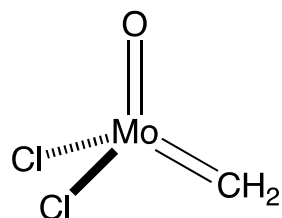


# Carbene Complexes: Electronic Structure and Reactivity

Historically, metal carbene complexes have been classified into two classes

Schrock "alkylidenes"  
[MoCl<sub>2</sub>(O)(CR<sub>2</sub>):]



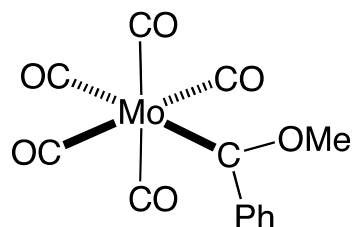
The Schrock-type carbene complexes contain an early transition metal in a formal high oxidation state (often in the d<sup>0</sup> electron configuration) stabilized by strong  $\pi$ -donor ligands.

Generally, the carbene ligand is not stabilized by the presence of heteroatoms and is regarded as negatively charged (alkylidene). Accordingly, most Schrock alkylidenes are nucleophilic.

Most of these complexes have an electron count below 18 and are, thus, coordinatively unsaturated. Therefore, nucleophilic attack involving the metal is possible because of the electron deficiency.

Fischer "carbenes"

$[\text{Mo}(=\text{C}(\text{OMe})\text{Ph})(\text{CO})_5]:$



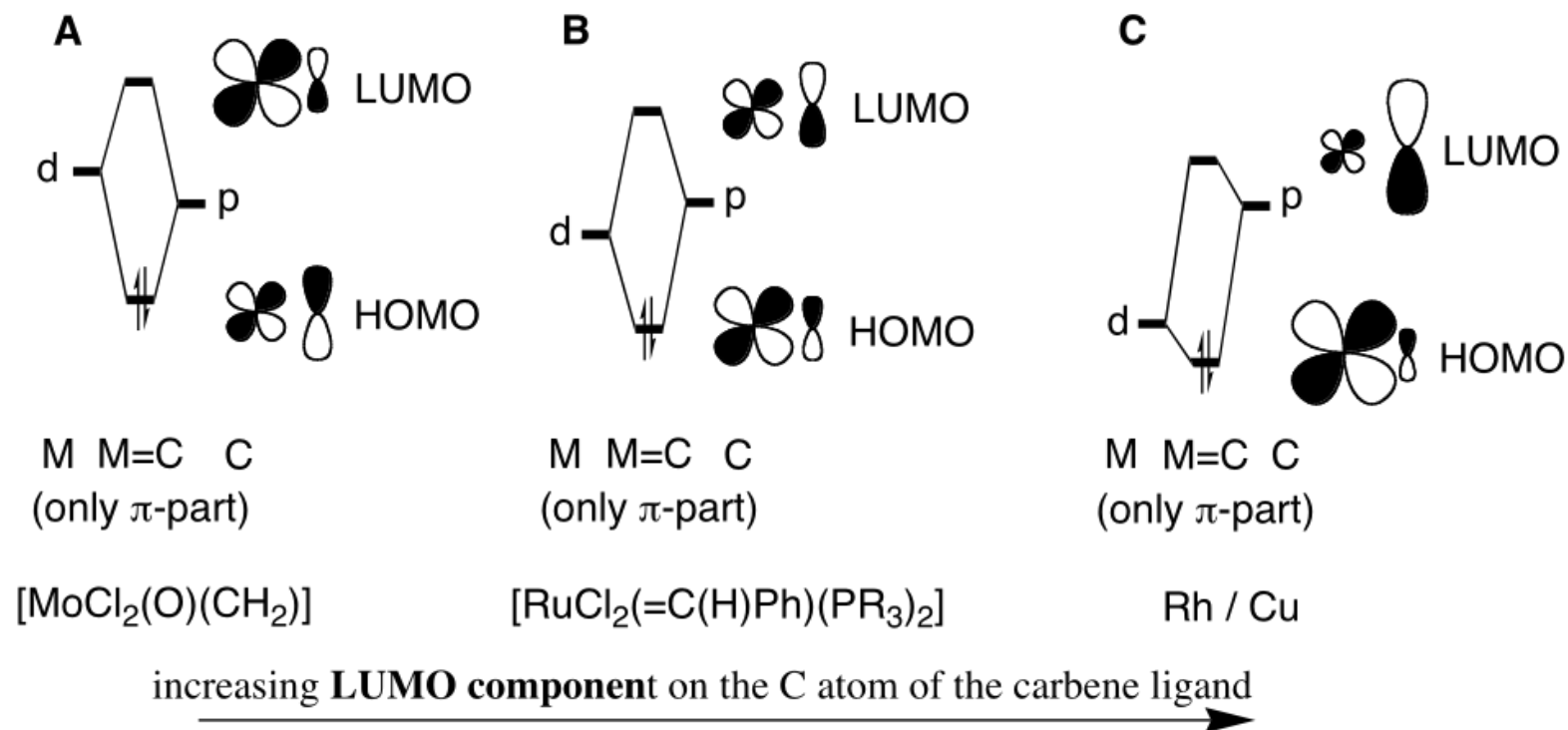
The Fischer-type carbene complexes are low-valent complexes stabilized by strong  $\pi$ -accepting ligands (often CO).

