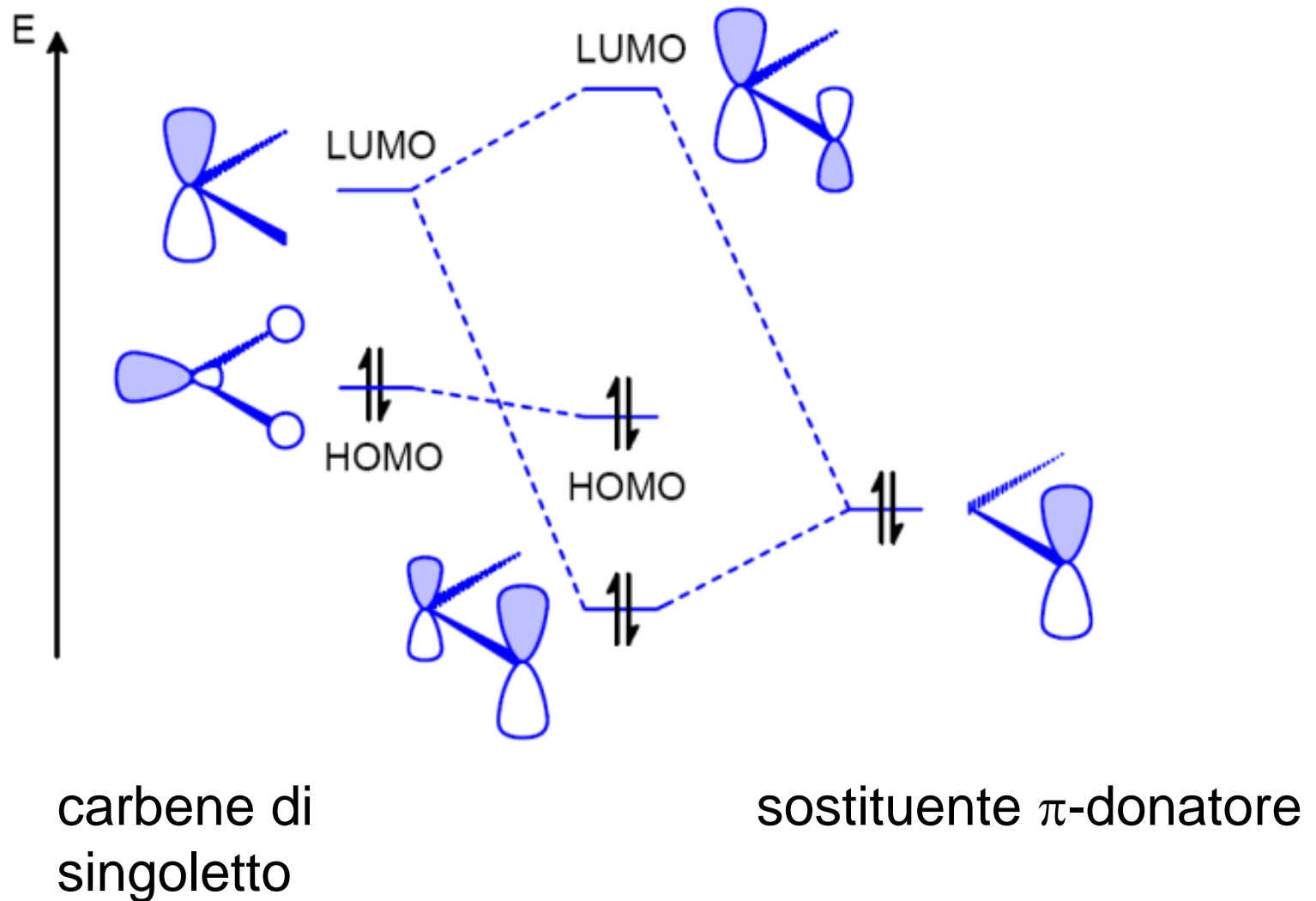


Interazioni C–H *agostiche*

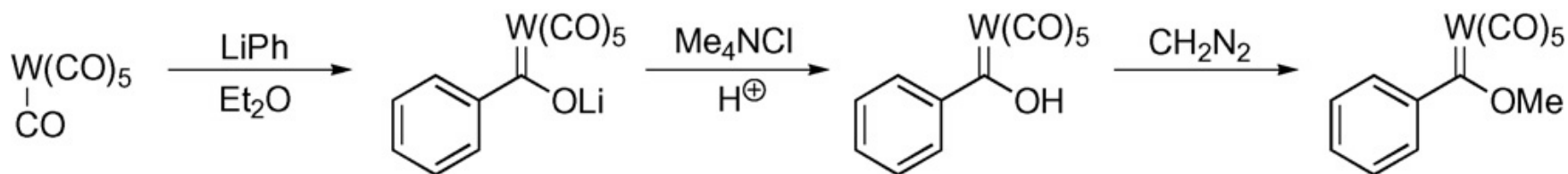
Carbeni



Sostituenti π -donatori stabilizzano lo stato di singoletto

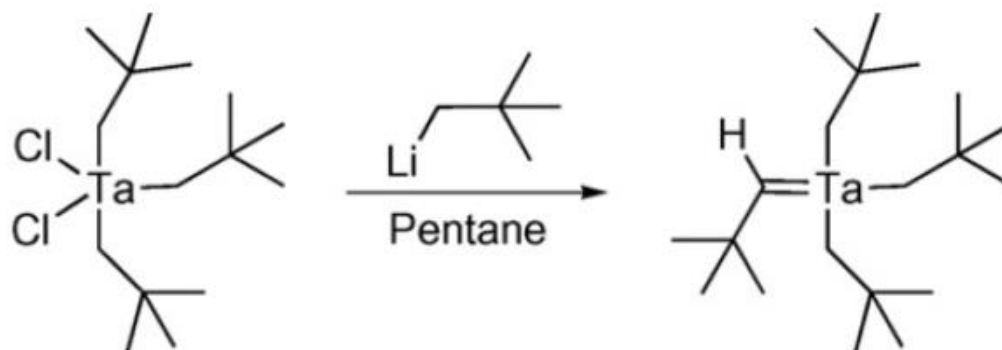


1964: primo complesso metallo-carbene (*Fischer*)



