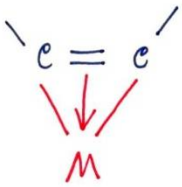
Transition Metal – Alkyne Complexes

Alkyne : Ligand Coordination Variety

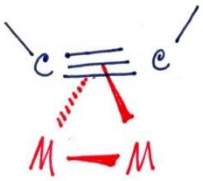
monodentate

bidentate

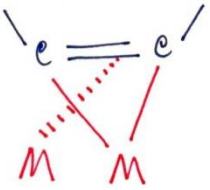
- alkyne acts as 2e'-donor
- (M) – metal fragment is ELECTRON RICH



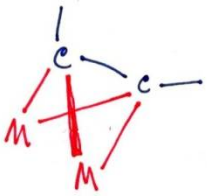
bidentate



bidentate



tridentate



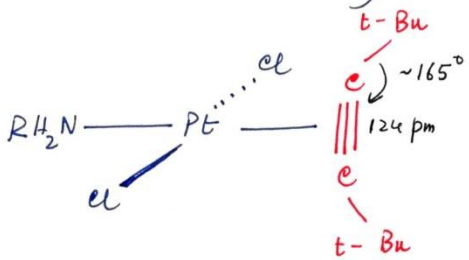
tetradentate

- alkyne acts as 4e'-donor
- (M) – metal fragment is ELECTRON POOR

Synthesis

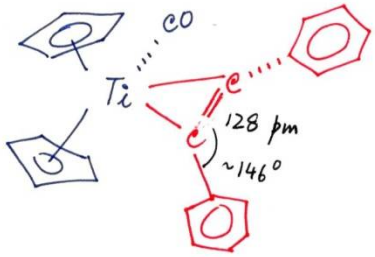
- **Alkynes as 2e⁻ donor** (mainly by Substitution Reactions)

$$Na_2[PtCl_4] \xrightarrow[ii)\ R\text{-}NH_2]{i)\ t\text{-}Bu_2C_2,\ EtOH} \quad (R = 4\text{-}MeC_6H_4)$$



$\bar{\nu}_{CC} = 2028\ cm^{-1}$

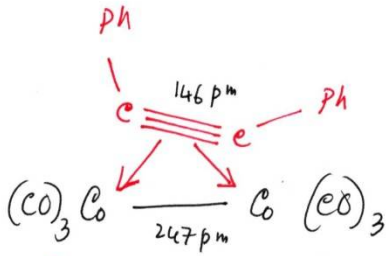
$$Cp_2Ti(CO)_2 + PhC\equiv CPh \xrightarrow[25°C,\ 3\ h]{\text{heptane, vacuum}}$$



