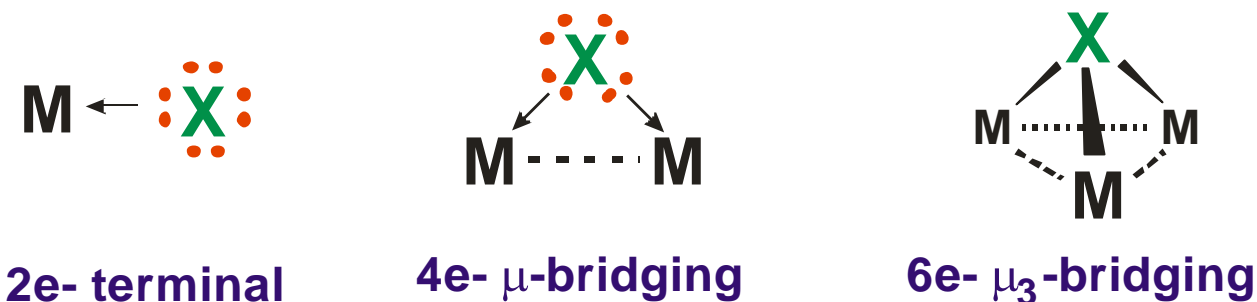
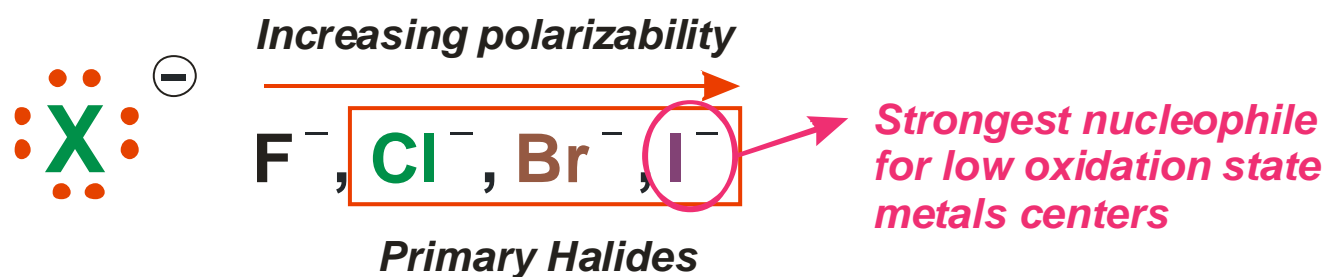


## Lewis Base Ligands

Non-carbon donor ligands that have one or more lone pairs of e- that can be donated into empty orbitals on the metal center.

Although *phosphine* ligands ( $\text{PR}_3$ ) are formally **Lewis Base** ligands, their importance in organometallic chemistry is such that we will treat them separately later.

### Halide Donors



The halides are anionic donors that generally only donate 2e- to a metal center.

Due to their relatively high

electronegativity they are not especially good  $\sigma$ -donor ligands.

Although they can theoretically act as  $\pi$ -donor ligands, once again, the higher electronegativity limits them to simple 2e- donor ligands.

*Fluoride is generally NOT a good ligand except for very high oxidation state metal centers. It is too electronegative to donate much of its electron density to a "normal" metal center.*

One possible exception to the 2e- donor “*rule*” when they are coordinating to a single metal center is for **iodide**. It is the least electronegative of the halides (not counting astatine) and is the best donor group. This is some evidence that **iodide** is a good enough donor and has enough orbital extension to act as a 4e-  $\sigma$ - and  $\pi$ -donor in some cases.

**Common Misconception:** Since we treat the halides as anionic halide ligands their relatively high electronegativity does NOT make them electron-withdrawing ligands as thought of in organic chemistry. In organic chemistry the halogens are treated as neutral ligands and as such drain electron density from whatever they are attached to. But in inorganic and organometallic chemistry they are anionic and are perfectly happy with that charge. What their electronegativity does in organometallic chemistry is to NOT make the halides particularly good donor ligands. As one moves down the periodic table from F<sup>-</sup> to I<sup>-</sup>, we do see steadily increasing donor ability as the electronegativity drops.

When halides act as bridging ligands (relatively common) they donate 2e- to each metal center that they are coordinated to.