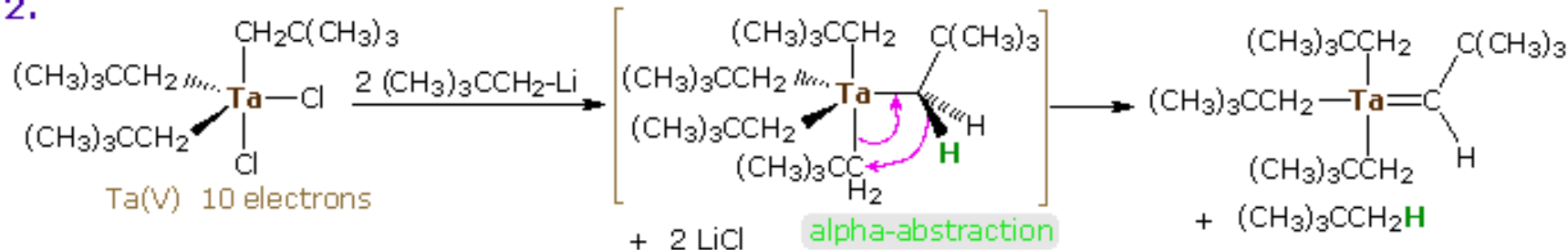
metossifenilmetilene tungsteno(0) pentacarbonile

1974: primo complesso metallo-alchilidene (*Schrock*)

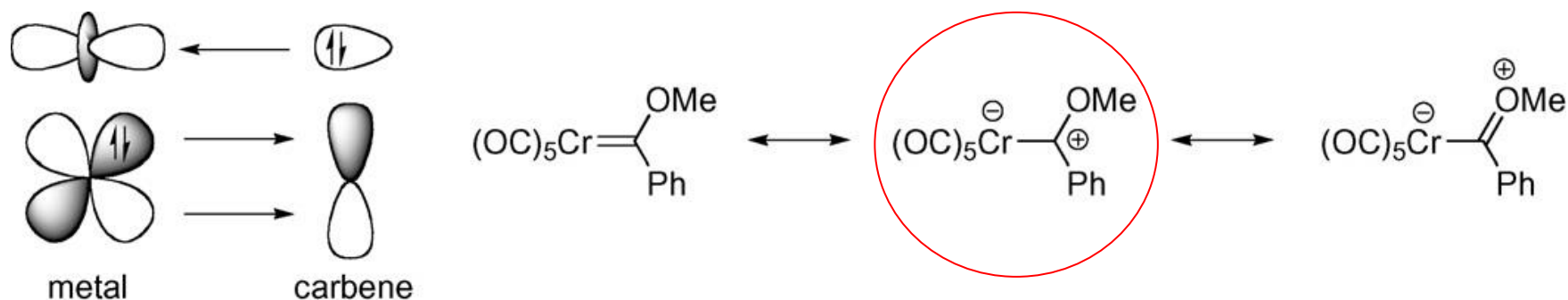


α -hydrogen abstraction

2.

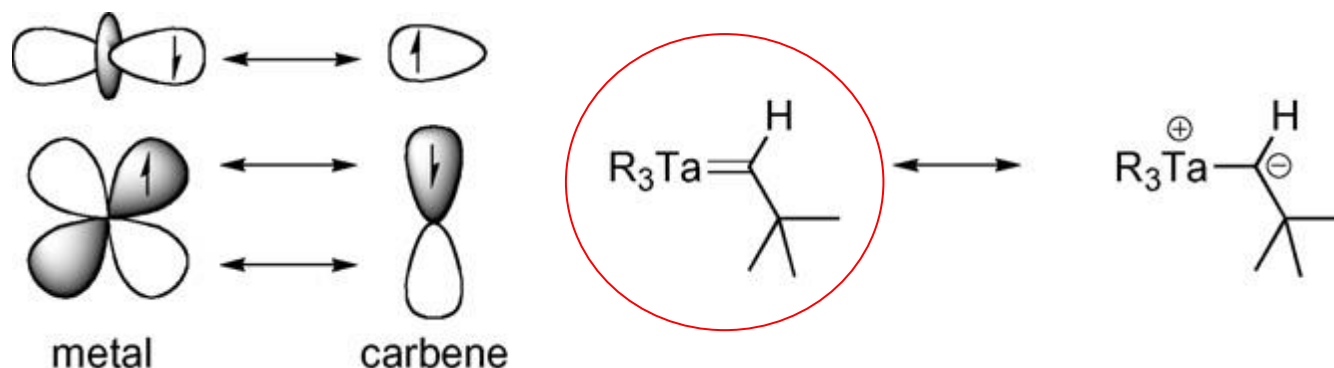


Carbeni di Fischer



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

Carbeni di Schrock

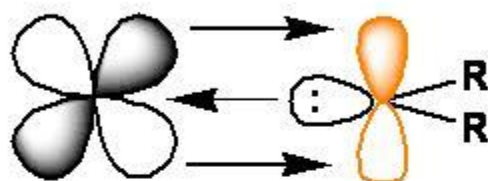


1. Carbeni debolmente stabilizzati (alchilideni)
2. *Early transition metals* in alto stato di ossidazione, con leganti ancillari σ - e π -donatori
3. È un vero doppio legame, polarizzato verso il carbonio
4. Nucleofili al legame carbonio–metallo (C elettrone-ricco)

