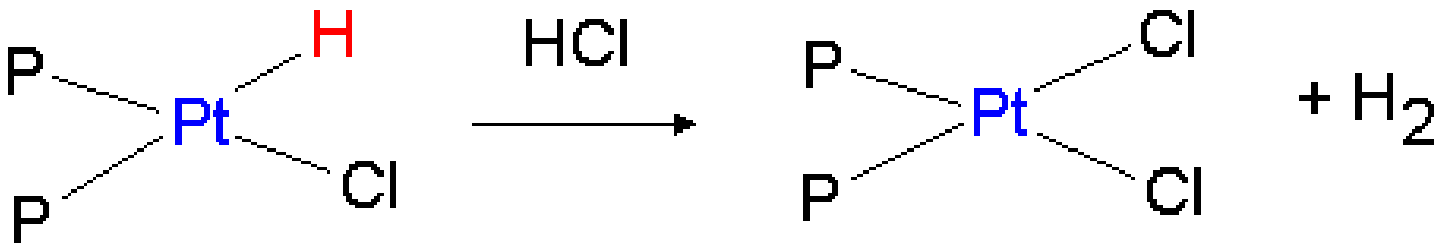
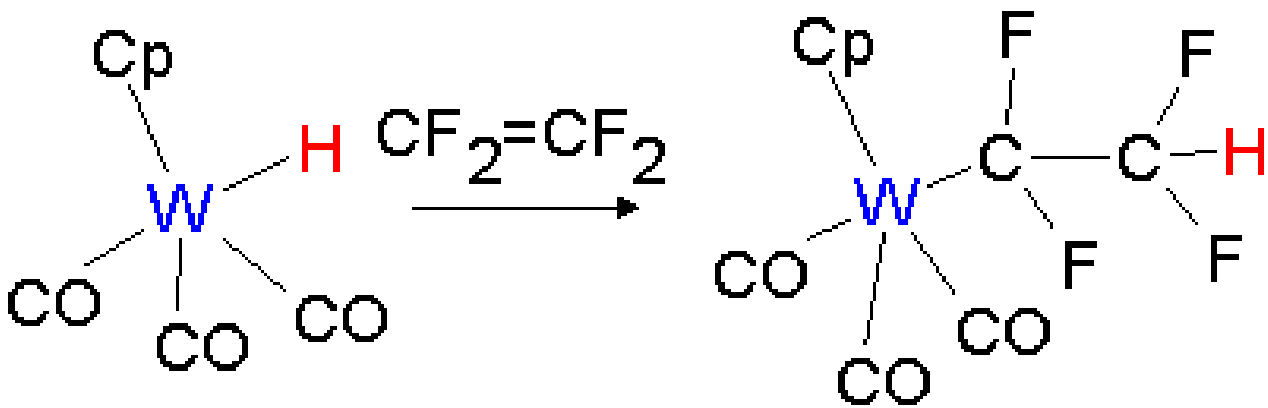
Reactions of Hydrides

- **Acid/Base Chemistry**
- some acidic, some hydridic
- $H_3Re_3(CO)_{12} + KOH \rightarrow K[H_2Re_3(CO)_{12}] + H_2O$
- $HCo(CO)_4$ $K_a = 2$; strong acid
- $HCo(PPh_3)(CO)_3$ $K_a = 1.1 \times 10^{-7}$; weak acid

