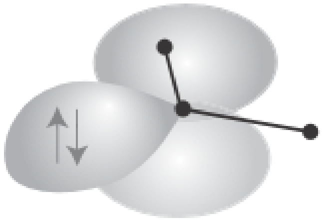
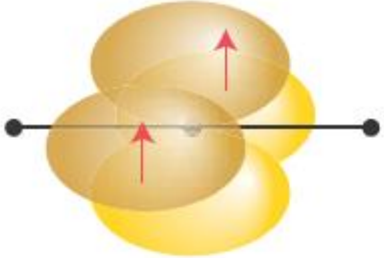
Carbenes

$:CH_2$ $:CR_2$ = alkylidene



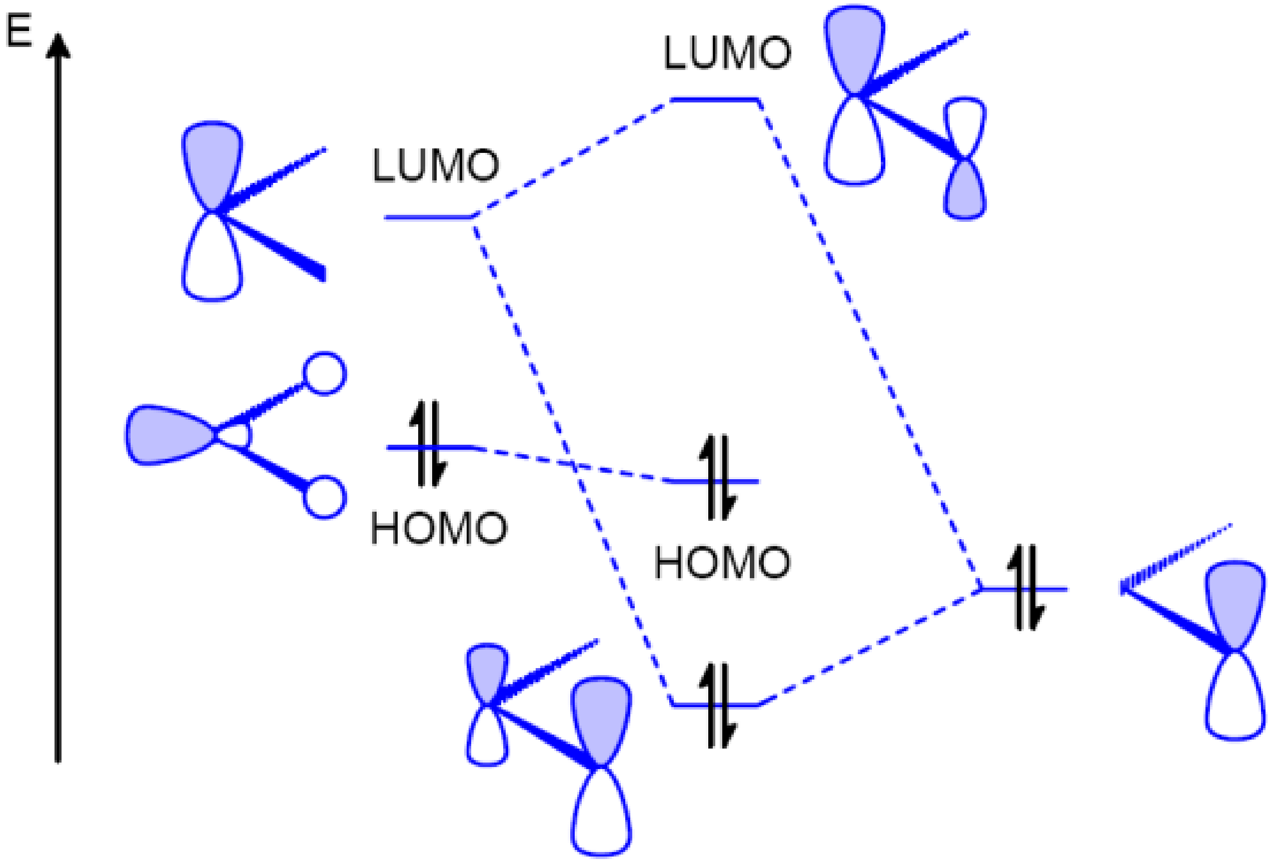
Singlet (C hybridized sp^2; S = 0: $2e^-$ coupled with opposite spin)



Triplet (C hybridized sp; S = 1: $2e^-$ with parallel spin)

in $:CH_2$ the singlet carbene has higher energy

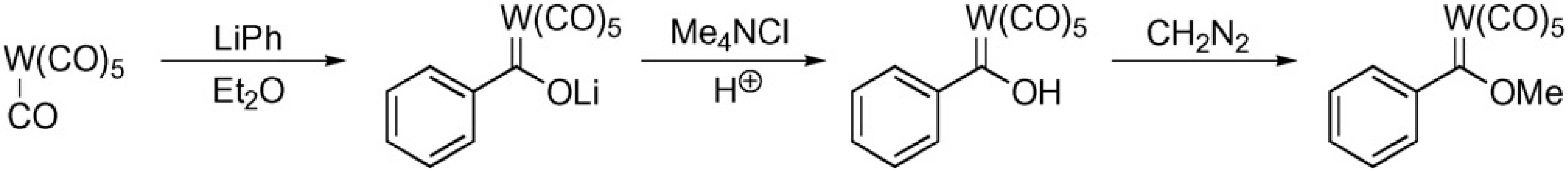
π-donor substituents stabilize the singlet state



Singlet
carbene

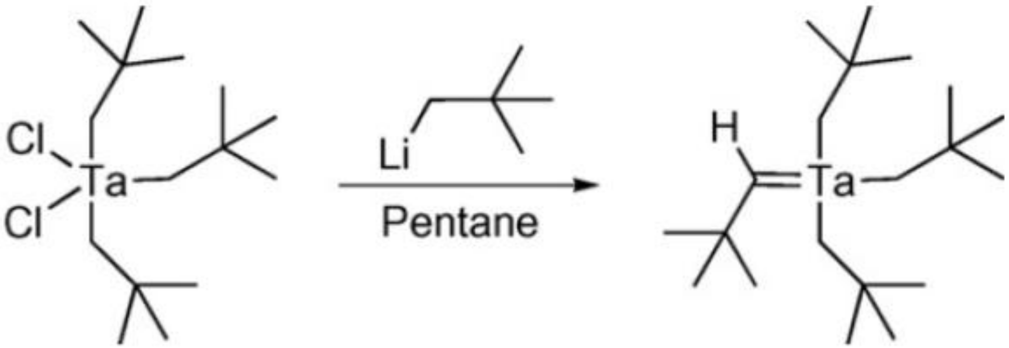
π-donor substituent

1964: first metal-carbene compound (*Fischer*)