Typical Ligands – Transition Metal Carbene Complexes

FISCHER

- Electrophilic Carbon



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

strong σ -donor
poor or OK π -acceptor

2-electron donor

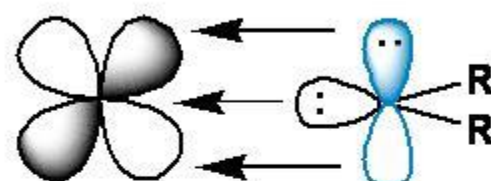
R = π -donor
(OR, NR_2 , Ph)

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

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

SCHROCK

- Nucleophilic Carbon



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

strong σ -donor
strong π -donor

4-electron donor

R = H, Alkyl

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

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

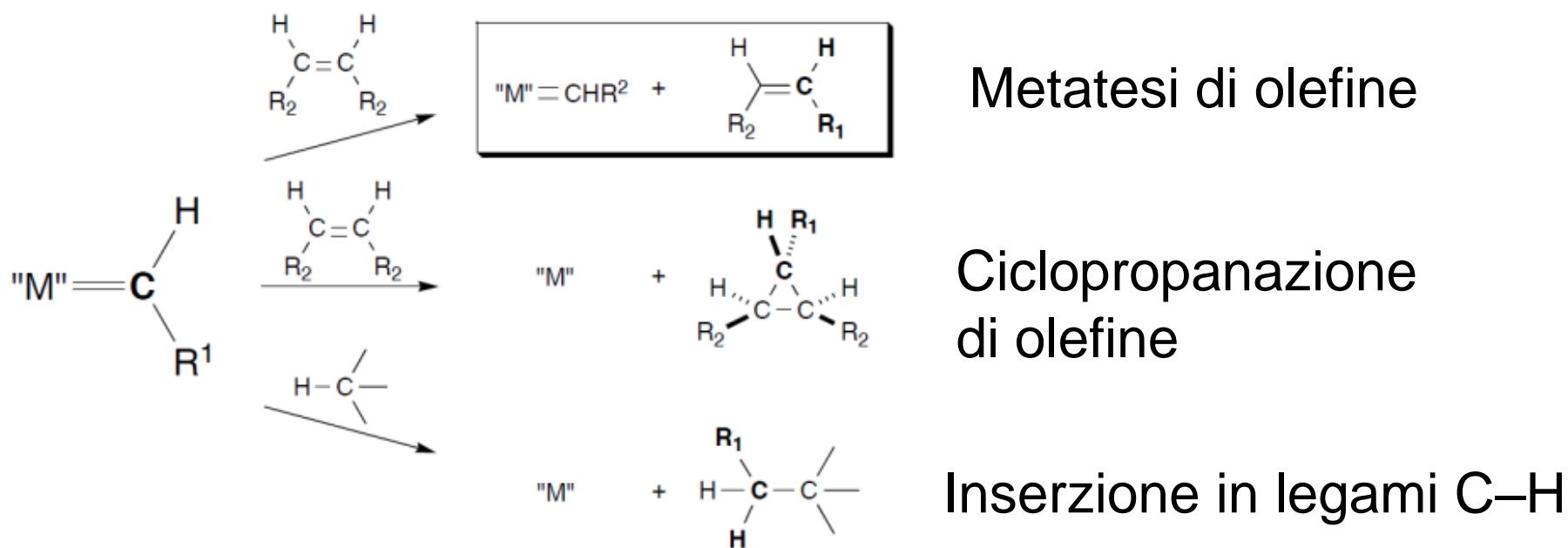
properties

typical R groups in CR_2

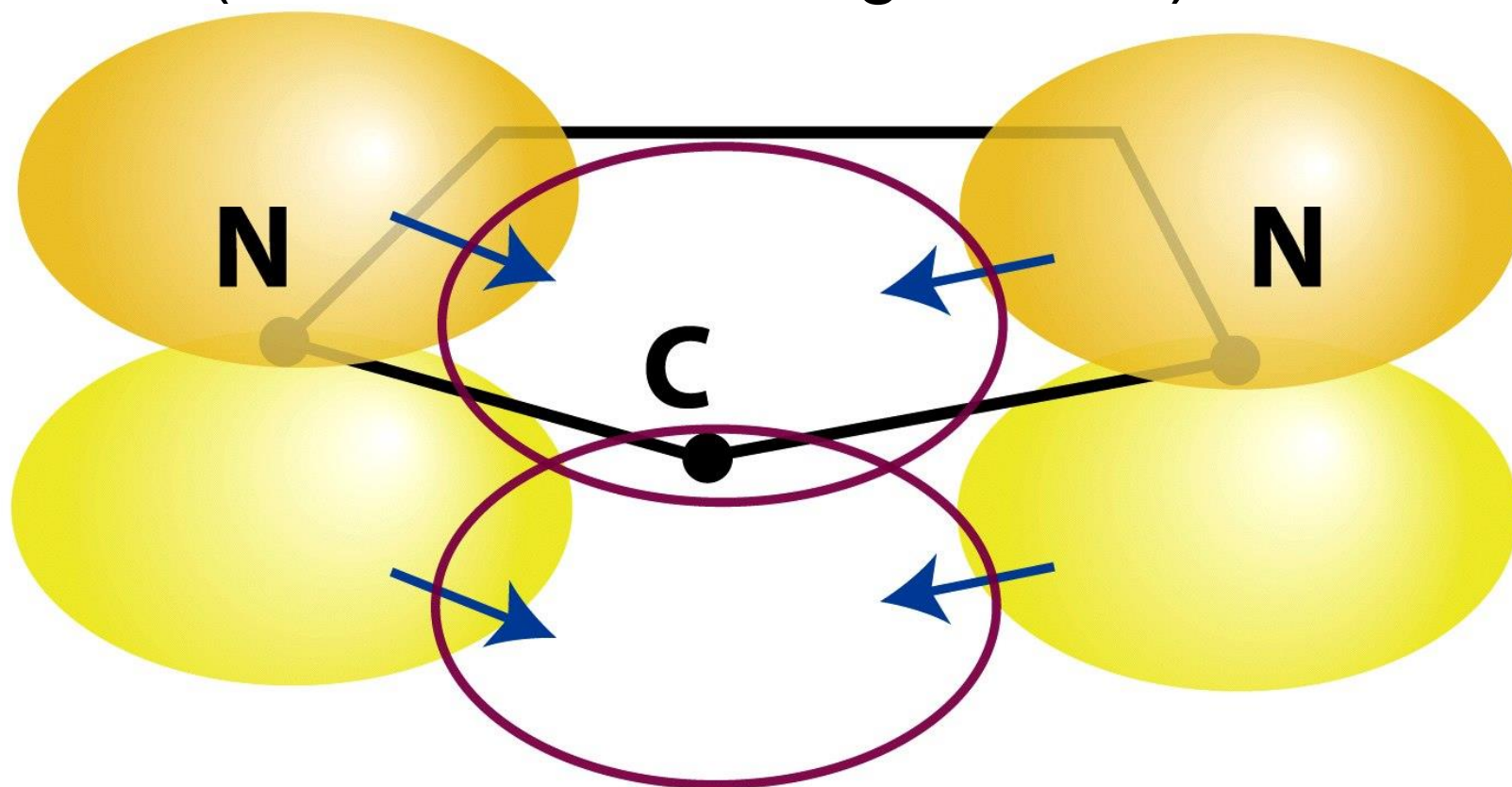
typical metals

typical co-ligands

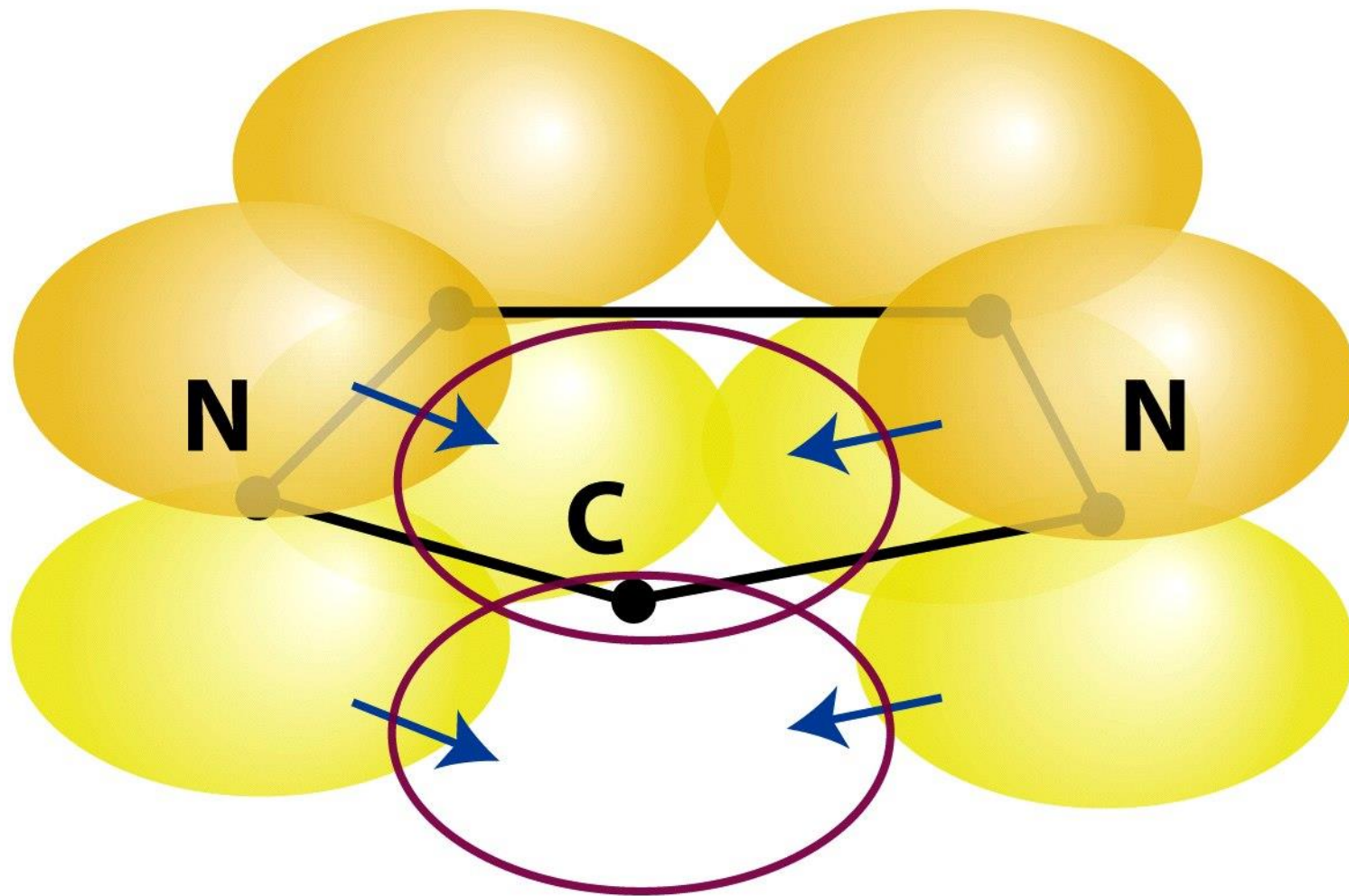
Applicazioni in catalisi dei carbeni di Schrock e carbeni di Fischer



