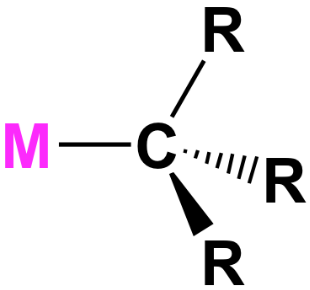
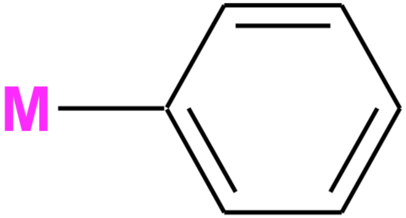
Alkyl, Aryl, Carbene, Alkylidene & Carbyne Ligands

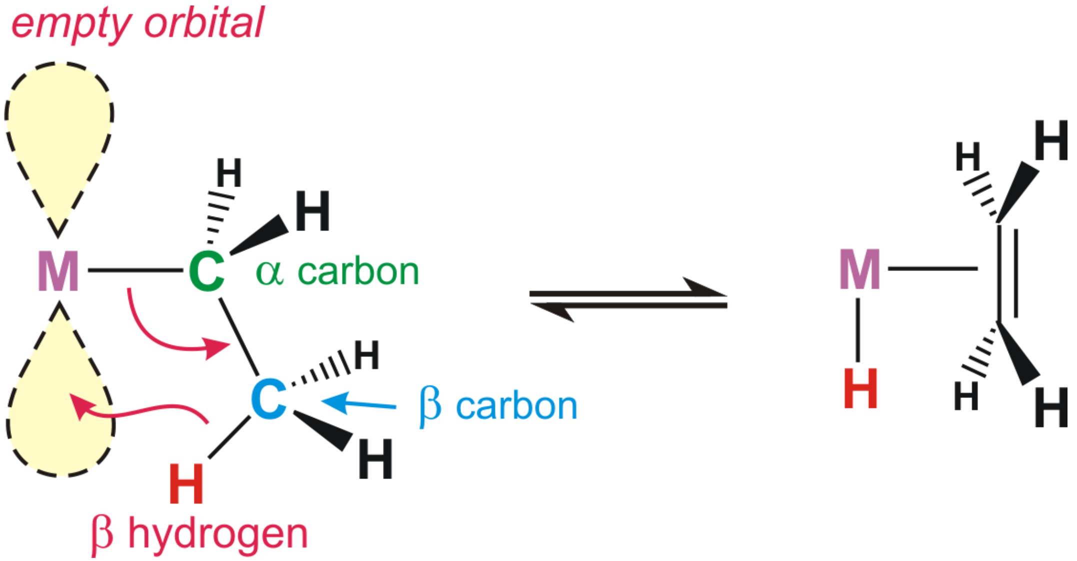
$M-CH_3$





Anionic
2 e- donors

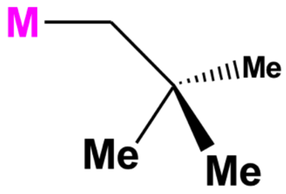
β-Hydride Elimination



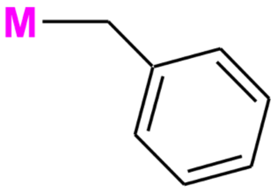
Ligands that avoid β-hydride elimination