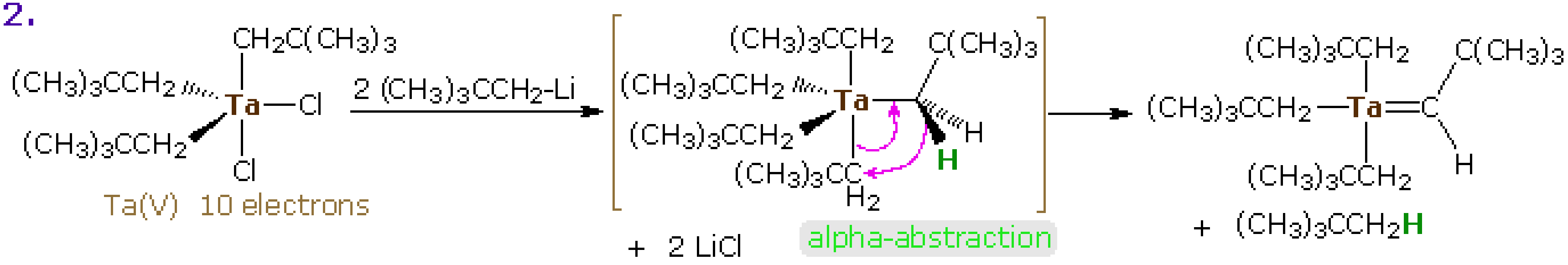
metoxyphenylmethylenepentacarbonyltungsten(0)

1974: first metal-alkylidene compound (*Schrock*)

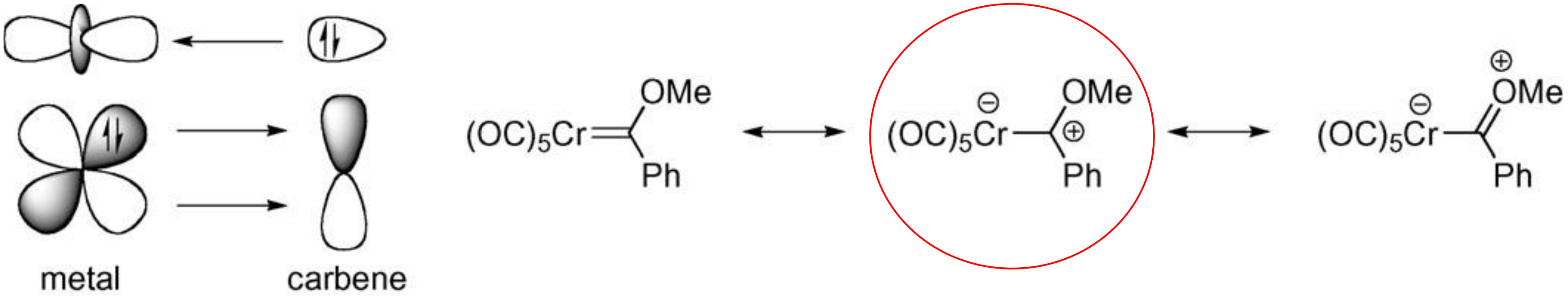


α-hydrogen abstraction

2.

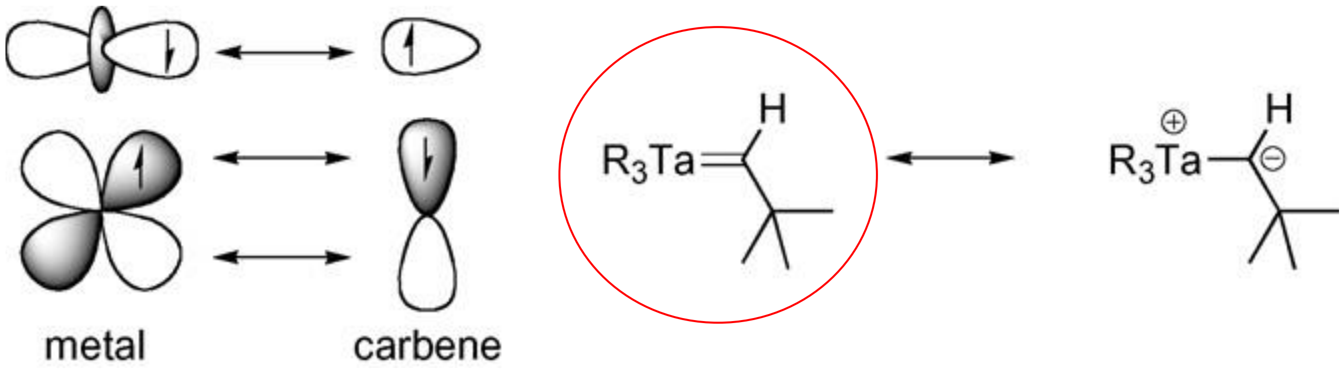


Fischer Carbenes



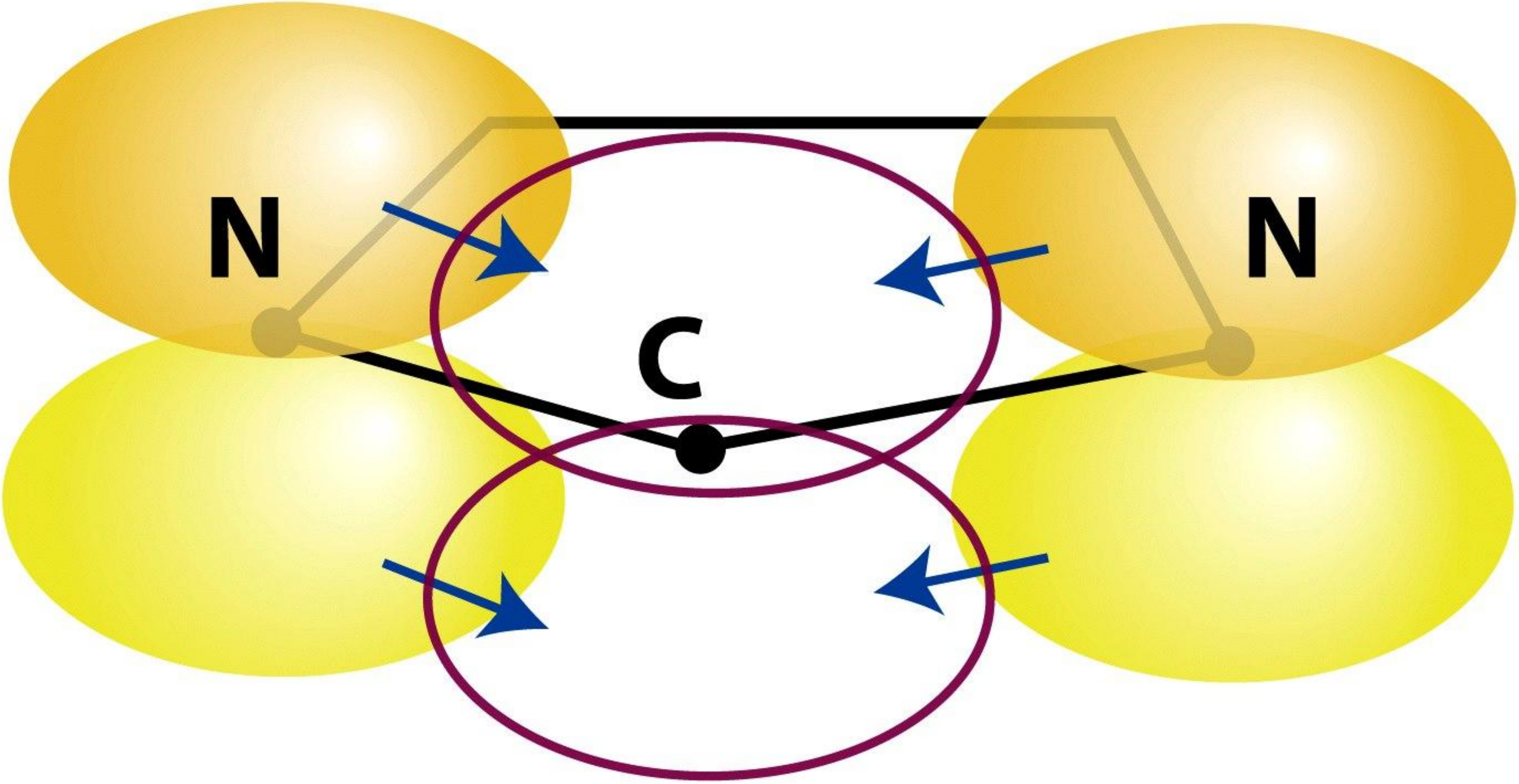
1. Singlet carbenes are stabilized by heteroatoms (*e.g.* aminocarbenes and alcoxycarbenes)
2. Metal in low oxidation state, π-acceptor ancillary ligands
3. Electrons are π polarized towards the metal (see resonance forms)
4. Electrophiles at the carbon–metal bond (C electron-poor) (*Fisher* = *Electrophilic Reagent*)