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

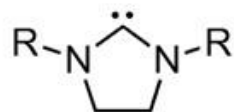


Carbeni tipo Fischer

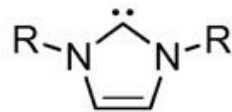


struttura di risonanza aromatica
sei elettroni

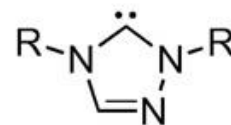
Principali NHC



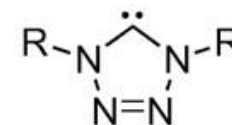
Imidazolidin-



Imidazol-

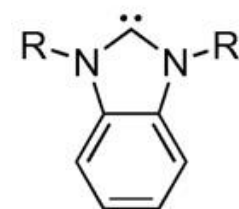


Triazol-

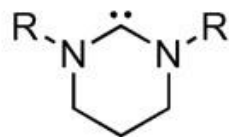


Tetrazol-

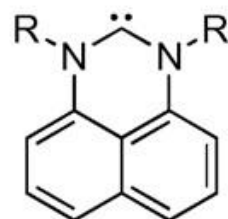
R = Alkyl, aryl



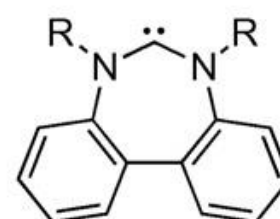
Benzimidazol-



Hexahydropyrimidin-



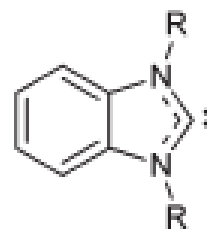
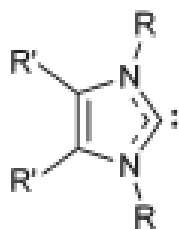
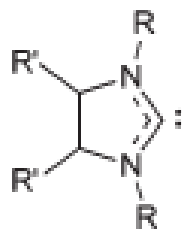
Dihydroperimidin-



Dihydro-dibenzo-diazepin-

-ylidene

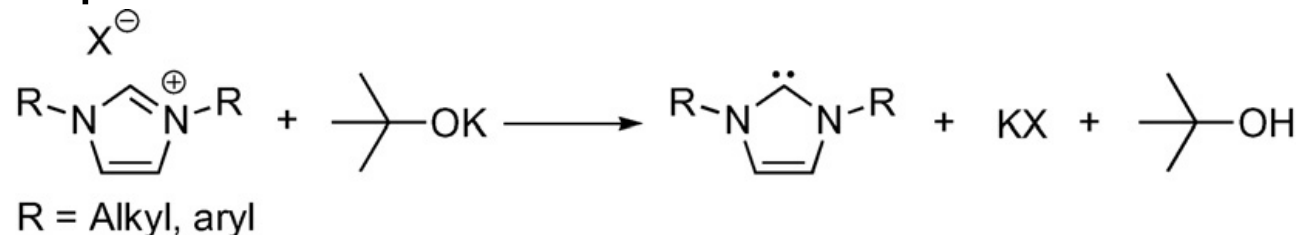
imidazolidinylieni, imidazolylieni, benzimidazolylieni



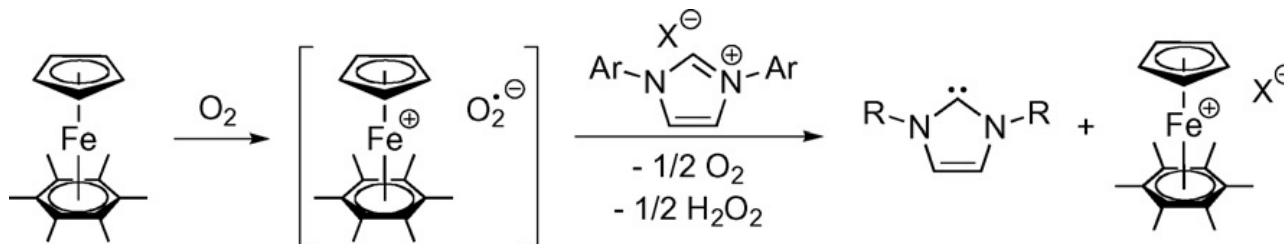
R, R' =
e.g. alkyl, aryl, halogen

Metodi per ottenere NHC stabili

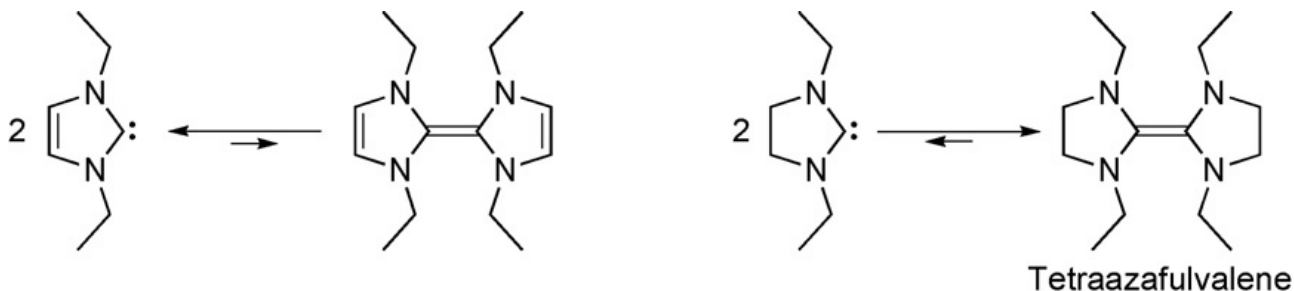
Deprotonazione di sali di imidazolio con basi forti



