ORGANOMETALLIC CHEMISTRY

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Organometallic Chemistry (Evans)

Michael Evans

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Licensing

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CHAPTER OVERVIEW

1: Introduction to Organometallic Chemistry

1.1: Resources for Organometallic Chemistry
1.2: What is Organometallic Chemistry?

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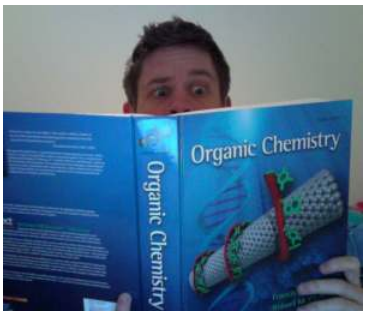
1.1: Resources for Organometallic Chemistry

Let's face it: organometallic chemistry is a somewhat esoteric subject. Unfortunately, this fact makes it difficult to find cheap, current textbooks on the subject, but there are a few used gems for sale on the Internet. Crabtree's Organometallic Chemistry of the Transition Metals is a short but solid book that's a good jumping-off point for deeper studies. Spessard and Miessler's Organometallic Chemistry is a longer but still informative classic. Hartwig's "biblical" Organotransition Metal Chemistry is a nice reference work, but I wouldn't start off with this back-breaking tome. If you do, skip around and avoid the vast sections of text describing "what's known" with little explanation.



What resources are available for the interested organometallics student?

For the penny-pinching student or layman, there are several good resources for organometallic chemistry on the Web. Nothing as exhaustive as Reusch's Virtual Textbook of Organic Chemistry exists for organometallic chemistry, but the base of resources available on the Web is growing. Rob Toreki's Organometallic HyperTextBook could use a CSS refresh, but contains some nice introductions to different organometallic concepts and reactions. Try the electron-counting quiz!

VIPER is a collection of electronic resources for teaching and learning inorganic chemistry, and includes a nice section on organometallic chemistry featuring laboratory assignments, lecture notes, and classroom activities. Awesome public lecture notes are available from Budzelaar at the University of Manitoba and Shaughnessy at Alabama (Roll Tide?). For practice problems, check out Fu's OpenCourseWare material from MIT and Shaughnessy's problem sets.

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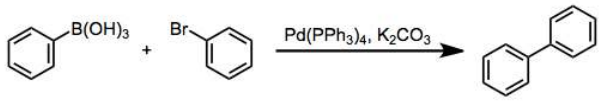
1.2: What is Organometallic Chemistry?

Let's begin with a few simple questions: what is organometallic chemistry? What, after studying organometallic chemistry, will we know about the world that we didn't know before? Why is the subject worth studying? And what kinds of problems is the subject meant to address? The purpose of this post is to give the best answers I currently know of to these questions. The goal of this otherwise content-free post is twofold: (1) to help motivate us as we move forward (that is, to constantly remind us that there is a point to all this!); and (2) to illustrate the kinds of problems we'll be able to address using concepts from the field. You might be surprised by the spine-chilling power you feel after learning about the behavior of organometallic compounds and reactions!

Put most bluntly, organometallic (OM) chemistry is the study of compounds containing, and reactions involving, metal-carbon bonds. The metal-carbon bond may be transient or temporary, but if one exists during a reaction or in a compound of interest, we're squarely in the domain of organometallic chemistry. Despite the denotational importance of the M-C bond, bonds between metals and the other common elements of organic chemistry also appear in OM chemistry: metal-nitrogen, metal-oxygen, metal-halogen, and even metal-hydrogen bonds all play a role. Metals cover a vast swath of the periodic table and include the alkali metals (group 1), alkali earth metals (group 2), transition metals (groups 3-12), the main group metals (groups 13-15, "under the stairs"), and the lanthanides and actinides. We will focus most prominently on the behavior of the transition metals, so called because they cover the transition between the electropositive group 2 elements and the more electron-rich main group elements.

Why is the subject worth studying? Well, for me, it mostly comes down to synthetic flexibility. There's a reason the "organo" comes first in "organometallic chemistry"—our goal is usually the creation of new bonds in organic compounds. The metals tend to just be along for the ride (although their influence, obviously, is essential). And the fact is that you can do things with organometallic chemistry that you cannot do using straight-up organic chemistry. Case in point:



The venerable Suzuki reaction...unthinkable without palladium!

