# 2.10: π Systems

With this post, we finally reach our first class of dative **actor** ligands, **π systems**. In contrast to the **spectator** L-type ligands we've seen so far, π systems most often play an important role in the reactivity of the OM complexes of which they are a part (since they act in reactions, they're called "actors"). π Systems do useful chemistry, not just with the metal center, but also with other ligands and external reagents. Thus, in addition to thinking about how π systems affect the steric and electronic properties of the metal center, we need to start considering the metal's effect on the ligand and how we might expect the ligand to behave as an active participant in reactions. To the extent that structure determines reactivity—a commonly repeated, and extremely powerful maxim in organic chemistry—we can think about possibilities for chemical change without knowing the elementary steps of organometallic chemistry in detail yet.
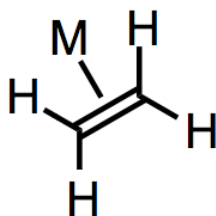


## General Properties

The π bonding orbitals of alkenes, alkynes, carbonyls, and other unsaturated compounds may overlap with dσ orbitals on metal centers. This is the classic ligand HOMO → metal LUMO interaction that we've beaten into the ground over the last few posts. Because of this electron donation from the π system to the metal center, coordinated π systems often act electrophilic, even if the starting alkene was nucleophilic (the **Wacker oxidation** is a classic example; water attacks a palladium-coordinated alkene). The π → dσ orbital interaction is central to the structure and reactivity of π-system complexes.

Then again, a theme of the last three posts has been the importance of orbital interactions with the opposite sense: metal HOMO → ligand LUMO. Like CO, phosphines, and NHCs, π systems are often subject to important backbonding interactions. We'll focus on alkenes here, but these same ideas apply to carbonyls, alkynes, and other unsaturated ligands bound through their π clouds. For alkene ligands, the relative importance of "normal" bonding and backbonding is nicely captured by the relative importance of the two resonance structures in the figure below.



Resonance forms of alkene ligands.

Complexes of weakly backbonding metals, such as the electronegative late metals, are best represented by the traditional dative resonance structure **1**. But complexes of strong backbonders, such as electropositive Ti(II), are often best drawn in the **metallacyclopropane** form **2**. Organic hardliners may have a tough time believing that **1** and **2** are truly resonance forms, but several studies—e.g. of the Kulinkovich cyclopropanation—have shown that independent synthetic routes to metallacyclopropanes and alkene complexes containing the same atoms result in the same compound. Furthermore, bond lengths and angles in the alkene change substantially upon coordination to a strongly backbonding metal. We see an elongation of the C=C bond (consistent with decreased bond order) and some pyramidalization of the alkene carbons (consistent with a change in hybridization from sp2 to sp3). A complete orbital picture of "normal" bonding and backbonding in alkenes is shown in the figure below.
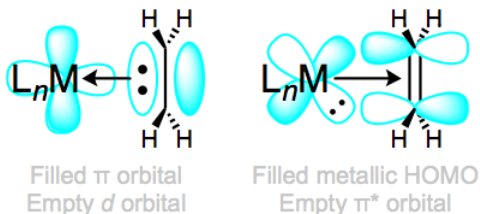


Normal bonding and backbonding in alkene complexes.

Here's an interesting question with stereochemical implications: what is the orientation of the alkene relative to the other ligands? From what we've discussed so far, we can surmise that one face of the alkene must point toward the metal center. Put differently, the bonding axis must be normal to the plane of the alkene. However, this restriction says nothing about rotation about the bonding axis, which spins the alkene ligand like a pinwheel. Is a particular orientation preferred, or can we think about the alkene as a circular smudge over time? The figure below depicts two possible orientations of the alkene ligand in a trigonal planar complex. Other orientations make less sense because they would involve inefficient orbital overlap with the metal's orthogonal d orbitals. Which one is favored?
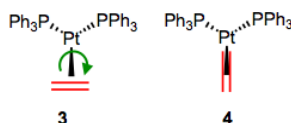


Two limiting cases for alkene orientation in a trigonal planar complex.

First of all, we need to notice that these two complexes are **diastereomeric**. They have different energies as a result, so one must be favored over the other. Naive steric considerations suggest that complex **4** ought to be more stable (in most complexes, steric factors dictate alkene orientation). To dig a little deeper, let's consider any electronic factors that may influence the preferred geometry. We've already seen that electronic factors can overcome steric considerations when it comes to complex geometry! To begin, we need to consider the crystal field orbitals of the complex as a whole. Verify on your own that in this d10, Pt(0) complex, the crystal-field HOMOs are the $d_{xy}$ and $d_{x^2-y^2}$ orbitals. Where are these orbitals located in space? In the xy-plane! Only the alkene in **3** can engage in efficient backbonding with the metal center. In cases when the metal is electron rich and/or the alkene is electron poor, complexes like **3** can sometimes be favored in spite of sterics. The thought process here is very similar to the one developed in an earlier post on geometry. However, please note that this situation is fairly rare—steric considerations often either match or dominate electronics where alkenes are concerned.