$M-CH_3$

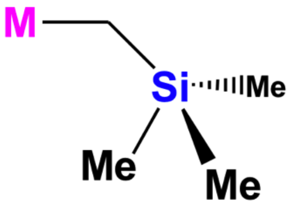
methyl



neopentyl

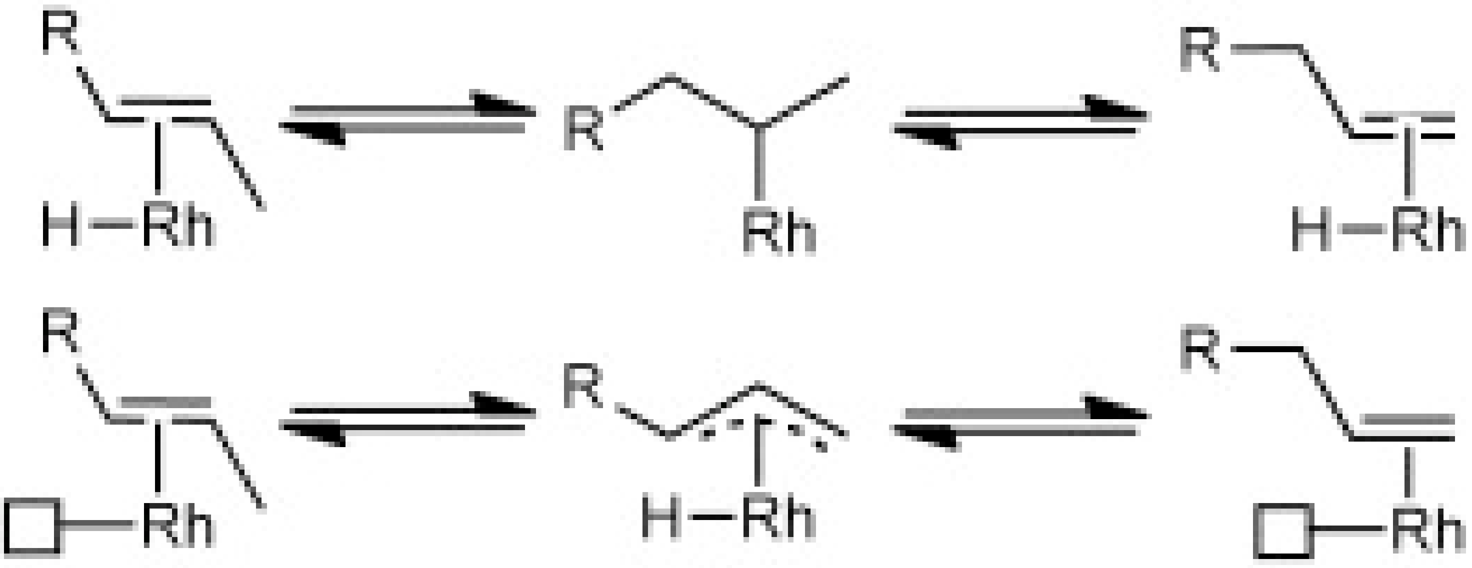


benzyl



trimethylsilylmethyl

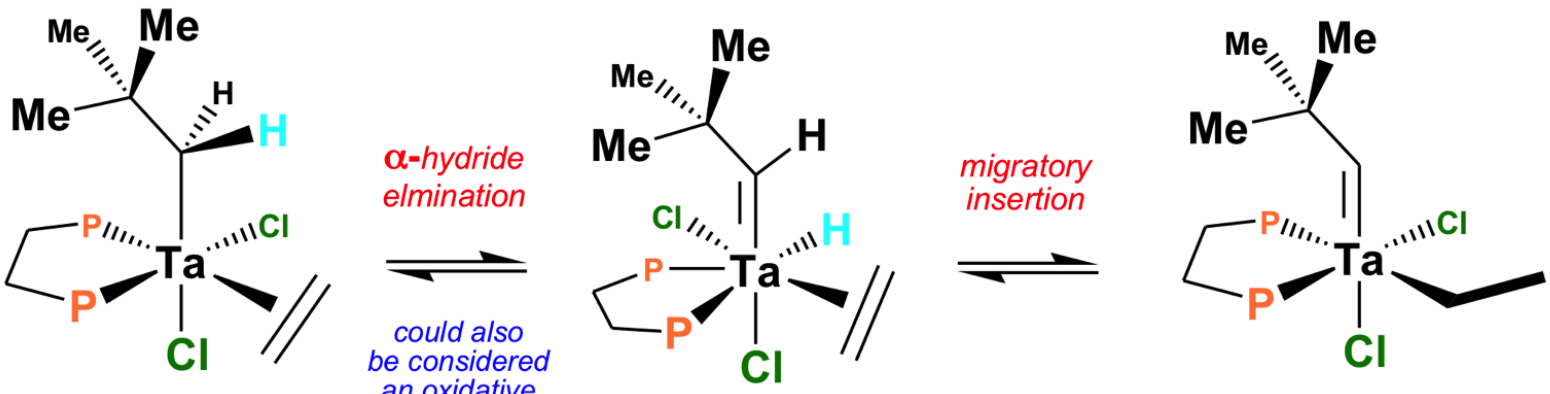
Olefin Isomerization Mechanisms



(1)

(2)