The establishment of the bond between the phenyl rings through a means other than dumb luck seems unthinkable to the organic chemist, but it's natural for the palladium-equipped metal-organicker. Bromobenzene looks like a potential electrophile at the bromine-bearing carbon, and if you're familiar with hydroboration you might see phenylboronic acid as a potential nucleophile at the boron-bearing carbon. Catalytic palladium makes it all happen! Organometallic chemistry is full of these mind-bending transformations, and can expand the synthetic toolbox of the organic chemist considerably.

To throw another motive into the mix for the non-specialist (or the synthesis-spurning chemist), organometallic chemistry is full of intriguing stories of scientific inquiry and discovery. Exploring how researchers take a new organometallic reaction from "ooh pretty" to strong predictive power is instructive for anyone interested in "how science works," in a practical sense. We'll examine a number of classical experiments in organometallic chemistry, both for their value to the field and their contributions to the general nature of scientific inquiry.

What kinds of problems should we be able to address as we move forward? Here's a bulleted list of the most commonly encountered types of problems in an organometallic chemistry course:

- Describe the structure of an organometallic complex…
- Predict the product of the given reaction conditions…
- Draw a reasonable mechanism based on evidence…
- Devise a synthetic route to synthesize a target organometallic compound…
- Explain the observation(s)…
- Predict the results of a series of experiments…

The first four are pretty standard organic-esque problems, but it's the last two, more general classes that really make organometallic chemistry compelling. Just imagine putting yourself in the shoes of the pioneers and making the same predictions they did!

There you have it, a short introduction to organometallic chemistry and why it's worth studying. Of course, we'll use the remainder of space in the blog to fully describe what organometallic chemistry really is…but it's helpful to keep these motives in mind as you

study. Keep a thirst for predictive power, and it's hard to go wrong with organometallic chemistry!

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CHAPTER OVERVIEW

2: Organometallic Ligands

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2.2: Carbon Monoxide
2.3: σ Complexes
2.4: Dative Ligands of N, O, and S
2.5: Metal Alkyls
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2.10: π Systems

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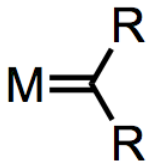
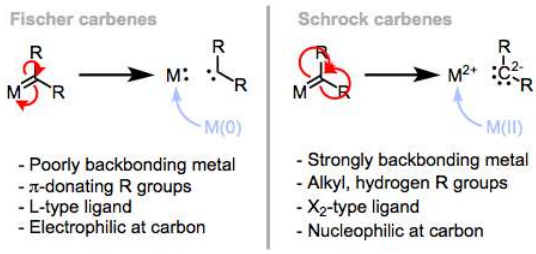
2.1: Carbenes

In a previous post, we were introduced to the N-heterocyclic carbenes, a special class of carbene best envisioned as an L-type ligand. In this post, we'll investigate other classes of carbenes, which are all characterized by a metal-carbon double bond. Fischer carbenes, Shrock carbenes, and vinylidenes are usually actor ligands, but they may be either nucleophilic or electrophilic, depending on the nature of the R groups and metal. In addition, these ligands present some interesting synthetic problems: because free carbenes are quite unstable, ligand substitution does not cut the mustard for metal carbene synthesis.



General Properties

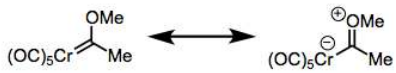
Metal carbenes all possess a metal-carbon double bond. That's kind of a given. What's interesting for us about this double bond is that there are multiple ways to deconstruct it to determine the metal's oxidation state and number of d electrons. We could give one pair of electrons to the metal center and one to the ligand, as we did for the NHCs. This procedure nicely illustrates why compounds containing M=C bonds are called "metal carbenoids"—the deconstructed ligand is an L-type carbenoid. Alternatively, we could give both pairs of electrons to the ligand and think of it as an X2-type ligand. The appropriate procedure depends on the ligand's substituents and the electronic nature of the metal. The figure below summarizes the two deconstruction procedures.



The proper method of deconstruction depends on the electronic nature of the ligand and metal.

