# Transition metal carbenes
# Metathesis

Robert H. Crabtree: Pages 309 -378

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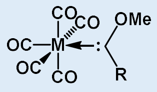
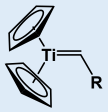
## Metal-carbon multiple bonds

- Many transition metals form not only M-C single bonds but also M=C and (more rare) even M≡C bonds
- Complexes containing an M=C bond are called carbene complexes
  - The ligand without the metal would be a free carbene
  - $CR_2$ → alkylidene ($L_nM=CHMe$ → ethylidene complex)
- Complexes with M≡C bonds are called carbyne complexes
  - CR → alkylidyne (LnM ≡ CPh → benzylidyne complex)
- Both types of complexes tend to be reactive, and useful in catalysis
- We distinguish between Fischer-type and Schrock-type carbene (and carbyne) complexes

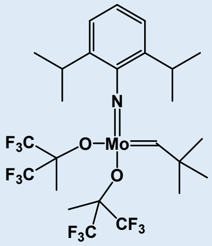


M = Cr, Mo, W

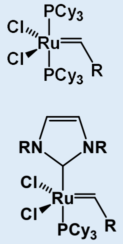
**Electrophilic Fisher Carbenes**



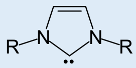
**Nucleophilic Schrock Carbenes**



**Schrock's metathesis catalyst**



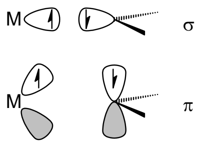
**Grubbs' metathesis catalyst**

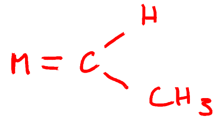


**Arduengo's carbenes**

# Schrock-type carbene complexes

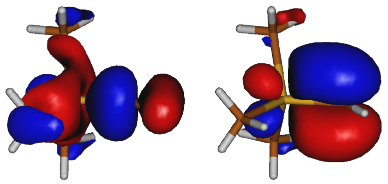
- "Standard" M=C bond:
  normal σ and π bonds,
  both polarized as in $M^{\delta+}$-$C^{\delta-}$
- Carbene binds by two unpaired electrons
  – not stabilized
  – H, alkyl substituents
- Early/middle transition metals,
  high oxidation state, stabilized by strong donor ligands such as Cp
  - count carbene as 2- (increase in the metal oxidation state by 2)
- Carbene carbon is ***nucleophilic***





ethylidene

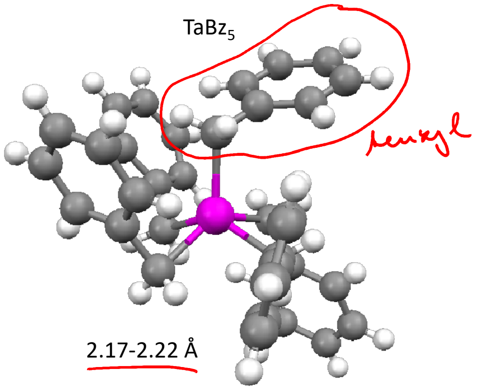
TaMe$_3$(=CH$_2$)



σ bond π bond

# Real M=C double bonds

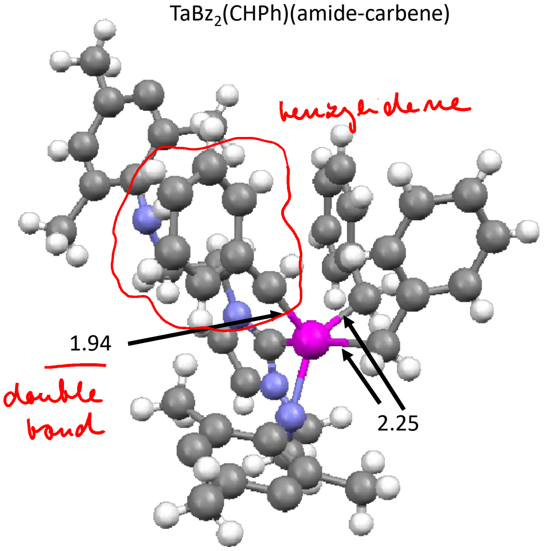
TaBz$_5$



benzyl

2.17-2.22 Å

TaBz$_2$(CHPh)(amide-carbene)



