



CARBENE AND OTHER M-C AND M-X MULTIPLE BONDS

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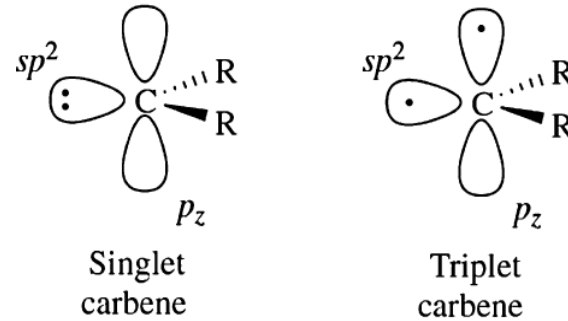
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3.1 FREE CARBENES



Reactive intermediate with a divalent carbon atom w/ 1 non-bonding orbital of π -symmetry and 1 non-bonding orbital of σ -symmetry.

Either singlet spin state (EWG substituents) or triplet (H/alkyl groups).

1991, Arduengo, first stable, crystalline, singlet carbene (NHC), now common ancillary ligand.

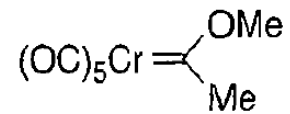


3.2 CARBENE COMPLEXES

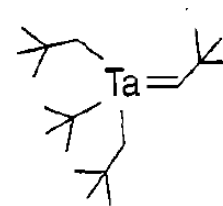
Coordination to the metal can stabilize reactive carbenes.

Carbene complex not synthesized from nor give carbenes (NHC exception).

2 major types:



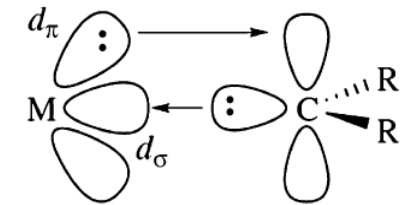
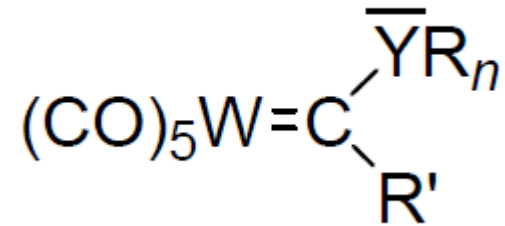
A The first
“Fischer carbene
complex”



B The first
“Schrock carbene
complex”

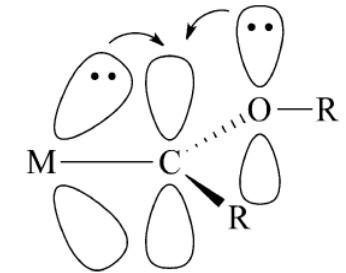


3.2.1 METAL-CARBENES – FISCHER TYPE



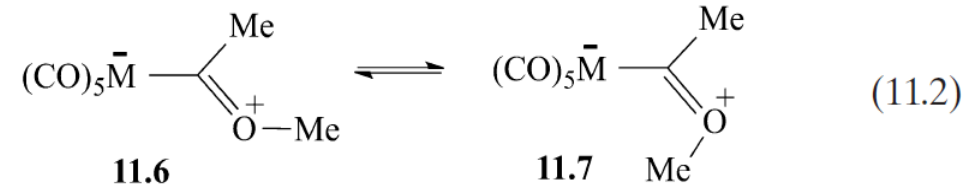
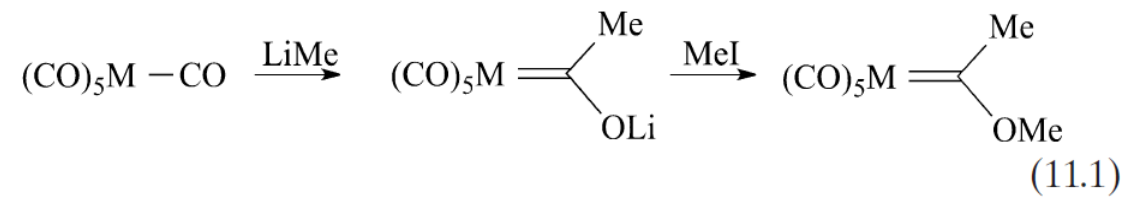
Fischer carbene