When the metal possesses π-acidic ligands and the R groups are π-basic, the complex is best described as an L-type Fischer carbene and the oxidation state of the metal is unaffected by the carbene ligand. When the ligands are "neutral" (R = H, alkyl) and the metal is a good backbonder—that is, in the absence of π-acidic ligands and electronegative late metals—the complex is best described as an X2-type Schrock carbene. Notice that the oxidation state of the metal depends on our deconstruction method! Thus, we see that even the oxidation state formalism isn't perfect.

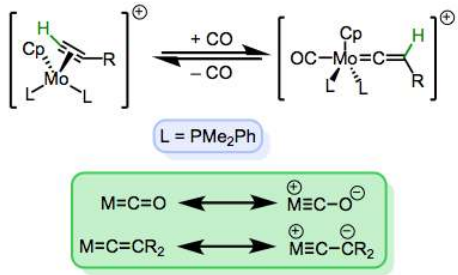
Deconstruction reveals the typical behavior of the methylene carbon in each class of complex. The methylene carbon of Schrock carbenes, on which electron density is piled through backbonding, is nucleophilic (the 2– charge screams nucleophilic!). On the other hand, the methylene carbon of Fischer carbons is electrophilic, because backbonding is weak and does not compensate for σ-donation from the ligand to the metal. To spot a Fischer carbene, be on the lookout for reasonable zwitterionic resonance structures like the one at right below.



Thanks to the pi-accepting CO ligands, the metal handles the negative charge well. This is a Fischer carbene.

The clever reader may notice that we haven't mentioned π-acidic R groups, such as carbonyls. Complexes of this type are best described as Fischer carbenes as well, as the ligand is still electrophilic. However, complexes of this type are difficult to handle and crazy reactive (see below) without a π-basic substituent to hold them in check.

Vinylidenes are the organometallic analogues of allenes, and are best described as intermediate in behavior between Fischer and Schrock carbenes. They are electrophilic at the α carbon and nucleophilic at the β carbon—in fact, a nice analogy can be made between vinylidenes and carbon monoxide. Tautomerization to form alkyne π-complexes is common, as the vinylidene and alkyne complexes are often comparable in stability.



Vinylidene tautomerization, and an analogy between vinylidenes and CO.

Take care when diagnosing the behavior of metal carbenes. In these complexes, there is often a subtle interplay between the R groups on the carbene and other ligands on the metal. In practice, many carbenes are intermediate between the Fischer and Schrock ideals.

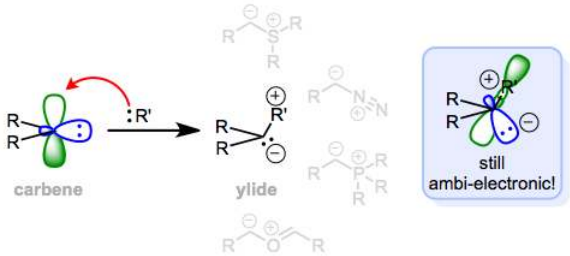
Synthesis

Metal carbenes present a fascinating synthetic problem. A cursory look at the deconstruction procedures above reveals that these complexes cannot be made using ligand substitution reactions, because the free ligands are far too unstable. Although the synthetic methods introduced here will be new for us, the attuned organic chemist will find them familiar. The conceptual foundations of metal carbene synthesis are similar to methods for the synthesis of alkenes in organic chemistry.

In the post on NHCs, we saw that the free carbene is both nucleophilic (via the lone pair in its σ system) and electrophilic (via its empty 2pz orbital). Organic precursors to metal carbenes and alkenes also possess this property—they can act both as nucleophiles and electrophiles. Fundamentally, this “ambi-electronic” behavior is useful for the creation of double bonds. One bond comes from “forward flow,” and the other from “reverse flow.” Naturally, the other reacting partner also needs to be ambi-electronic for this method to work.

A fundamental paradigm for double bond synthesis: ambi-electronic compounds doing what they do.

What sets carbene precursors apart from free carbenes? What other kinds of molecules may act as both nucleophiles and electrophiles at the same atom? Watch what happens when we tack a third group onto the free carbene…the figure below shows the result in general and a few specific examples in gray.

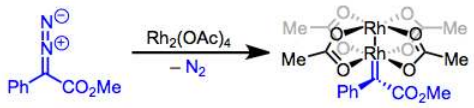


A "dative ligand" R' is the difference between a carbene and an ylide. Both are ambi-electronic.