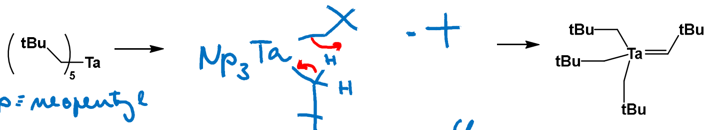
benzylidene

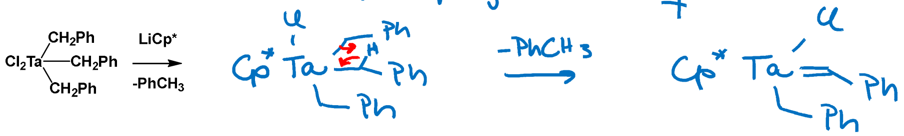
double bond

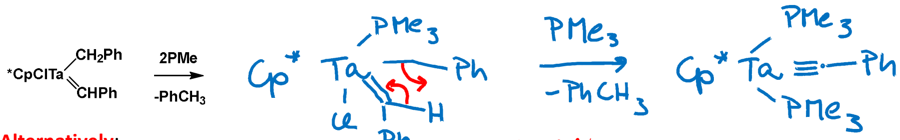
# Synthesis of Schrock carbenes

Usually from decomposition of alkyls

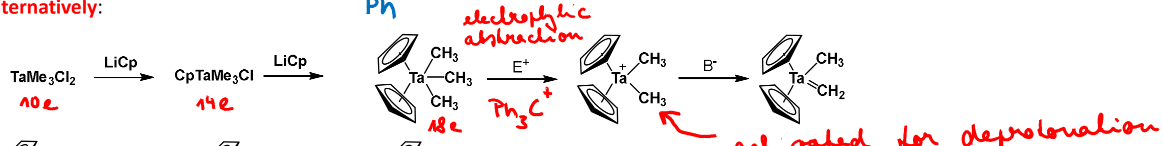
**α-elimination** – requires **bulky ligands**

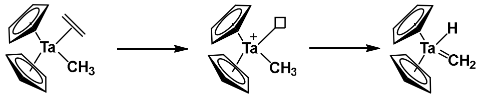






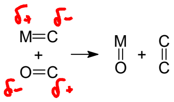
**Alternatively:**

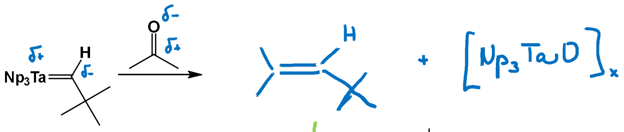




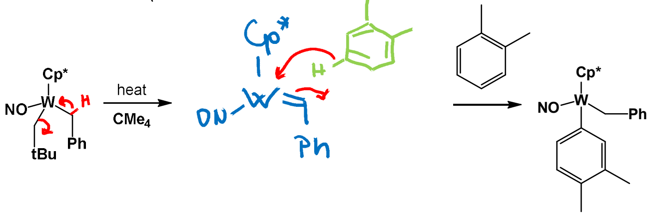
# Reactivity of Schrock carbenes

- With ketones: "Wittig"

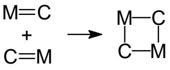




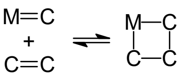
- Addition of X-H (X = C, N, O) bonds

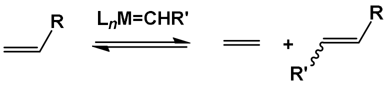


- With electrophiles: attack on carbene carbon
  Unhindered carbenes dimerize



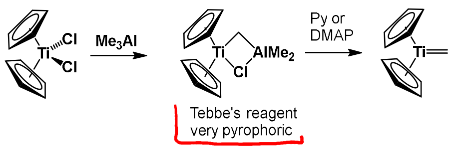
- With olefins: metallacycles
  - Metathesis catalysis – in detail bellow