- Y = O, NR, S
- M = low valent, middle-late TM, often 18e⁻, d6
- Nucleophilic attack on carbon atom favored (C electrophilic)
- Electrophilic attack on metal center favored (M nucleophilic)
- Carbene stabilized by heteroatom that can donate into the empty π orbital on C
- Weak M-C bond
- **L-type ligand**





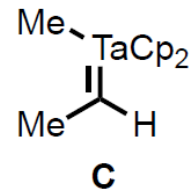
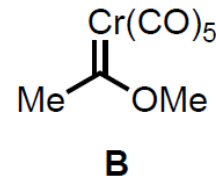
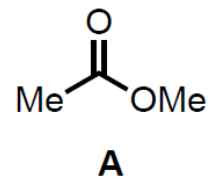
3.2.1 METAL-CARBENES – FISCHER TYPE SYNTHESIS





3.2.1 POD #2

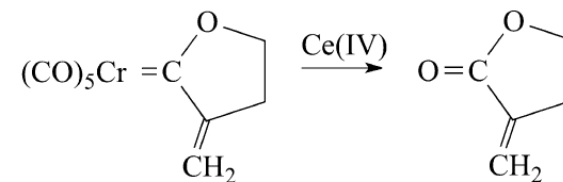
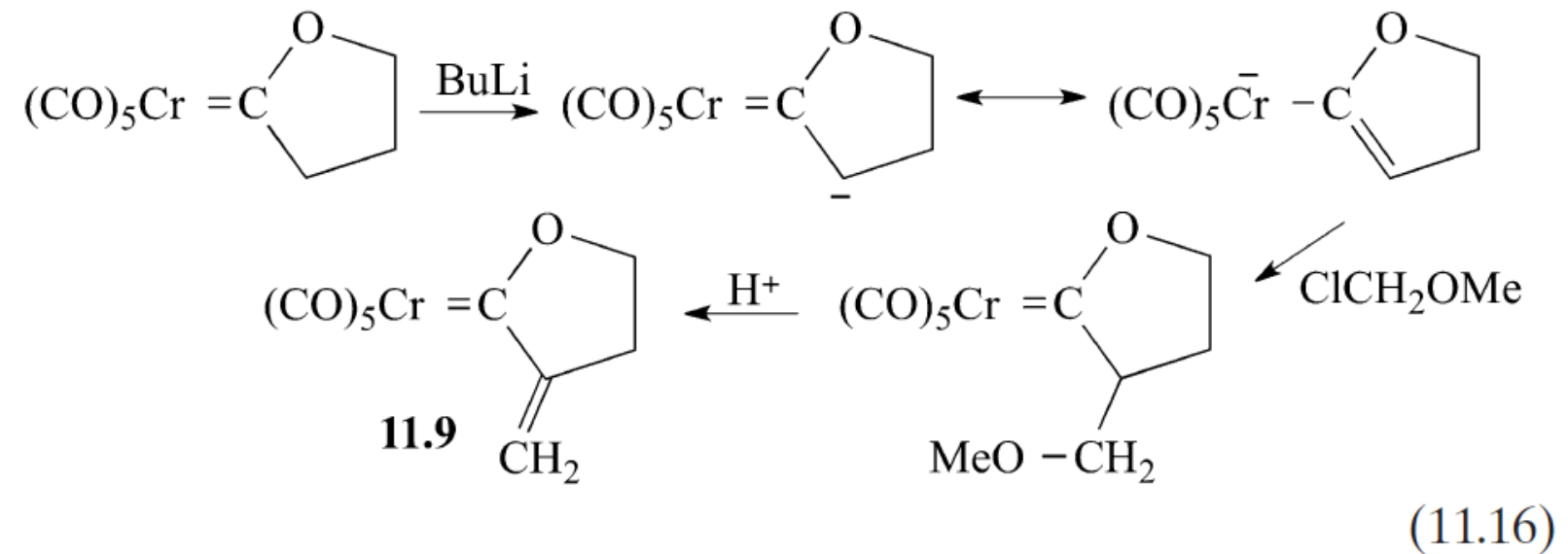
Consider the following three compounds. **Rank them in terms of increasing pKa**