An ylide, which contains adjacent positive and negative charges, results from this purely hypothetical process. Ylides (diazo compounds, specifically) are the most common precursors to metal carbene complexes. Like free carbenes, ylides are ambi-electronic. The electrophilic frontier orbital of an ylide is just the σ* orbital of the bond connecting the charged atoms, which

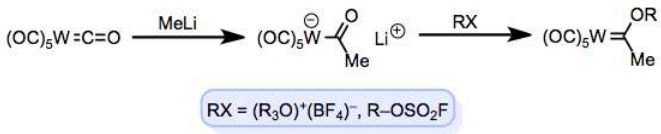
makes sense if we consider the positively charged fragment as a good leaving group (it always is). The lone pair is still nucleophilic. The figure above depicts some of the most famous ylides of organic chemistry, including those used for alkene synthesis (Corey-Chaykovsky and Wittig) and cycloaddition reactions (the carbonyl ylide).

Although diazo compounds are most commonly drawn with charges on the two nitrogen atoms, the diazo carbon is a good nucleophile and can attack electrophilic metal centers to initiate metal carbene formation. A slick 15N kinetic isotope effect study showed that C–N bond cleavage is the rate-limiting step of the reaction below. Visualize the carbanionic resonance structure to kick off the mechanism! Don't think too hard about the structure of rhodium(II) acetate here. Rhodium, copper, ruthenium, and iridium all form carbene complexes with diazo compounds in a similar way.



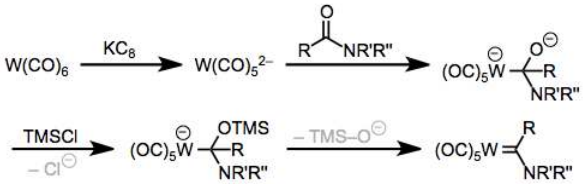
After association of the nucleophilic carbon to Rh, elimination with loss of nitrogen gas is the slow step of this reaction.

Diazo compounds work well for metal carbene formation when they possess an electron-withdrawing group, which stabilizes the ylide through conjugation. What about Fischer carbenes, which possess electron-donating groups on the carbene carbon? An interesting method that still involves a "push-and-pull" of electron flow (but not ylides) employs metal-CO complexes. Upon addition of a strong nucleophile ("forward flow") to the carbonyl carbon, a metalloenolate of sorts is produced. Treatment with an electrophile RX that prefers oxygen over the metal ("reverse flow") results in an OR-substituted Fischer carbene. Reactions reminiscent of transesterification trade out the OR group for an –SR group (using a thiol) or an –NR2 group (using a secondary amine).



Fischer's classical route to L-type carbenes.

As counterintuitive as it may seem, it's possible to use metal dianions for the synthesis of Fischer carbenes via a method pioneered by Hegedus and Semmelhack. Potassium intercalated in graphite—the mysterious "KC8"—reduces group 6 metal carbonyl complexes to the corresponding dianions, which subsequently unleash a deluge of electrons on a poor, unsuspecting amide to afford NR2-substituted Fischer carbenes after treatment with trimethylsilyl chloride.

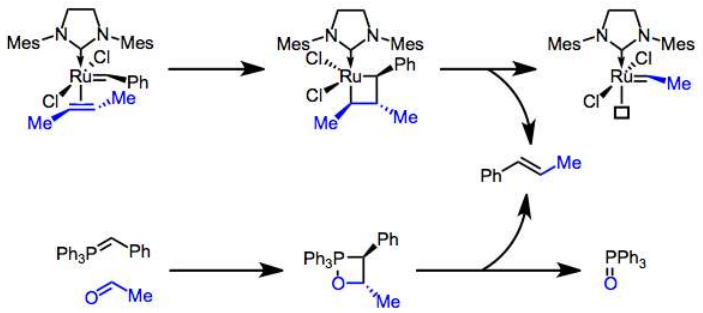


One-directional electron flow for Fischer carbene synthesis: the Hegedus-Semmelhack approach.

For other methods for the synthesis of Fischer carbenes, check out this nice review from the Baran group.