## Oxygen Donors



### Alkoxides

2 or 4e- donor

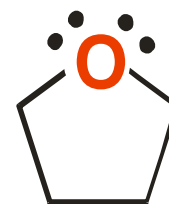
Terminal  
Bridging  
Triply bridging



### Oxide

4 or 6e- donor

Terminal  
Bridging  
Triply bridging  
Quad bridging

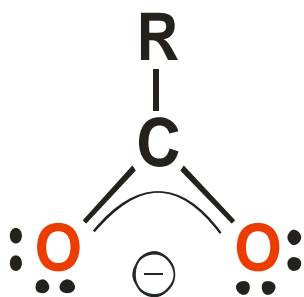


THF  
tetrahydrofuran

### Ethers

2e- donor

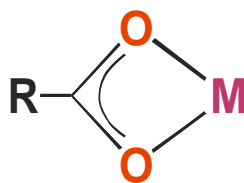
Typically  
weak donor



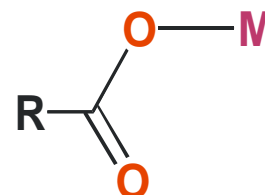
### Carboxylates

2 or 4e- donor

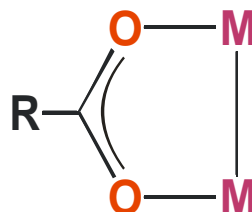
$\eta^1$ -terminal  
 $\eta^2$ -terminal  
Bridging



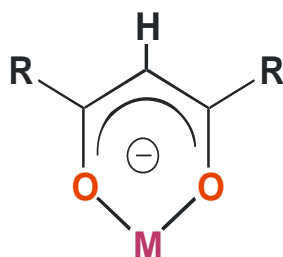
$\eta^2$ -chelating 4e-



$\eta^1$  2e- mode



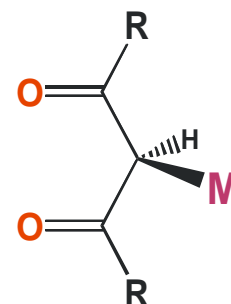
$\mu$ -bridging



### Acetoacetonates (acac)

2 or 4e- donor

Unusual C-bonded  
acac



## Sulfur Ligands



2e- or 4e- Terminal  
4e- Bridging  
6e- Triply bridging

*Easily oxidized  
to R-S-S-R*

**Thiolates**  
**Mercaptides**

Thiolates are powerful bridging ligands, particularly for low-oxidation state metal centers. The lower electronegativity relative to oxygen means that thiolates are also better donors.