- **Reactions with Acids**



- **Insertion Reactions**



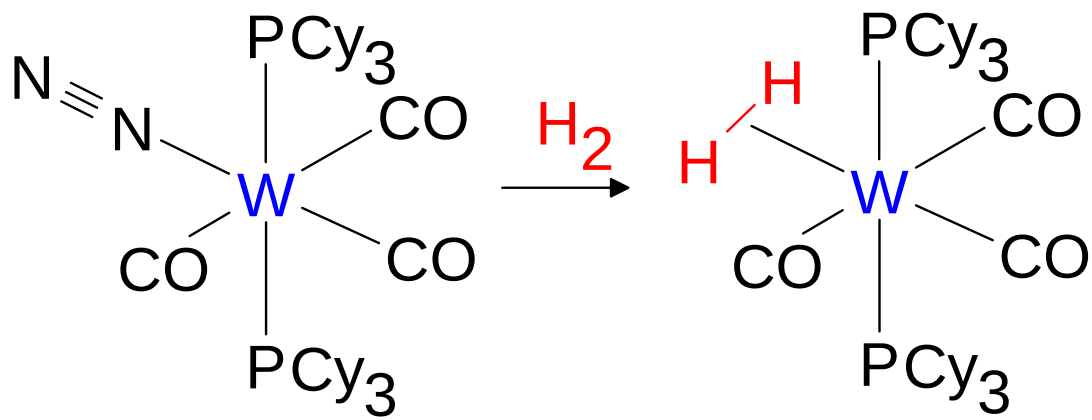
can be regiospecific

Other Small Molecules as Ligands

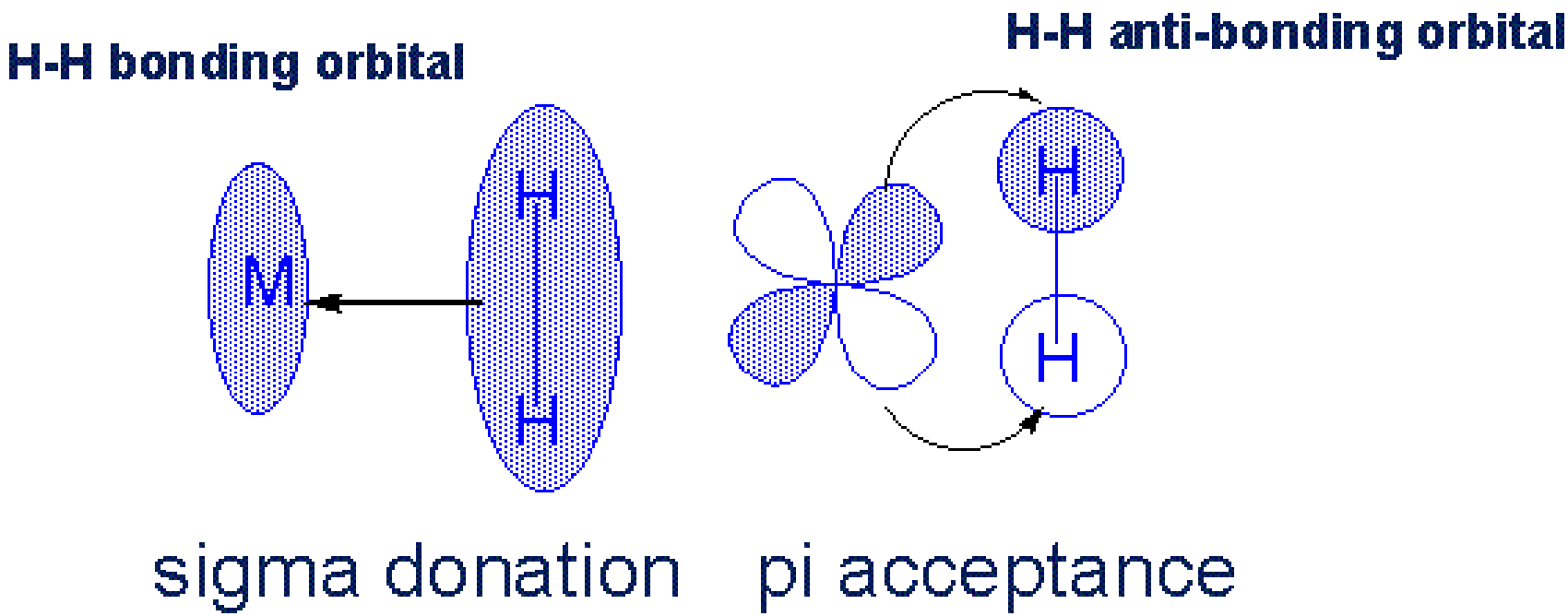
- **NO** **nitrous oxide**
- **O_2** **dioxygen**
- **CO_2** **carbon dioxide**
- **SO_2** **sulfir dioxide**
- **N_2** **dinitrogen**
- **H_2** **dihydrogen**

