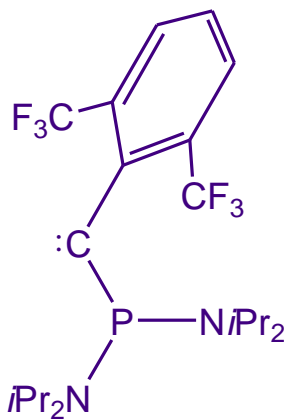
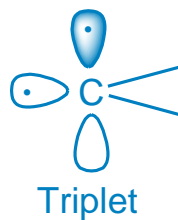
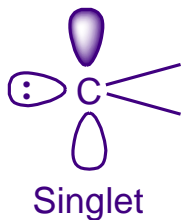


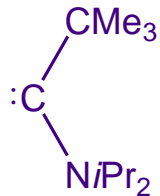
Carbenes

- Stable Free Carbenes :



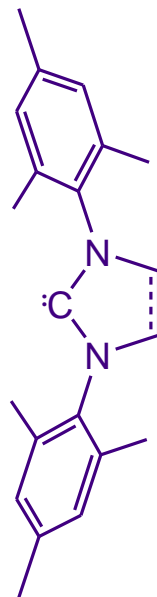
Science, **2000**,
288, 834

Guy Bertrand



JACS, **2004**, 8670

Arduengo Carbene or
NHC (N-Heterocyclic Carbene)



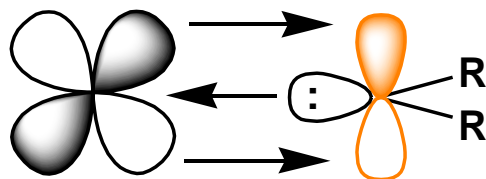
Triplet

Tomioka, *JACS*,
2003, 14664

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

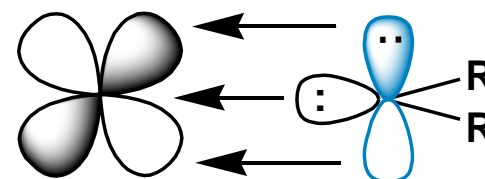
R = π -donor
(OR, NR_2 , Ph)

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

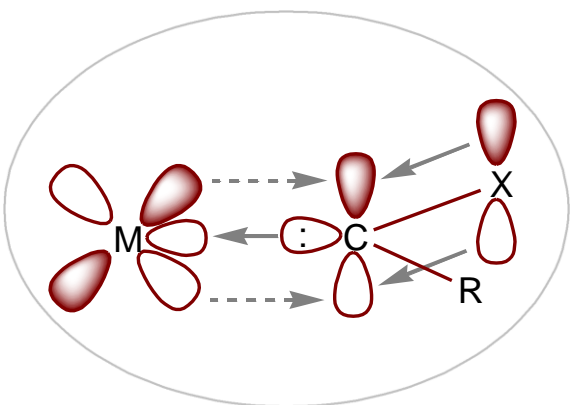
typical metals

typical co-ligands

Transition Metal Carbene Complexes

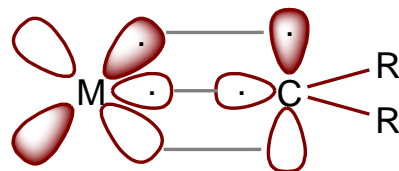
- **Carbenes (CR_2)** – these are not redox active ligands – *i.e.* Fischer or Schrock complexes have the same number of electrons. The difference is whether the carbene carbon is nucleophilic (Schrock) or electrophilic (Fischer).

Fischer Carbene



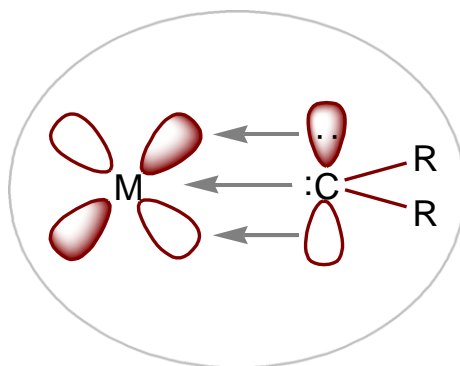
- only one way to look at a Fischer carbene
- neutral singlet carbene
- 1 donor covalent bond + weak π -backdonation
- 2 electron donor

