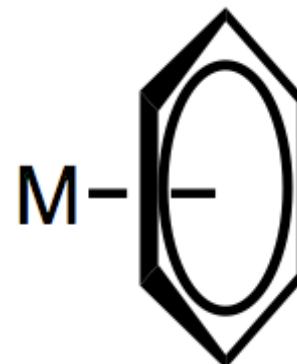


## EPIC LIGAND SURVEY: $\pi$ (II) SYSTEMS –II



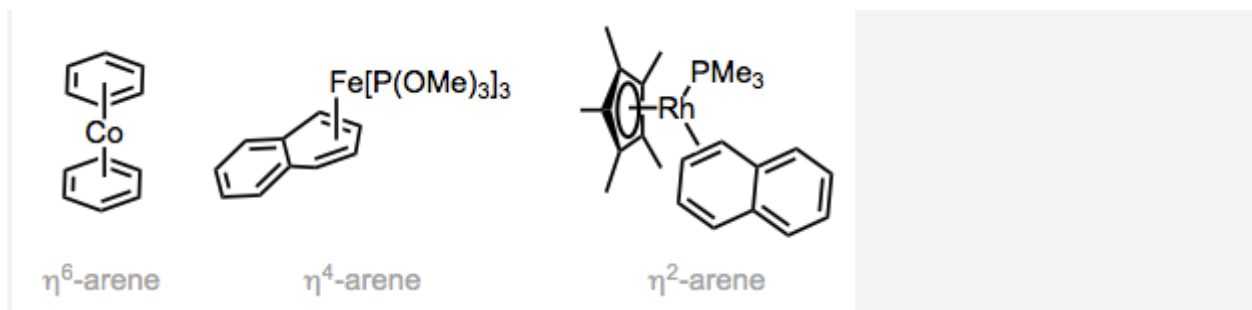
**Arene** or **aromatic ligands** are the subject of this post, the second in our series on  $\pi$ -system ligands. Arenes are dative, L-type ligands that may serve either as actors or spectators. Arenes commonly bind to metals through more than two atoms, although  $\eta^2$ -arene ligands are known. Structurally, most  $\eta^6$ -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  $\pi$  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.  $\pi \rightarrow d_\sigma$  (normal bonding) and  $d_\pi \rightarrow \pi^*$  (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  $\pi \rightarrow d_\sigma$  orbital interaction. Despite the single line, it is often useful to think about arenes as  $L_3$ -type ligands. For instance, we think of  $\eta^6$ -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 ( $\eta^6$ -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  $\eta^4$ -mode, so that the four atoms bound to the metal are coplanar while the other  $\pi$  bond is out of the plane.  $\eta^4$ -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  $\eta^6$ -arene ligand undergoes **ring slippage**—one of the  $\pi$  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.

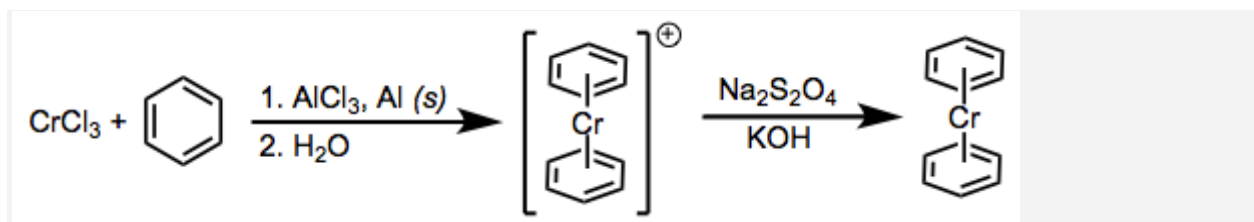
Even  $\eta^2$ -arene ligands bound through one double bond are [known](#). Coordination of one  $\pi$  bond results in **indearomatization** and makes  $\eta^2$ -benzene behave more like [butadiene](#), and furan act more like a [vinyl ether](#). With naphthalene as ligand, there are multiple  $\eta^2$  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  $\sigma$ ,  $\pi$ -binding (the arene is an LX-type ligand, and one C–M bond is covalent, not dative) and L<sub>2</sub>-type bridging through two distinct  $\pi$  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  $\pi$  complexes. Thiophene is perhaps the most [heavily](#) studied, as the [desulfurization of thiophene](#) from fossil fuels is an industrially useful process.

### Synthesis

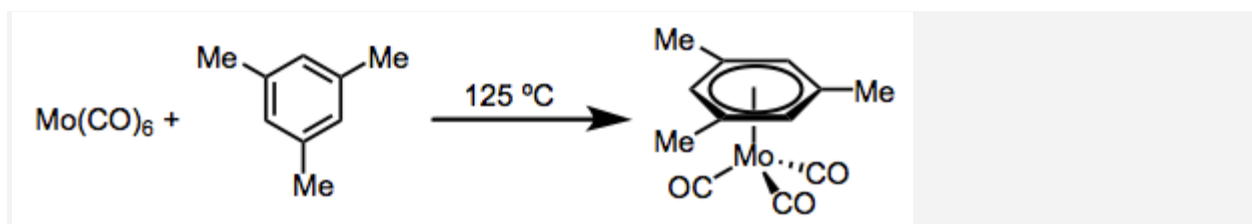
There are two common methods for the stoichiometric synthesis of arene “sandwich” complexes, in which a metal is squished between two arenes. Starting from a metal halide, treatment with a Lewis acid and mild reductant rips off the halogen atoms and replaces them with arene ligands. The scope of this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