α-Hydride Elimination: A divalent C as ligand



α-hydride elmination

could also be considered an oxidative addition

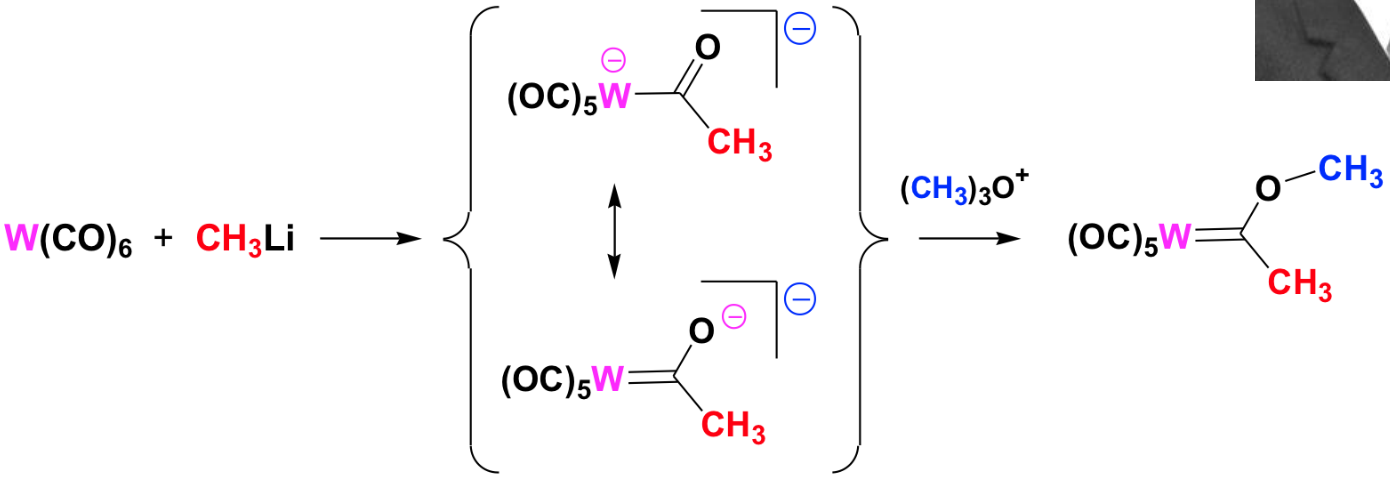
migratory insertion

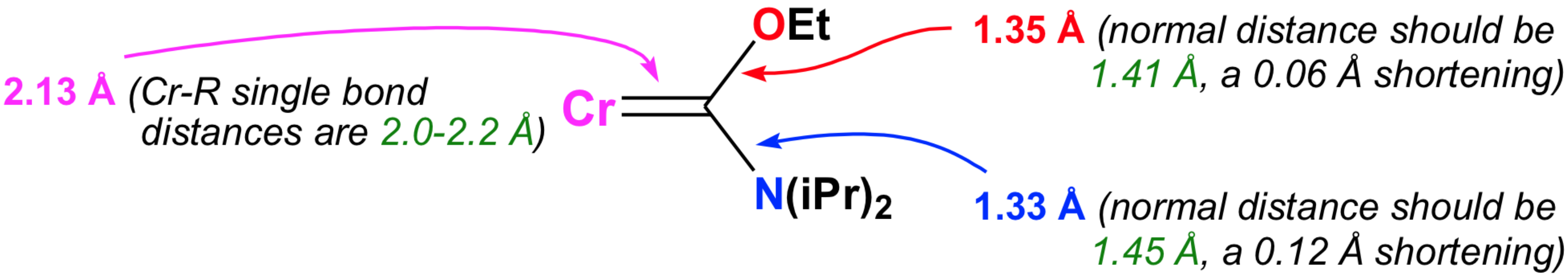
Practice your electron counting!!

Fischer Carbenes (Hetero-atom stabilized divalent carbon)

Example of 1) Nucleophilic attack on metal bound ligand

2) Electrophilic attack on metal-bound ligand

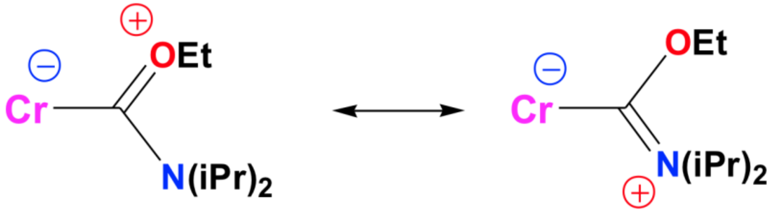




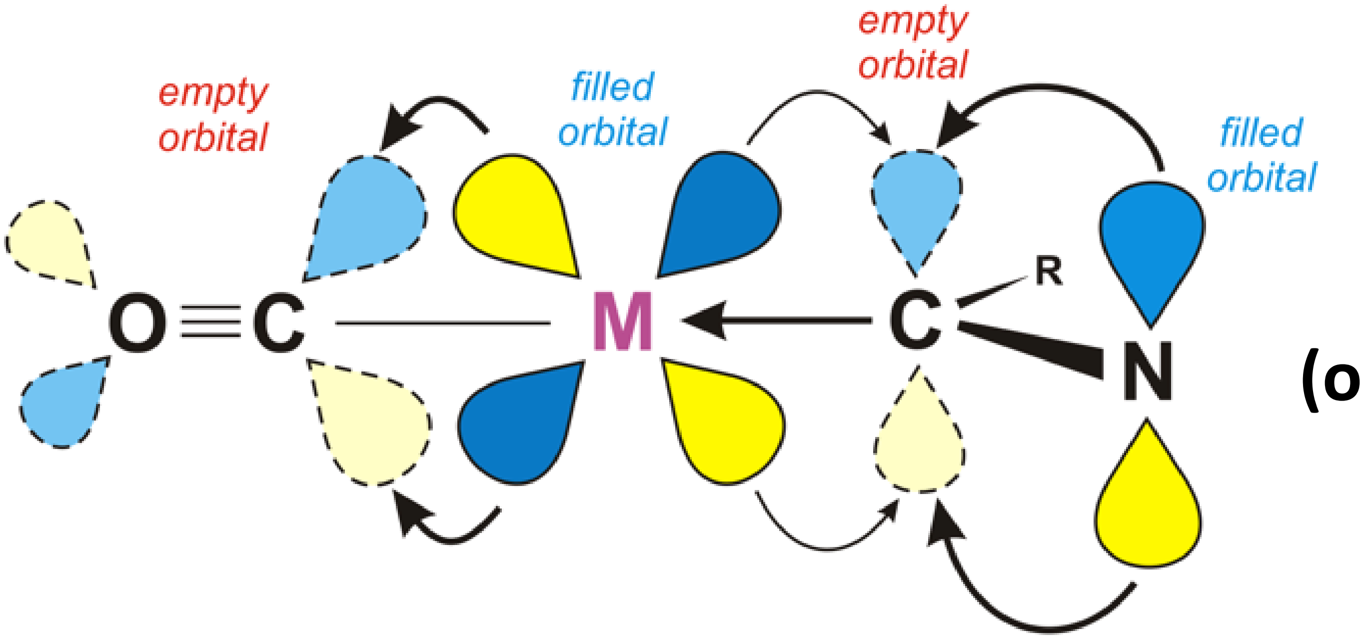
2.13 Å *(Cr-R single bond distances are 2.0-2.2 Å)*