## Synthesis

Alkene and alkyne complexes are most often made via **ligand substitution** reactions, which simply exchange one ligand for another. A nice example of a stable alkene complex synthesized via ligand substitution is [Ir(COD)Cl]2, made from IrCl3 and cyclooctadiene. Similarly, the inimitable Pd2(dba)3 may be prepared from PdCl42– and dibenzylideneacetone (dba). In truth, only a few stable alkene and alkyne complexes find use as organometallic precatalysts and/or catalysts. Substitutions of alkenes for phosphine ligands can be rendered easy, so phosphine precatalysts may be used in reactions that involve intermediate alkene complexes. In addition, unsaturated complexes containing an open coordination site often associate with alkenes and alkynes. Gold(I) chemistry is riddled with examples of this strategy, for example. The unsaturated complexes may be derived from precursors themselves, and the resulting π complexes may be short lived, but that's often the point! Some transformation of the π system is often desired.

I have to mention the metallacyclopropane route to alkene complexes from the Kulinkovich reaction, which is a surprising but awesome transformation. After displacement of two alkoxide ligands on titanium by ethylmagnesium bromide, a process described as either (1) β-hydride elimination followed by reductive elimination, or (2) concerted σ-bond metathesis leads to the liberation of ethane and formation of the alkene complex. The proof that the product is an alkene complex? Other olefins can displace ethylene, and ethylene can come right back in to re-form the product! Ti(II)'s strong backbonding ability almost certainly figures in to the driving force for the ethane-releasing step(s).
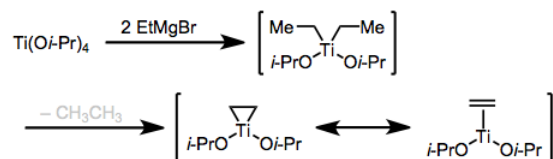


*Kulinkovich synthesis of alkene complexes. A remarkable loss of ethane!*

## Reactions

The reactivity patterns of alkene and alkyne ligands are remarkably similar to those of carbon monoxide: nucleophilic attack and migratory insertion dominate their chemistry. The important issues of **site selectivity** and **stereoselectivity** come into play when

considering alkenes and alkynes, however—the fundamental questions are…

- Which atom gets the nucleophile/migrating group?
- Which atom gets the metal?
- What is the relative orientation of the nucleophile/migrating group and the metal (cis or trans)?

The wide variety of what we might generally call "**atom-metallation**" processes (carbopalladation, carboauration, aminopalladation, oxypalladation, etc.) may involve external nucleophilic addition to the π system, with attachment of the metal to the carbon that was not attacked. The net result is the addition of atom and metal across the π bond, in a trans or anti orientation. The anti orientation results because the nucleophile attacks the face opposite the metal center. A cis orientation of nucleophile and metal is indicative of a migratory insertion pathway (see below). In the example in the following figure, the metal alkyl was converted into a chlorohydrin using copper(II) chloride and LiCl (with stereospecific inversion). Subsequent epoxide formation with NaOH afforded only the cis diastereomer, supporting the trans configuration of the metal alkyl.
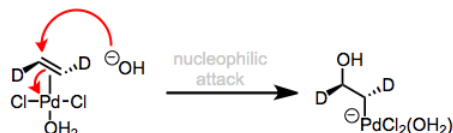


*Nucleophilic attack on a coordinated alkene or alkyne is always trans, or anti.*

Migratory insertion of alkenes and alkynes, like insertions of CO, can be thought of as an internal attack by a nucleophile already coordinated to the metal center. Migratory insertion is the C–C bond-forming step of **olefin polymerization**, and some fascinating studies of this reaction have shown that the alkyl group (the growing polymer chain) migrates to the location of the olefin (not the other way around). Migratory insertion is also important for the **Heck reaction**—in this case, the olefin inserts into a Pd–Csp2 bond. Finally, a large number of metal-catalyzed addition reactions rely on migratory insertion as the key C–X bond-forming step. cis-Aminopalladation is one example.
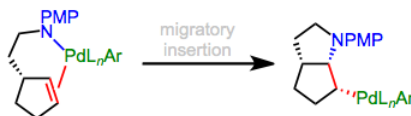


*cis-Aminopalladation via migratory insertion. Two new bonds are established with stereospecificity!*

Importantly, migratory insertion of alkenes and alkynes into M–X bonds takes place in a syn or cis fashion—the metal and the migrating group (X) end up on the same face of the π system. The site selectivity of migratory insertion may be controlled by either steric factors or the π system's electronics, although the former is more common, I'd say. Electronics are at play in Wacker oxidations of 1-alkenes, for example, which exclusively yield methyl ketones.