Schrock Carbenes

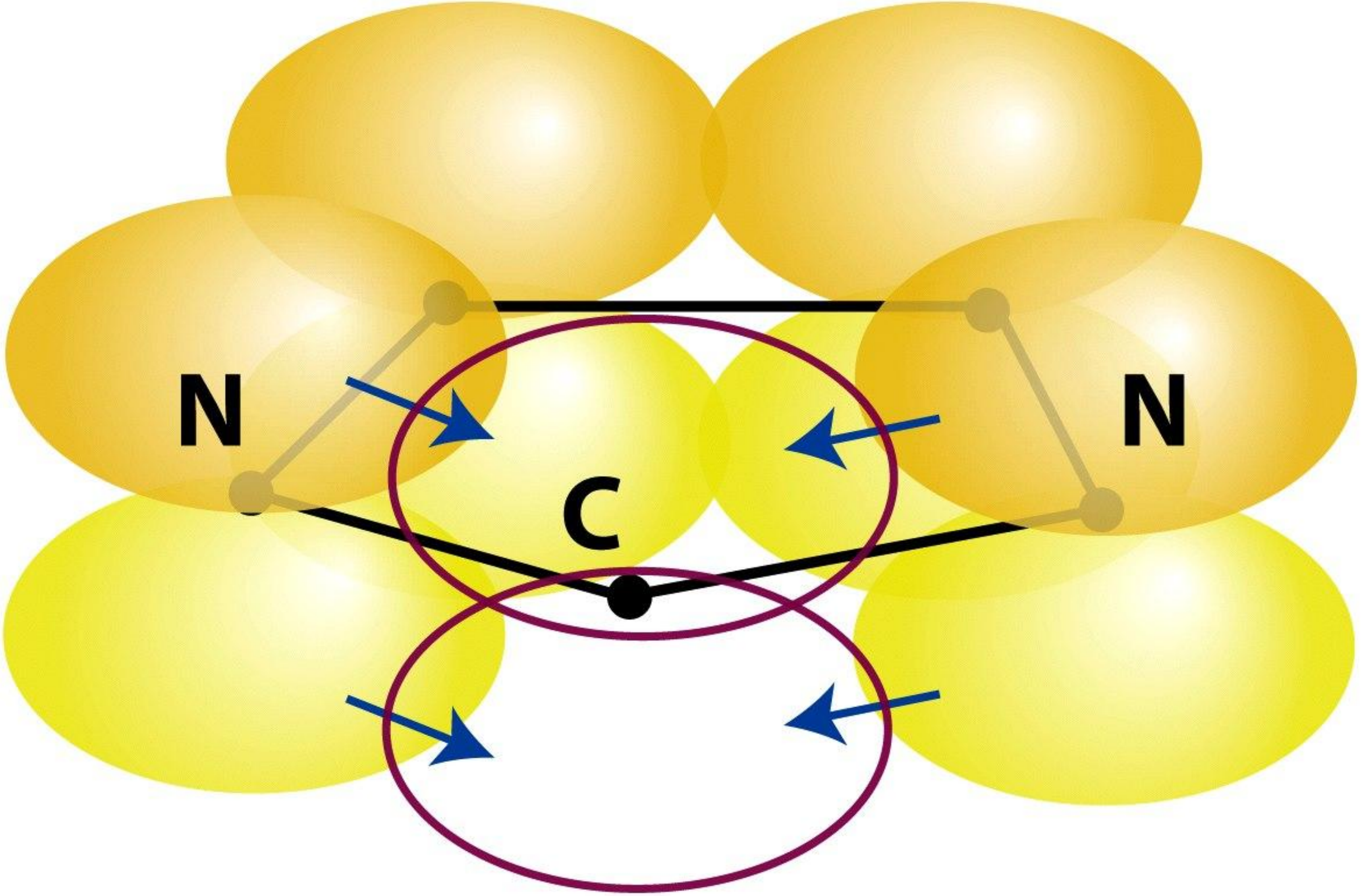


1. Carbenes are weakly stabilized (alkylidenes)
2. *Early transition metals* in high oxidation state, σ- and π-donor ancillary ligands
3. Proper double bond, polarized towards the carbon
4. Nuclephiles at the carbon–metal bond (C electron-rich)

*N-Heterocyclic Ca*rbenes, NHCs
(Arduengo Carbenes, 1991)