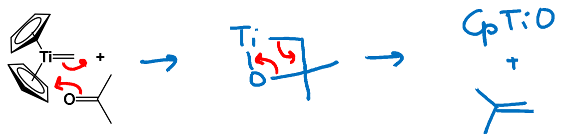




# Titanium Carbenes

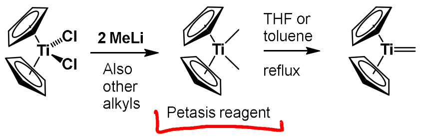
- For review see: J. Chem. Soc., Perkin Trans. 1, 2002, 2763.
- Tebbe's reagent
  - widely used for Wittig-type olefinations of carbonyl compounds
  - Also methylenation of esters, lactones, and amides
  - Not basic, methylenetes readily enolisable ketones and sterically hindered carbonyl groups

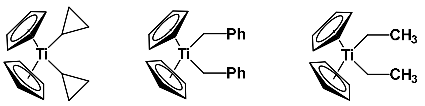




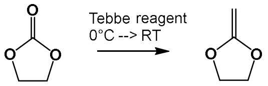
- Dimethyltitanocene – easier to prepare, more stable

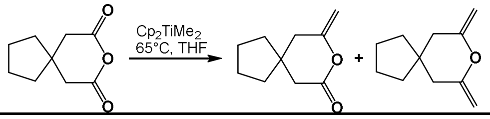
RANGE OF DIALKYLTITANOCENES





- Compare conditions:

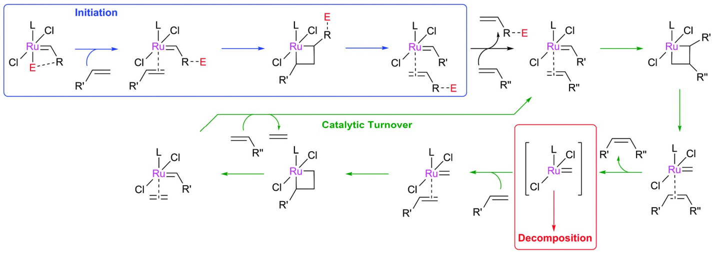


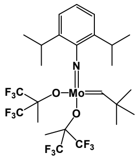


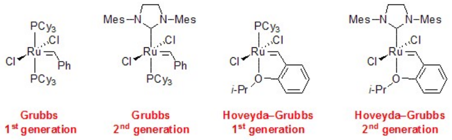
# Olefin metathesis catalysis

- Reviews: Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18; Schrock, *Angew. Chem. Int. Ed.* **2003**, *42*, 4592; Furstner, *Angew. Chem. Int. Ed.* **2000**, *39*, 3012.
- Olefin metathesis – powerful synthetic method, very general

CROSS METATHESIS
→ ONE PRODUCT REMOVED
(volatile $C_2H_4$)



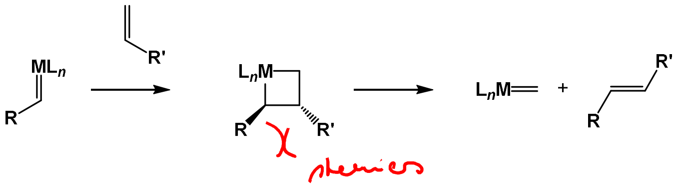




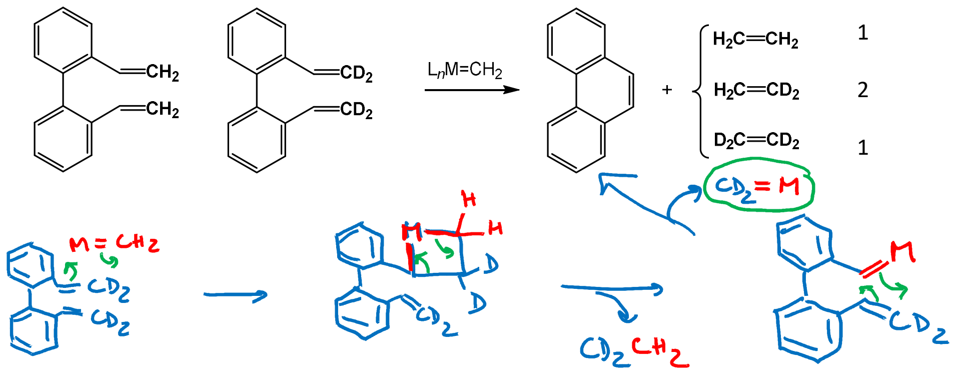
**The Schrock catalyst** is more active and allows formation of tri- and tetra-substituted double bonds, but is not tolerant of oxygen, water, alcohols, acids, or aldehydes.