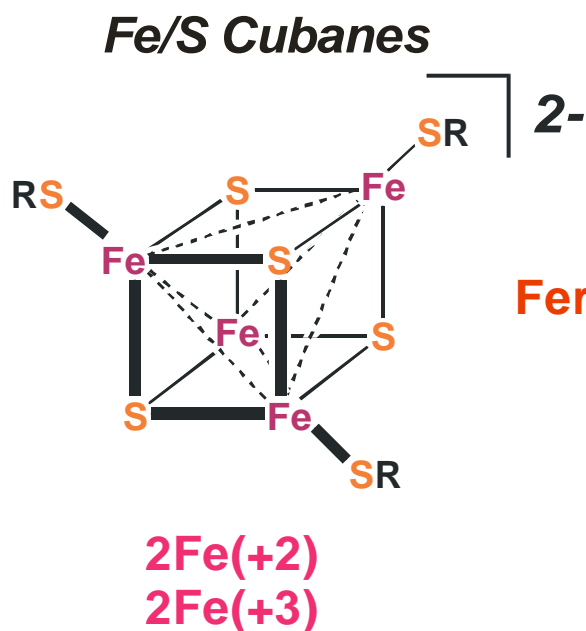


4e- Terminal  
4e- Bridging  
6e- Triply bridging  
8e- Quad bridging

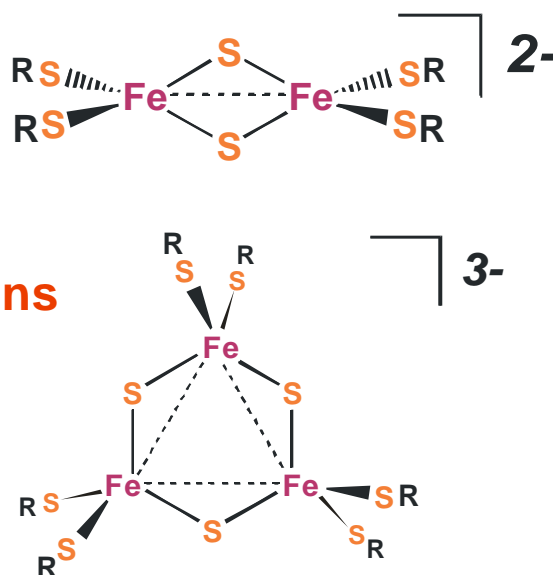
$\text{M}=\text{S}$  *Relatively*  
 $\text{M}\equiv\text{S}$  *rare*

**Sulfide**

Sulfides (and thiolates) are extremely effective *bridging* ligands and play a critically important role as such in bioinorganic chemistry:

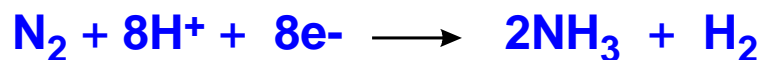


**Ferredoxins**



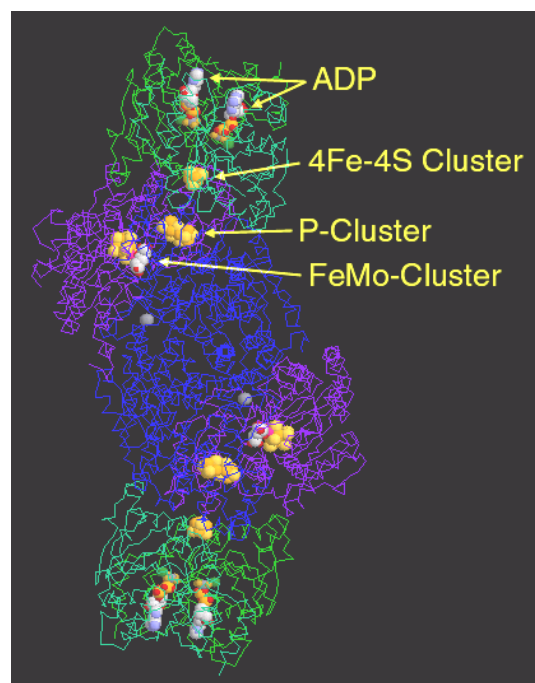
## Nitrogenase

The nitrogenase enzyme catalyzes the extremely difficult reaction:

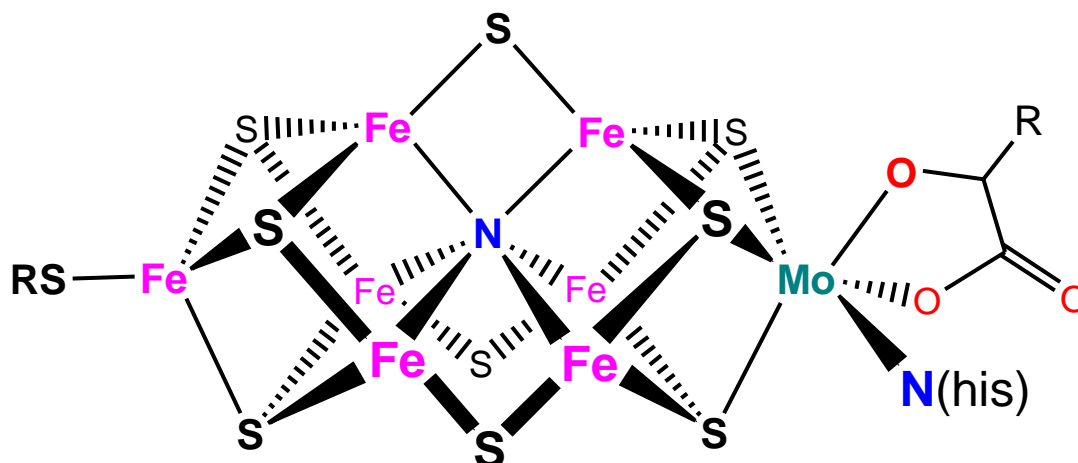


The conversion of atmospheric  $\text{N}_2$  into  $\text{NH}_3$  is a marvel of catalysis and provides the plant with its own fertilizer. In the **Haber** catalytic process for converting  $\text{N}_2 + 3\text{H}_2$  into  $\text{NH}_3$ , over  $400^\circ\text{C}$  and 400 atm of  $\text{H}_2/\text{N}_2$  pressure are required along with a heterogeneous Fe catalyst. Nitrogenase does this at room temperature and pressure.

