Carbenes

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Carbenes

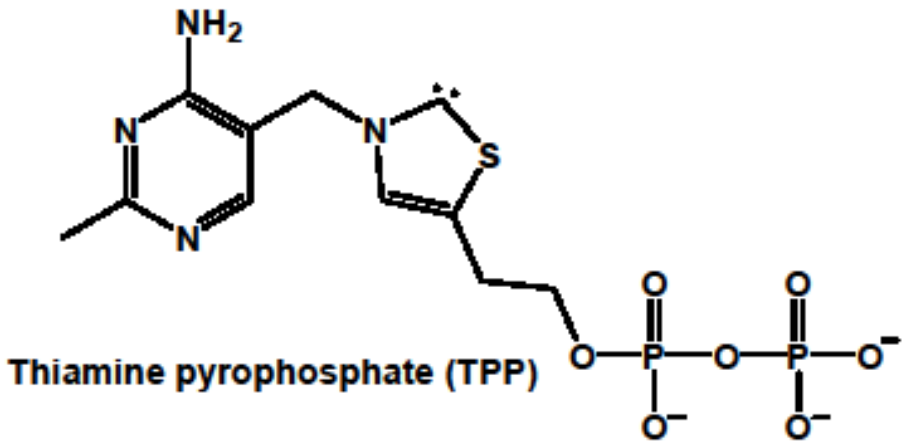
- Reagent (Intermediate) -> Direct participation
- **Stable carbene (Reagents/ligands/catalysts)**
- **Tamed** via transition metal complexes
  - Electrophilic (Fischer)
  - Nucleophilic (Schrock)
  - **Metathesis carbenes** (Grubb/ Schrock)

  Spectator ligand in transition metal complexes

  for smooth & effective chemical transformations.

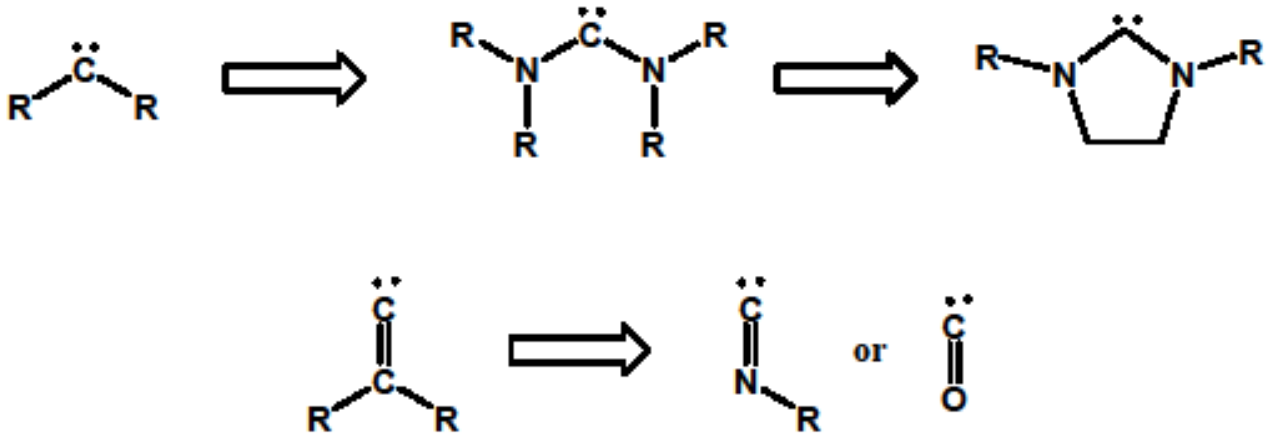
Thiamine

- Vitamin B_1 (Thiamine)
  - Coenzyme in many biochemical reactions
  - A dietary lack of thiamine results in beriberi



Thiamine pyrophosphate (TPP)