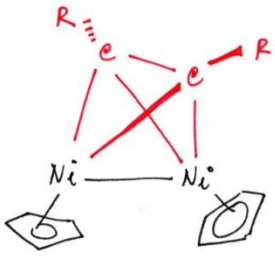
$\bar{\nu}_{CC} = 1780\ cm^{-1}$

- **Alkyne as 4e⁻ donor**
  - ↳ acts as BRIDGING ligands

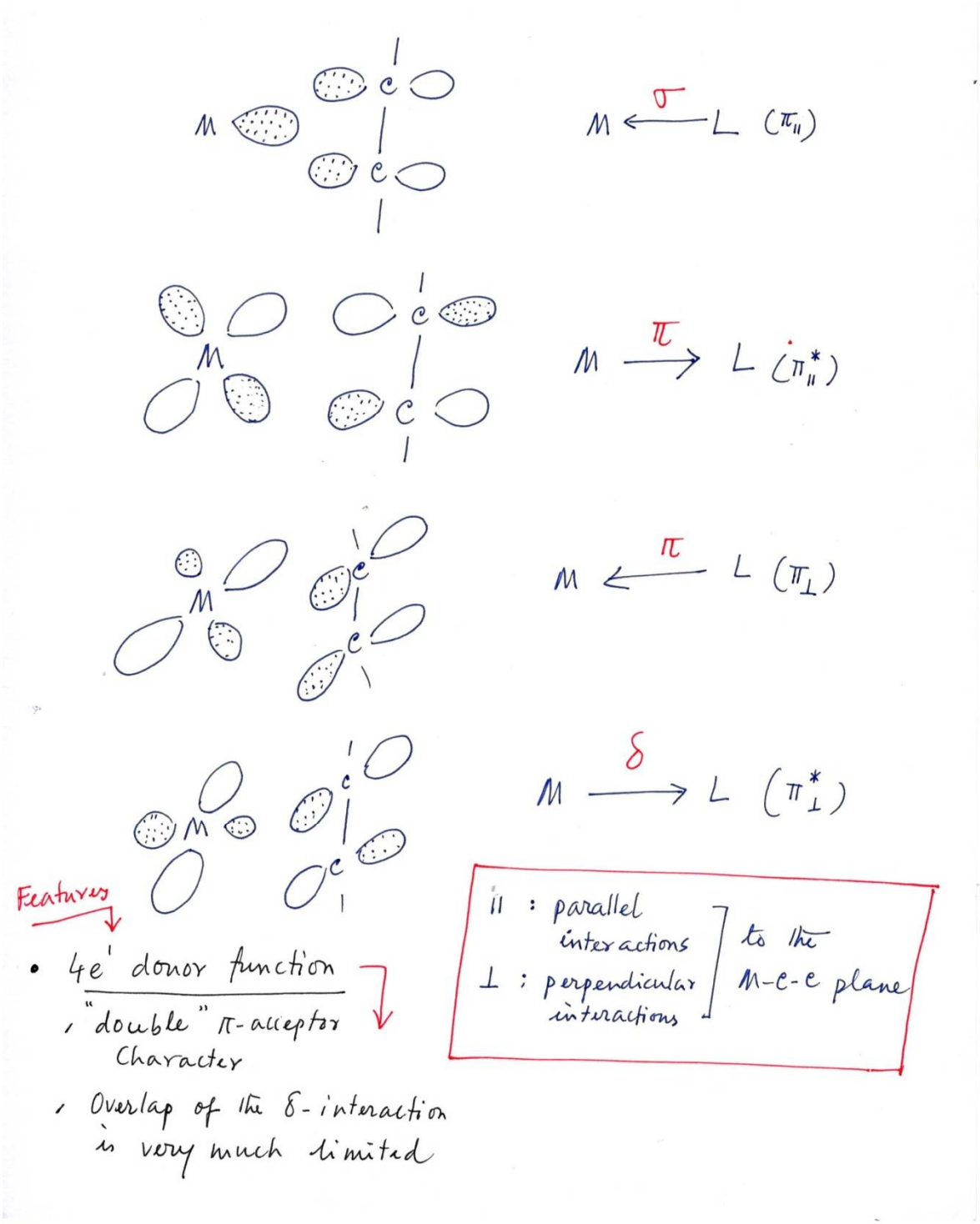
$$Co_2(CO)_8 + PhC\equiv CPh \xrightarrow[(-2CO)]{}$$