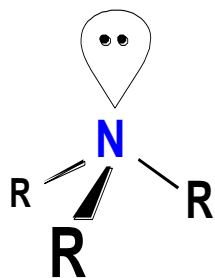
Nitrogenase, shown to the right, requires a steady source of electrons. The reaction requires the addition of 8 electrons for each nitrogen molecule that is split into two  $\text{NH}_3$  molecules and one “wasted”  $\text{H}_2$ . The Fe protein (green) uses the breakage of ATP to pump these electrons into the MoFe protein (blue-purple). Two molecules of ATP are consumed for each electron transferred.



The active catalytic site in the enzyme is believed to be this unusual Fe/Mo/S cluster – the central atom is believed to be a nitride ( $\text{N}^{3-}$ ), see *Science*, 2002, 297, 1696-1700.

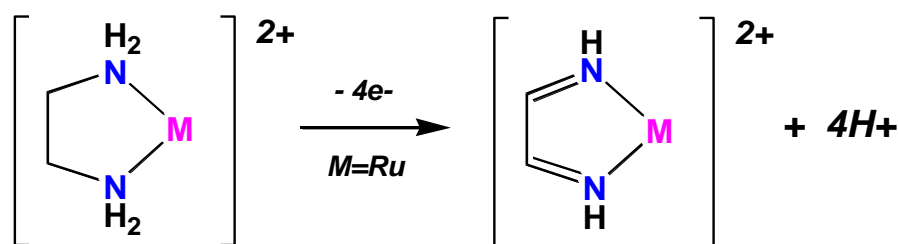


## Nitrogen Ligands



In general, alkylated **amines** are not particularly good ligands. This is mainly due to the relatively short N-C bond distances and the stereoelectronic problems generated from this.

Chelating amines have less steric problems and are better ligands for transition metal centers. Primary and secondary amines, however, are susceptible to oxidations:



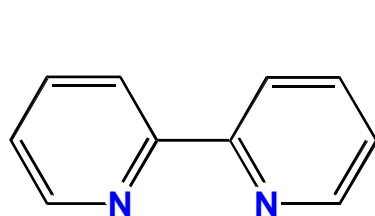
*Di-imine Complex*

**Tertiary** amines, on the other hand, are quite stable and not easily oxidized.

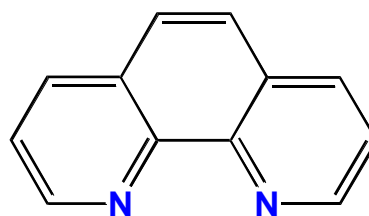


*TMEDA = tetramethylethylenediamine*

Perhaps the most famous neutral **nitrogen** donor ligand is **bipyridine** or **bipyridyl**, almost universally abbreviated **bipy**. Phenanthroline is a more rigid version of bipy that forms even stronger metal chelates.



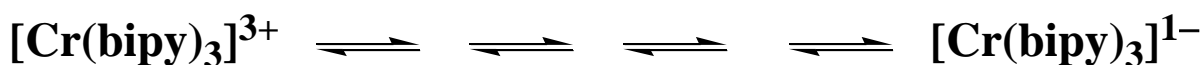
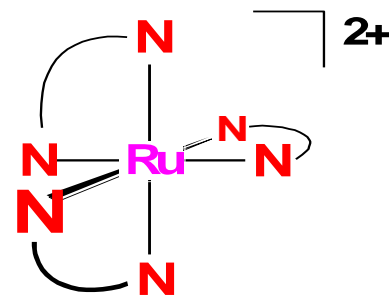
*Bipy = Bipyridine*



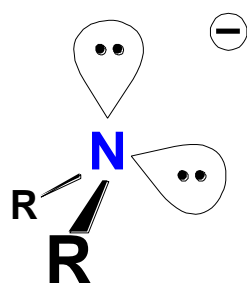
*Phen = phenanthroline*

The most famous bipy complex is  $[\text{Ru}(\text{bipy})_3]^{2+}$ , which has an extremely rich photoredox chemistry. There are probably over 1000 papers concerning  $[\text{Ru}(\text{bipy})_3]^{2+}$ .