One or two heteroatoms (O, N, or S) are bonded to the carbene carbon atom and stabilize it by delocalizing the positive formal charge. The carbene is formally regarded as a neutral ligand. Accordingly, Fischer carbenes are relatively inert, but tend to react as electrophiles.

In general, Fischer carbenes are  $18 e^-$ , coordinatively saturated complexes. Therefore, nucleophilic attack at the metal is not possible in general (unless ligand dissociation is induced thermally, photochemically, or chemically, see page 70).

## $\pi$ -Bonding in $M=CR_2$ Complexes

The effect of the decreasing energy of the  $d$ -orbitals on going from early to late  $d$ -metals:



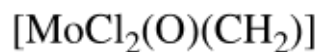
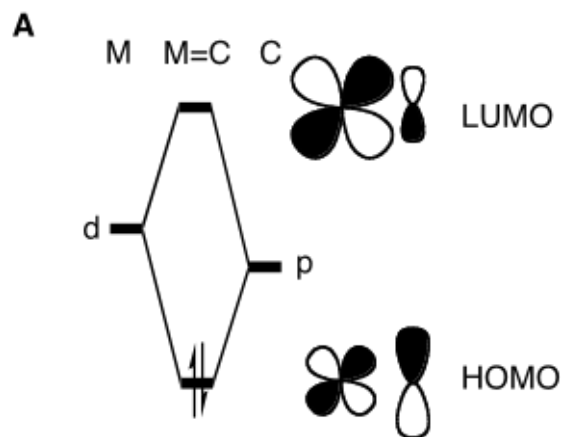
The M=C bond is covalent  
(like in ethylene)

A C $\rightarrow$ M dative  $\sigma$  bond and a M $\rightarrow$ C  
retrodonative  $\pi$  bond  
(like in carbonyl complexes)

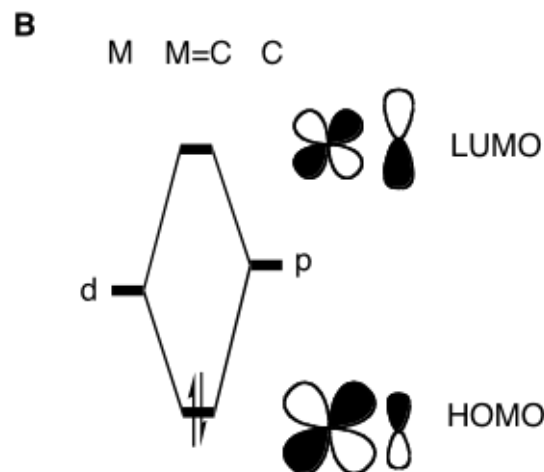
The localization of the LUMO changes from left to right of the periodic table. Effect on the reactivity?

# Electronic Structure and Reactivity

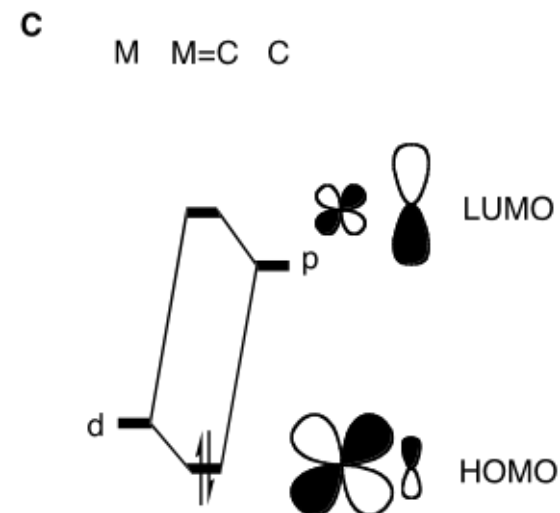
The reactions of  $\pi$ -bonded ligands (like those of C=C and C=O) are **frontier-orbital controlled** (NOT charge-controlled!):



