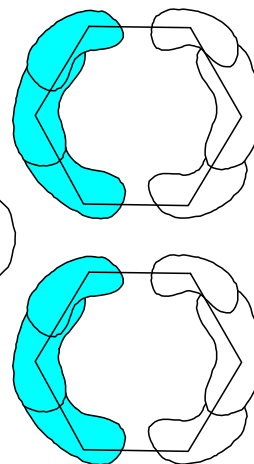
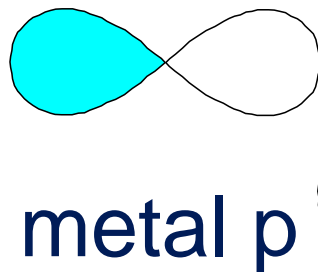
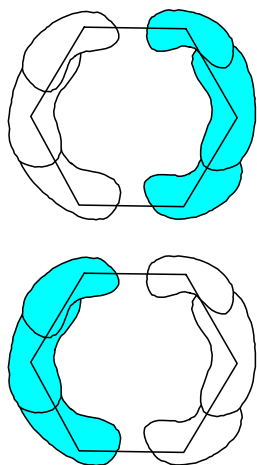
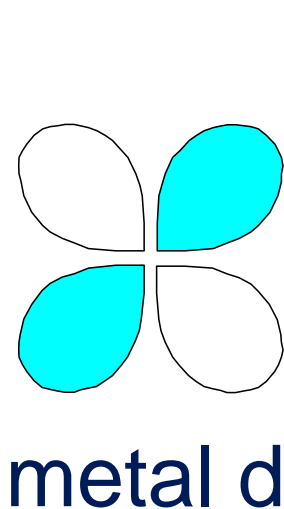
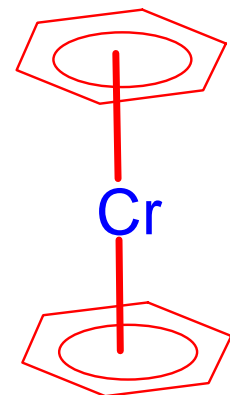
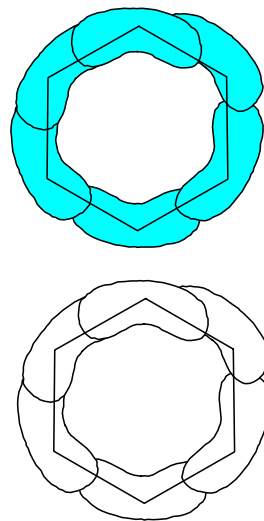
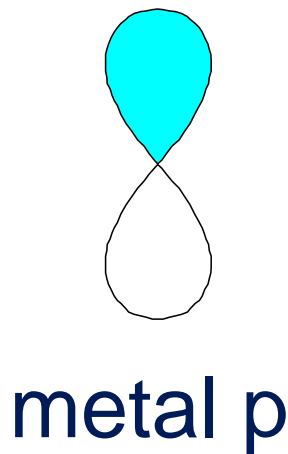
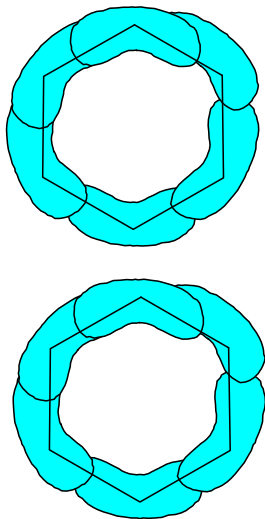
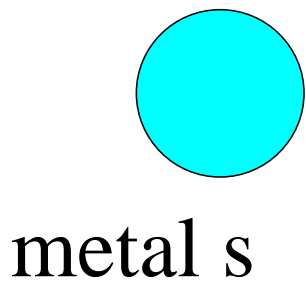
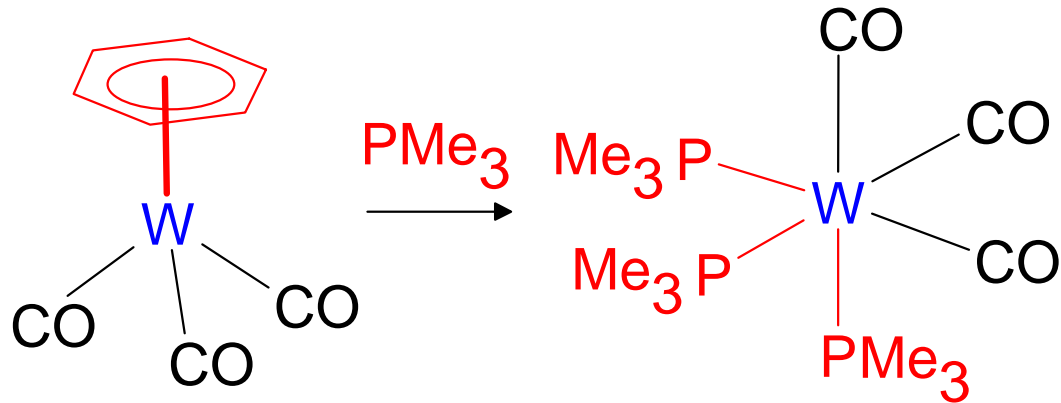