Schrock Carbene



- neutral triplet carbene
- 2 covalent bonds
- 2 electron donor

Ligands viewed as being neutral $2e^-$ donors

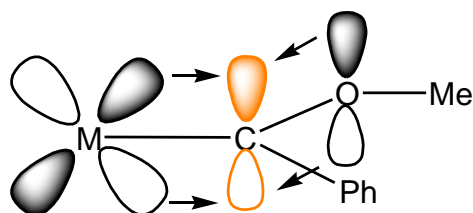
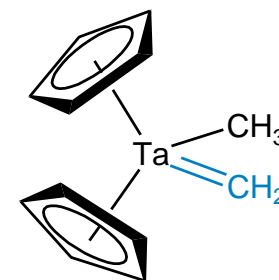
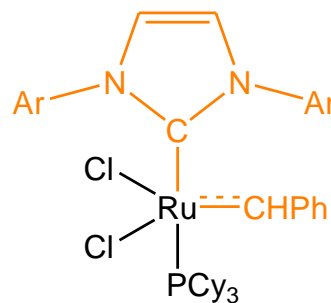
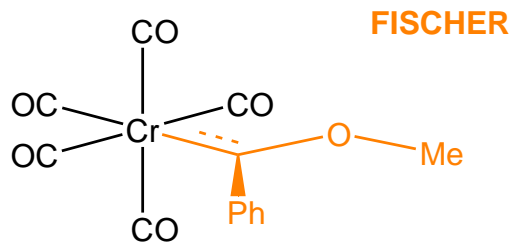


- dianionic CR_2^{2-}
- 2 bonds (σ and π donation)
- 4 electron donor

Ligands not neutral

Transition Metal Carbene Complexes

- Examples :



SCHROCK

- Exceptions :

If Schrock

$W^{VI} = d^0$

$2 \times Cp^- = 12$

$Me^- = 2$

$CH_2^{2-} = 4$

Total = 18

If Fischer

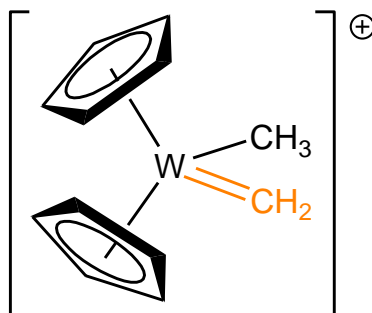
$W^{IV} = d^2$

$2 \times Cp^- = 12$

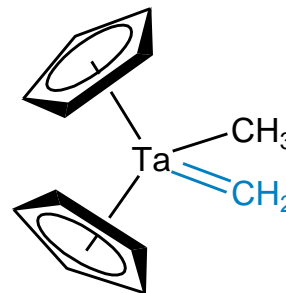
$Me^- = 2$

neutral $CH_2 = 2$

Total = 18



FISCHER !!!



SCHROCK

$Ta^V = d^0$

$2 \times Cp^- = 12$

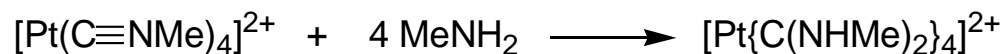
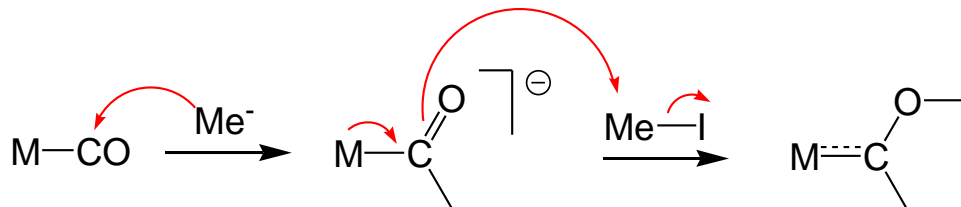
$Me^- = 2$

$CH_2^{2-} = 4$

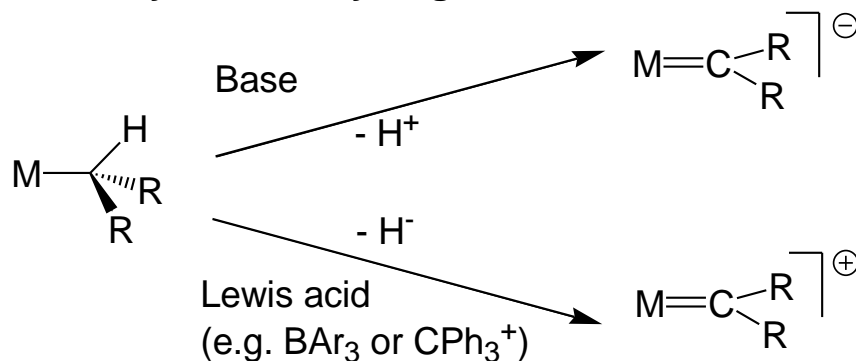
Total = 18

Synthesis of Carbene Complexes

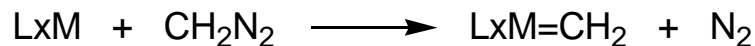
Acyl or Iminoacyl Complex + Electrophile :