Dihydrogen Complexes

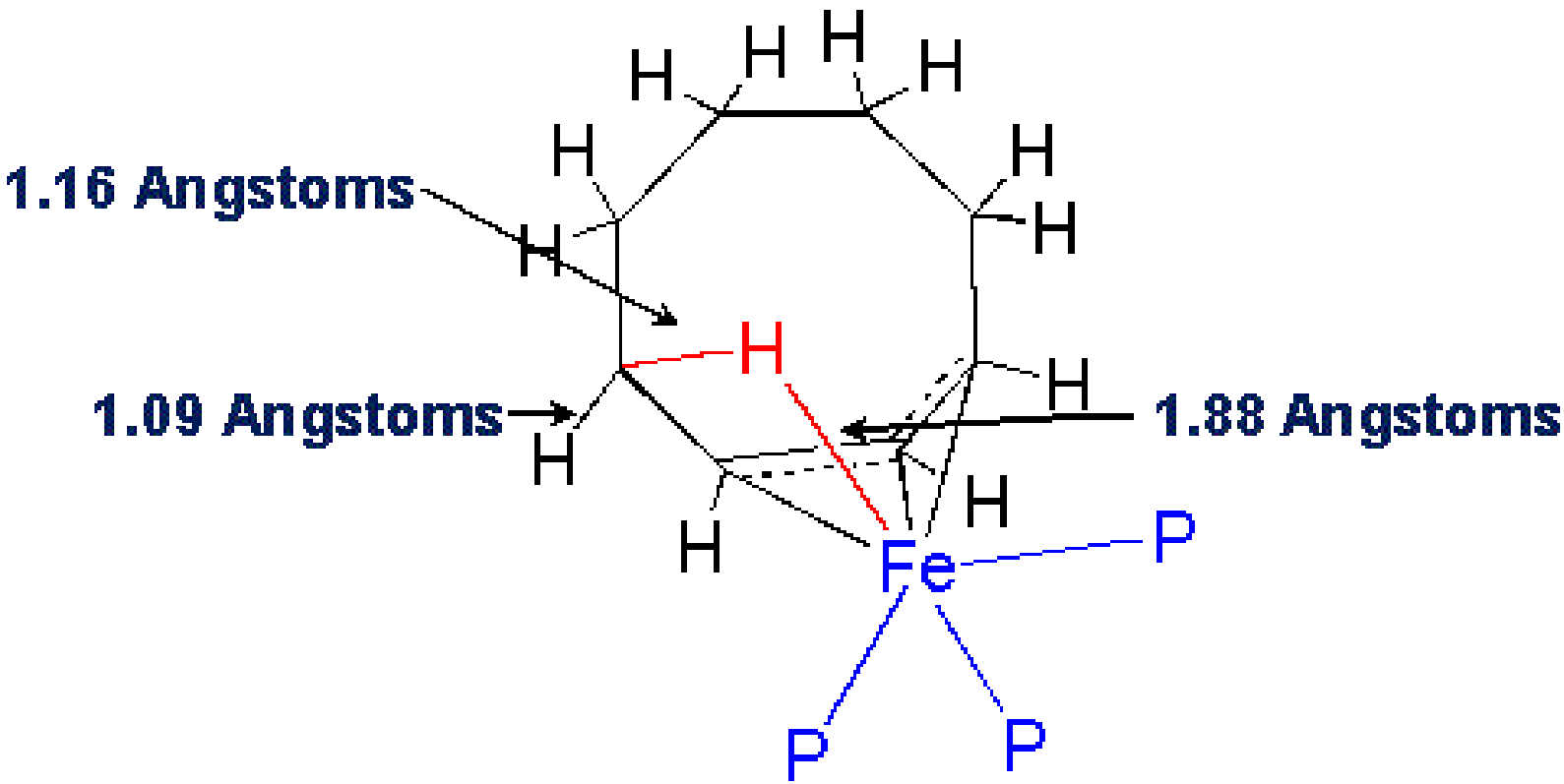
- proven by neutron diffraction η^2 binding
- H-H σ bond is the donor
- model for H_2 absorption on metal surface
- 1986 NMR technique distinguishes between H_2 complex and dihydride