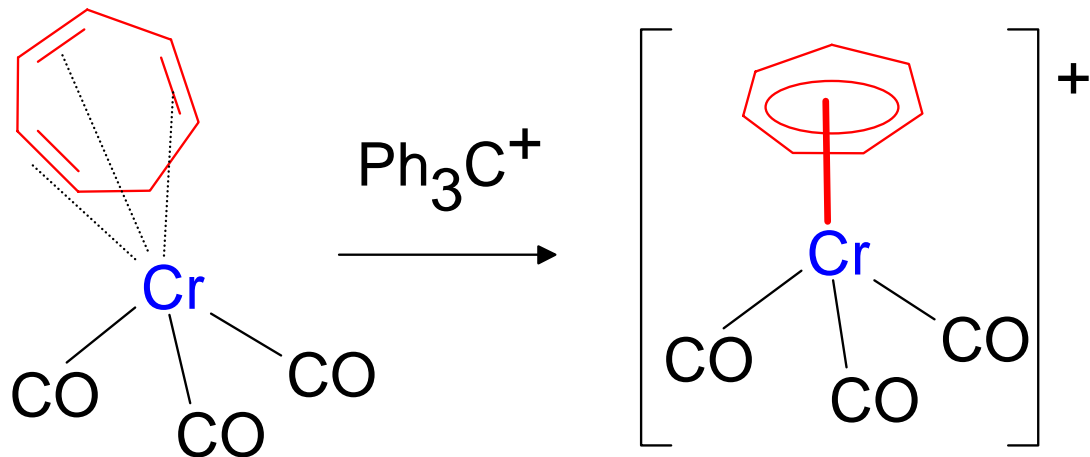
Correlation of Metal/Ligand Orbitals



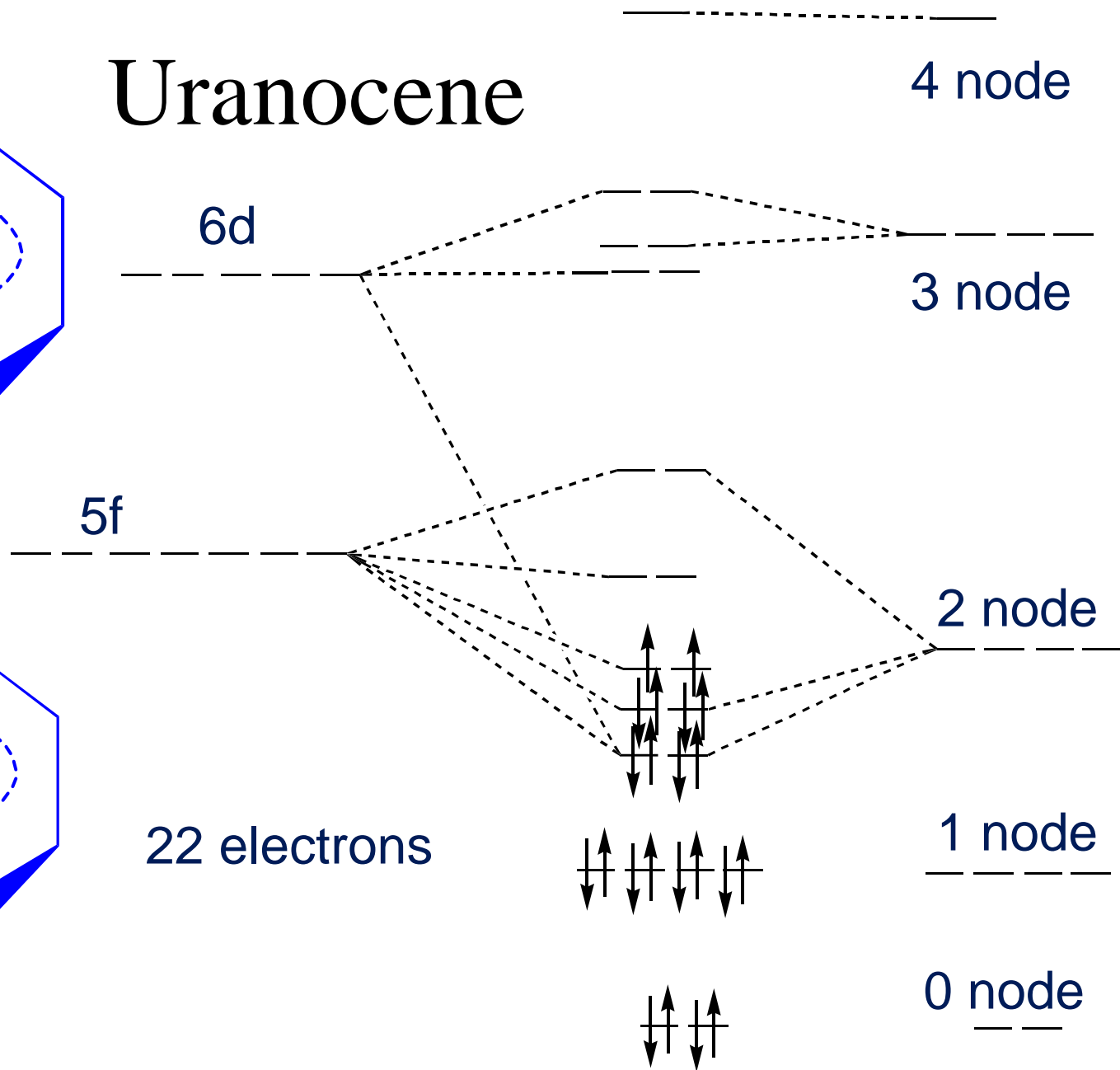