Finally, **electrophilic attack** on π systems coordinated to electron-rich metals can also happen, although it's much rarer than nucleophilic attack. Usually these reactions involve coordination of the electrophile to the metal, followed by migratory insertion. We'll hear more about this in a future post on electrophilic attack on coordinated ligands. Coming up next: cyclic π systems!

**Arene** or **aromatic ligands** are the subject of this post, the second in our series on π-system ligands. Arenes are dative, L-type ligands that may serve either as actors or spectators. Arenes commonly bind to metals through more than two atoms, although η2-arene ligands are known. Structurally, most η6-arenes tend to remain planar after binding to metals. Both "normal" bonding and backbonding are possible for arene ligands; however, arenes are stronger electron donors than CO and backbonding is less important for these ligands. The reactivity of arenes changes dramatically upon metal binding, along lines that we would expect for strongly electron-donating ligands. After coordinating to a transition metal, the arene usually becomes a better electrophile (particularly when the metal is electron poor). Thus, metal coordination can enable otherwise difficult **nucleophilic aromatic substitution** reactions.
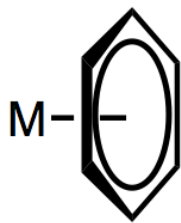
## General Properties

The coordination of an aromatic compound to a metal center through its aromatic π MOs removes electron density from the ring. I'm going to forego an in-depth orbital analysis in this post, because it's honestly not very useful (and overly complex) for arene ligands. π → dσ (normal bonding) and dπ → π* (backbonding) orbital interactions are possible for arene ligands, with the former being much more important, typically. To simplify drawings, you often see chemists draw "toilet-bowl" arenes involving a circle and single central line to represent the π → dσ orbital interaction. Despite the single line, it is often useful to think about arenes as L3-type ligands. For instance, we think of η6-arenes as six-electron donors.

Multiple coordination modes are possible for arene ligands. When all six atoms of a benzene ring are bound to the metal (η6-mode), the ring is flat and C–C bond lengths are slightly longer than those in the free arene. The ring is bent and non-aromatic in η4-mode, so that the four atoms bound to the metal are coplanar while the other π bond is out of the plane. η4-Arene ligands show up in both stable complexes (see the figure below) and reactive intermediates that possess an open coordination site. To generate the latter, the corresponding η6-arene ligand undergoes **ring slippage**—one of the π bonds "slips" off of the metal to create an open coordination site. We'll see ring slippage again in discussions of the aromatic cyclopentadienyl and indenyl ligands.
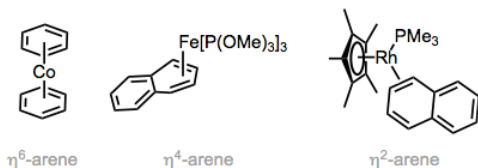


Arene ligands exhibit multiple coordination modes.

Even η2-arene ligands bound through one double bond are known. Coordination of one π bond results in **dearomatization** and makes η2-benzene behave more like butadiene, and furan act more like a vinyl ether. With naphthalene as ligand, there are multiple η2 isomers that could form; the isomer observed is the one that retains aromaticity in the free portion of the ligand. In fact, this result is general for polycyclic aromatic hydrocarbons: binding maximizes aromaticity in the free portion of the ligand. In the linked reference, the authors even observed the coordination of two different rhodium centers to naphthalene—a bridging arene ligand! Other bridging modes include σ, π-binding (the arene is an LX-type ligand, and one C–M bond is covalent, not dative) and L2-type bridging through two distinct π systems (as in biphenyl).