**The Grubbs catalyst** 1st generation is less active, allows formation of disubstituted double bonds, tolerant of aldehydes, acids, oxygen, water
The 2nd generation Grubbs catalyst is more active – more substituted double bonds

# Mechanism of metathesis

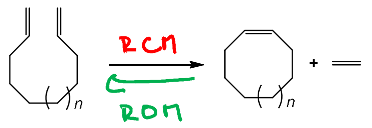


Preferentially trans



# Olefin metathesis catalysis

**Ring Closing Metathesis** (RCM)



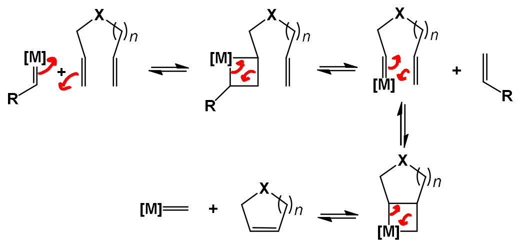
RCM → removal of $C_2H_4$

driving force

ROM → ring-strain release

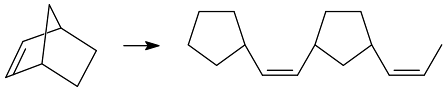
add excess $C_2H_4$

- Mechanism:



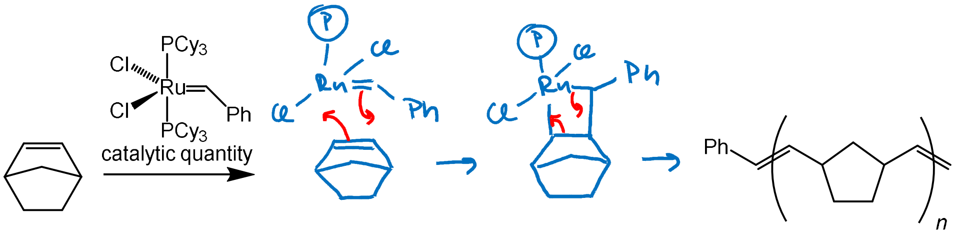
**Driving force**: the reaction driven by loss of ethylene

# Olefin metathesis catalysis



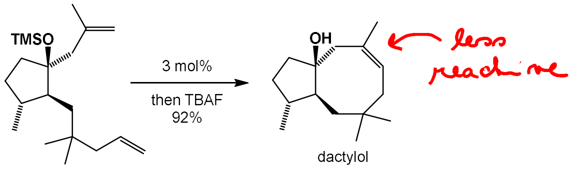
**Ring opening metathesis polymerization** (ROMP)

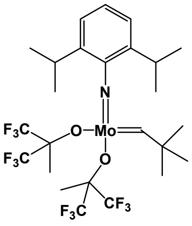
**Driving force**: decrease of ring strain



**Selectivity:**

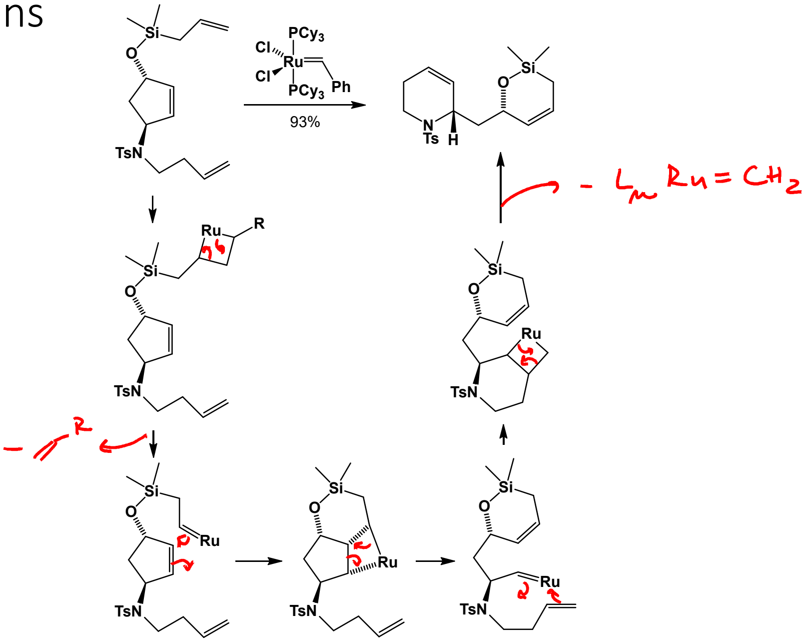
- The metathesis catalysts are sensitive to the substitution pattern of olefins and will coordinate terminal olefins in preference to other types of olefin and therefore it is often the case that the product is less reactive than the starting material