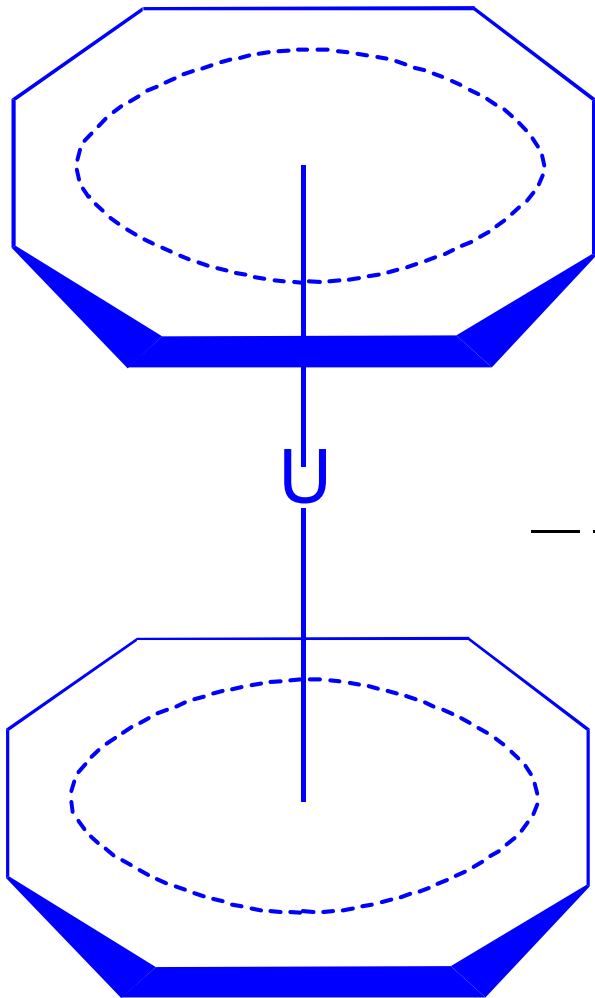
- **benzenoid complexes more sensitive and ligand is readily displaced**