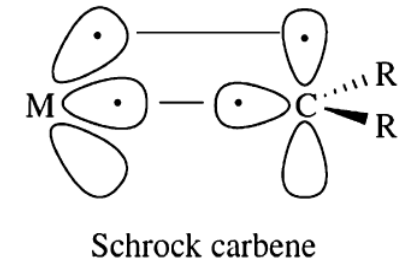
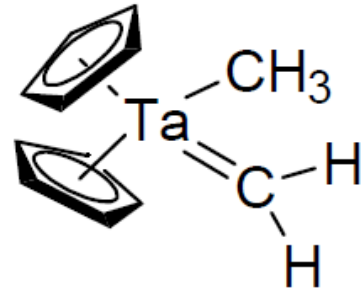
3.2.1 METAL-CARBENES – FISCHER TYPE REACTIVITY

Enolate-type





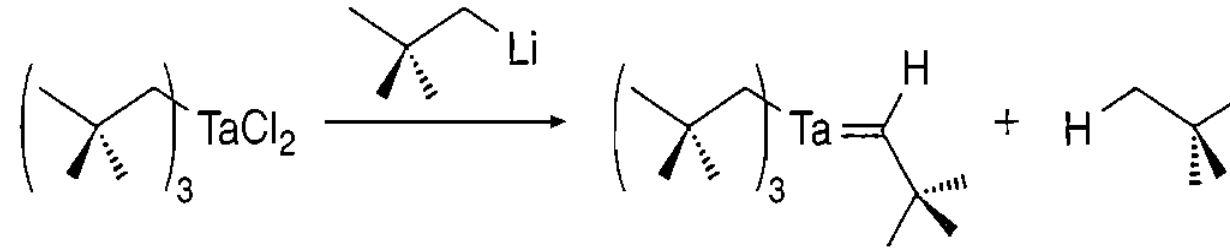
3.2.2 METAL-CARBENES – SCHROCK TYPE



- $R_1, R_2 = \text{Alkyl, H}$
- $M = \text{high valent, early-middle TM, } 14/16e^-, d^0/d^2$
- Electrophilic attack on carbon atom favored (C nucleophilic)
- Nucleophilic attack on metal center favored (M electrophilic)
- Carbene is destabilized by heteroatom that can π -bond to it
- Strong M-C bond
- **X_2 -type ligand** (“dianionic”)



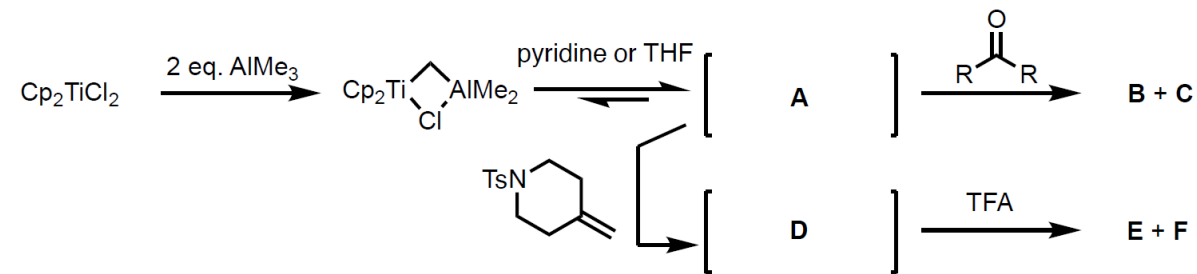
3.2.2 METAL-CARBENES – SCHROCK TYPE SYNTHESIS





3.2.2 POD #3

Consider the following reaction sequences. **Provide structures for A–F and the name of reagent A.** Propose an explanation for why these reactions cannot be readily turned over catalytically.