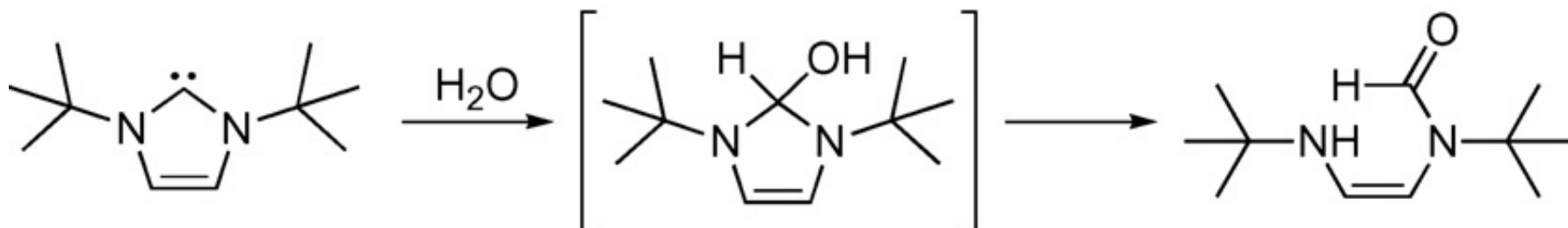
Deprotonazione radicalica di sali di imidazolio con O_2^-



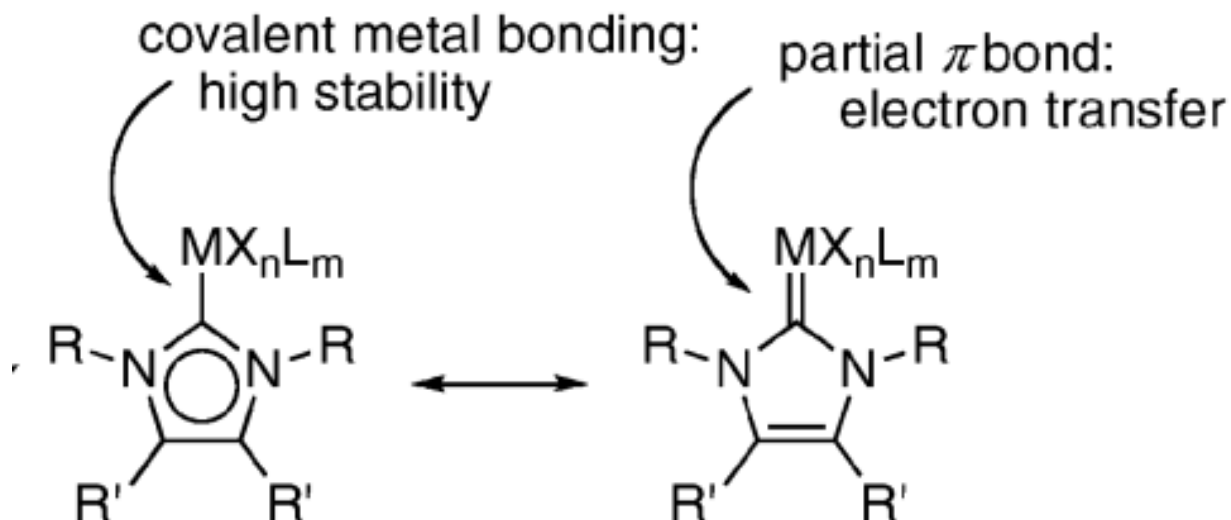
Possibile dimerizzazione



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



Legame M-C nei carbeni NHC



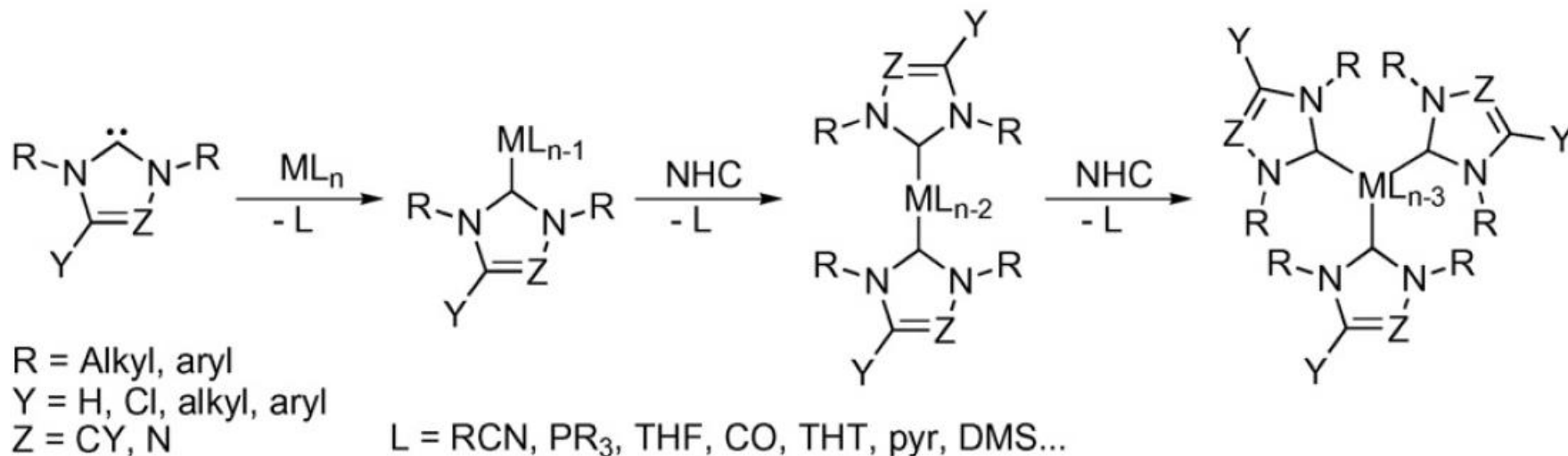
1. Forti σ -donatori
2. Contributi π modesti
3. TEP inferiori a quelli delle fosfine
4. Flessibilità sintetica (variazioni dei gruppi R ed R')