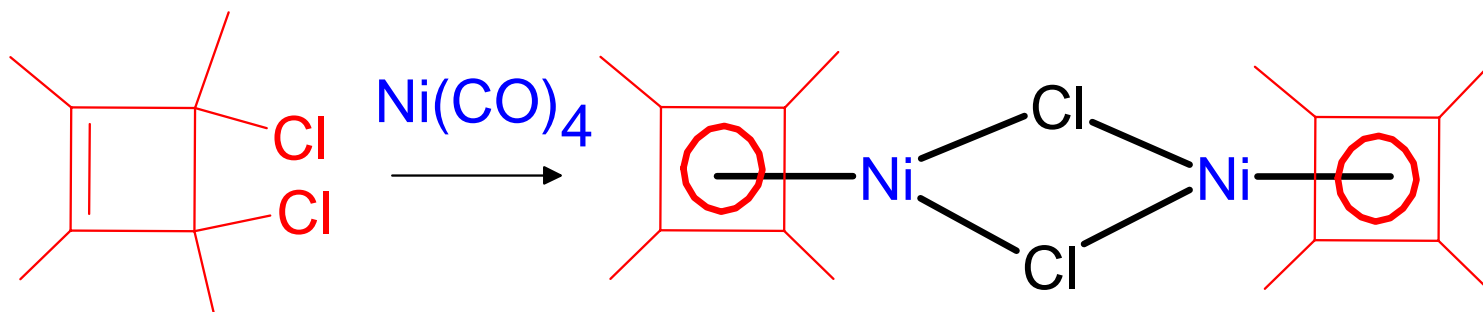
- **Cycloheptatrienyl Cation Complex**



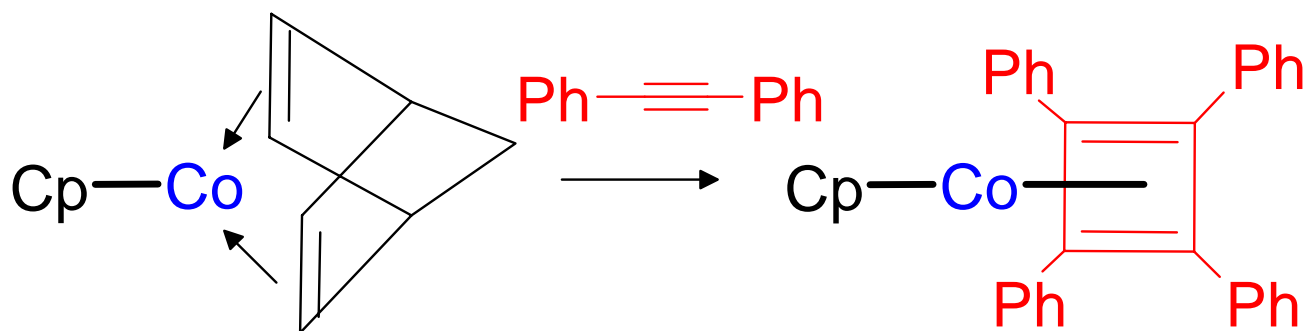
Uranocene



- **Cyclobutadiene Complex**



anti-aromatic (4π -electrons)
isolable if R is bulky

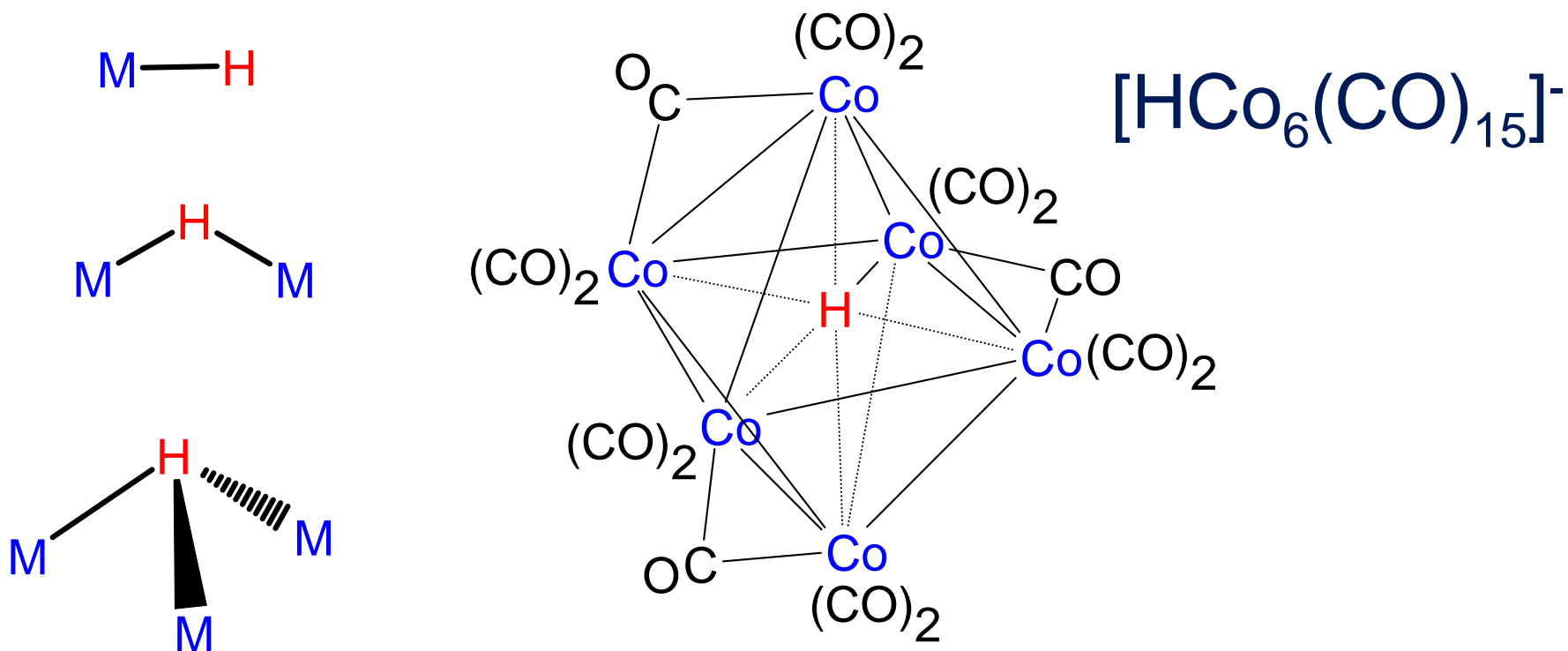


Transition Metal Hydrides

- kinetic and thermodynamic stability increase going down a group
- $(\text{Et}_3\text{P})_2\text{NiHCl}$ -only detected spectroscopically
- $(\text{Et}_3\text{P})_2\text{PdHCl}$ -solid slowly decomposes
- $(\text{Et}_3\text{P})_2\text{PtHCl}$ -distill under high vacuum

Transition Metal Hydrides

- $(\text{Ph}_3\text{P})_3\text{CoH}$ K_2ReH_9 $\text{HCo}(\text{CO})_4$
- $(\text{Ph}_3\text{P})_3\text{IrH}_2\text{Cl}$ Cp_2ZrHCl $\text{H}_2\text{Ru}_6(\text{CO})_{18}$
- terminal, bridging, triply bridging or interstitial



^1H NMR of Hydrides

- ^1H NMR distinctive chemical shifts (usually)

Early Metal
Hydrides