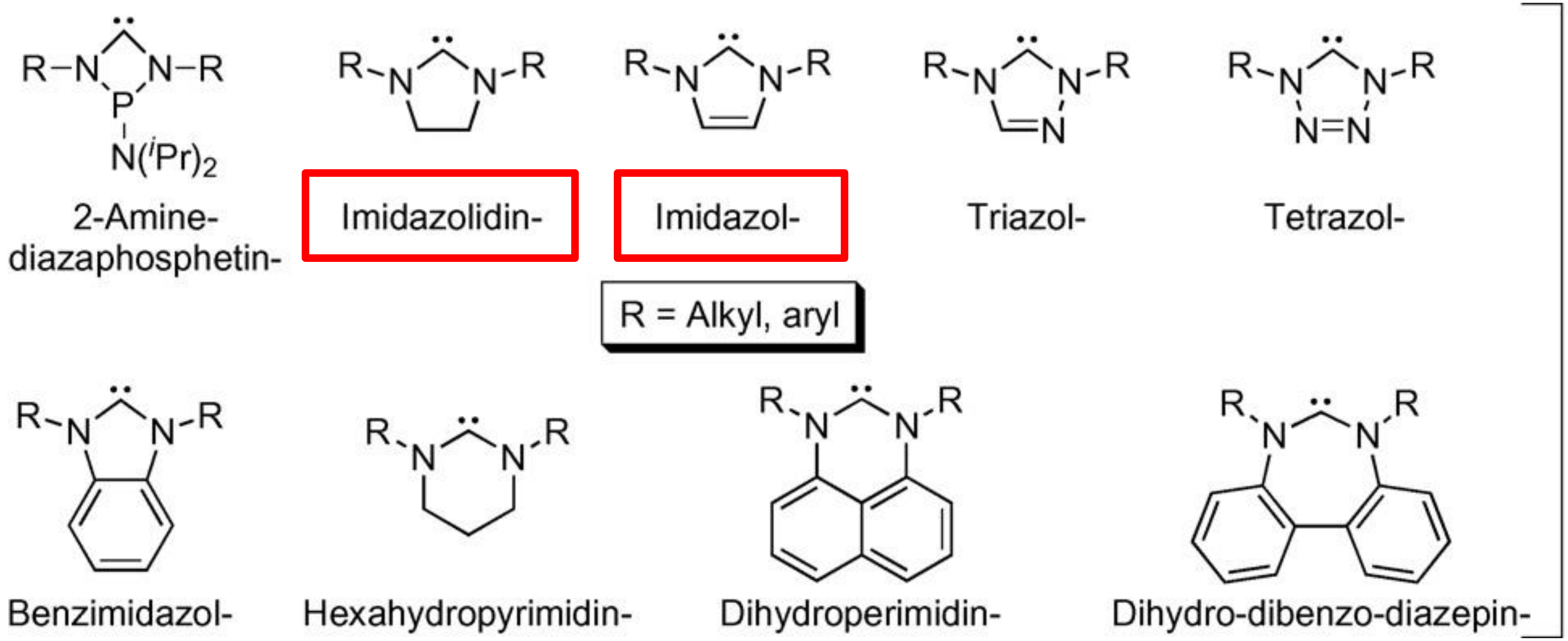


Fischer Carbenes



Aromatic resonance structure with 6 e⁻

Main NHCs



2-Amine-diazaphosphetin-

Imidazolidin-

Imidazol-

Triazol-

Tetrazol-

R = Alkyl, aryl

Benzimidazol-

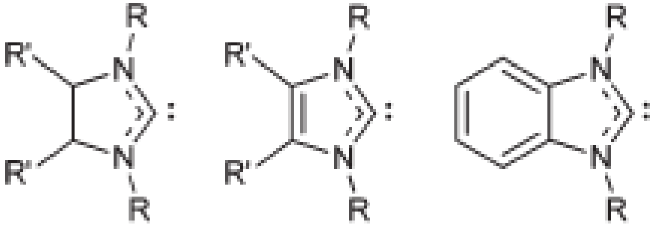
Hexahydropyrimidin-

Dihydroperimidin-

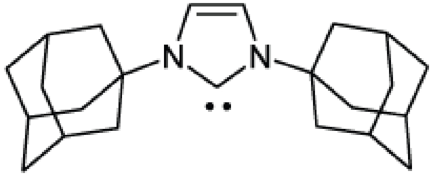
Dihydro-dibenzo-diazepin-

-ylidene

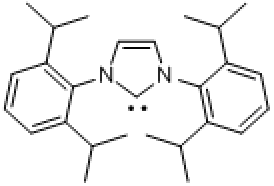
imidazolidinylidenes, **imidazol**ylidenes, benzimidazolylidenes



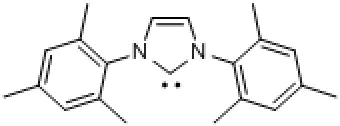
R,R' =
e.g. alkyl, aryl, halogen



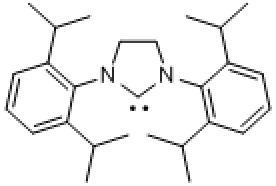
IAd



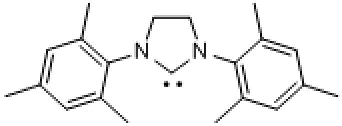
IPr



IMes



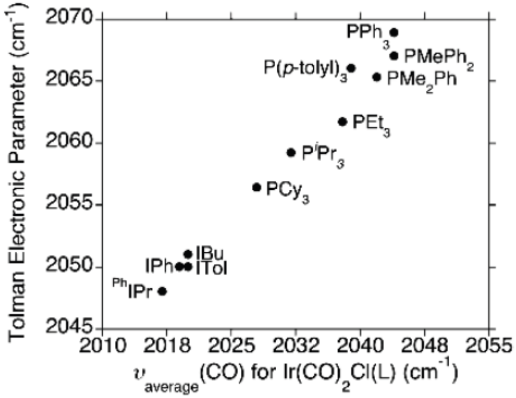
SIPr

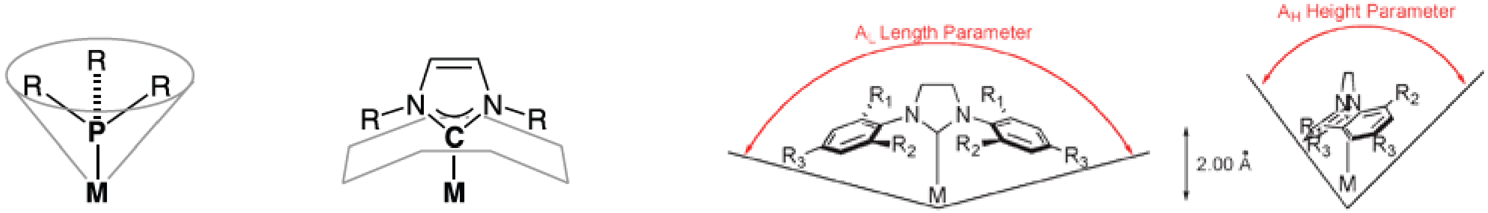


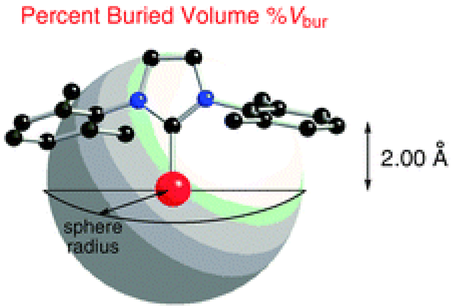
SIMes

Table 1 IR values for the carbonyl stretching frequencies in $LNi(CO)_3$ measured in CH_2Cl_2 [23, 26]

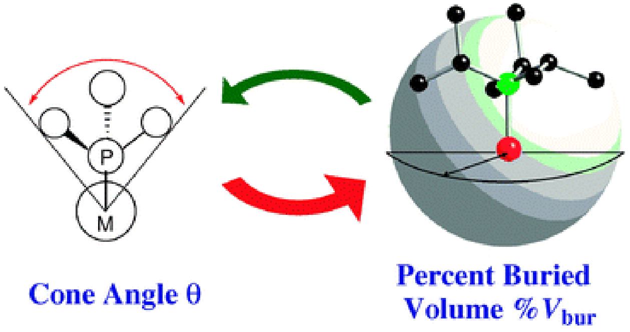
Ligand	υ_{CO} (A_1) [cm^{-1}]	υ_{CO} (E) [cm^{-1}]
IMes	2050.7	1969.8
SIMes	2051.5	1970.6
IPr	2051.5	1970.0
SIPr	2052.2	1971.3
ICy	2049.6	1964.6
PPh_3	2068.9	1990
PCy_3	2056.4	1973
$PtBu_3$	2056.1	1971







"Percent buried volume" ($\%V_{bur}$) defined as the percent of the total volume of a sphere occupied by a ligand. The sphere has a defined radius and has the metal center at the core. $\%V_{bur}$ is calculated using crystallographic data. The volume of this sphere represents the potential coordination sphere space around the metal occupied by a ligand/ligand fragment.