1.35 Å *(normal distance should be 1.41 Å, a 0.06 Å shortening)*

1.33 Å *(normal distance should be 1.45 Å, a 0.12 Å shortening)*

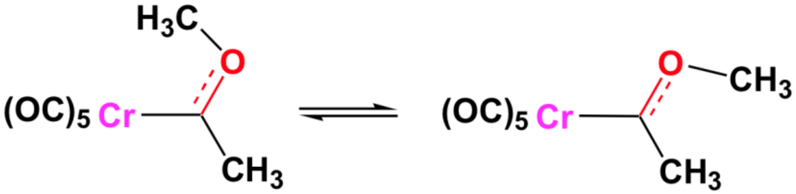


How does the heteroatom stabilize the carbene donor?



(or O)

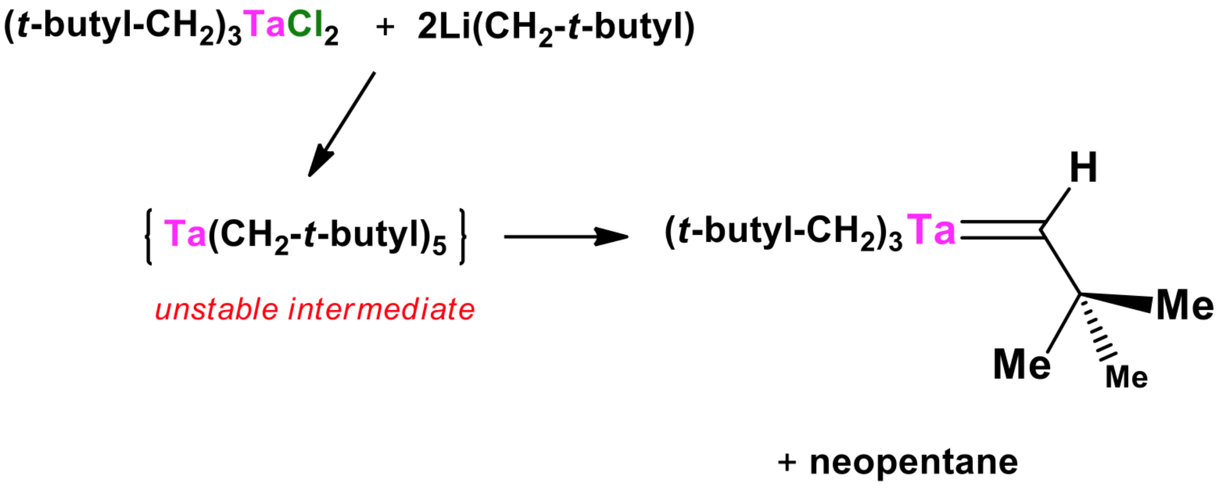
competition for π-backbonding from the metal and the lone pair orbital(s) on the functional group(s) to the carbene empty orbital (N and S the best, then O, Ph, and other π-donating or lone pair containing groups)