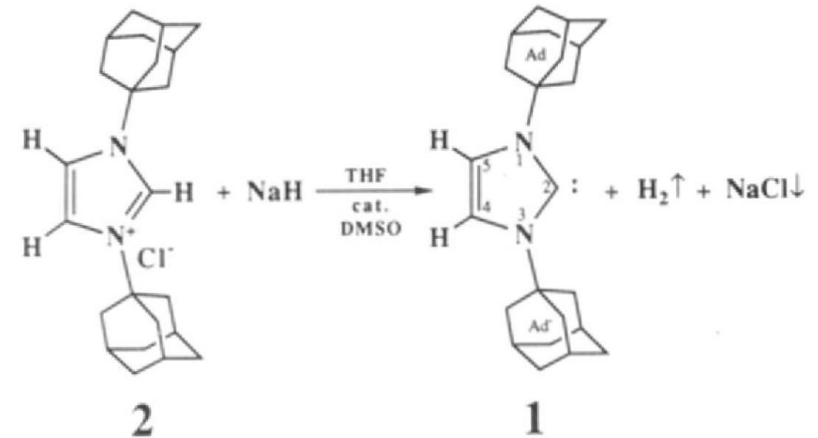


Frederich, *ACIE*, **2021**, 60, 14360. DOI: [10.1002/anie.202103278](https://doi.org/10.1002/anie.202103278)



3.3 N-HETEROCYCLIC CARBENE (NHC) COMPLEXES

- Generally spectators
- “phosphine like”
 - strong σ -donor
 - Weak π -acceptor
- Stronger trans effect than PR_3
- Arduengo / Wanzlick carbene
- **L-type ligand**

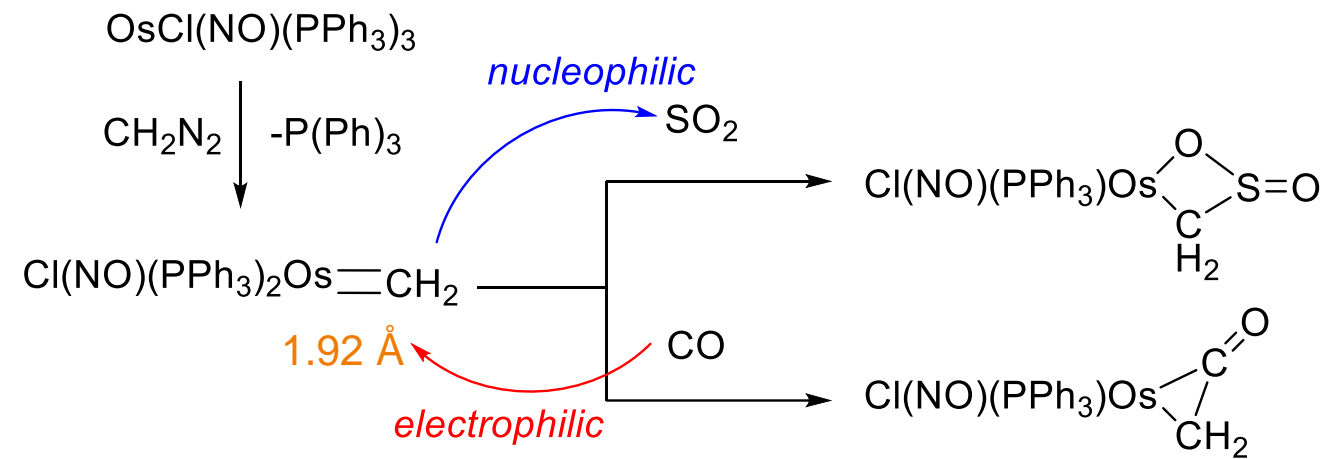


Arduengo, JACS, **1991**, 113, 361. DOI: [10.1021/ja00001a054](https://doi.org/10.1021/ja00001a054)