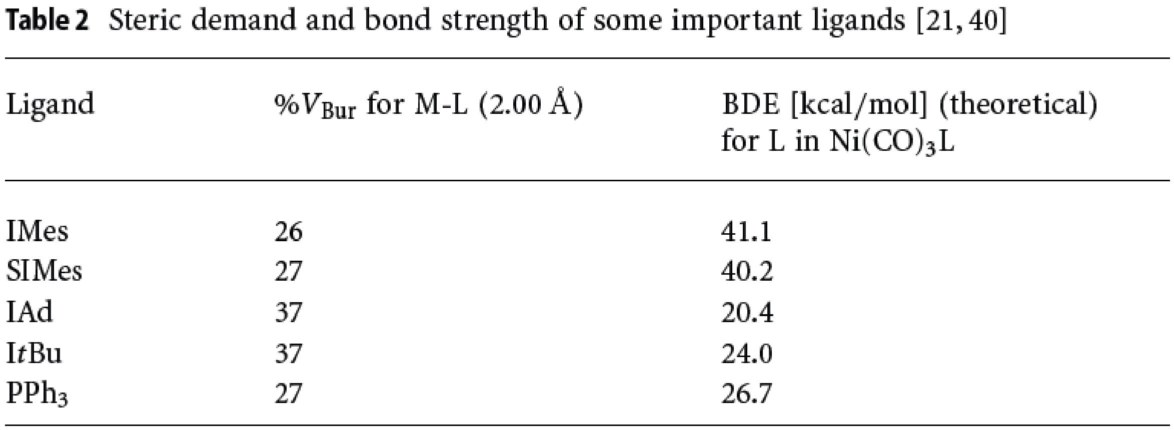
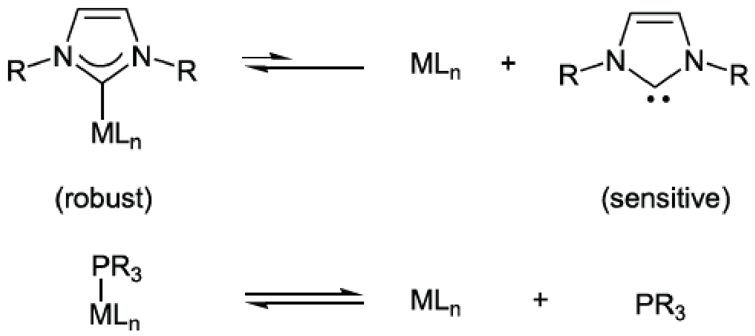


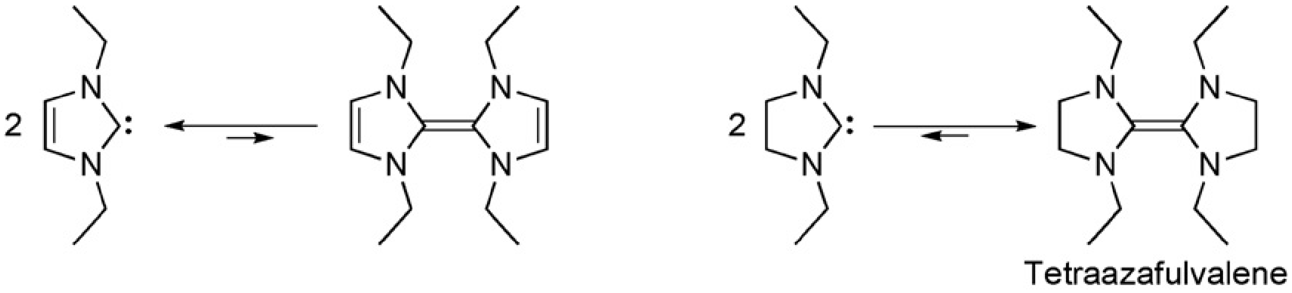
Table 2 Steric demand and bond strength of some important ligands [21, 40]

Ligand	%V_{Bur} for M-L (2.00 Å)	BDE [kcal/mol] (theoretical) for L in $Ni(CO)_3L$
IMes	26	41.1
SIMes	27	40.2
IAd	37	20.4
I*t*Bu	37	24.0
PPh_3	27	26.7

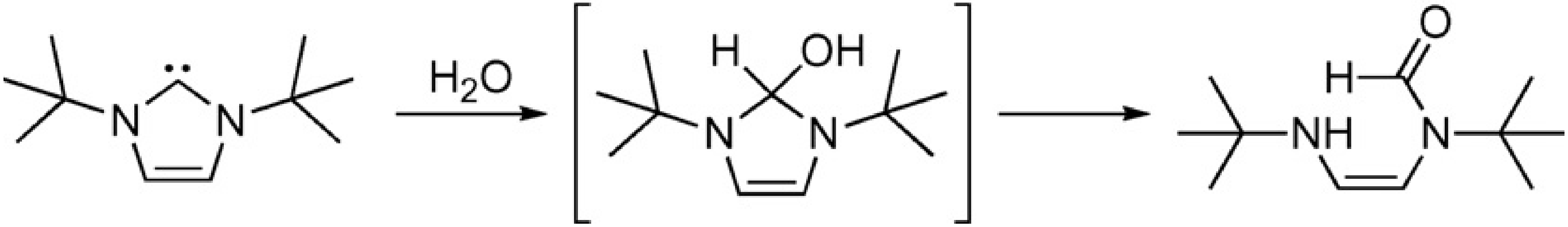


the equilibrium between the free carbene and the carbene metal complex lies far more on the side of the complex than is the case for phosphines. This minimizes the amount of free NHC in solution and thus increases the life time of the complex as well as its robustness against heat, air and moisture.

Potential dimerization



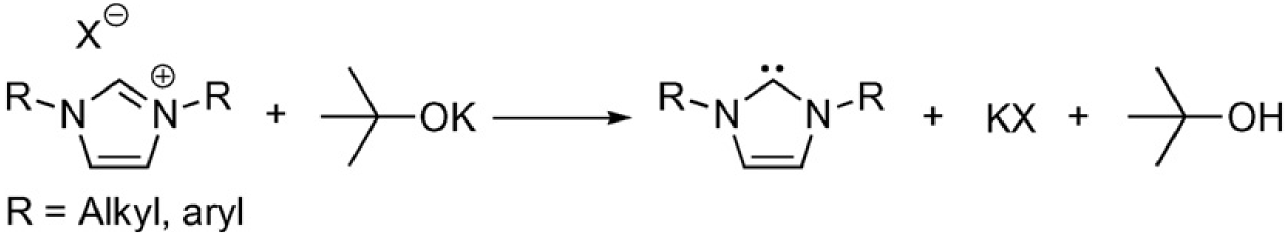
NHCs are strongly sensitive to moisture, but are kinetically stable towards triplet oxygen