Bonding H_2 Complexes



Agostic Hydrogens



Nitrous Oxide

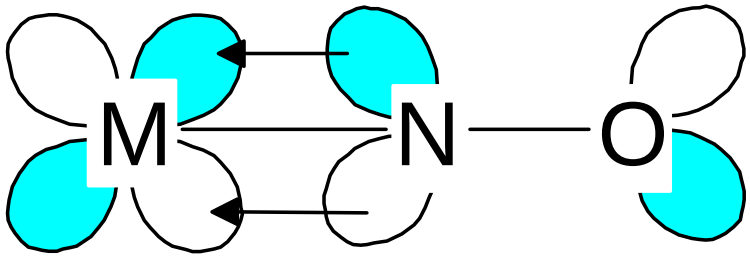
- can act as a 3 or 1 electron donor
- result is linear (180^{o}) or bent (120-140^{o})
- most are linear as in **Cp-Ni-N-O**
- can be considered NO^{+} (2 e^{-} donor) where the third e^{-} is transfer to the metal
- **M(0)-N=O** (3 e^{-}) or **M(-1)-$^{+}$N=O** (2 e^{-}) net e^{-} count is the same

$^{+}$N=O is isoelectronic with CO

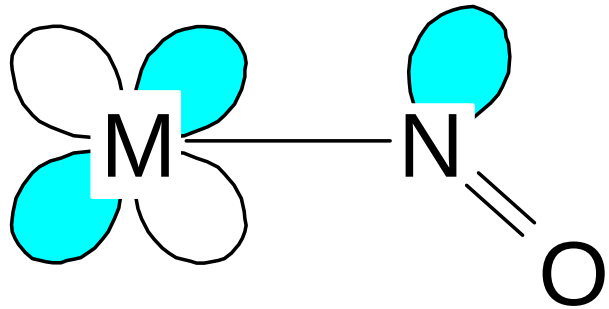
NO and Infrared Spectra

- νNO for neutral complexes 1610-1820 cm^{-1}
- νNO for anionic complexes ca. 1455 cm^{-1}
- νNO for cationic complexes ca. 1945 cm^{-1}
- νNO for $NO^{+}PF_6^{-}$ 2220 cm^{-1}
- decreased νNO shows strong back bonding
- can not use IR to distinguish bent and linear
- $(Ph_3P)_2Ir(CO)Cl(NO)$ 1660-1720 cm^{-1} bent

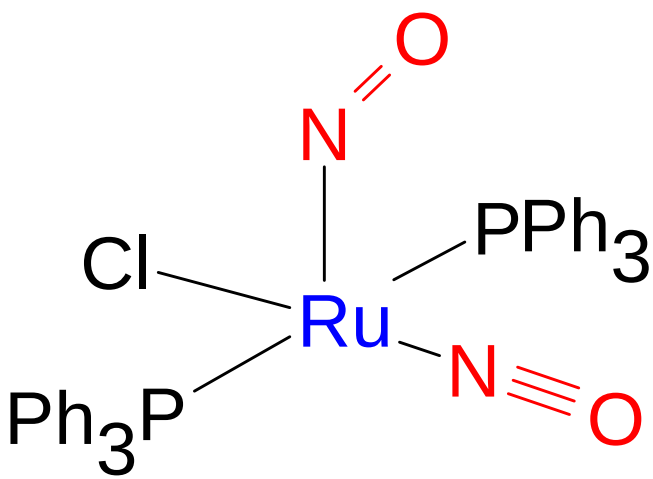
Examples of NO Complexes



$3e^-$ donor (NO^+, $2e^-$)



$1e^-$ donor (NO^-, $2e^-$)