3.4 BORDERLINE CARBENES

Common for group 8 (Ru, Os)



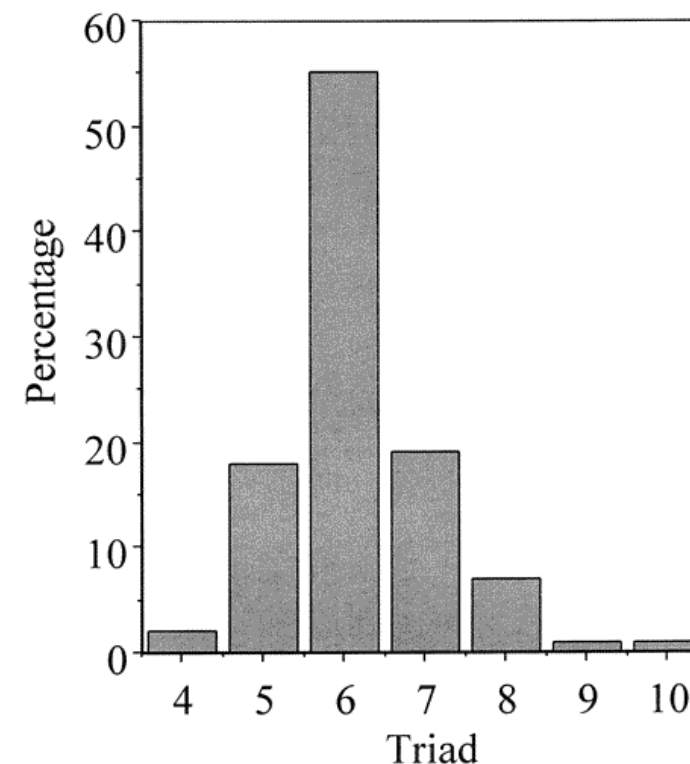
Roper, *J Organomet Chem*, **1986**, 300, 167. DOI: [ffgz9g](https://doi.org/10.1016/0162-2145(86)00099-9)



3.4 OTHER METAL—LIGAND MULTIPLE BONDS

Structure		name	ligand type	e ⁻ donated
$\begin{array}{c} \text{M}=\text{N} \\ \quad \quad \quad \backslash \\ \quad \quad \quad \text{R} \end{array}$	(bent, sp ²)	imido	X ₂	4
$\begin{array}{c} \leftarrow \cdots \\ \text{M}=\text{N}-\text{R} \end{array}$	(linear, sp)	imido	LX ₂	6
M≡N		nitrido	X ₃	6
M=O	(sp ²)	oxo	X ₂	4
$\begin{array}{c} \leftarrow \cdots \\ \text{M}=\text{O} \end{array}$	(sp)	oxo	X ₃	6
$\begin{array}{c} \text{R} \\ \quad \quad \quad \backslash \\ \text{M}=\text{C}=\text{C} \\ \quad \quad \quad / \\ \text{R} \end{array}$		vinylidene	L	2
$\begin{array}{c} \text{M} \quad \quad \quad \text{O} \\ \quad \quad \quad \backslash \quad / \\ \quad \quad \quad \text{C}=\text{C} \\ \quad \quad \quad / \quad \backslash \\ \text{R} \quad \quad \quad \text{R} \end{array}$		carbenoid	L	2
M≡—R	(Fischer)	carbyne	LX	4
M≡—R	(Schrock)	carbyne	X ₃	6

Occurrence of TM=MG Complexes in the Cambridge Structural Database



+ sylene (M=Si), phosphinidene (M=P), borylene...



POD #1 – ELECTRON COUNTING CARBENE METAL COMPLEXES

For the structures below, provide the **coordination number**, **metal oxidation state**, **d-electron count**, and **overall electron count**.