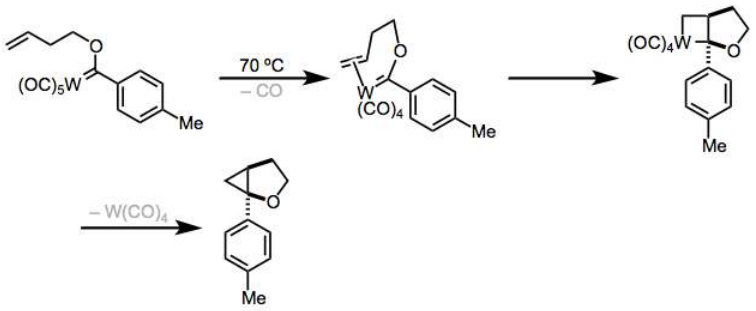
Reactions

In many ways, the reactivity of metal carbenes parallels that of ylides. Olefin metathesis catapulted metal carbenes to international stardom, but in many ways, metathesis is conceptually similar to the Wittig reaction, which employs phosphorus ylides. During both mechanisms, an ylide/carbene hooks up with another doubly bound molecule to form a four-membered ring. This step is followed by what we might call "orthogonal breakdown" to yield two new double bonds.



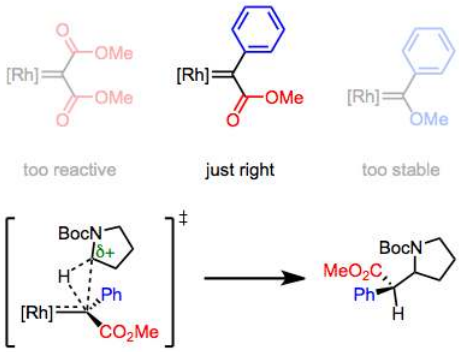
Wittig, Grubbs, and Schrock: Lords of the Chemical Dance. Ambi-electronic molecules are the dancers!

In my opinion, bond insertion reactions are the most interesting processes in which carbenes regularly engage. Bond insertions may be subdivided into cyclopropanation (π-bond insertion) and σ-bond insertion. Evidence suggests that most cyclopropanations take place by a mechanism that overlaps with metathesis—instead of orthogonal breakdown, reductive elimination occurs to release the three carbon atoms as a cyclopropane.



The metallacyclobutane mechanism of cyclopropanation.

σ-Bond insertion involves electron-rich C–H bonds most prominently, suggesting that electrophilic Fischer carbenes should be best for this chemistry. Fischer carbenes incorporating electron-withdrawing groups love to dimerize to form olefins and/or cyclopropanate olefins—how might we put the brakes on this behavior? If we simply tack a π-basic substituent onto the carbene carbon, the reactivity of these complexes is “just right” for C–H insertion. Notably, no covalent organometallic intermediates are involved; the electrophilic carbene carbon snuggles in between C and H in a single step. The transition state of this step resembles the transfer of a hydride from the organic substrate to the carbene, with “rebound” of electron density toward the partial positive charge.



Donor-acceptor carbenoids are the "Goldilocks complexes" of C–H insertion.

Let’s end with a nod to the similarity between Fischer carbenes and carboxylic acid derivatives (esters and amides). Transesterification-type reactions allow the chemist to swap out heteroatomic substituents on the carbene carbon at will (see above). Alkyl substitutents can even be deprotonated at the α carbon, just like esters! When we see the electronic similarities between the M=C bond of a Fischer carbene and the O=C bond of carboxylic acid derivatives, the similar behavior is only natural.

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2.2: Carbon Monoxide

As a young, growing field, organometallic chemistry may be taught in many ways. Some professors (e.g., Shaugnessy) spend a significant chunk of time discussing ligands, while others forego ligand surveys (e.g., White) to dive right in to reactions and mechanisms. I like the ligand survey approach because it lays out many of the general concerns associated with certain ligand sets before organometallic intermediates pop up. With the general concerns in hand, it becomes easier to generate explanations for certain observed effects on reactions that depend on ligands. Instead of generalizing from complex, specific examples in the context of reaction mechanisms, we'll look at general trends first and apply these to reaction intermediates and mechanisms later. This post kicks off our epic ligand survey with carbon monoxide, a simple but fascinating ligand.