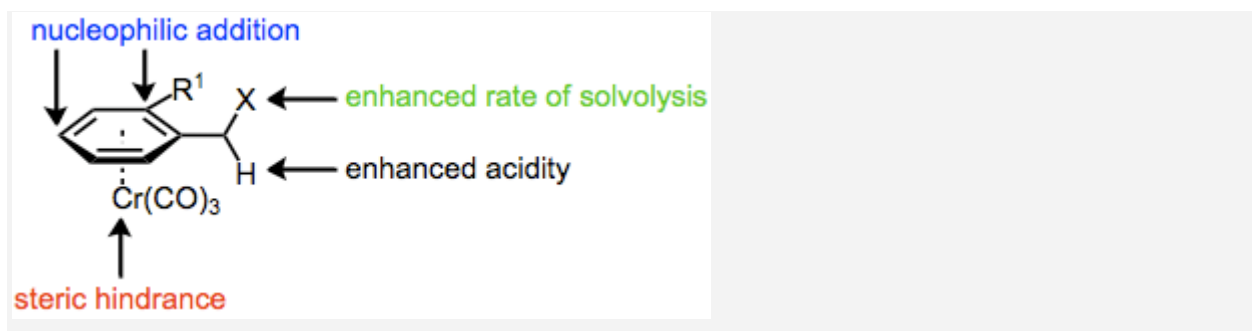
Syntheses of metal arene carbonyl complexes take advantage of the fact that arenes are strongly binding, “chelating” ligands. Infrared spectroscopic studies have shown that a single benzene ligand is a stronger electron donor than three CO ligands—C–O stretching frequencies are lower in metal arene carbonyls 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

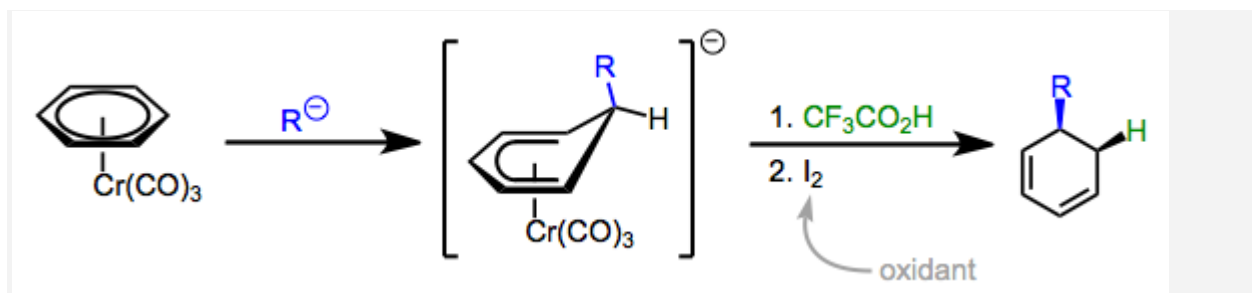
It's important here to distinguish aromatic X-type ligands from the topic of this post,  $L_n$ -type arenes bound only through their  $\pi$  systems. The figure below nicely summarizes the typical behavior of arene ligands coordinated through their  $\pi$  clouds. Although the figure is for [chromium 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.

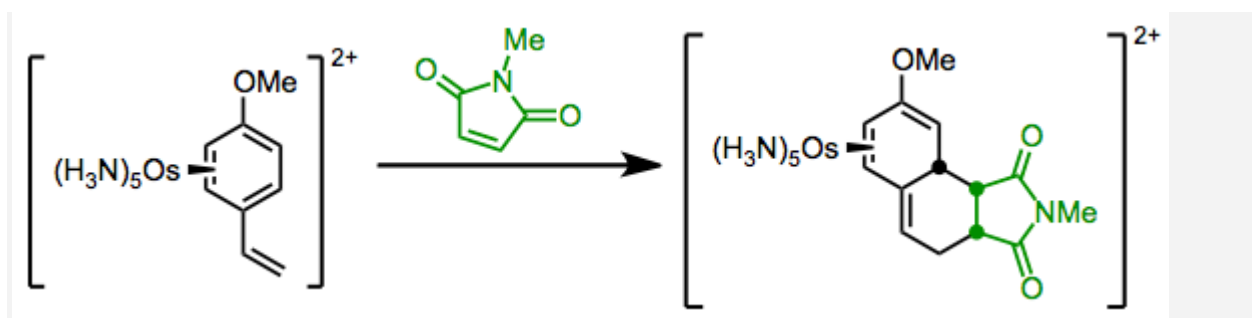
Steric hindrance on the side of the arene bound to the metal is a second important factor to consider. Nucleophilic addition takes place on the face opposite the coordinated metal. If rearomatization through the loss of a leaving group isn't fast, an electrophile can be introduced after nucleophilic addition, resulting in the *cis* addition of nucleophile and electrophile across an aromatic  $\pi$  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  $\pi$ -system ligands. However, we'll encounter ligands that bear great similarity to alkenes and arenes in the near future.  $\pi$  Systems that contain an odd number of atoms, unlike  $\pi$  systems we've seen so far, are L<sub>n</sub>X-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.). Don't touch that dial!

Source : <http://organometallicchem.wordpress.com/2012/02/02/epic-ligand-survey-%CF%80-systems-part-2/>