#### Lewis Base Ligands

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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 (PR3) and hydrides (H) are formally Lewis Base ligands, their importance in organometallic chemistry is such that we will treat them in separate chapters.

##### 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 -donor ligands. Although they can theoretically act as -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 common 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- - and -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 to I, 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



**THF**

tetrahydrofuran

##### Sulfur Ligands



**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.**



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



***Nitrogenase***

**The nitrogenase enzyme catalyzes the extremely difficult reaction:**

**N2** + **8H+** + **8e-  2NH3** + **H2**

**The conversion of atmospheric N2 into NH3 is a marvel of catalysis and provides the plant with its own fertilizer. In the Haber catalytic process for converting N2 + 3H2 into NH3, over 400ºC and 400 atm of H2/N2 pressure are required along with a heterogeneous Fe catalyst. Nitrogenase does this at room temperature and pressure.**



**Nitrogenase, shown to the right,[[1]](#footnote-1) requires a steady source of electrons. The reaction requires the addition of 8 electrons for each nitrogen molecule that is split into two NH3 molecules and one “wasted” H2. 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 was initially believed to be a nitride (N3),** seeScience, **2002**, *297*, 1696-1700, **but most researchers now favor a C4, carbide, based on XPS and better X-ray structures.**

***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:

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

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**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.**

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**The most famous bipy complex is [Ru(bipy)3]2+, which has an extremely rich photoredox chemistry. There are probably over 1000 papers concerning [Ru(bipy)3]2+.**



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

**[Cr(bipy)3]3+   [Cr(bipy)3]1**

###### Inorganic Amides



The lone pairs in an amide are about 2eV higher in energy than in OR. This makes an amide a considerably stronger donor.

Typical formation reaction:

MXn + nLiNR2 M(NR2)n + nLiX

Amides that act as 2e- donors have *pyramidal geometry* (sp3-like) with a free lone pair, while amides that donate 4e- have a *trigonal* *planar (sp2-like) geometry*. There are, of course, in-between structural cases that indicate intermediate bonding situations.



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 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- 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- donor when all three nitrogens are coordinated to a metal center, just like Cp-.

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



1. This figure is freely available from the protein databank. <http://pdb101.rcsb.org/motm/26> [↑](#footnote-ref-1)