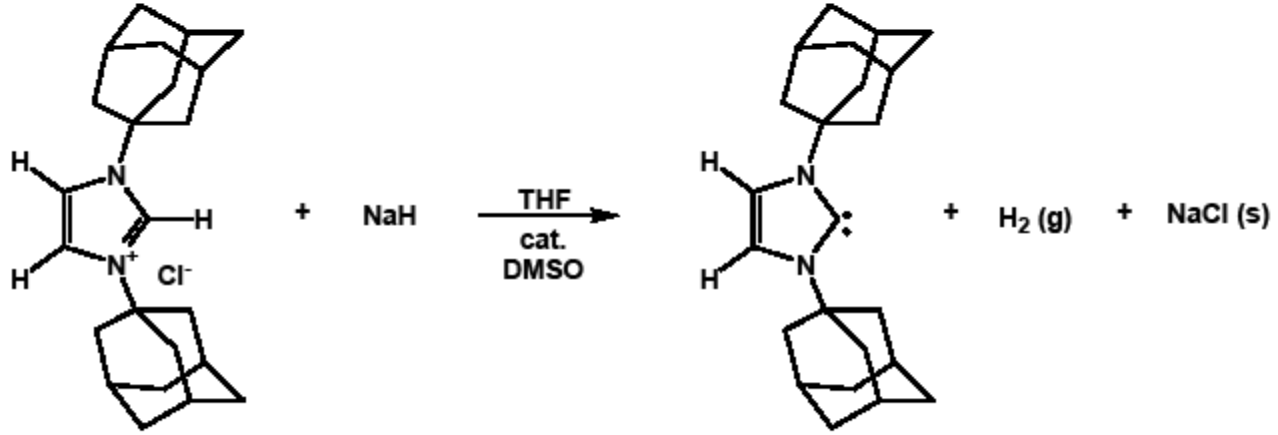
A Quest for Stable Carbenes



- 1960's – Wanzlick attempts isolation of a stable carbene
  - Electrophilic nature of carbenes will be decreased if substituents are strong π-donors
  - Generate nucleophilic, singlet carbenes

Wanzlick, H. W.; Schonher, H. J. *Angew. Chem. Int. Ed.,* **1968**, 7, 141.

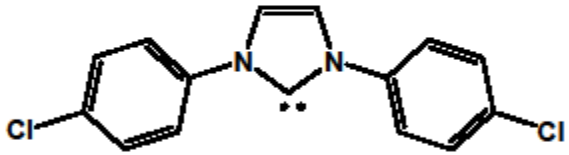
Isolation of a Stable Carbene



- 1991 – Arduengo isolates first stable carbene
- Stable in absence of O_2 and H_2O
- Does not decompose upon melting (240°C)

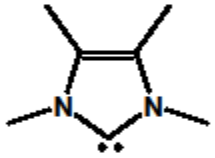
Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.*, **1991**, 113, 361

Stable Carbenes



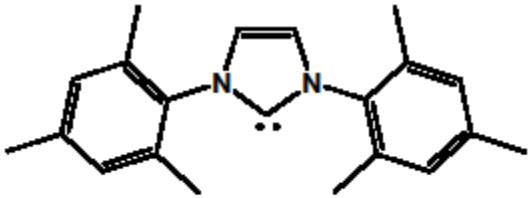
m.p. = 153 - 155 °C

$\theta_{N\text{-}C2\text{-}N}$ = 101.7°



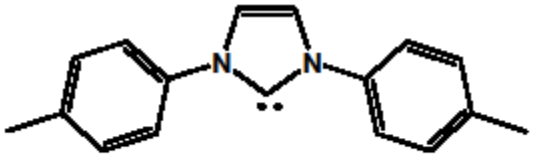
m.p. = 109 - 110 °C

$\theta_{N\text{-}C2\text{-}N}$ = 101.5°



m.p. = 150 - 155 °C

$\theta_{N\text{-}C2\text{-}N}$ = 101.4°



m.p. = 156 - 158 °C

$\theta_{N\text{-}C2\text{-}N}$ = 101.2°

- Bond angles resemble those of acyclic, singlet carbenes

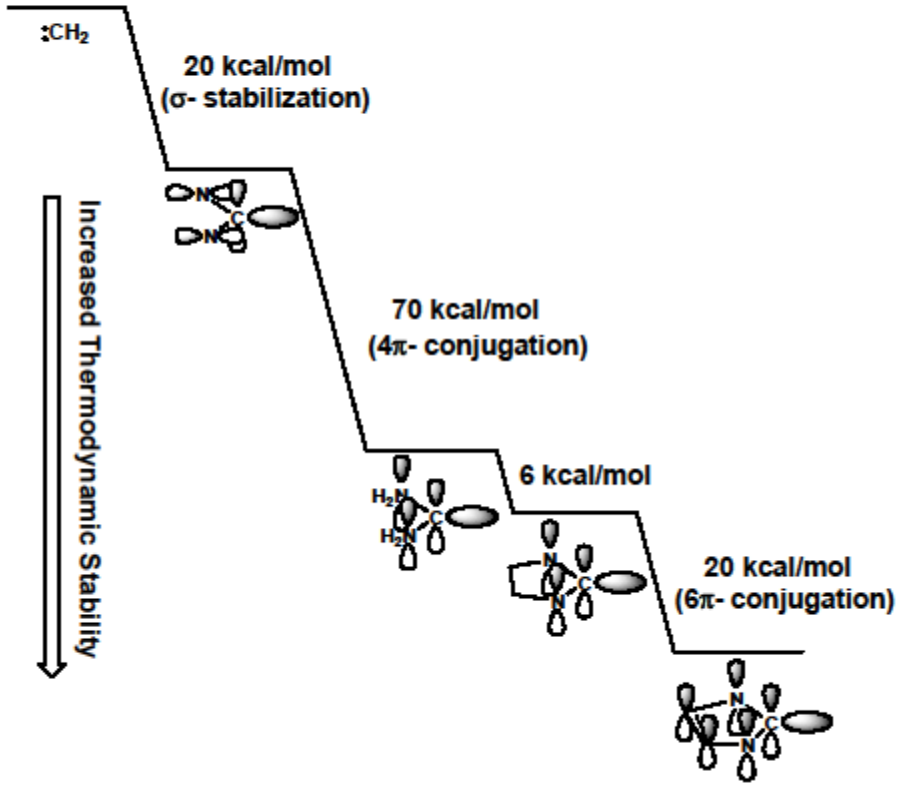
Arduengo, A. J.; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, 114, 5530.