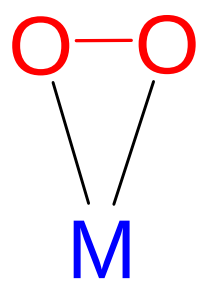


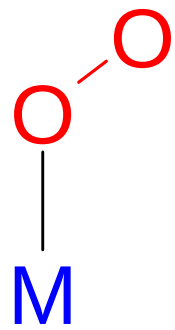
^{15}N NMR -rapid interconverting

Dioxygen Complexes

- **Biological importance**
  free O_2 1556 cm^{-1}, O-O 1.21 Å

η^2 peroxide

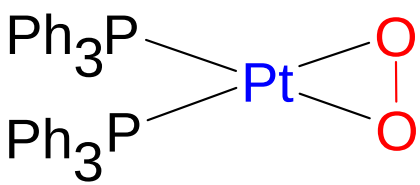


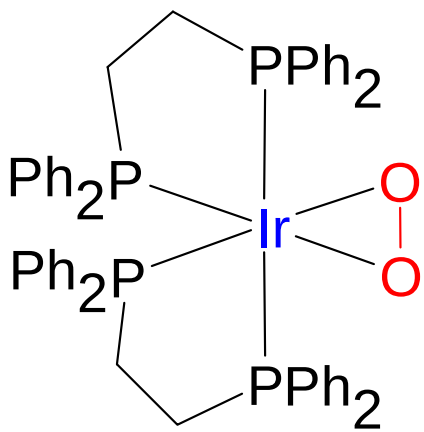


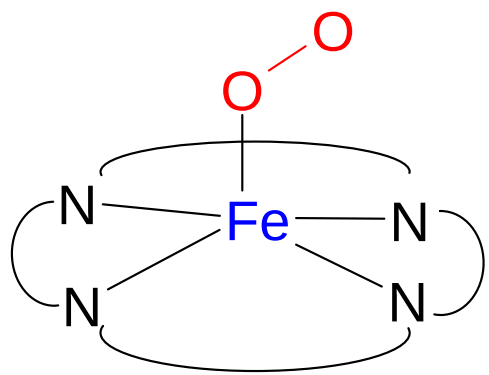
η^1 superoxide

850-860 cm^{-1}

O-O 1.43-1.50 Å

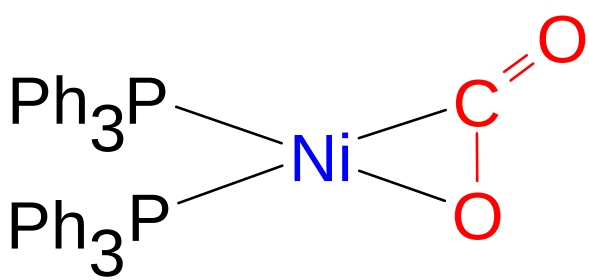


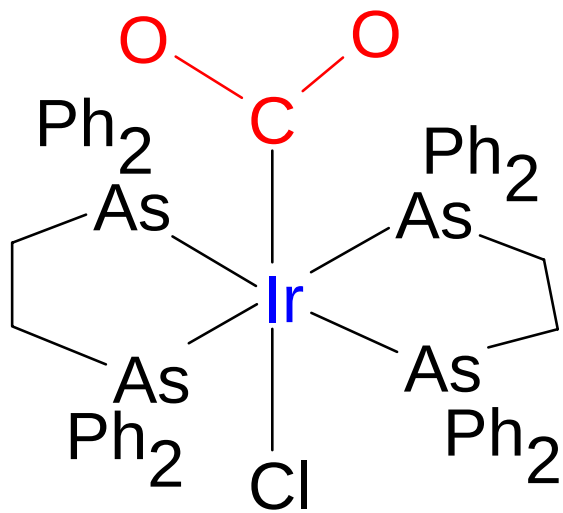




Carbon Dioxide Complexes

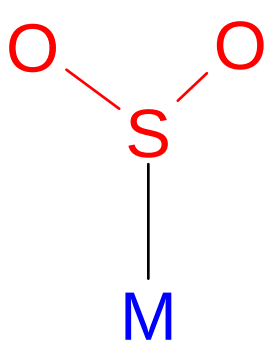
- CO_2 very weak electrophile, readily available