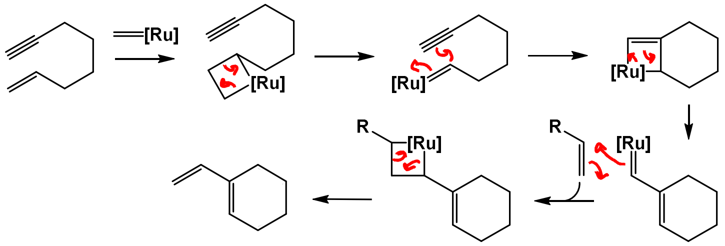
Schrock's catalyst

# Cascade reactions

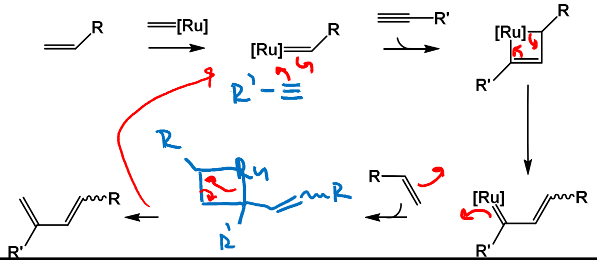


# Enyne metathesis

- Both intramolecular and intermolecular enyne metathesis are know using Grubbs' catalysts
- Intramolecular enyne metathesis tends to give 1,2-substituted dienes



- Intramolecular enene metathesis → 1,3-substituted dienes



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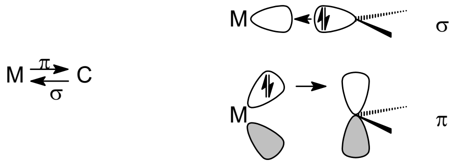
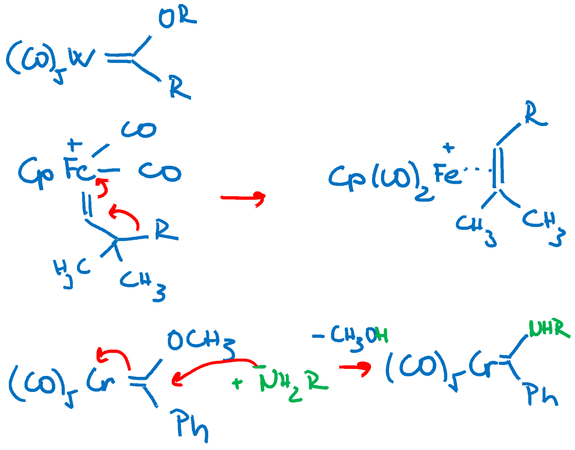
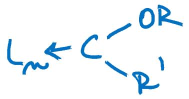
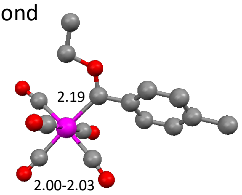
# Fischer-type carbene complexes



- Ligand best described as strong σ-donor, medium-weak π-acceptor
- Carbene has a singlet ground state
  - because of π-donor substituents (OMe, NMe$_2$)
- Metal: late, low oxidation state
  - count carbene as neutral ligand
- Carbene carbon is ***electrophilic***
- Good ligands, not a real double bond
  - Often depicted by an arrow