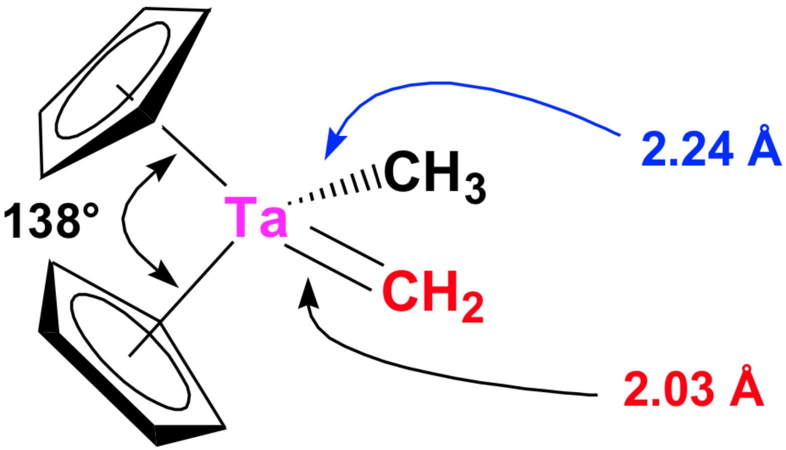
trans ***cis***

Schrock Alkylidenes

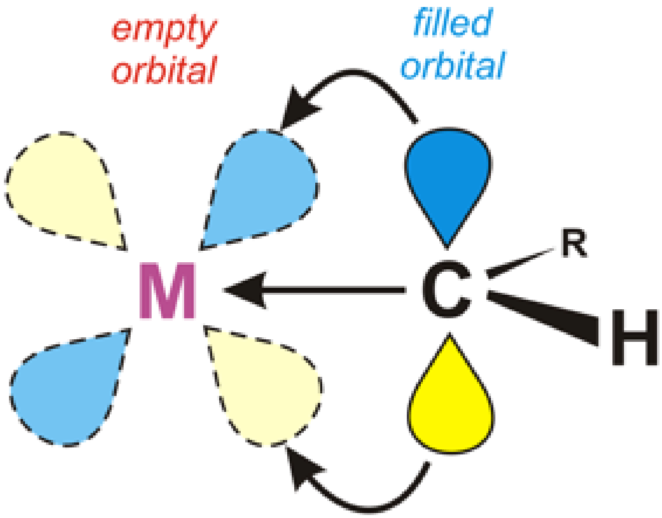
In 1973 Richard Schrock, while working at DuPont central research, prepared the first early transition metal complex with a metal=carbon double bond:



Richard Schrock
MIT
Picture from "Richard R. Schrock - Facts". Nobelprize.org. Nobel Media AB 2014. Web. 29 Jul 2016. <http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/schrock-facts.html>



The Ta=CH$_2$ bond is distinctly shorter than the Ta-CH$_3$ single bond!



both the sp^2 and p orbitals on the alkylidene are filled (thus the -2 charge) and both can strongly donate to the empty orbitals on the early transition metal (only one empty d orbital is shown)

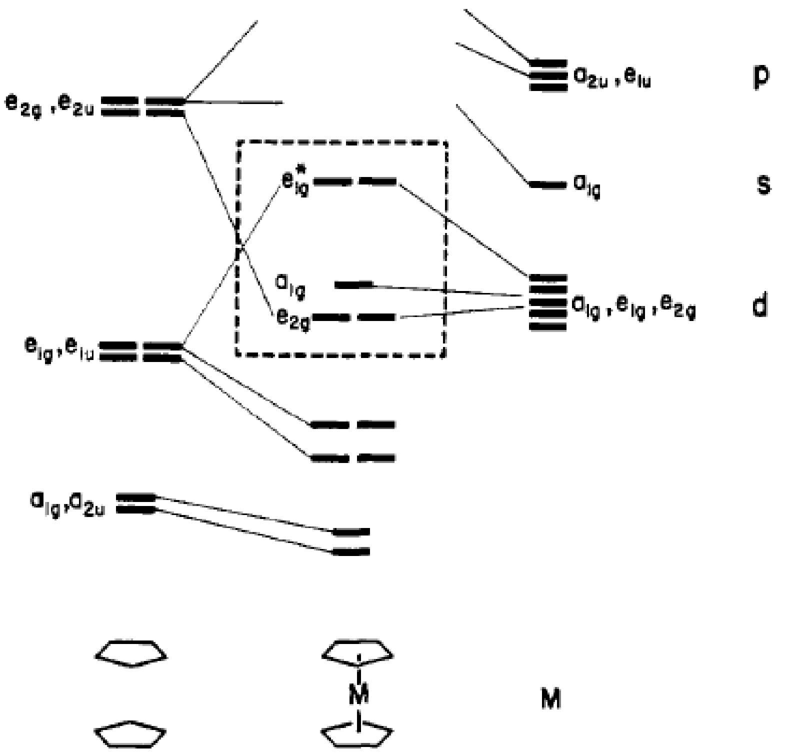


Figure 1. Interaction diagram for a D_{5d} metallocene. The frontier orbitals are in the box.