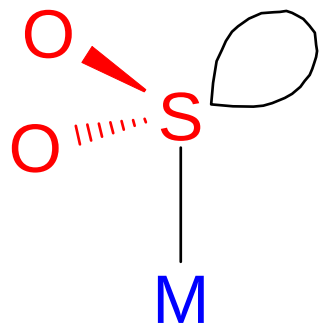


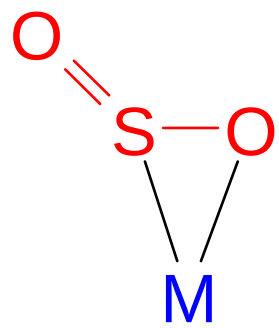


Sulfur Dioxide Complexes

- removal of S from feedstock is of interest





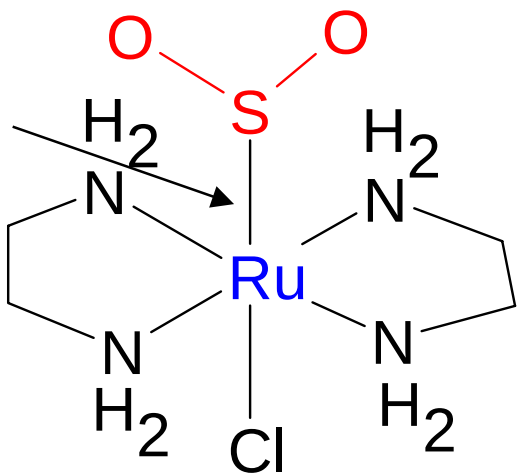


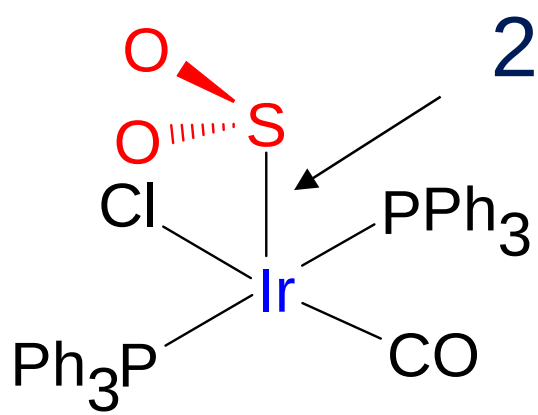
η^1 planar η^1 pyramidal η^2 planar

valence tautomers

- SO_2 has empty π acceptor orbital
- filled σ donor orbital
- in extreme metal e^-'s transferred to S orbital

2.07 Å





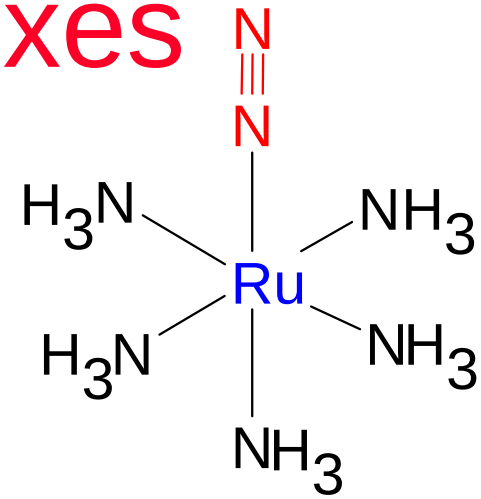
2.49 Å

1301, 1278, 1100 cm^{-1} 1198, 1185, 1048 cm^{-1}

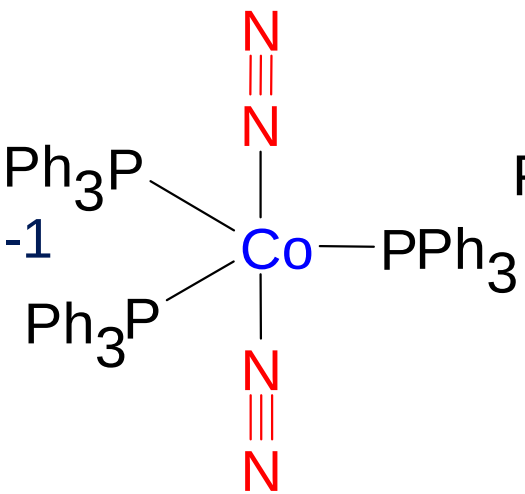
SO_2 plane-M-S angle

120° **180°**

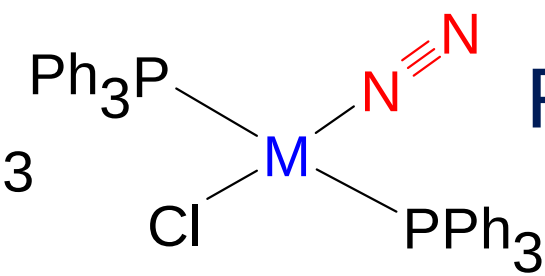
Dinitrogen Complexes



- first N_2 complex prepared by A.D.Allen (U of T)
- weaker s donor than CO
- weaker p acceptor than CO
- N-N bond 0.1-0.3 Å longer when bound to M
- ν_{NN} shifts to lower energy (free N_2 2331 cm^{-1})