Schrock:  
nucleophilic alkylidene ligand.  
Early transition metal, coordinatively  
unsaturated complex: nucleophilic  
attack at the metal is possible



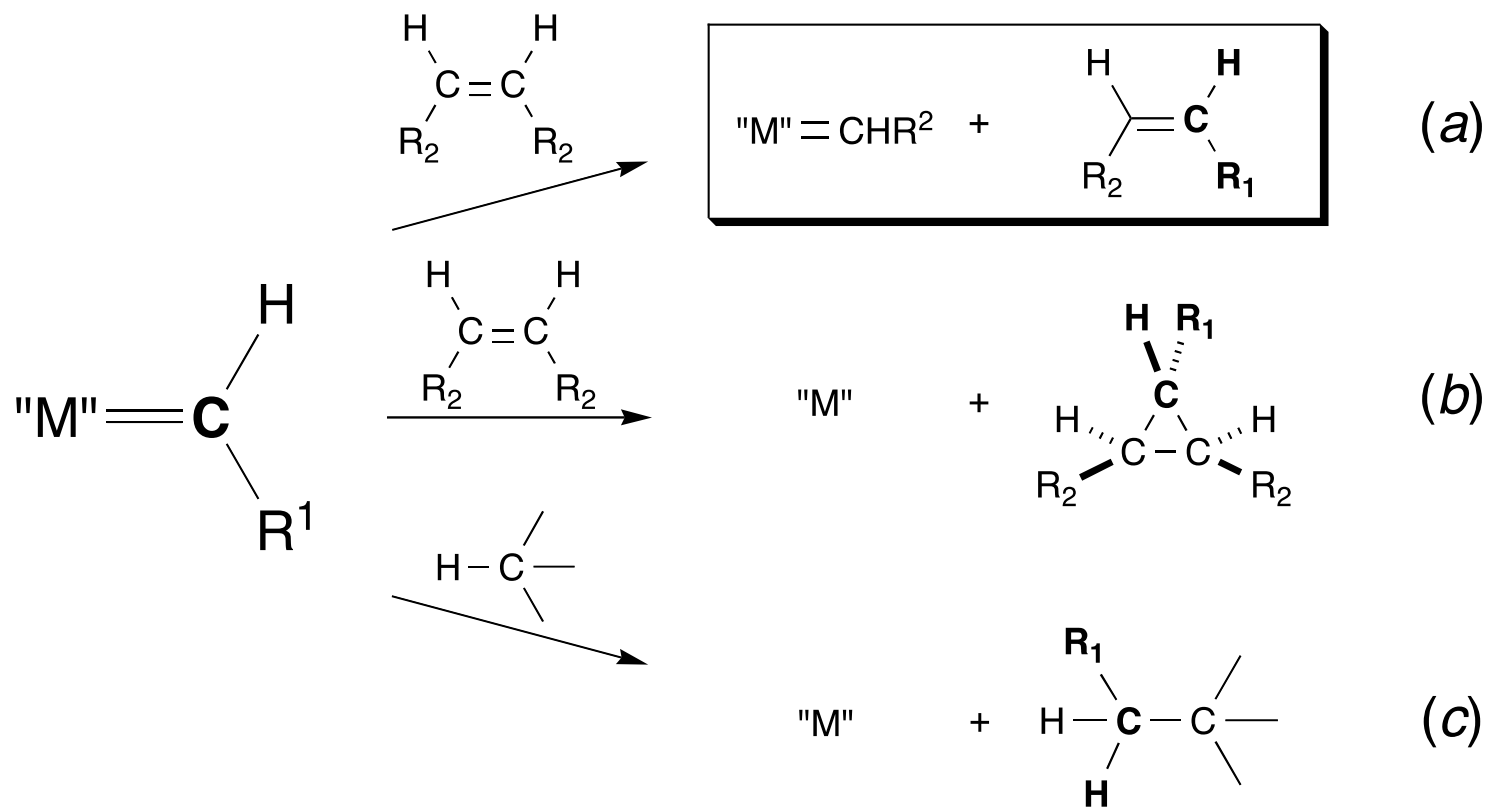
the carbene is neither a good  
electrophile nor a good nucleophile,  
apolar mechanisms are favored, like  
in metathesis, provided that the  
complex is coord. unsaturated