$$[CpNi(CO)]_2 + RC\equiv CR \xrightarrow[(-2CO)]{}$$



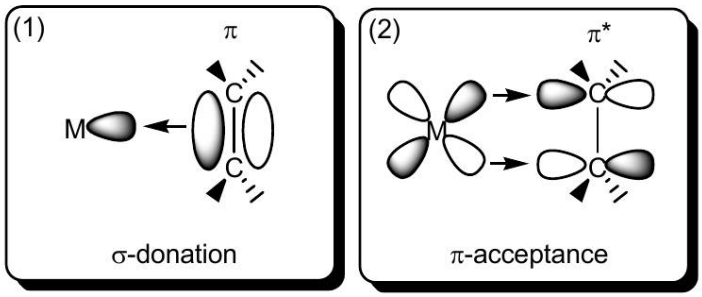
[TM] - Alkyne Complex: Bonding



Dewar – Chatt – Duncanson Model: DCD Model

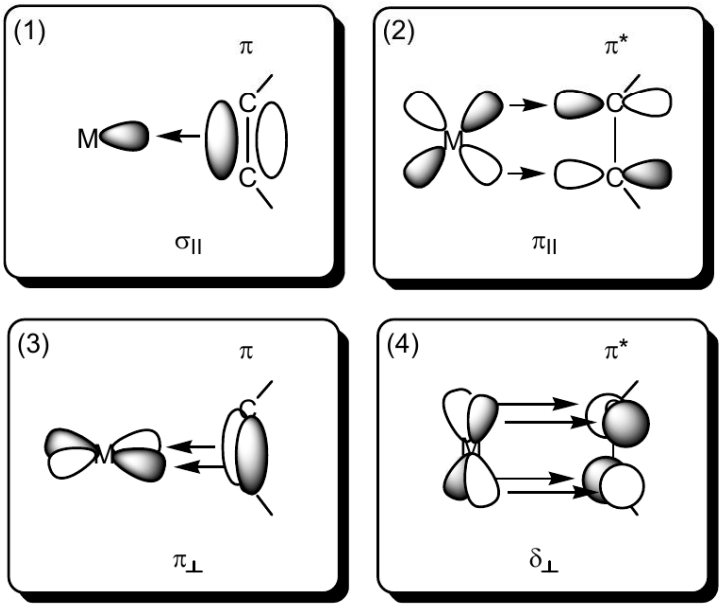
Comparison: [TM] - Alkene Complex vs. [TM] - Alkyne Complex

Alkene complexes: Dewar-Chatt-Duncanson Bonding Model



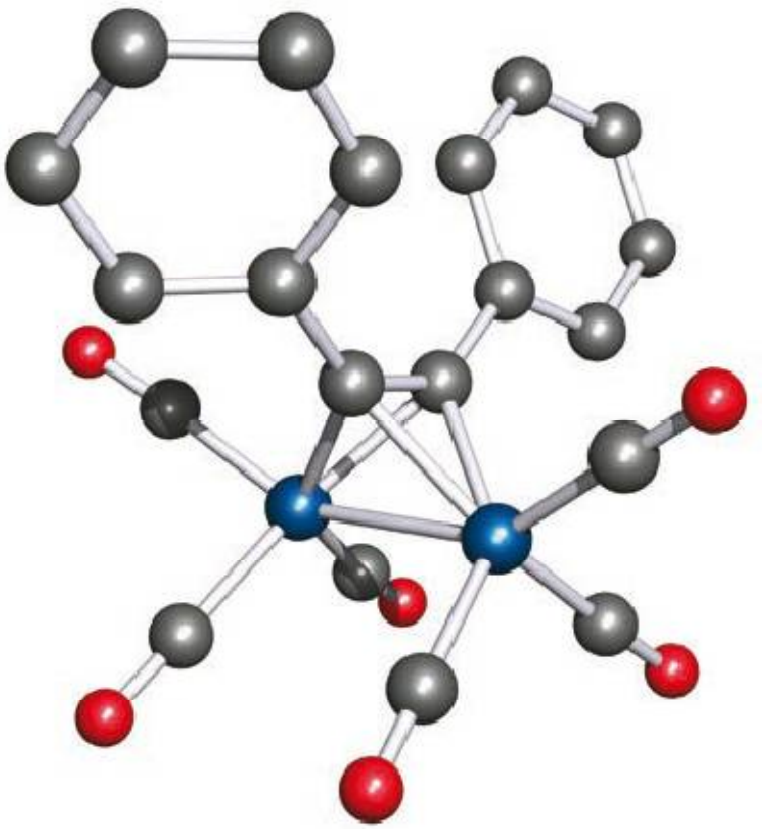
- Synergic Bonding
- Both σ-donation and π-acceptance weakens the CC bond

Alkyne complexes: Dewar-Chatt-Duncanson Bonding Model



- Synergic Bonding
- All four possible bonding interactions weaken the CC bond
- Alkynes can be 2 or 4 electron donors, depending on whether the $\pi_{\perp}$ interaction is significant for a given complex

The structure (X-ray diffraction) of $Co_2(CO)_6(C_2Ph_2)$



Reference:
[D. Gregson et al. (1983) Acta Crystallogr., Sect. C, vol. 39, p. 1024]. Hydrogen atoms are omitted for clarity; colour code: Co, blue; C, grey; O, red.