2085 cm^{-1}

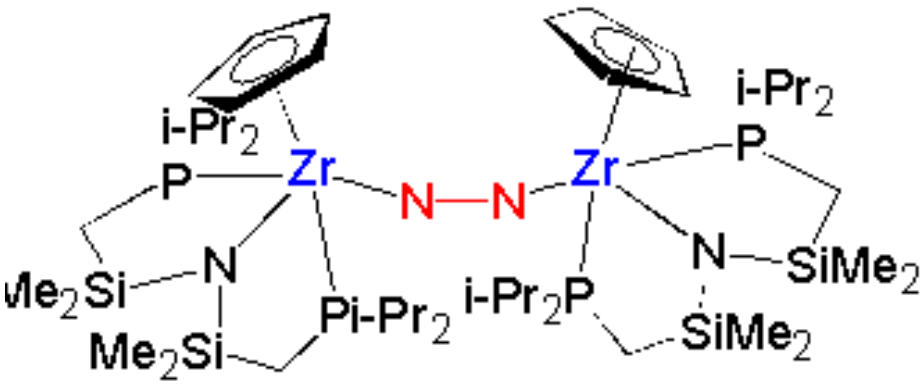


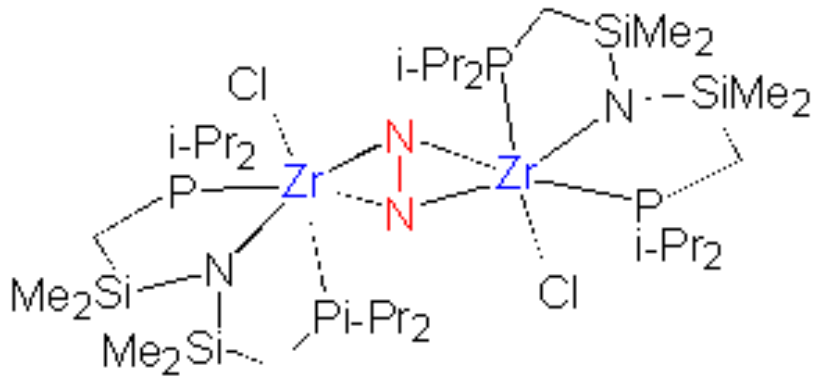
Rh:2152 cm^{-1}

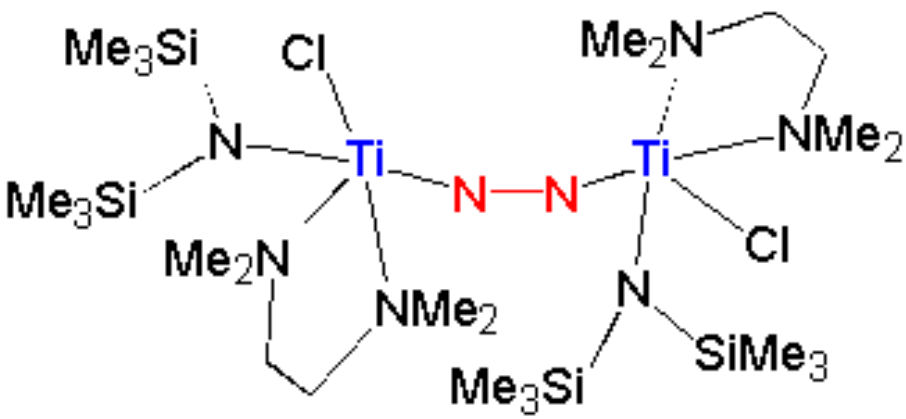
Ir: 2105 cm^{-1}

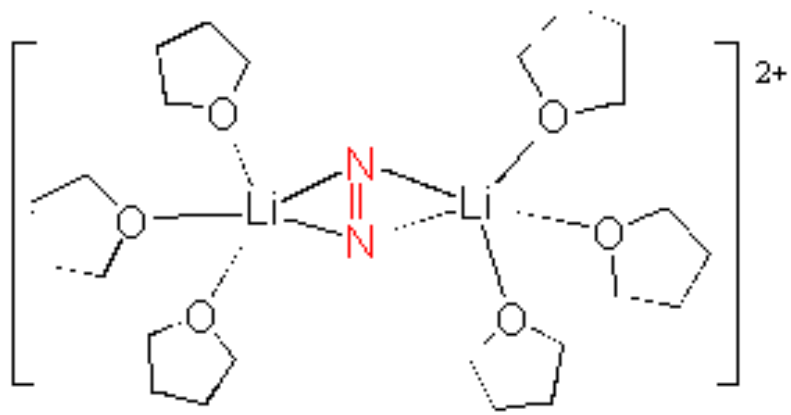
Other N_2 Complexes

- bridging, end-on or side-on complexes









$[Cp_2Zr(PR)]_2^{2-}$