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

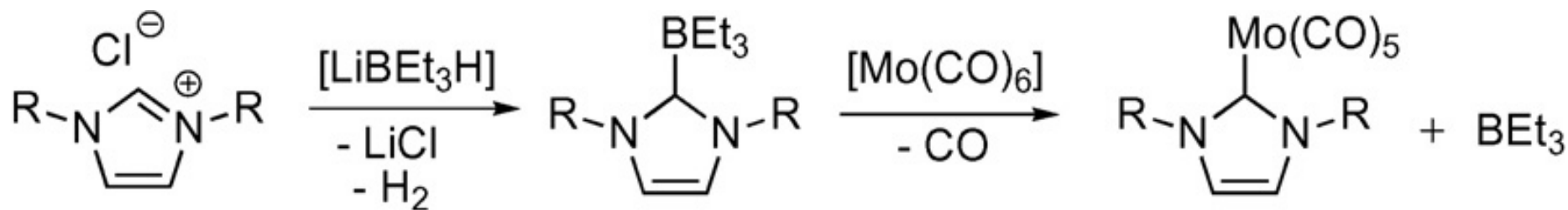
Legame M–C nei carbeni

- Capacità π -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 σ , mentre il contributo di π -retrodonazione è quasi sempre trascurabile.
- La componente π diventa significativa con i metalli del Gruppo 11, cioè rame, argento e oro.
- Esistono esempi con tutti i metalli dal Gruppo 4 al 12

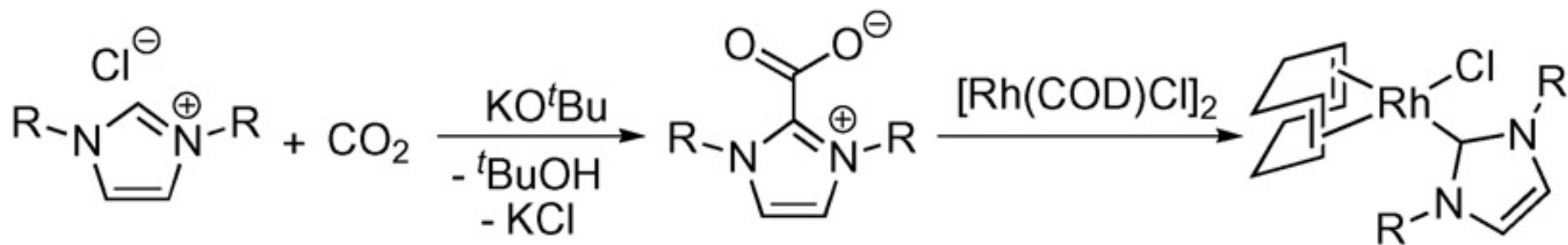
Sintesi di composti M-NHC a partire da NHC stabili per sostituzione