From alkyls with α -hydrogens

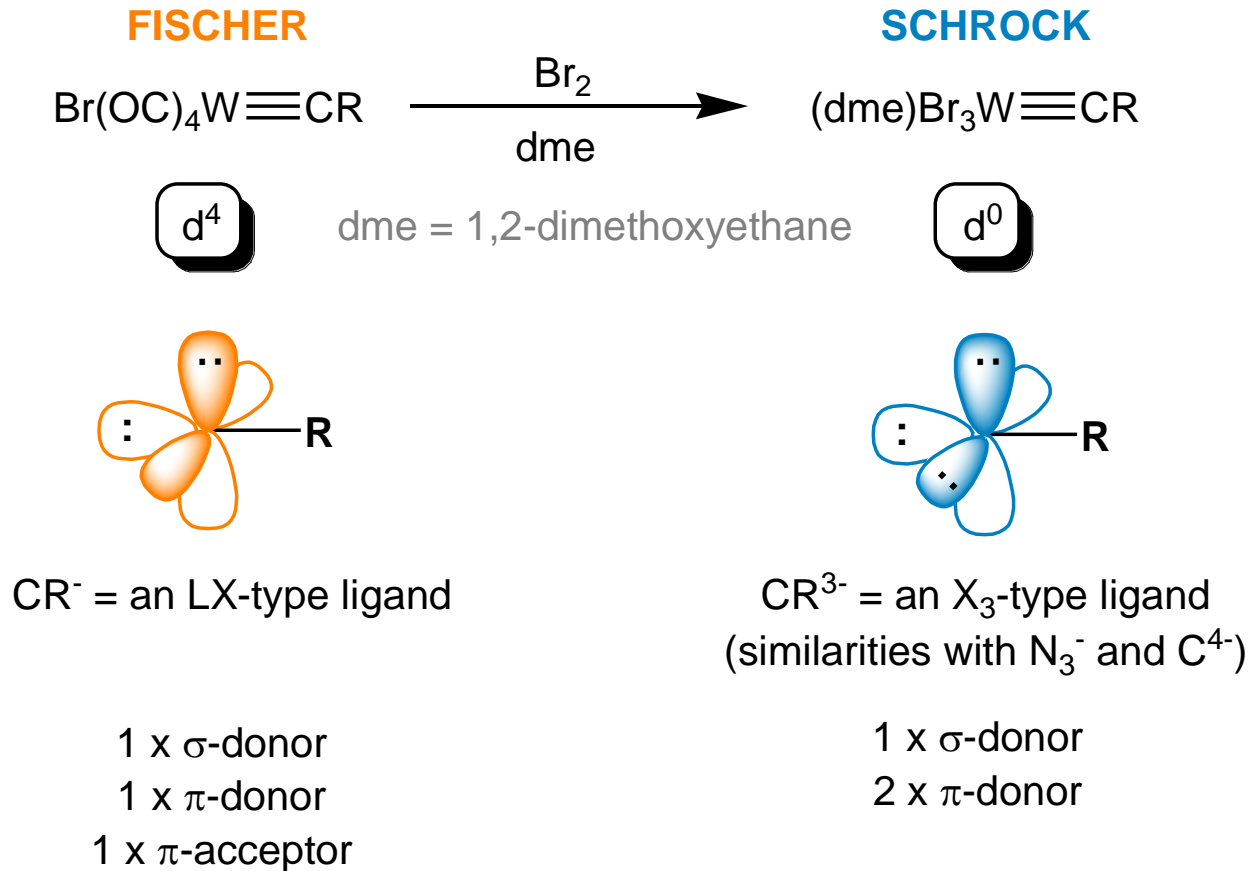


Using a carbene source (e.g. a diazoalkane, $R_2C=N=N$)



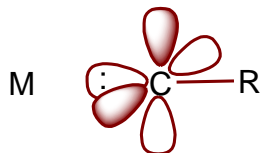
Metal Carbyne Complexes

- Also Fischer and Schrock bonding extremes, but the distinction is less marked → considerable ambiguity in many cases.

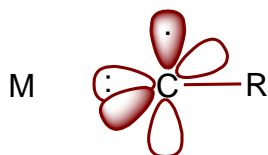


Metal Carbyne Complexes

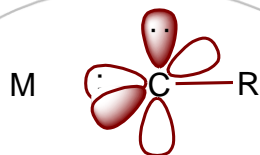
Fischer Carbyne



- cationic CR^+ ($2 e^-$ donor)
- 1 donor covalent bond + 2 vacant p-orbitals for $M \rightarrow L$ π -backdonation



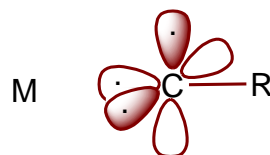
- neutral doublet CR ($3 e^-$ donor)
- 2 covalent bonds + 1 vacant p-orbital for $M \rightarrow L$ π -backdonation



