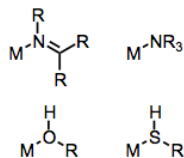


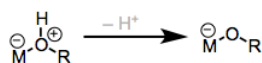
2.4: Dative Ligands of N, O, and S

In this post, we'll take a quick look at L-type ligands of nitrogen, oxygen, and sulfur. Ligands of this type are important for at least two reasons: (1) coordination to a metal can modify the reactivity of the bound functional group, and (2) dative coordination is a critical element of organometallic reactions that depend on intramolecular **directing group** effects. "Long-term" ligands containing two-connected nitrogens, such as pyridines and oxazolines, are now among the most commonly used for organometallic reactions. The behavior of coordinated dinitrogen is also a hot research area right now. Although they look boring on the surface, dative ligands of N, O, and S are rich in chemistry!



General Properties

This might be the first class of ligand for which we can reliably say that backbonding is rarely important. Dative coordination of amines and alcohols involves a straightforward $n \rightarrow d\sigma$ orbital interaction. Intuitively, we should expect the acidity of amines, alcohols, and thiols to increase upon coordination, because removal of electron density from nitrogen and oxygen through coordination makes these atoms more electrophilic. Consider the charged model of dative bonding at left in the figure below.

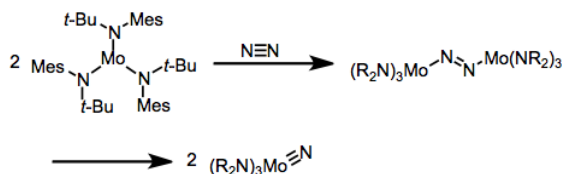


Coordination increases acidity.

Transfer of the lost proton to an organic substrate is an important aspect of hydrogenation reactions employing amine ligands (see below).

Food for thought: why aren't (cheaper) amines found in place of phosphines in organometallic catalysts? History has ruled against tertiary amines, but are there any good reasons why? Yes—for one thing, amine nitrogens are more sterically hindered than analogous phosphorus atoms, because N–C bonds are shorter than P–C bonds. Plus, the cone angles of amines are generally wider than those of phosphines. Getting amines to play nice with hindered metal centers can thus be very difficult.

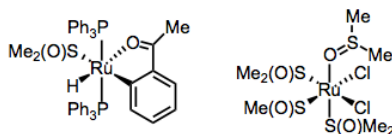
Although dinitrogen (N_2) is isoelectronic with carbon monoxide, it's been a tough nut for organometallic chemists to crack. An electron-rich metal center lacking π -acidic ligands is an absolute must for dinitrogen-containing complexes, as the π^*NN orbital does not easily participate in backbonding. What sets nitrogen apart from CO is its ability to participate in side-on bonding and bridging through its π system—for this application, dinitrogen's higher-energy orbitals are a perk over CO. While migratory insertion and nucleophilic addition reactions of N_2 bound "end-on" (through a non-bonding lone pair) are virtually unknown, functionalization of "side-on" nitrogen ligands is a growing field. Dinitrogen has been known to bridge multiple metals in "end-end," "side-end," and "side-side" modes.



Activation of dinitrogen by molybdenum—a complex containing an "end-end," linear bridging dinitrogen (not shown) is proposed as an intermediate in this mechanism.

Imines are another important class of ligands that fit into this post; unlike carbonyl compounds, imines more commonly bind through the nitrogen atom rather than the π system. These are very common directing groups but are also important for hydrogenation and hydroamination reactions.

DMSO is an interesting, archetypal sulfur-containing ligand that may bind through either S or O. As sulfur is softer and more polarizable than oxygen, sulfur binds to softer (low-valent) metals and oxygen to harder metal centers.

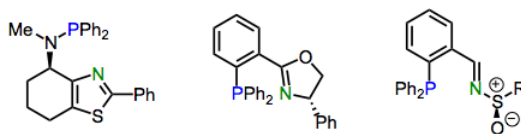


The soft Ru(II) center with hydrocarbonyl ligands contains S-bound DMSO, while the harder Ru(II) with chloride ligands includes one O-bound DMSO.

Most ligands binding through dative sulfur require chelation, as M–S bond strengths tend to be low.

Synthesis

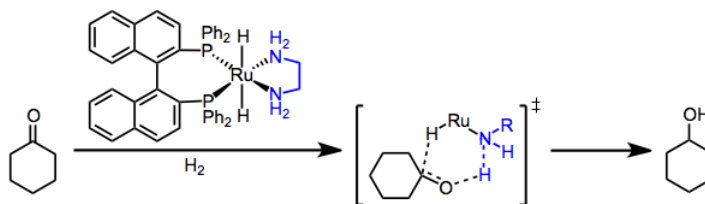
Ligand substitution reactions are most commonly used to load dative ligands of N, O, and S onto metal centers. In some cases, when the heteroatom bears a hydrogen atom, deprotonation can produce a covalent, X-type ligand. Usually, however, these types of ligands are incorporated into organic substrates and used as directing groups—coordination brings the metal center into close contact with a target functional group, such as an alkene, C–H bond, or C–X bond. They may also be part of chelating ligands containing a second, more robust electron donor, like a phosphine.



P,N ligands for organometallic chemistry.

Reactions

I'll showcase only one reaction in this section: the Noyori hydrogenation employing amine ligands as proton donors. The reaction is a nice illustration of the influence of metal coordination on the reactivity of amines.



"External" hydrogenation without substrate binding. The metal is a hydride source, and the ligand a proton source.

Easy, breezy, beautiful, right? Dative ligands of N, O, and S are usually employed as spectators, not actors, so reactions like this are somewhat hard to come by. I'll pass on discussing the reactivity of dinitrogen complexes in detail, but for an interesting recent example of metal-dinitrogen chemistry, check this out.

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