Ar

TMS

Most Transition Metal Hydrides

10

8

0

-3

ppm

-30

- very high field due to shielding by metal
- strong coupling to magnetically active metals
- $J_{\text{M-H}} = 30\text{-}1400\text{Hz}$, ^{103}Rh , ^{183}W , ^{187}Os , ^{95}Mo , ^{57}Fe
- early metal hydrides sometimes at low field due to electron deficient metal

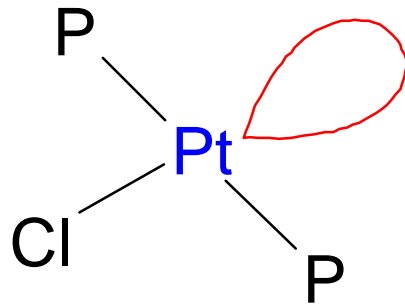
Infrared of Hydrides

- M-H stretches are weak 1900-2250 cm⁻¹
- difficult to observe
- M-H-M also weak ca 1000 cm⁻¹ overlap with organic moieties
- can use ²D to confirm assignment of bands

$$\frac{\nu(\text{M-H})}{\nu(\text{M-D})} = 2^{0.5}$$

X-ray Diffraction and Hydrides

- X-rays are diffracted by electron density
- M-H only 1 electron near a larger number
- difficult to "see"; often don't, find a hole



circumstantial
evidence

- M-H distances 1.5-1.7 Å
- can find by neutron diffraction studies
- neutrons are diffracted by protons