Bipy (and its related systems) can stabilize multiple oxidation states on metal complexes:



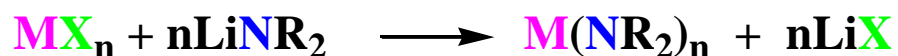
## Inorganic Amides



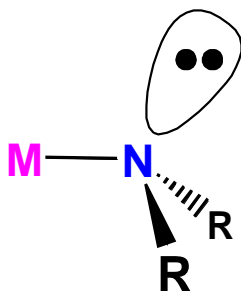
**Strong Base & Nucelophile**  
**Terminal (2 or 4e-) donor**  
**4e- Bridging donor**

The lone pairs in an amide are about 2eV higher in energy than in  $\text{OR}^-$ . This makes an amide a considerably stronger donor.

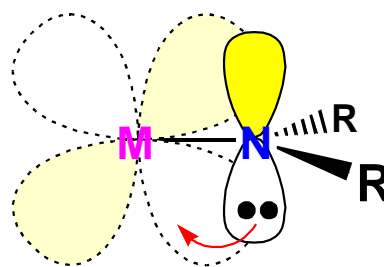
Typical formation reaction:



Amides that act as 2e- donors have *pyramidal geometry* ( $\text{sp}^3$ -like) with a free lone pair, while amides that donate 4e- have a *trigonal planar* ( $\text{sp}^2$ -like) *geometry*. There are, of course, in-between structural cases that indicate intermediate bonding situations.

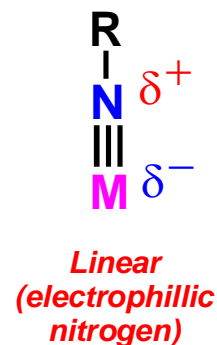
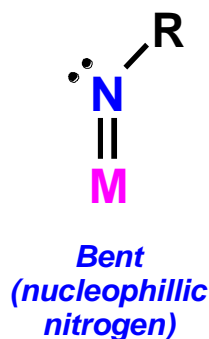
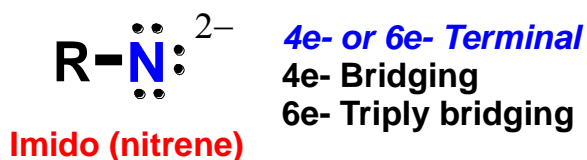


*2e- donor*  
*pyramidal geometry*



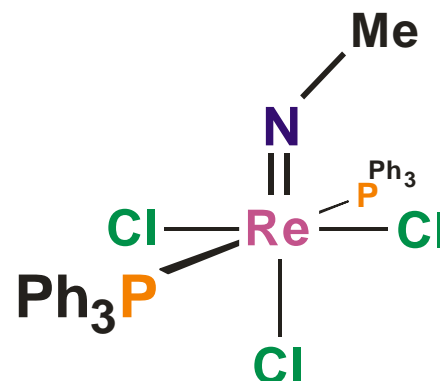
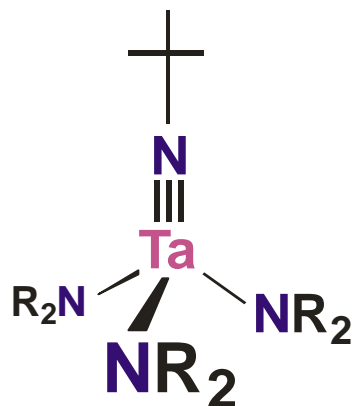
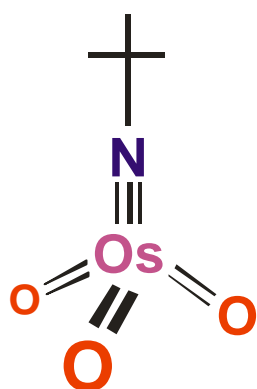
*4e- donor*  
*trigonal planar*

## Alkyl-Imido (nitrene) Ligand



In the bent mode the imido ligand is formally only a 4e- donor, while in the linear mode it donates 6e- to the metal center. As with the other ligands we have seen that can donate variable numbers of electrons to the metal center, you initially count it as a 4e- donor and then boost it up to 6e- if you need to increase the electron count on the metal to get up to 16 or 18 e-.