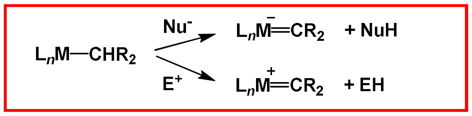




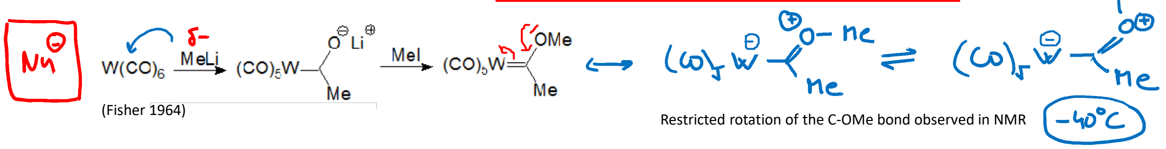


# Synthesis of Fischer carbenes

- Usually from CO or RNC complexes via
  - Nucleophilic attack
  - Electrophilic attack (e-count + 2!)


$L_nM{-}CHR_2 \xrightarrow{Nu^-} L_n\overset{-}{M}{=}CR_2 + NuH$

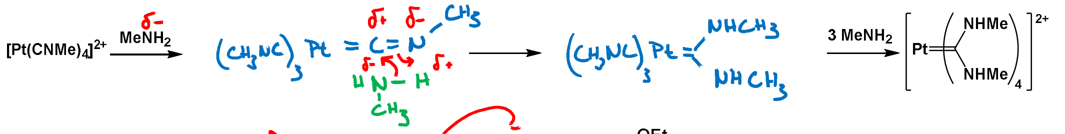
$L_nM{-}CHR_2 \xrightarrow{E^+} L_n\overset{+}{M}{=}CR_2 + EH$

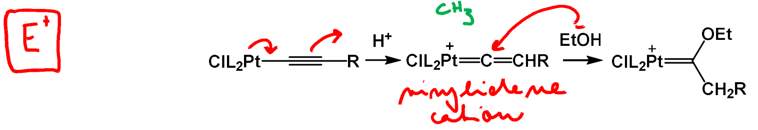


(Fisher 1964)

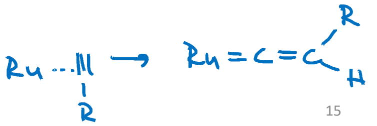
Restricted rotation of the C-OMe bond observed in NMR

−40°C





- Transfer of $CH_2$ from diazomethane $ML_n + CH_2N_2 \longrightarrow L_n\overset{-}{M}{=}CH_2 + N_2$
- Spontaneous isomerization of vinyl, olefin or acetylene complexes (Ru)



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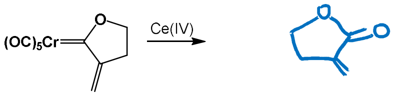
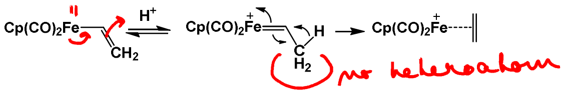
# Reactivity of Fischer carbenes

- Decomposition:
  - a) Dimer of carbene (C=C)
  - b) Olefin, via isomerization of carbene

- Oxidation to ketone (oxidative cleavage)
  Ce(IV), pyridine N-oxide, air

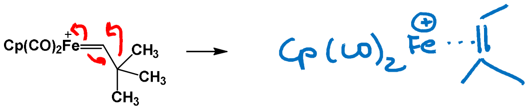


- Isomerization (1,2-shift of R⁻)
  thermodynamically driven:

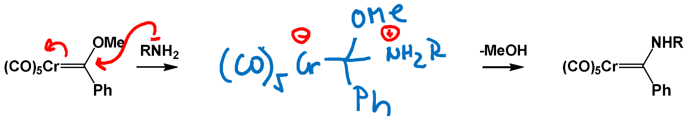


no heteroatom → very reactive

even carbenes without β-hydrogen atom unstable → 1,2-migration of R⊖

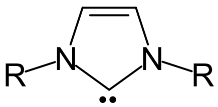


- Nucleophilic substitution on carbene carbon



# Arduengo carbenes

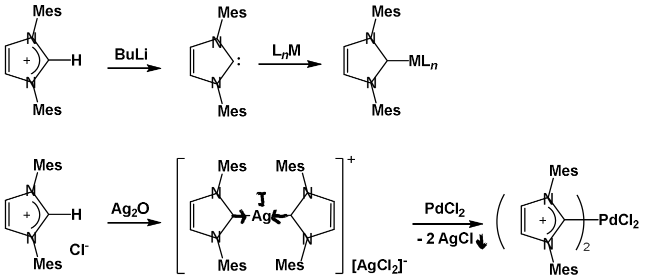
- Free, stable carbenes



(Fischer)