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



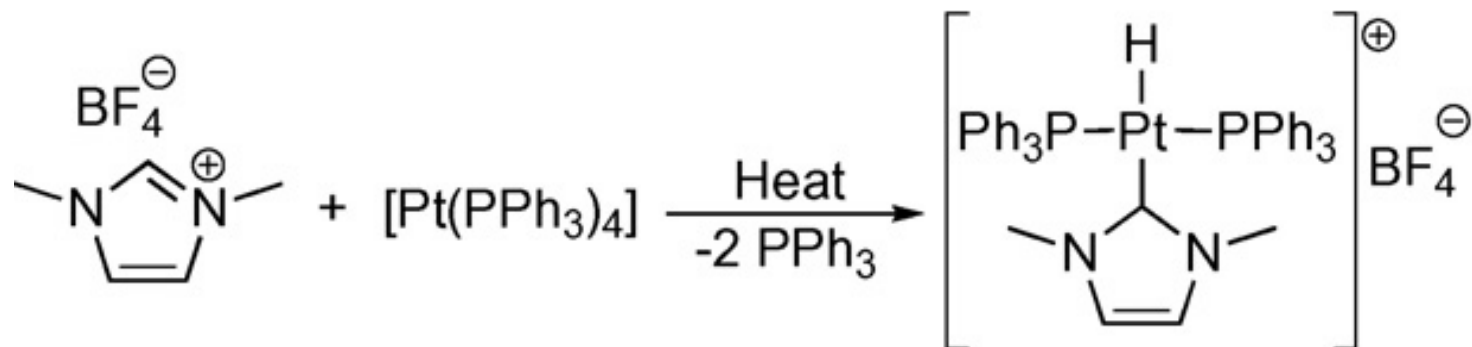
trialchilborano-2-imidazolo



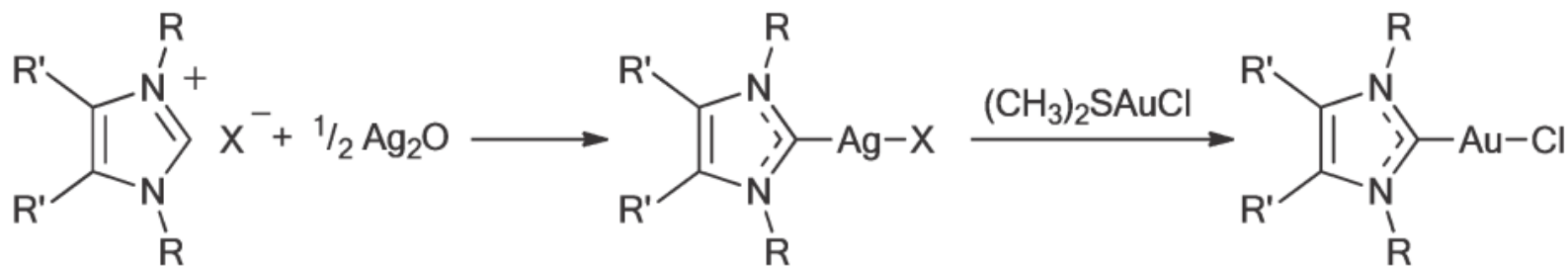
carbossilato-2-imidazolo

Sintesi di composti M-NHC

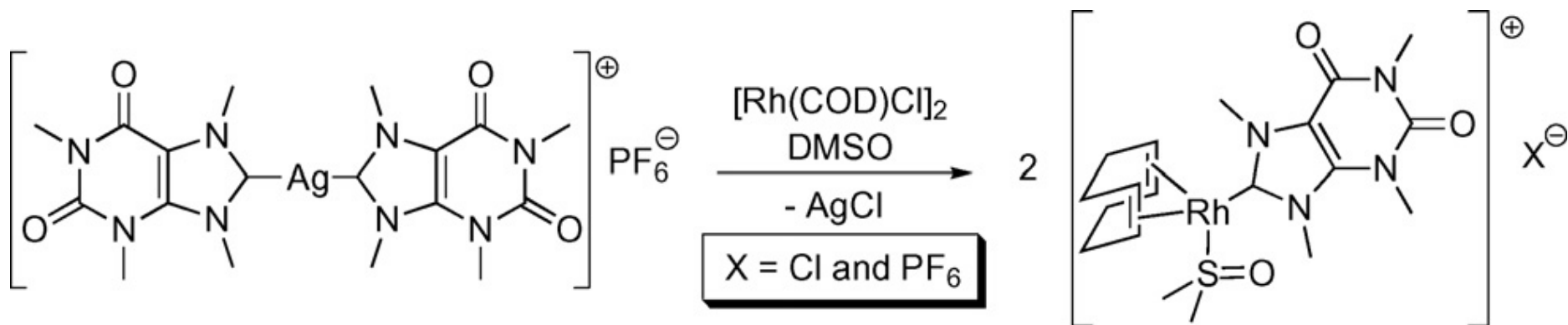
addizione ossidativa di sali di imidazolio su precursori zerovalenti

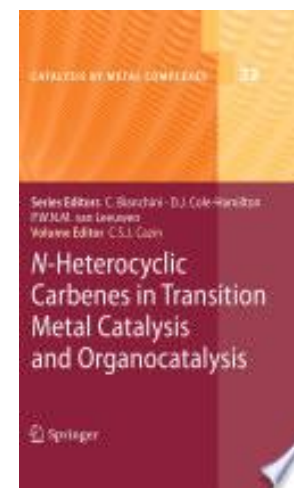
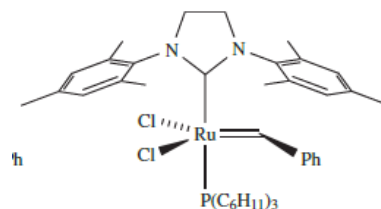
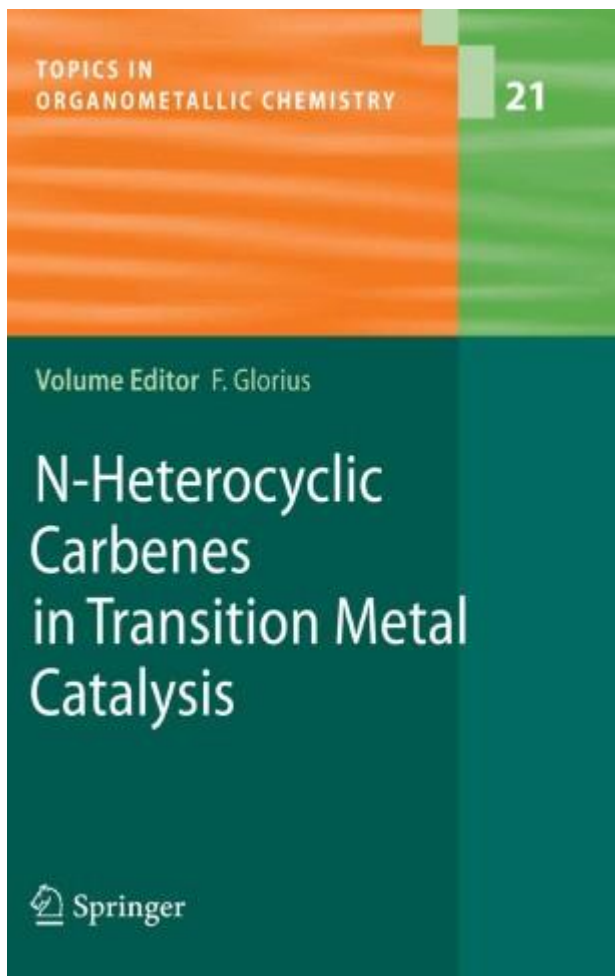


trans-metallazione a partire da alogenuri di Ag-NHC



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





Organocatalysis

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N-Heterocyclic Carbenes as Organocatalysts

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