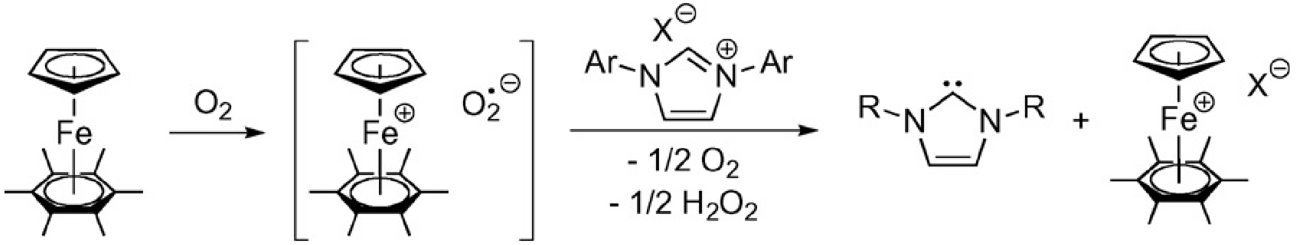
formimide

Methods to isolate stable NHCs

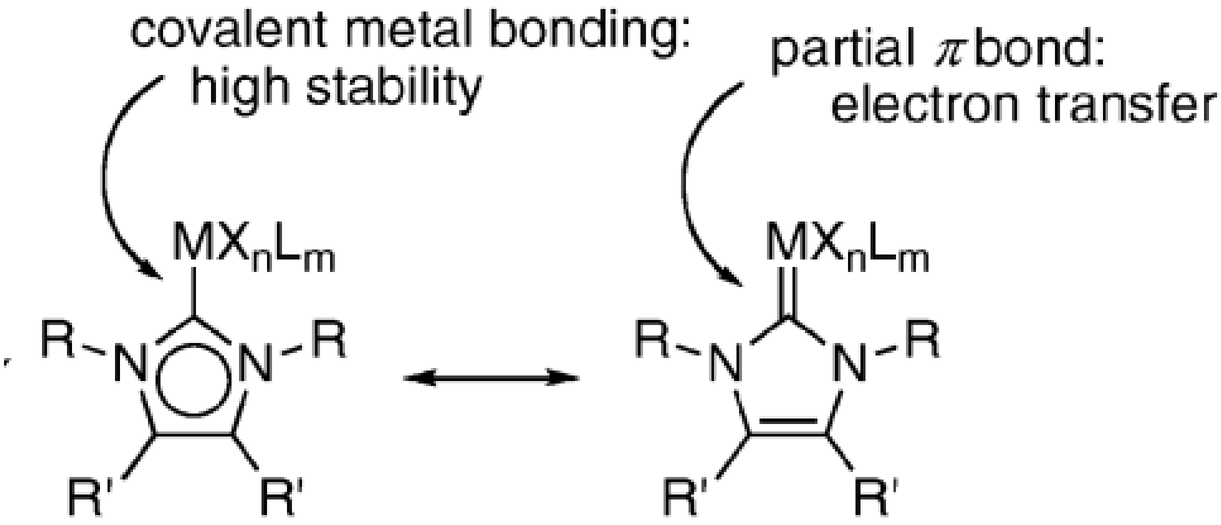
Deprotonation of imidazolium salts



Radical deprotonation of imidazolium salts with $^{\bullet}O_2^{-}$



M−C bond in NHC carbenes



1. Strong σ-donor
2. Modest π contribution
3. TEP smaller than phosphines
4. Sythethic flexibility (variation of R and R’ groups)

NHC ligands are in general stronger σ-donor than the vast majority of phosphines (even the more basic ones).

M−C bond in NHC carbenes

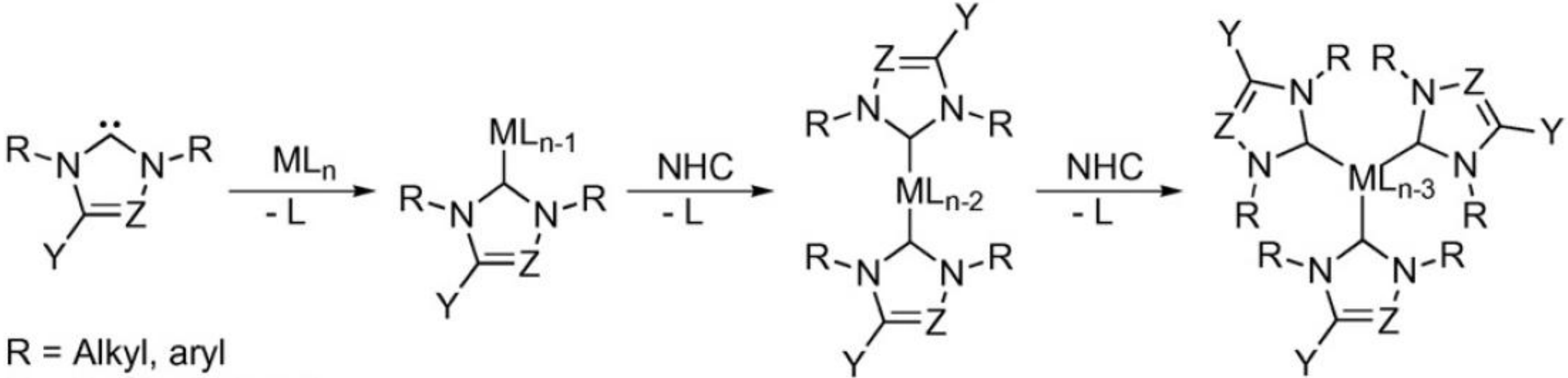
-π-acceptor ability of carbenes bound to metals decreases from Schrock carbens to Fischer (non-diamminocarbenes) to NHCs.

-NHCs are strongly bound to metals via σ, while the π-backdonation contribution is mostly negligible.

-The π component becomes significant for Group 11 metals (i.e. *copper, silver and gold).*

-There are examples of NHCs compounds with metals from Group 4 to 12.

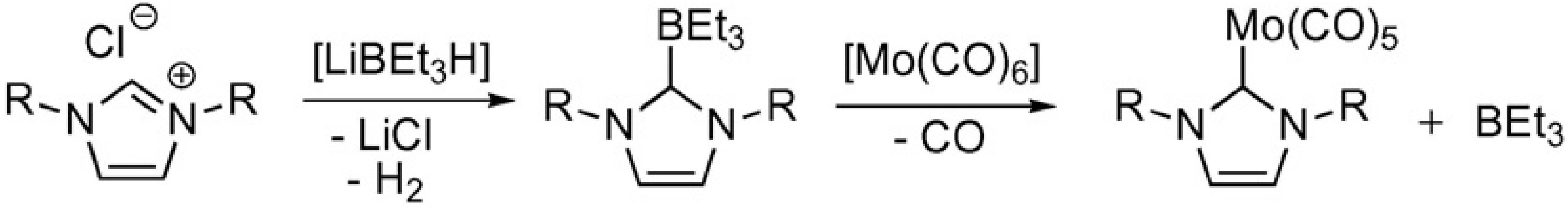
Synthesis of M−NHC compounds from stable NHCs *via* substitution