Arene ligands are usually hydrocarbons, not heterocycles. Why? Aromatic heterocycles, such as pyridine, more commonly bind using their basic lone pairs. That said, a few heterocycles form important π complexes. Thiophene is perhaps the most heavily studied, as the desulfurization of thiophene from fossil fuels is an industrially useful process.
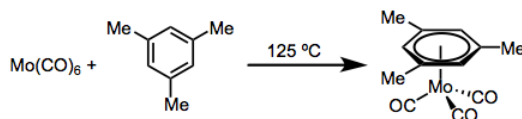
## Synthesis

There are two common methods for the stoichiometric synthesis of arene "sandwich" complexes, in which a metal is squished between two arenes. Starting from a metal halide, treatment with a Lewis acid and mild reductant rips off the halogen atoms and replaces them with arene ligands. The scope of this method is fairly broad metal-wise.
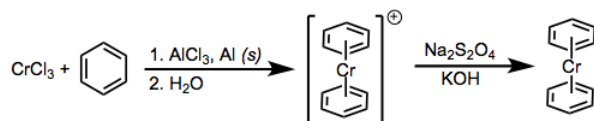


*The Fischer-Hafner synthesis. Reduction of metal halides in the presence of arene.*

A second method, "co-condensation," involves the simultaneous condensation of metal atom and arene vapor onto a cold (-196 °C) surface.

Syntheses of metal arene carbonyl complexes take advantage of the fact that arenes are strongly binding, "chelating" ligands. Infrared spectroscopic studies have shown that a single benzene ligand is a stronger electron donor than three CO ligands—C–O stretching frequencies are lower in metal arene carbonyls than homoleptic metal carbonyls. Since the process is entropically driven, a little heat can get the job done.



*Entropically driven synthesis of arene complexes: three molecules for the price of one!*

## Reactions

It's important here to distinguish aromatic X-type ligands from the topic of this post, Ln-type arenes bound only through their π systems. The figure below nicely summarizes the typical behavior of arene ligands coordinated through their π clouds. Although the figure is for chromium carbonyls specifically, other metals apply as well. Note the reactivity of the benzylic position: both cations and anions are stabilized by the metal.
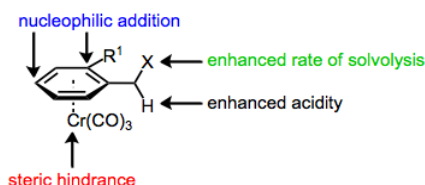


*The magic of metal coordination: increased acidity and electrophilicity and steric hindrance.*

Since the coordination of arenes to metals depletes electron density on the arene, it makes sense that metal-arene complexes should be susceptible to nucleophilic aromatic substitution (NAS). In fact, NAS on metal-coordinated arene ligands has been extensively developed for several different metals. However, all of these NAS methods are stoichiometric because the product ligands are as good as (or better than) the starting ligands at coordinating metal. A stoichiometric amount of another reagent—typically an oxidant—is used to free up the arene. Why are oxidants effective at freeing arene ligands from metal centers? Oxidation worsens the metal's ability to backbond and consequently decreases the enthalpic advantage of arene binding. Entropy is thus able to take over and release the ligand.

Steric hindrance on the side of the arene bound to the metal is a second important factor to consider. Nucleophilic addition takes place on the face opposite the coordinated metal. If rearomatization through the loss of a leaving group isn't fast, an electrophile can be introduced after nucleophilic addition, resulting in the cis addition of nucleophile and electrophile across an aromatic π bond. Take that, aromaticity!
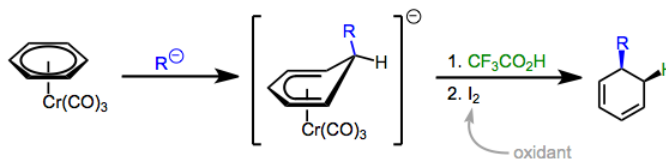


*Aromaticity takes a beating, thanks to chromium!*

We already touched a little on the interesting behavior of $\eta_2$-arene complexes, which behave more like their analogues possessing one less double bond. Here's a nifty example from Harman of a Diels-Alder reaction in which a substituted styrene is the diene. Strike two for aromaticity!
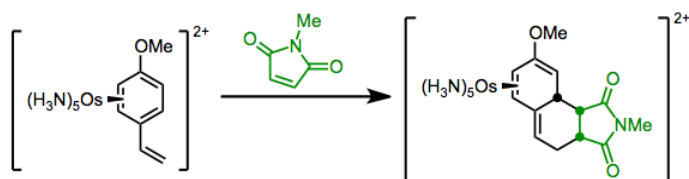
*Harman's Os(II) arene chemistry. Styrene is uniquely acting like a diene!*

If you're interested in learning more about this fascinating chemistry, check out Harman's review (linked above). The behavior of furan is particularly intriguing.

This brings us to the end of our short series on L-type π-system ligands. However, we'll encounter ligands that bear great similarity to alkenes and arenes in the near future. π Systems that contain an odd number of atoms, unlike π systems we've seen so far, are LnX-type ligands with one covalent M–X bond and n dative bonds. We'll return to this interesting class of ligands after finishing off the dative ligands with metal carbenes and introducing a few simple X-type ligands (hydrides, alkyls, alkoxides, etc.).

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