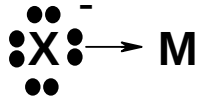
Common Ligand Types

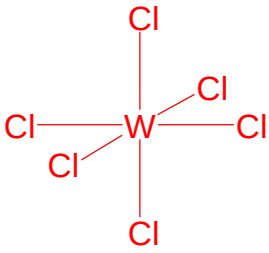
X type ligands: halides F^-, Cl^-, Br^-, I^-



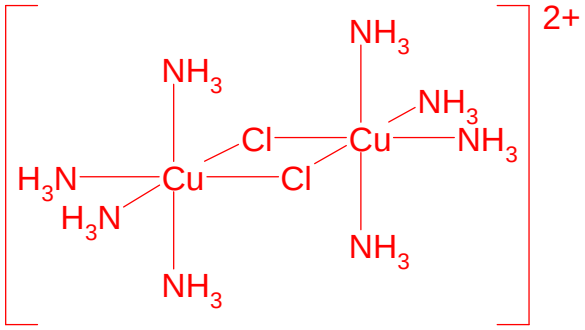
'halo'

formally anionic:

terminal — reduced basicity relative to 'free' halide



bridging (μ)



'pseudo-halogens': many other monodentate 1^- ligands

egs. CN^- ***'cyano'*** or cyanide anion (terminal through C but can also bridge using N)

SCN^- ***'thiocyano'*** or thiocyanate anion

OH^- ***'hydroxo'*** or hydroxide ion, can also bridge

Oxygen donors

water (OH_2) alcohols (ROH) and ethers (R_2O) are most important

aqua H_2O → hydroxo HO^- → oxo O^{2-}

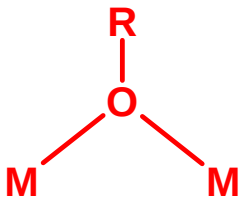
alcohol ROH → alkoxo RO^-

ether R_2O

S equivalents

alkyl / arylthiol	alkyl / arylthiolato	sulphido
thioether	or alkyl / arylsulphido	

charged species far more likely to bridge:



R = H μ-hydroxo

R = alkyl or aryl μ-alkoxo or aryloxo

M═O terminal

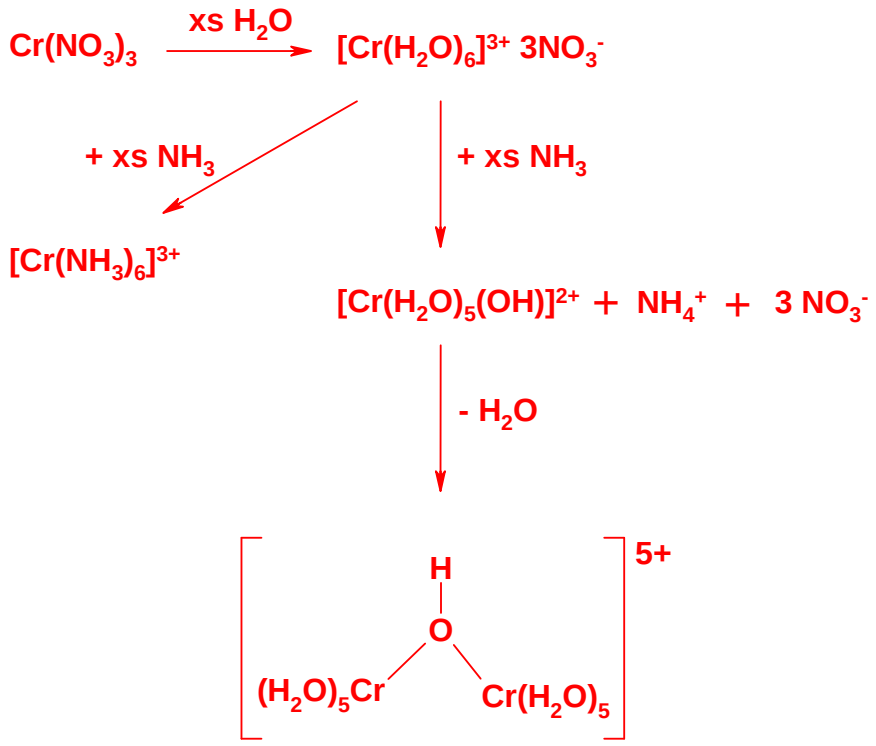
M—O—M bridging

oxo

pK_a of water drops sharply on coordination to a Lewis acid:

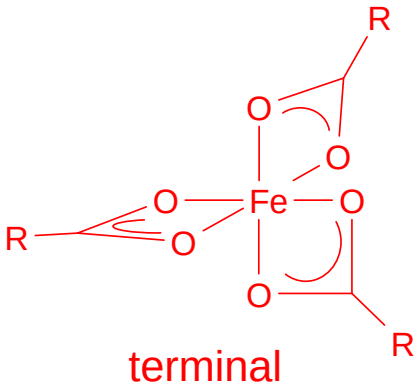
'free' water $pK_w = 14$ but $[Fe(OH_2)_6]^{3+}$ has a pK_a of ca. 2
d^n number? d^5 hexaaquairon(III)

Increased acidity of coordinated water can have important consequences on solution chemistry:

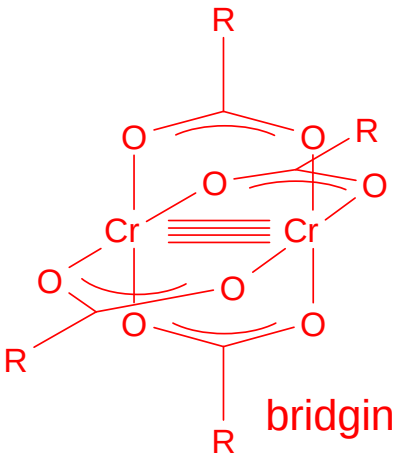


carboxylates, RCO_2^-

terminal or μ-acetato (R = Me)



terminal

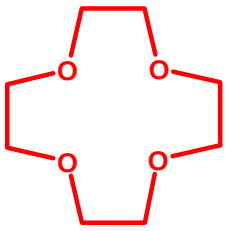


bridging

chelating oxygen donors

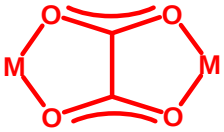
neutral: polyethers including crowns and acyclic types

anionic: di- or higher carboxylates (eg. oxalate)
β-diketonates (eg. acac)

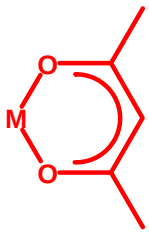


12-crown-4

dme

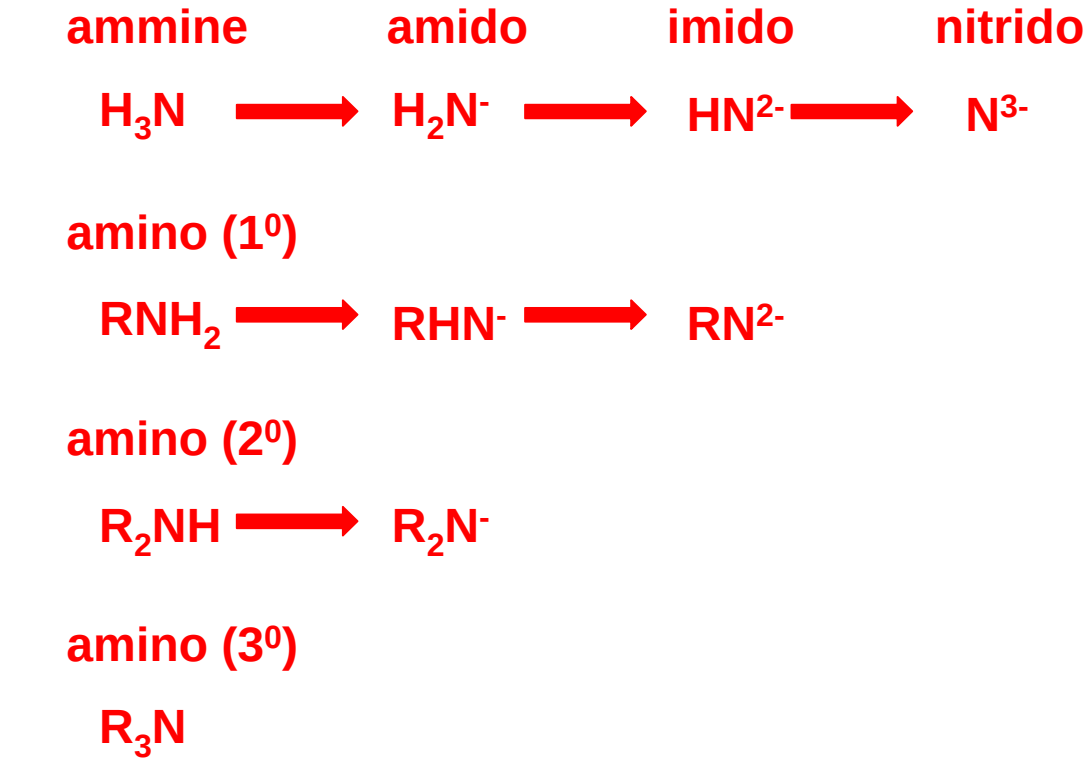


Ox



acac

Nitrogen and phosphorus donors



P equivalents

phosphino ➡ phosphido ➡ phospheno
or
phosphinideno

anionic versions (amido and imido) are generally good at bridging

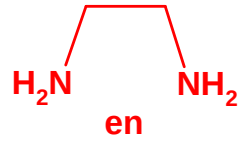
amides and phosphides are X^- type ligands

pK_a drop on coordination is even more dramatic here:

NH_3 ($pK_a \sim 30$-33) $M \leftarrow NH_3$ ($pK_a \sim 19$-22)

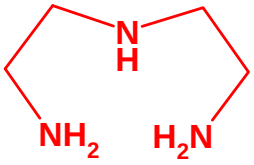
Chelating amines and phosphines:

ethylenediamine (en)



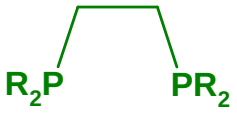
en

diethylenetriamine (dien)

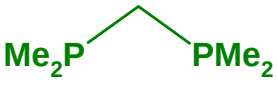


dien

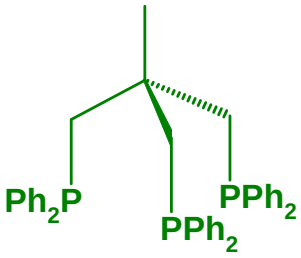
bis(diphenylphosphino)ethane (**dppe** or **diphos**); related members of this family (**dmpe**, **dppm**); ***tripodal*** versions such as tris(diphenylphosphinomethyl)ethane (**triphos**) and ***chiral*** variants such as **BINAP**:



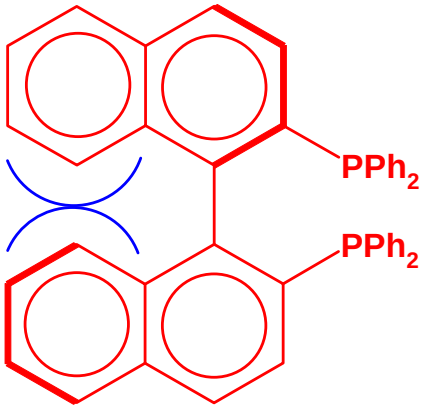
dppe (R = Ph)
dmpe (R = Me)



dmpm



triphos

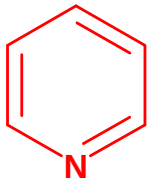


S-BINAP

sp^2 N donors:

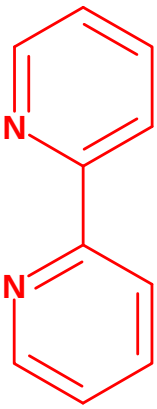
neutral:

pyridine (**py**) is the prototype



py

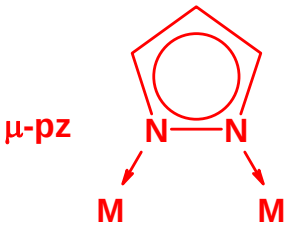
chelates common here too:



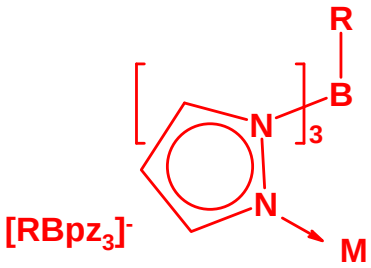
bipy

anionic:

pyrazolyls (pz)



tris(pyrazolyl)borates



sp N donors:

nitriles such as acetonitrile (CH_3CN)

dinitrogen (N_2)

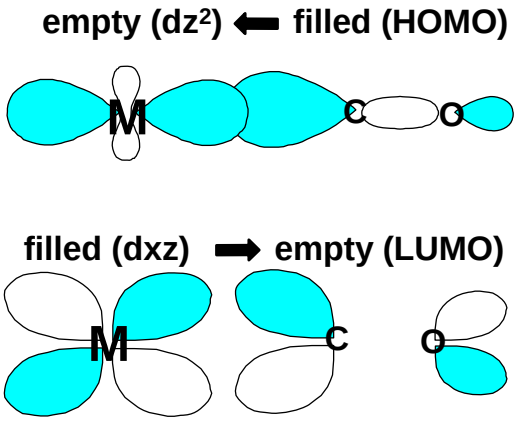
Carbon monoxide (CO)

Not just a pretty donor!

donates through C end (HOMO is more localized on C)

BUT also

acceptor into empty π* levels (LUMO):



Can bridge through carbon (most common) but bridges through C and O are also known (***isocarbonyls***):