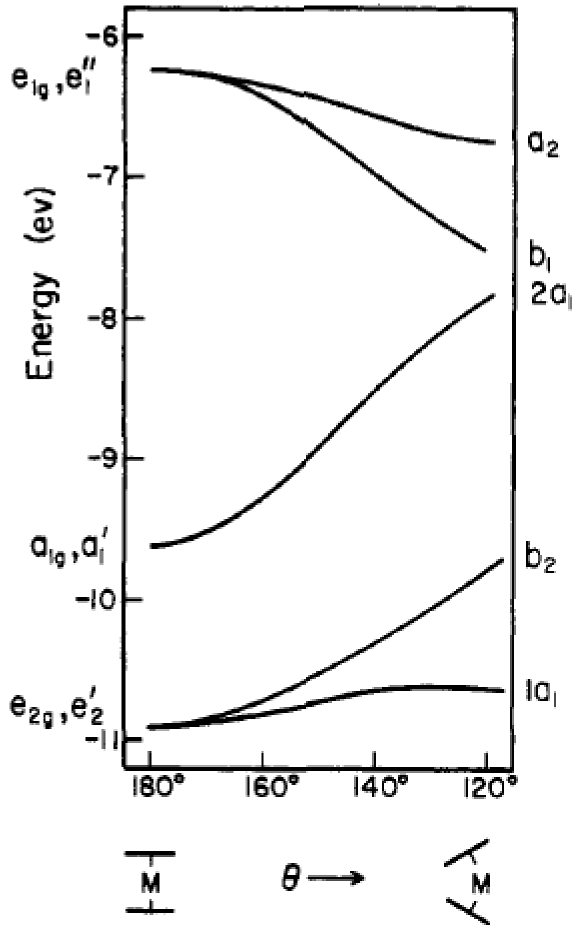
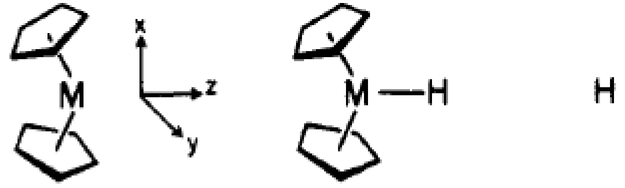


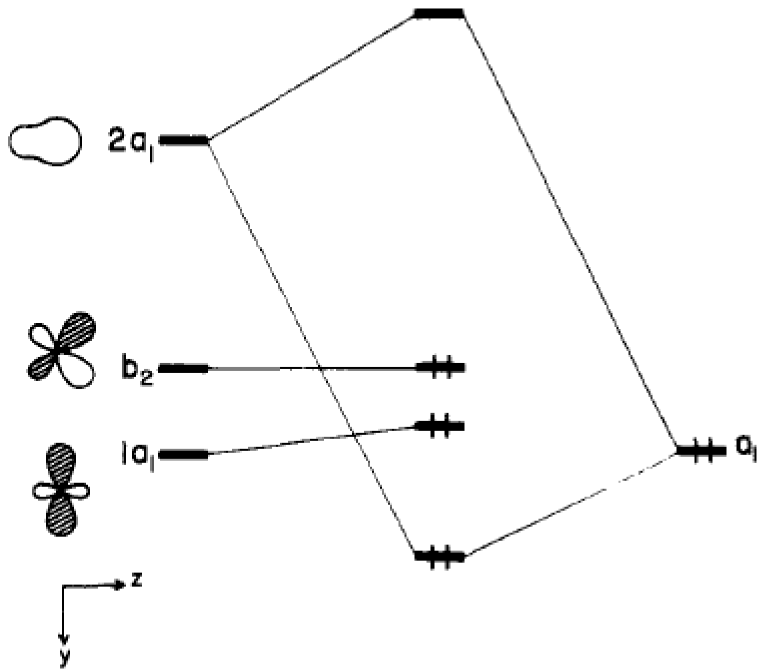
Figure 2. Cp$_2$M orbitals as a function of the bending angle θ. Bending is from an eclipsed D_{5d} form, but the labels at left are given for both D_{5d} and D_{5h} geometries.