General Properties

CO is a dative, L-type ligand that does not affect the oxidation state of the metal center upon binding, but does increase the total electron count by two units. We've recently seen that there are really two bonding interactions at play in the carbonyl ligand: a ligand-to-metal $n \rightarrow d_\sigma$ interaction and a metal-to-ligand $d_\pi \rightarrow \pi^*$ interaction. The latter interaction is called **backbonding**, because the metal donates electron density back to the ligand. To remind myself of the existence of backbonding, I like to use the right-hand resonance structure whenever possible; however, it's important to remember to treat CO as an L-type ligand no matter what resonance form is drawn.

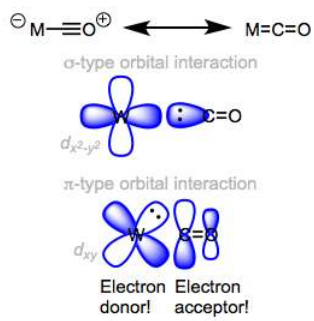

Figure 2.2.1: Orbital interactions in M=C=O. (Copyright; Michael Evans)

CO is a fair σ-donor (or σ-base) and a good π-acceptor (or π-acid). The properties of ligated CO depend profoundly upon the identity of the metal center. More specifically, the electronic properties of the metal center dictate the importance of backbonding in metal carbonyl complexes. Most bluntly, *more electron-rich metal centers are better at backbonding to CO.* Why is it important to ascertain the strength of backbonding? I'll leave that question hanging for the moment, but we'll have an answer very soon. Read on!

Infrared spectroscopy has famously been used to empirically support the idea of backbonding. The table below arranges some metal carbonyl complexes in "periodic" order and provides the frequency corresponding to the C=O stretching mode. Notice that without exception, every complexed CO has a stretching frequency lower than that of free CO. Backbonding is to blame! The C–O bond order in complexed carbon monoxide is (almost always) lower than that of free CO.

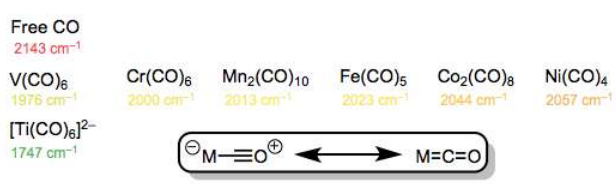

Figure 2.2.2: C=O stretching frequencies in metal-carbonyl complexes. Does something seem off here? (Copyright; Michael Evans)

The figure above depicts a clear increase in frequency (an increase in C–O bond order) as we move left to right across the periodic table. This finding may seem odd if we consider that the number of *d* electrons in the neutral metal increases as we move left to right. Shouldn't metal centers with more *d* electrons be better at backbonding (and more "electron rich")? What's going on here? Recall the periodic trend in *orbital energy*. As we move left to right, the *d* orbital energies decrease and the energies of the d_π and π* orbitals separate. As a result, the backbonding orbital interaction becomes worse (remember that strong orbital interactions require well-matched orbital energies) as we move toward the more electronegative late transition metals! We can draw an analogy

to enamines and enols from organic chemistry. The more electronegative oxygen atom in the enol is a worse electron donor than the enamine's nitrogen atom.

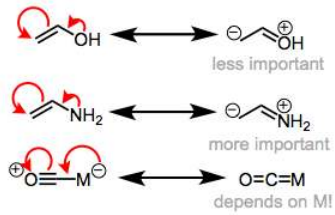

Figure 2.2.3: The importance of backbonding depends on the electronegativity of the metal and its electron density. (Copyright; Michael Evans)

Of course, the contribution of other ligands on the metal center to backbonding cannot be forgotten, either. Logically, electron-donating ligands will tend to make the backbond stronger (they make the metal a better electron donor), while electron-withdrawing ligands will worsen backbonding. Adding electron-rich phosphine ligands to a metal center, for instance, *decreases* the CO stretching frequency due to *improved* backbonding.

Carbonyl ligands are famously able to **bridge** multiple metal centers. Bonding in bridged carbonyl complexes may be either "traditional" or delocalized, depending on the structure of the complex and the bridging mode. The variety of bridging modes stems from the different electron donors and acceptors present on the CO ligand (and the possibility of delocalized bonding). Known bridging modes are shown in the figure below.