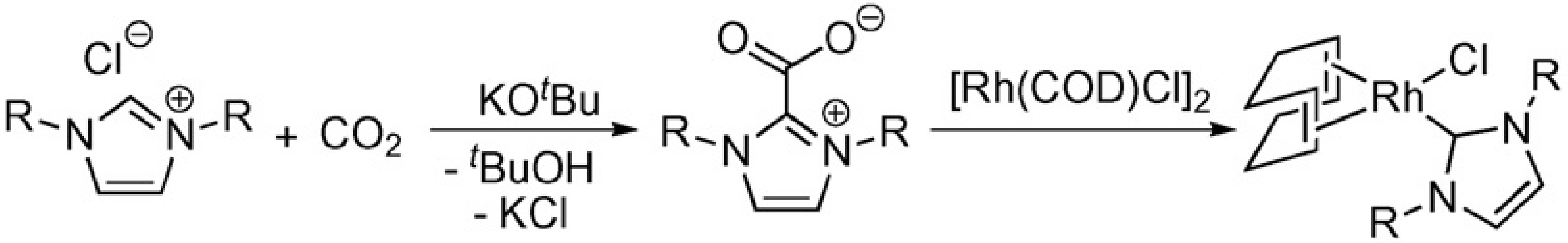
R = Alkyl, aryl
Y = H, Cl, alkyl, aryl
Z = CY, N

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

Synthesis of M−NHC compounds from «masked carbenes»



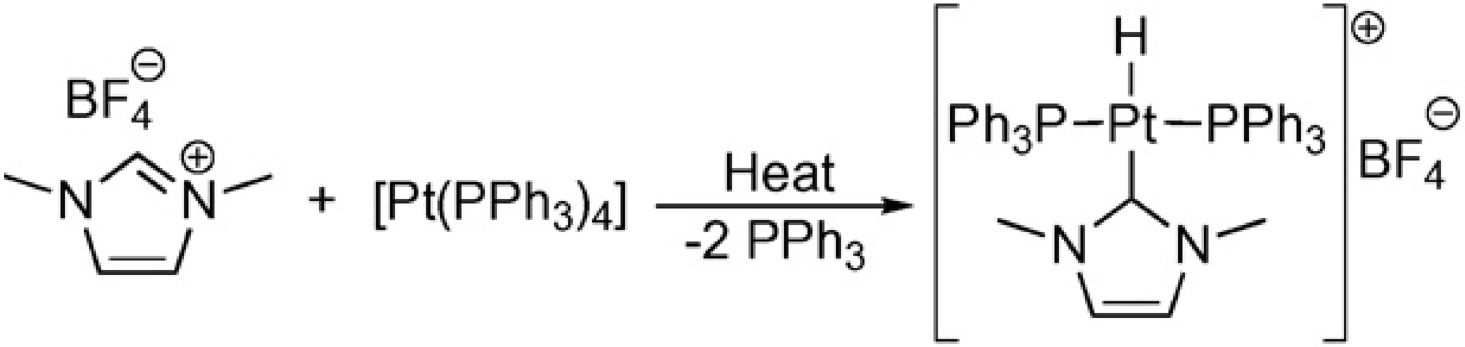
trialkylborane-2-imidazole



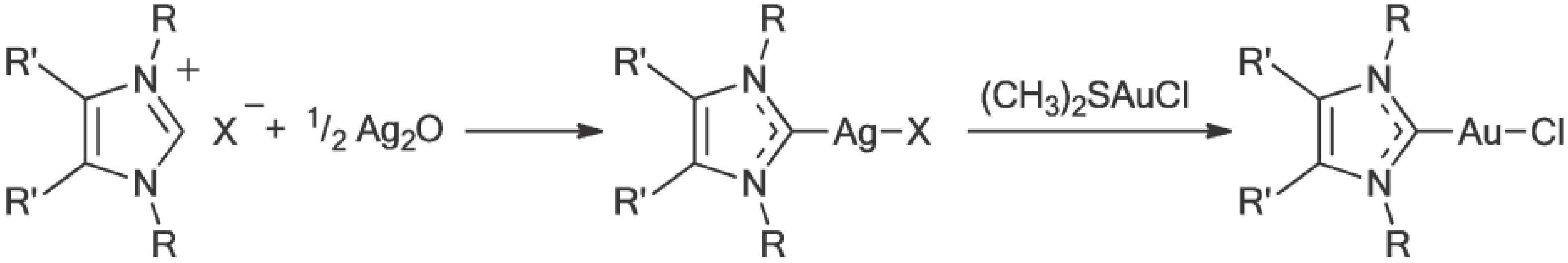
carboxylate-2-imidazole

Synthesis of M−NHC compounds

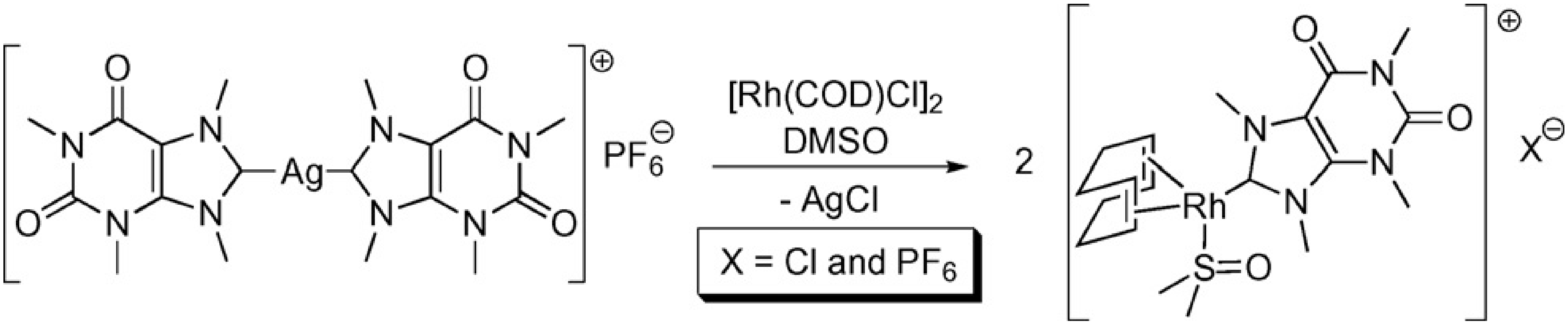
Oxydative addition of imidazolium salts to zero-valent precursors