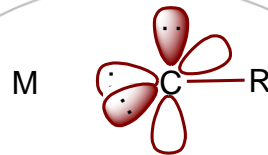
- anionic CR^- ($4 e^-$ donor)
- 2 donor covalent bonds + 1 vacant p-orbital for $M \rightarrow L$ π -backdonation

Schrock Carbyne

- Carbynes (CR) are not redox active ligands



- neutral quartet CR ($3 e^-$ donor)
- 3 covalent bonds



- trianionic CR^{3-} ($6 e^-$ donor)
- 3 donor covalent bonds

Ligand cationic

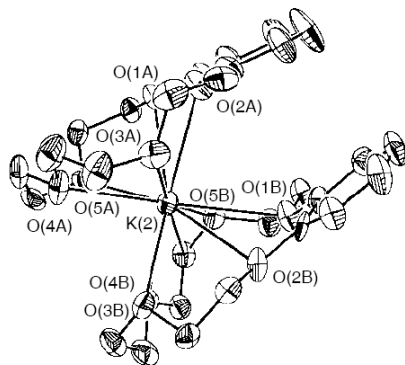
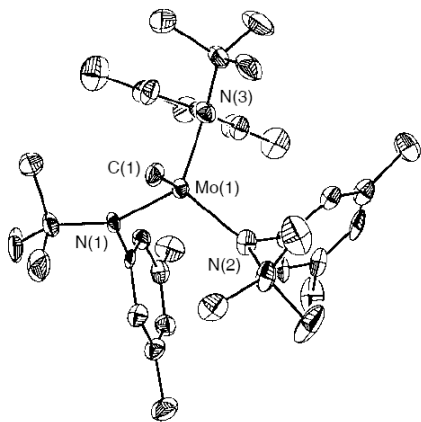
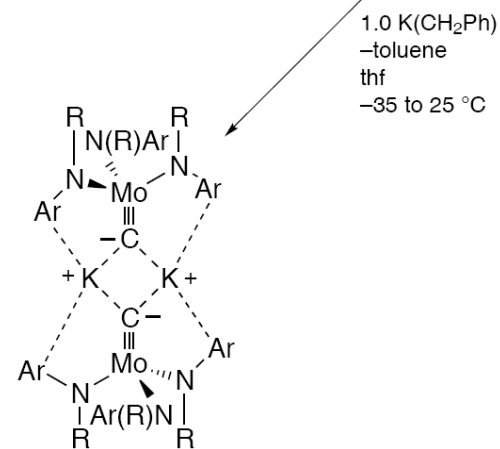
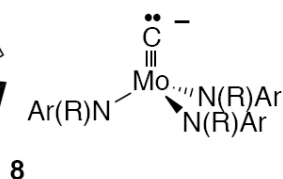
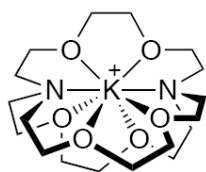
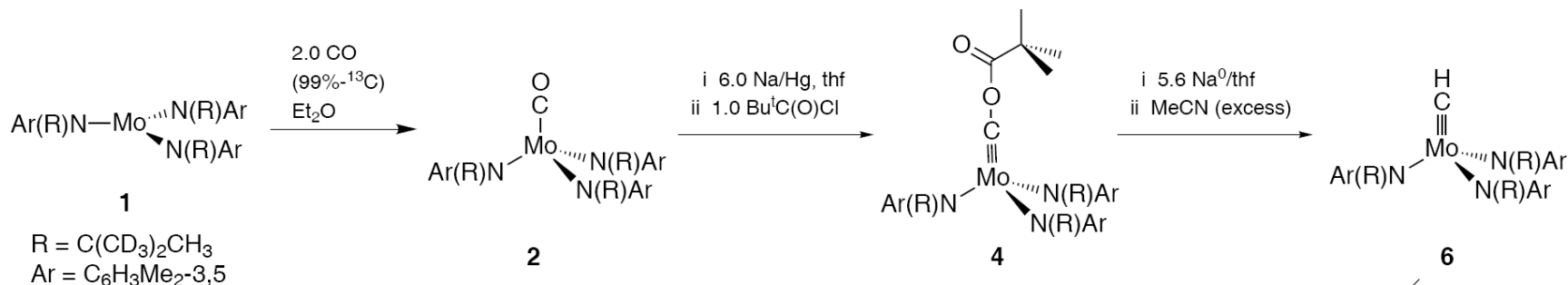
Ligands viewed as being neutral $3e^-$ donors

- useful for electron counting if you don't know if a CR_2 ligand is a Fischer or Schrock carbene.

Ligands anionic

- Better method for working out the formal oxidation state of a metal coordinated to a CR_2 ligand. Using this method, Schrock carbynes are almost always found with d^0 -metals

Metal Carbide Complexes



C. C. Cummins *et al.*,
Chem. Commun., **1997**, 1995