Structure and chemistry of bis(cyclopentadienyl)-MLn complexes

Lauher, J. W.; Hoffmann, R. , *J. Am. Chem. Soc.*, **1976**, 98, pp 1729–1742



4



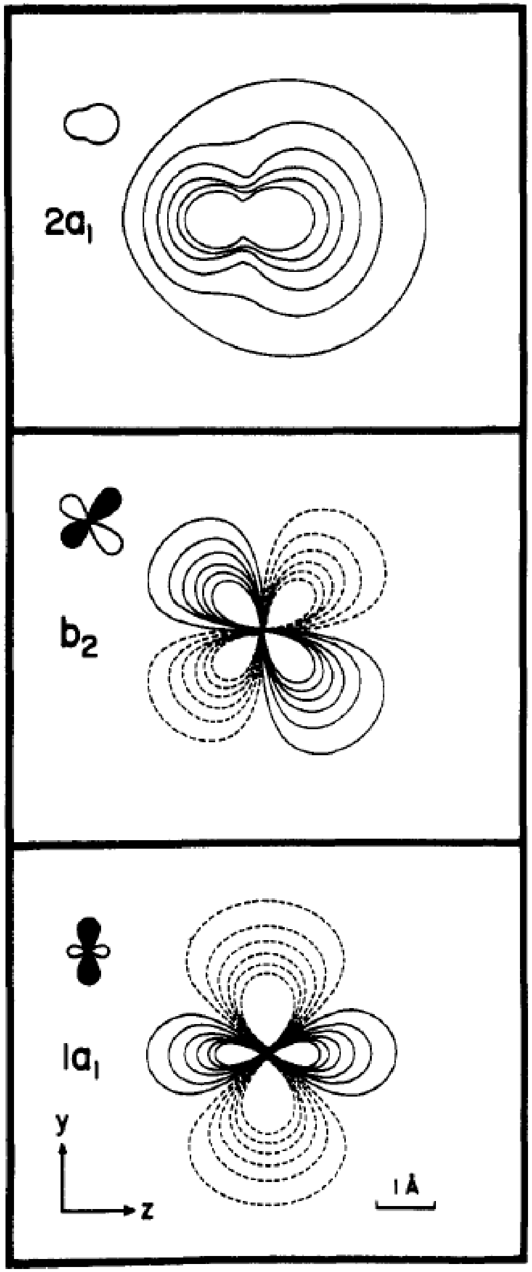
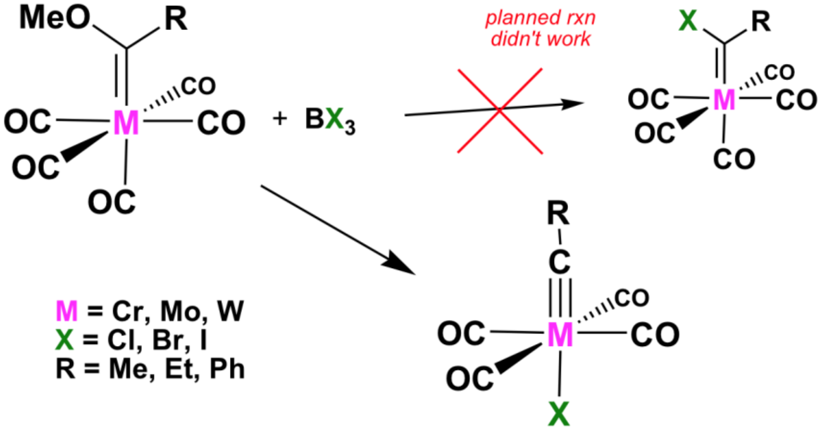


Figure 3. Contour diagram, in the *yz* plane, of the three important Cp_2M orbitals, computed at $\theta = 136°$. From top to bottom: $2a_1$, b_2, $1a_1$. Solid line = positive and dashed line = negative contour of the wave function. The contours are at intervals of 0.02.

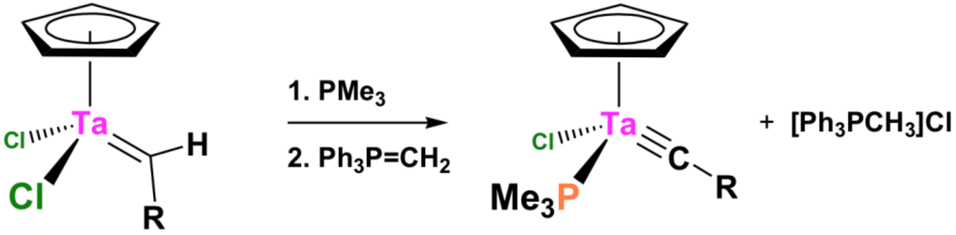
Comparison of Fischer and Schrock Divalent Carbon Ligands

Fischer Carbenes	**Schrock Alkylidenes**
Nucleophillic attacks at carbon atom of carbene (carbon is electron deficient)	Electrophillic attacks at carbon atom of alkylidene (carbon is electron-rich)
Electrophillic attacks on metal center (metal is more electron-rich, often d^6 18 e- system)	Nucleophillic attacks on metal center (metal is electron-deficient, usually d^2 or d^0 16 or 14 e- count)
Carbene is *stabilized* by heteroatom groups that can π-bond to it. Likes NR_2, SR, OR, or Ph groups.	Alkylidene is *destabilized* by heteroatom groups that can π-bond to it. Strongly prefers H or simple alkyl groups.
Later transition metals favored, especially with d^6 counts (carbene as neutral 2e- donor ligand)	Early transition metals favored, especially with d^0 centers (alkylidene as dianionic 4e- donor)

Carbynes and Akylidynes



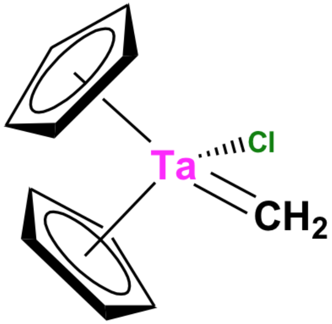
M = Cr, Mo, W
X = Cl, Br, I
R = Me, Et, Ph



Electron Counting

As far as the overall electron-count is concerned, it DOESN’T matter which electron-counting method you use, since both give you the same overall electron-count!!