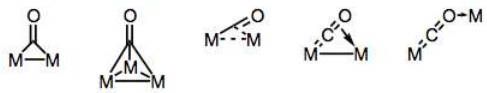

Figure 2.2.4: Building bridges with carbonyl ligands! (Copyright; Michael Evans)

Synthesis

Metal carbonyl complexes containing only CO ligands abound, but most cannot be synthesized by the method we all wish worked, bathing the elemental metal in an atmosphere of carbon monoxide (entropy is a problem, as we already discussed for $W(CO)_6$). This method does work for nickel(0) and iron(0) carbonyls, however.

$M + n\,CO \rightarrow M(CO)_n$ [M = Fe, n = 5; M = Ni, n = 4]

Other metal carbonyl complexes can be prepared by **reductive carbonylation**, the treatment of a high-oxidation-state complex with CO. These methods usually require significant heat and pressure. One example:

$WCl_6 + CO + \text{heat, pressure} \rightarrow W(CO)_6$

Still other methods employ **deinsertion** from organic carbonyl compounds like dimethylformamide. These methods are particularly useful for preparing mixed carbonyl complexes in the presence of reducing ligands like phosphines.

$IrCl_3(H_2O)_3 + 3\,PPh_3 + HCONMe_2 + PhNH_2 \rightarrow IrCl(CO)(PPh_3)_2 + (Me_2NH_2)Cl + OPPh_3 + (PhNH_3)Cl + 2\,H_2O$

The key thing to notice about the reaction above is that the CO ligand is derived from dimethylformamide (DMF).

Reactions

The dissociation of carbonyl ligands is common in reactions that require an open coordination site at the metal. Naturally, the favorability of dissociation is governed by electron density at the metal—weaker backbonding metals lose CO more easily. This is one reason understanding trends in backbonding strength is important!

Like the carbonyl carbon in organic compounds, the carbon of ligated CO is often an exquisite electrophile—particularly when the metal is a poor π-base, leaving the carbonyl carbon starved of electrons. CO ligands are susceptible to nucleophilic attack at the carbonyl carbon in the presence of strong nucleophiles. Treating the adduct with an electrophile yields a Fischer carbene complex. If we imagine M=C=O as an analogue of ketene, this reactivity just corresponds to classic nucleophilic addition across the C=O bond.

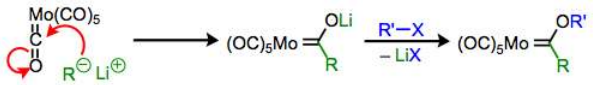

Figure 2.2.5: Metal carbene complexes from metal carbonyls via nucleophilic addition. (Copyright; Michael Evans)

Perhaps the most important elementary step in which the CO ligand participates is **migratory insertion**, a step typical of oxidized organic ligands (CO, alkenes, alkynes, etc.). The net result of the process is the insertion of the carbonyl carbon into an M–X bond (X is most commonly C or H, but can be any X-type ligand). An empty coordination site—the strange-looking box in the figure below—is left behind after migration. The **hydroformylation** reaction involves the insertion of CO into an M–C bond as a key step. We'll talk about this fascinating processes in more detail in a later post.

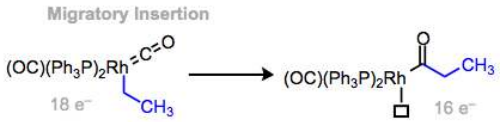

Figure 2.2.6: Migratory insertion, a powerful method for C–C bond construction on transition metal centers.Copy and Paste Caption here. (Copyright; Michael Evans)

For CO, it's useful to think about migratory insertion as a sort of intramolecular nucleophilic attack by the X-type ligand on coordinated CO. In this respect its similar to the intermolecular nucleophilic addition process leading to carbenes described above. Just view the carbonyl carbon as an electrophile (as if you don't already!) and it becomes easy to keep these ideas in mind. We'll see migratory insertion in more detail in a future post as well.