Rh / Cu:

the carbene ligand is  
strongly electrophilic:  
it attacks olefins  
and gives insertion into  
C-H bonds

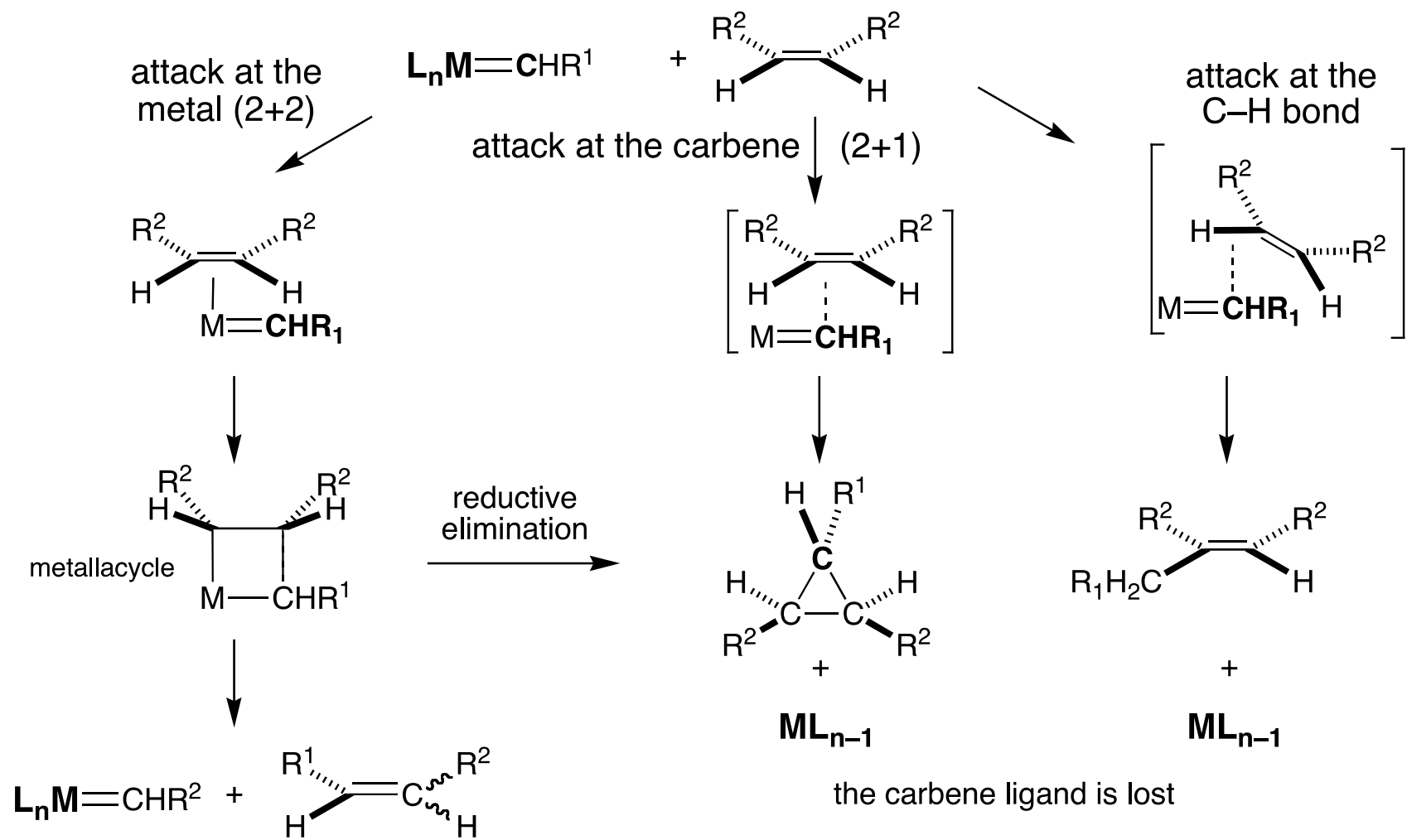
# Carbene Complexes and Olefin Metathesis



In principle, 3 different reactions are possible:

(a) Olefin Metathesis / (b) Olefin Cyclopropanation / (c) Insertion into C-H-Bonds (or N-H, O-H)

# A General Mechanism



# Reactivity

Originally, the Fischer / Schrock classification was based on reactivity, with the Schrock alkylidenes being nucleophilic and the Fischer carbenes being electrophilic. However, these differences are not very pronounced, because the carbene C atom bears a small charge both in Fischer- and in Schrock-type carbenes as discussed above. Therefore, the preference for attack at M or C is similar, and other effects play a role, too. In particular, the electron count at the metal influences the kind of reactivity observed.