- Good ligands, strong σ-donors
- More reluctant to dissociate than phosphines
- Shape very different from that of typical phosphines

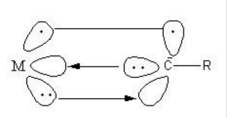
- Easy and convenient synthesis from imidazolium salts



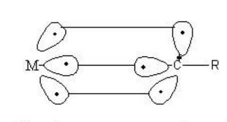
# Carbyne complexes

**Fischer carbynes**

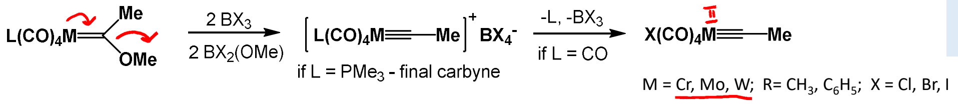
- First made in 1973 by Fischer - via electrophilic abstraction of methoxide from a methoxide methyl carbene
- Classified by being able to be stabilized by heteroatoms
- Typically bonded with low oxidation state transition metals (usually late transition metals)
- Usually - π–acceptor ligands on the metal making the carbyne essentially electrophilic
- The carbyne complexes - usually 18 electrons because the CR bond is mostly covalent. The ligand is LX type.



Fischer, or doublet type carbyne



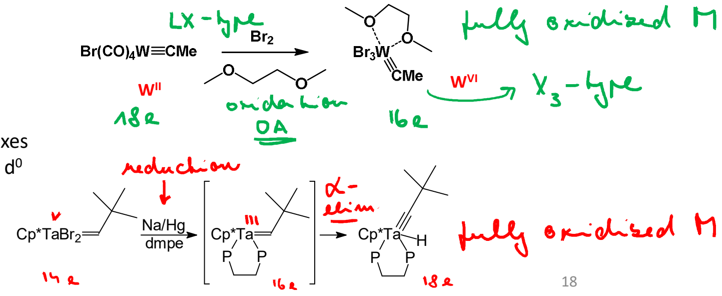
Schrock, or quartet type carbyne



M = Cr, Mo, W; R= $CH_3$, $C_6H_5$; X = Cl, Br, I

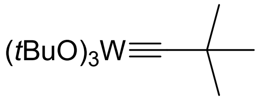
**Schrock carbynes**

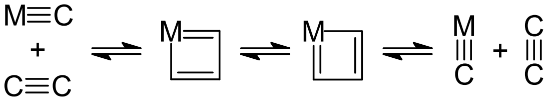
- No heteroatoms, ligands are usually strong σ-donors
  → carbon nucleophilic
- High oxidation state metals (early transition metals)
- The ligand is of the $X_3$ type. They usually form complexes with less than 18 electrons and the metals tend to be $d^0$
- Preparation
  - by oxidizing a Fischer carbyne
  - by α-elimination



# Alkyne metathesis catalysis

e.g. with





Very sensitive to functional groups.
Not (yet) very useful in organic synthesis.

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# What did you learn today?

- Carbenes – Fischer and Schrock extremes

| Property | Fischer | Schrock |
|---|---|---|
| Reactivity of carbene carbon | Electrophilic | Nucleophilic |
| Typical R groups on carbon | π donor (e.g., -OR) | Alkyl, H |
| Typical metal | Mo(0), Fe(0) | Ta(V), W(VI) |
| Typical ligands on the metal | π acceptor (e.g., CO) | Cl, Cp, alkyl |
| E-count | 2e (L) | 2e (X2) |
| Oxidation state change | 0 | +2 |
| Back bonding to carbene | weak | strong |

- N-heterocyclic carbenes – spectator ligands, useful for catalysts
- Metathesis reactions