Carbenes or Ylides?

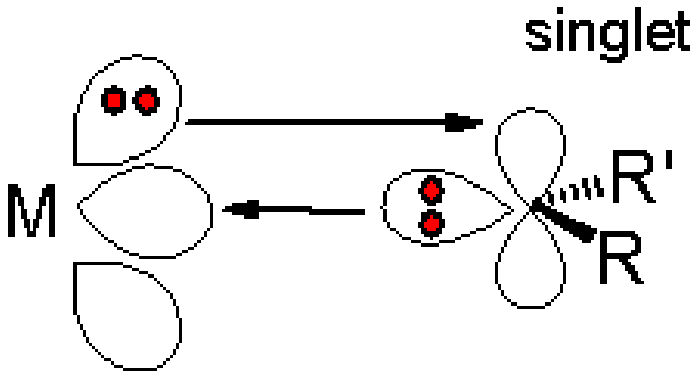
- Carbene center stabilized by a “push-pull” effect
  - Electronegative nitrogens “pull” electron density away from the carbene center – σ-stabilization
  - Nitrogen lone pairs can “push” electron density into the empty p-orbital – π-stabilization

Evidence for Ylides

ab initio calculations suggest significant thermodynamic stabilization due to π-conjugation

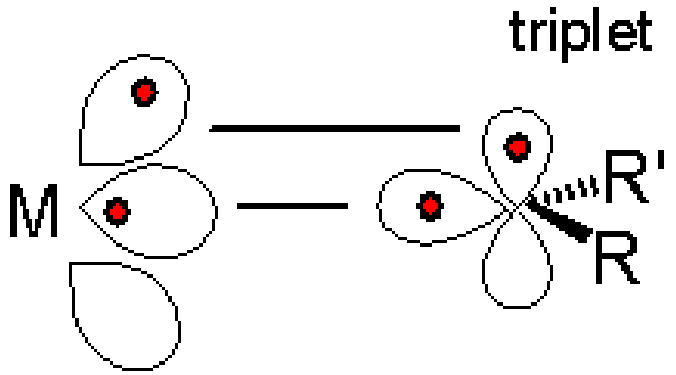


Heinemann, C.; Muller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.*, **1996**, 118, 2023