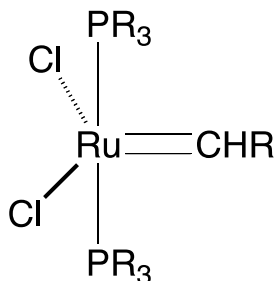
As an example of the importance of the electron count, we mention here that Fischer-type carbene complexes do not normally initiate the chain metathesis of olefins, since they are both coordinatively and electronically saturated (18-electron complexes). However, they can sometimes be activated for metathesis by heating, or by reaction with a co-catalyst, or photochemically:

Complex	Activator	Substrate
$(\text{CO})_5\text{Mo}=\text{C}(\text{OPh})\text{NBu}_4^a$	$\text{MeAlCl}_2$	$\text{PrCH}=\text{CH}_2$
$(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Et}$	$\text{Bu}_4\text{NCl}$	$\text{PrCH}=\text{CH}_2$
$(\text{CO})_5\text{W}=\text{C}(\text{OEt})\text{Bu}$	$\text{TiCl}_4$	Cyclopentene
$(\text{CO})_5\text{W}=\text{CPh}_2^b$	Heat (38°C)	<i>cis</i> -Cycloalkenes
	21–25°C	$\text{EtCH}=\text{CHMe}$
$(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}$	Heat (50°C)	Cyclobutene, norbornene
	Heat (40°C)	$\text{RC}\equiv\text{CR}$
	$\text{PhC}\equiv\text{CH}$	Cyclopentene
	<i>hν</i>	Cycloocta-1,5-diene
	Halides	$\text{PrCH}=\text{CH}_2$

K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, **1997**, p. 16.

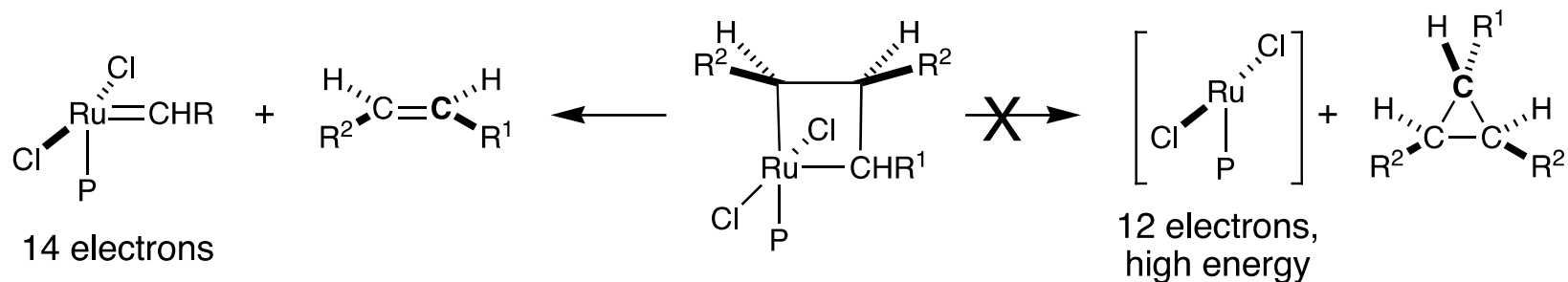
Eventually, with the development of different classes of carbene complexes, in particular Grubb's catalyst (see below) and the Arduengo / Herrmann carbene ligands (not discussed), the Fischer / Schrock distinction has lost some of its usefulness.

# Grubbs' Catalyst: $[\text{RuCl}_2(=\text{CHR})(\text{PR}')_3]$



Meets the conditions for metathesis: attack at the metal, no reductive elimination.

- A significant part of the LUMO is localized on Ru (not Fischer, middle transition metal).
- Neutral: C is less electrophilic than a rhodium or copper carbene complex.
- Coordinatively unsaturated (16 electrons, but the active species has only 14 e. Formation of the metallacycle is preferred over elimination, which would give a 12-e complex:



Grubbs' complex gives metathesis because ruthenium needs **at least** 4 ligands (14 electron count).

Review on olefin metathesis: R. H. Grubbs *Tetrahedron* **2004**, 60, 7117.