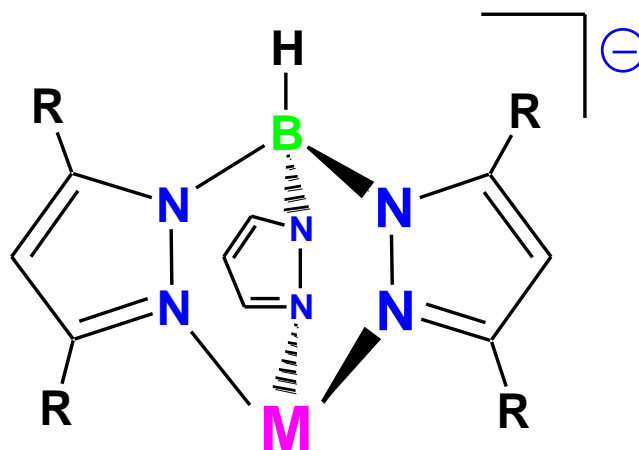
Some examples:



*As one moves to the right-hand side of the periodic table, one tends to get less M-L multiple bonding*

As with amides, you can have intermediate cases where the bending of the alkyl group is in-between linear and bent. It is difficult to predict when the imido ligand will act as a 4e- or 6e- donor. So long as you give me a reasonable electron count I will not be picky about whether you use 4e- or 6e-. If you use 6e- you should realize that the imido and alkyl group should be drawn linear.

## Tris(pyrazolyl)borate Ligand

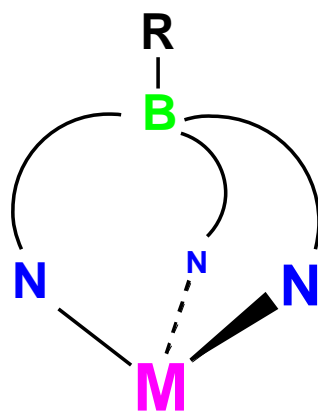


- *Anionic*
- *6e<sup>-</sup> donor*
- *coordination via the three lower nitrogen centers*
- *Moderate donor*
- *Steric effects adjusted via R groups*

The tris(pyrazolyl)borate (Tp) ligand has become extremely popular in the last decade and is sometimes called the inorganic Cp ligand. It is **anionic** and is a 6e<sup>-</sup> donor when all three nitrogens are coordinated to a metal center, just like Cp<sup>-</sup>.

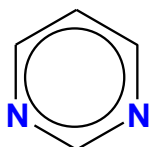
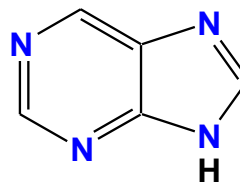
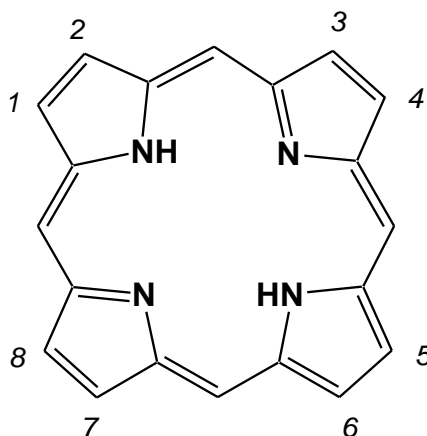
It is considerably bulkier (much bulkier if one uses large bottom R groups) and, due to the higher nitrogen electronegativity, it is not as good a donor relative to Cp.

When drawing the ligand, you can abbreviate it as follows:



Most inorganic and organometallic chemists will understand what you are talking about with this simplified drawing.

## A Few Biologically Important N-Ligands

*imidazolate**pyrimidine**purine*

*Porphine*  
(metalloporphyrin when bound to a metal)