Fischer

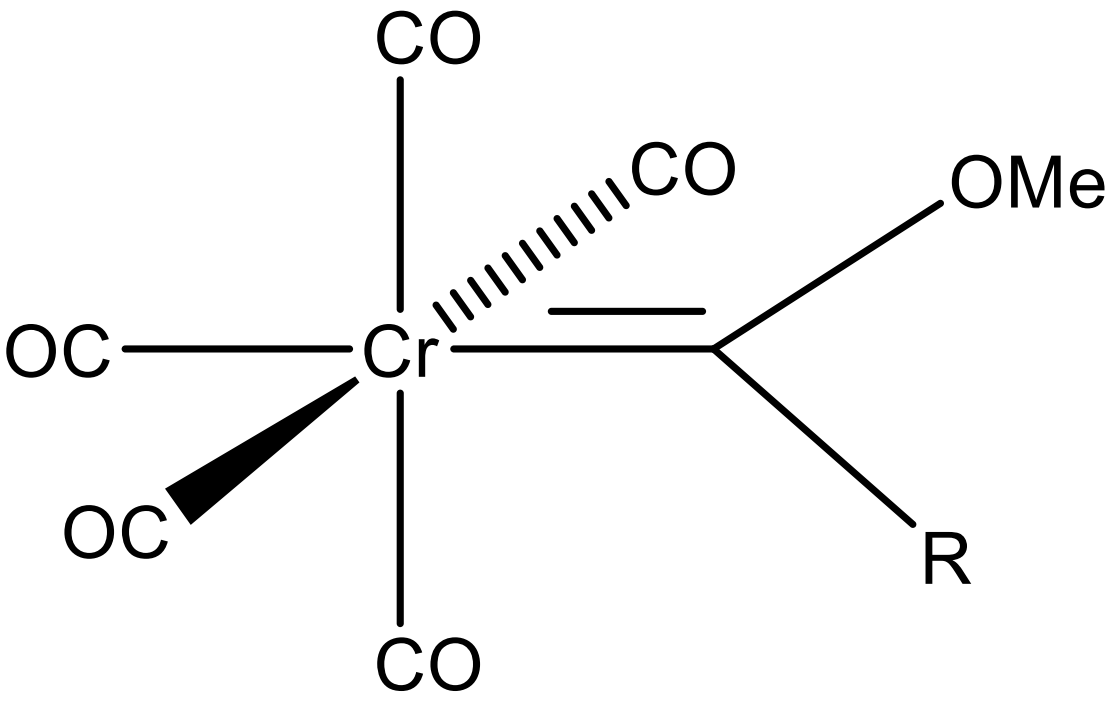
- low oxidation state metals
- middle and late transition metals Fe(0), Mo(0), Cr(0)
- pi electron acceptor metal ligands
- pi-donor substituents on methylene group such as alkoxy and alkylated amino groups



Schrock

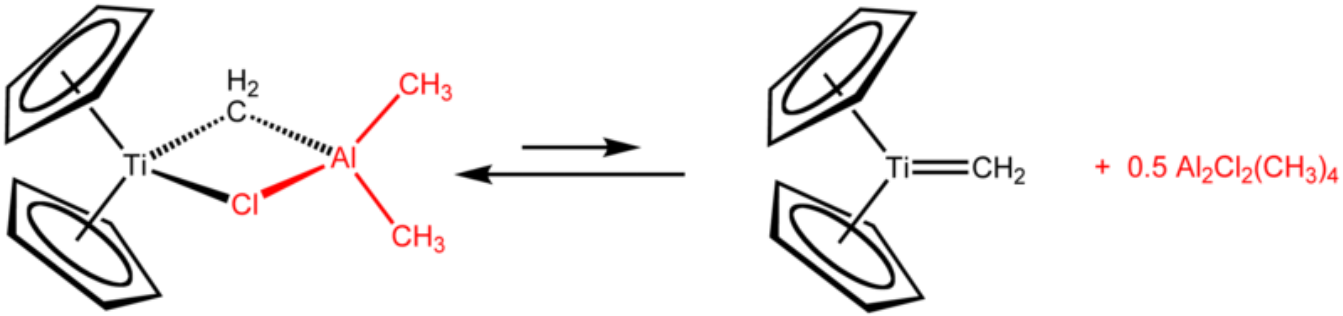
- high oxidation states
- early transition metals Ti(IV), Ta(V)
- pi-donor ligands
- hydrogen and alkyl substituents on carbenoid carbon

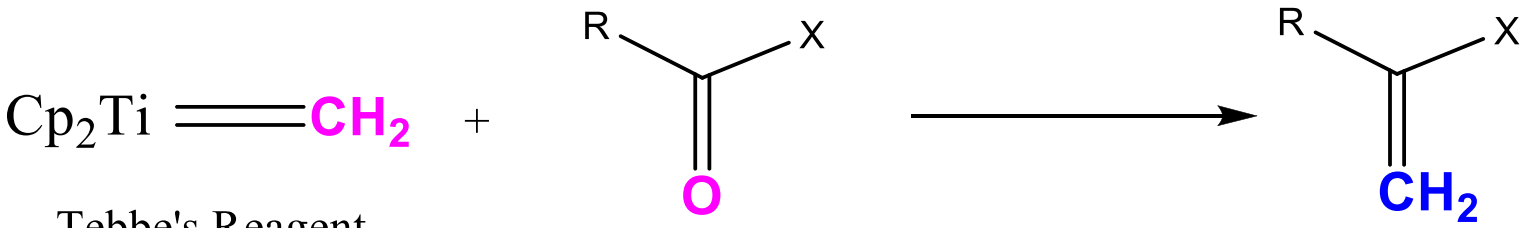
Electrophilic Heteroatom Stabilised ‘Fischer’ Carbene Complexes



Nucleophilic 'Schrock' Carbene Complexes

- **Tebbe's reagent**





Tebbe's Reagent

X = R, H, OR, NR_2