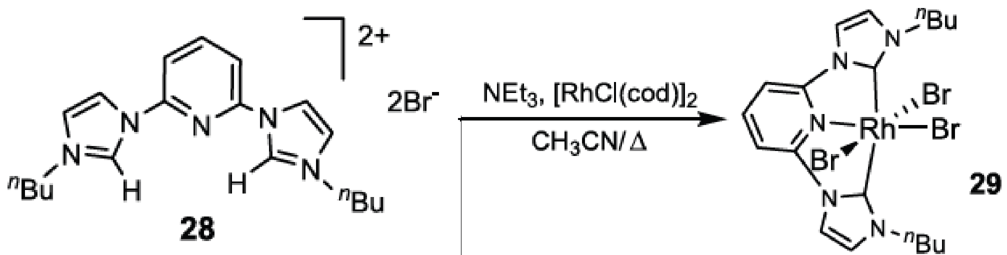


trans-metalation from halide Ag–NHC



Synthesis of M−NHC compounds via *trans*-metalation of Ag-NHCs





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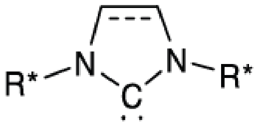
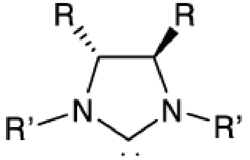
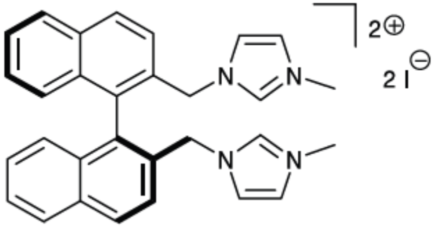
Chiral N-Heterocyclic Carbenes as Stereodirecting Ligands in Asymmetric Catalysis

1. NHC ligands with N-substituents containing centers of chirality;
2. NHC ligands containing chiral elements within the N-heterocycle;
3. NHC ligands containing an element of axial chirality;

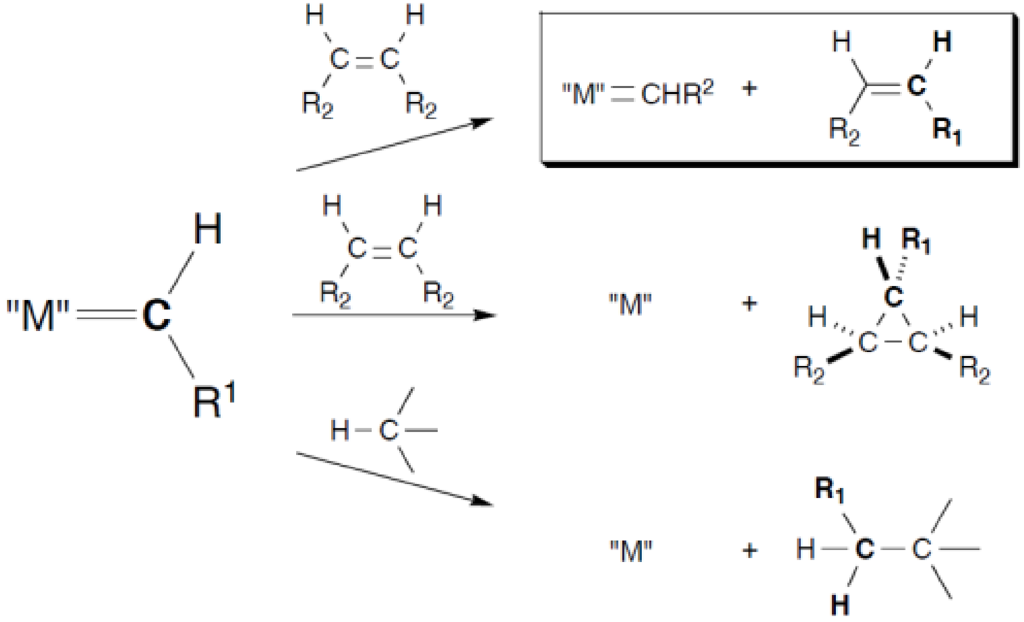






30

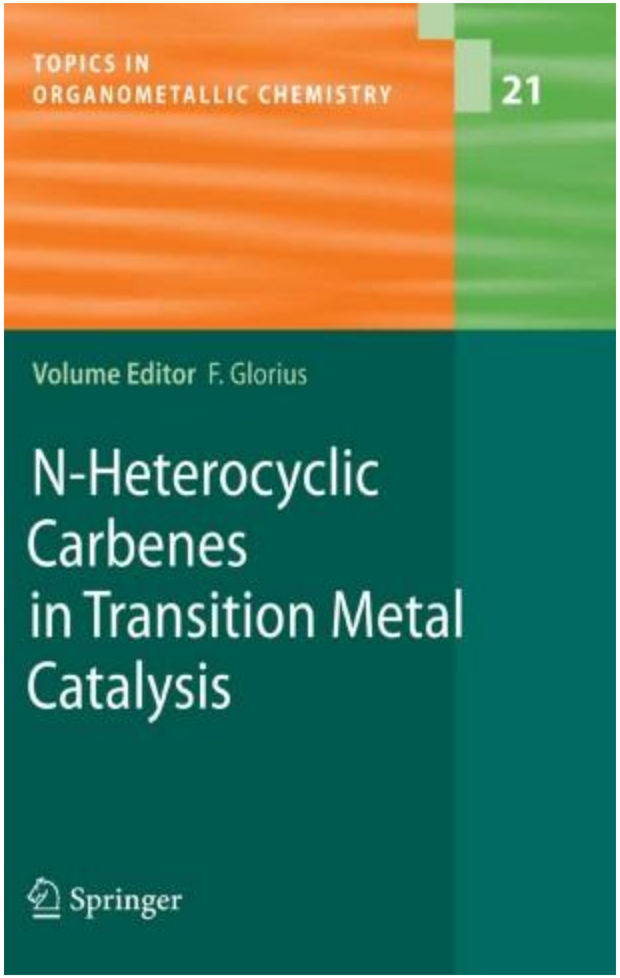
Applications in catalysis of Schrock and Fischer carbenes



Olefin metathesis

Olefin cyclopropanation

C–H bond insertion



TOPICS IN ORGANOMETALLIC CHEMISTRY 21

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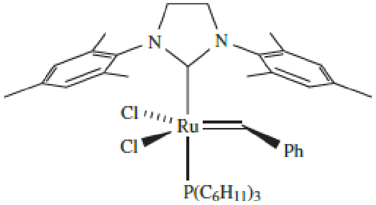
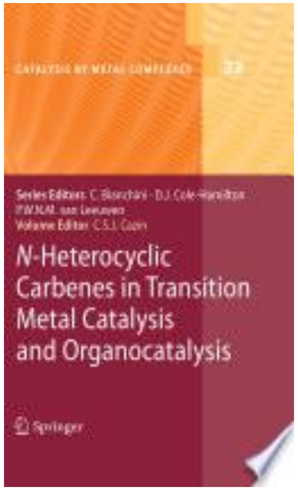
N-Heterocyclic Carbenes in Transition Metal Catalysis

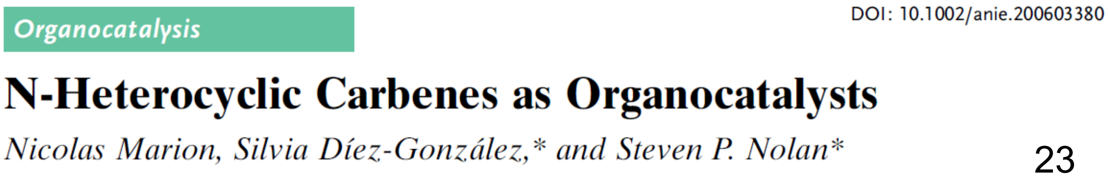
Springer





N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis

Springer



Organocatalysis

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N-Heterocyclic Carbenes as Organocatalysts

Nicolas Marion, Silvia Díez-González, and Steven P. Nolan**