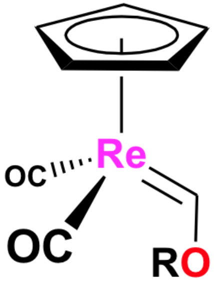
Example: Identify the following complexes as Fischer carbene or Schrock alkylidene.



neutral carbene

Ta(+3)	d^2
2 Cp^-	12 e-
Cl^-	2 e-
CH_2	2 e-
	18 e-

d^2 early TM using neutral carbene indicates a Schrock alkylidene complex

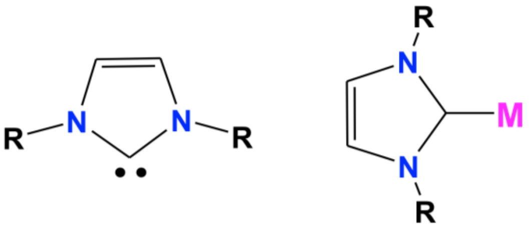


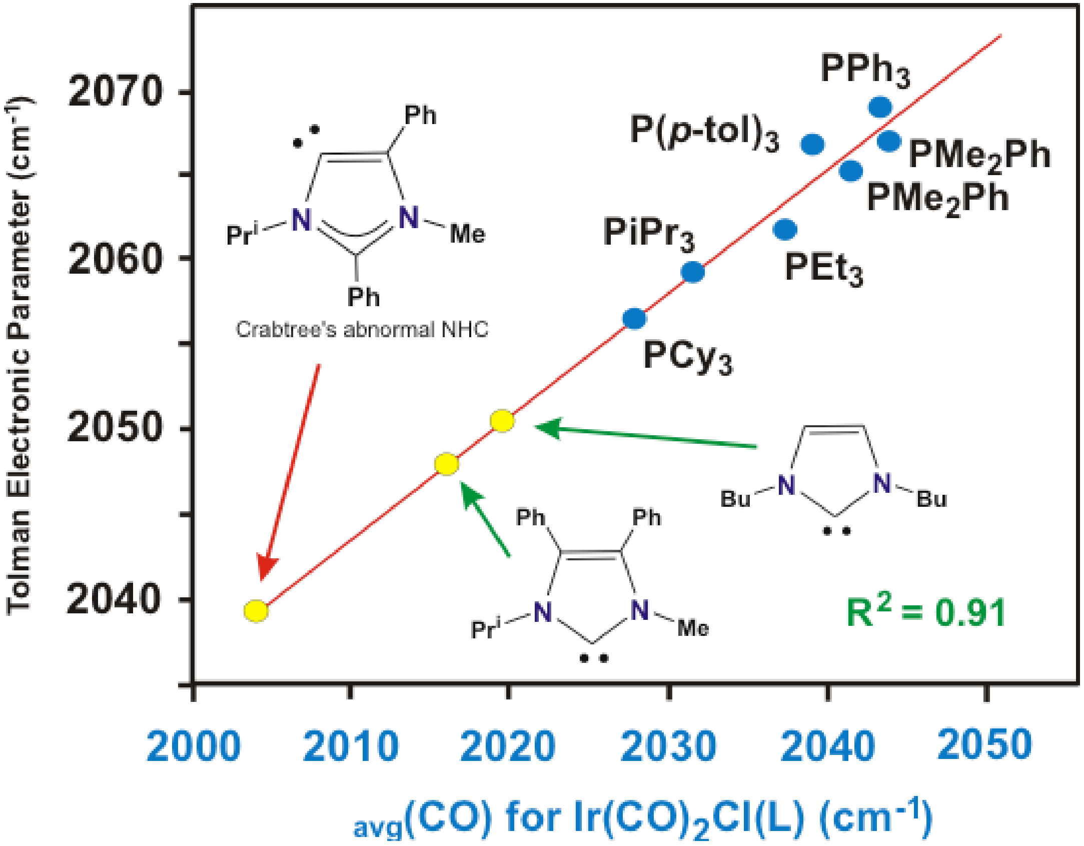
neutral carbene

Re(+1)	d^6
Cp^-	6 e-
2CO	4 e-
C(OR)H	2 e-
	18 e-

d^6 mid-TM using neutral carbene indicates a Fisher carbene complex

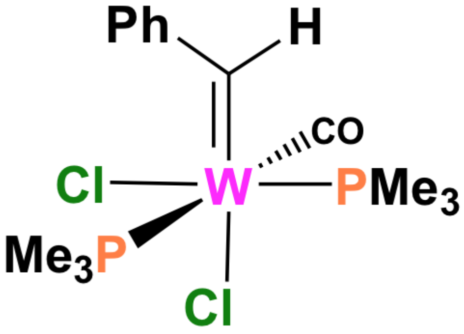
The wonderful N-Heterocyclic Carbene Ligand

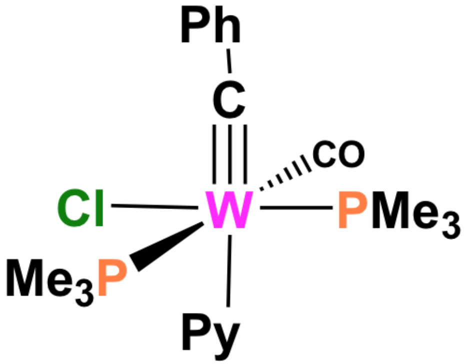




The Nature of the alkylidene/dyne ligands:

νCO = 1938 cm^{-1}





νCO = 1870 cm^{-1}