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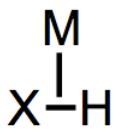
2.3: σ Complexes

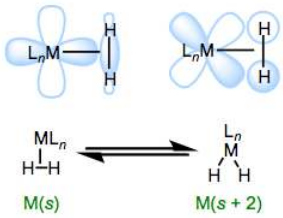
Ligands can, shockingly enough, bind through their σ electrons in an L-type fashion. This binding mode depends as much on the metal center as it does on the ligand itself—to see why, we need only recognize that σ complexes look like intermediates in concerted oxidative additions. With a slight reorganization of electrons and geometry, an L-type σ ligand can become two X-type ligands. Why, then, are σ complexes stable? How can we control the ratio of σ complex to X_2 complex in a given situation? How does complexation of a σ bond change the ligand's properties? We'll address these questions and more in this post.

General Properties

The first thing to realize about σ complexes is that they are highly sensitive to steric bulk. Any old σ bond won't do; hydrogen at one end of the binding bond or the other (or both) is necessary. The best studied σ complexes involve dihydrogen (H2), so let's start there.

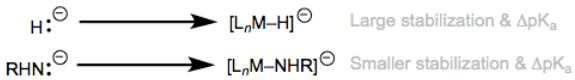


Mildly backbonding metals may bind dihydrogen "side on." Like side-on binding in π complexes, there are two important orbital interactions at play here: σH–H → dσ and dπ → σ*H–H. Dihydrogen complexes can "tautomerize" to $(H)_2$ isomers through oxidative addition of the H–H bond to the metal.



Orbital interactions and L-X_2 equilibrium in σ complexes.

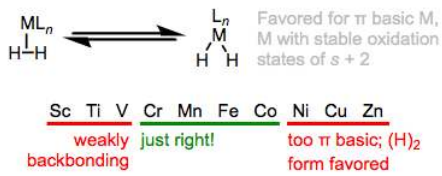
H_2 binding in an L-type fashion massively acidifies the ligand—changes in pKa of over thirty units are known! Analogous acidifications of X–H bonds, which we touched on in a previous post, rarely exhibit ΔpKa > 5. What gives? What's causing the different behavior of X–H and H–H ligands? The key is to consider the conjugate base of the ligand—in particular, how much it's stabilized by a metal center relative to the corresponding free anion. The principle here is analogous to the famous dictum of organic chemistry: consider charged species when making acid/base comparisons. Stabilization of the unhindered anion H– by a metal is much greater than stabilization of larger, more electronegative anions like HO– and NH_2– by a metal. As a result, it's more favorable to remove a proton from metal-complexed H_2 than from larger, more electronegative X–H ligands.



Remarkably large stabilization by an acidic metal fragment, without any counterbalancing from steric factors, explains the extreme acidification of dihydrogen upon metal binding.

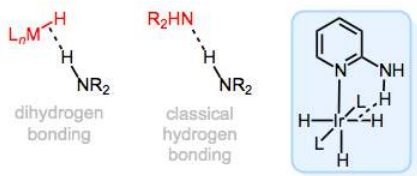
The electronic nature of the metal center has two important effects on σ complexes. The first concerns the acidity of H2 upon metal binding. The principle here is consistent with what we've hammered into the ground so far. In the same way cationic organic acids are stronger than their neutral counterparts, σ complexes of electron-poor metals—including (and especially) cations—are stronger acids than related complexes of electron-rich metals. The second concerns the ratio of L-type to X_2-type binding. We should expect more electron-rich metal centers to favor the X2 isomer, since these should donate more strongly into the σ*H–H orbital. This idea was masterfully demonstrated in a study by Morris, in which he showed that H2 complexes of π-basic metal centers show all the signs of X2 complexes, rather than L complexes. More generally, metal centers in σ complexes need a good balance of π basicity

and σ acidity (I like to call this the “Goldilocks effect”). Because of the need for balance, σ complexes are most common for centrally located metals (groups 6-9).



Oxidative addition of H2 is important for electron-rich, π-basic metal centers. Groups 6-9 hit the "Goldilocks" spot.

The M–H bond in hydride complexes is a good base—anyone who’s ever quenched lithium aluminum hydride can attest to this! Intriguingly, because it’s a good base, the M–H bond can participate in hydrogen bonding with an acidic X–H bond, where X is a heteroatom. This kind of bonding, called dihydrogen bonding (since two hydrogen atoms are involved), is best described as a sort of σM–H→σ*X–H orbital interaction. Think of it as analogous to a traditional hydrogen bond, but using a σ bond instead of a lone pair. Crazy, right?!

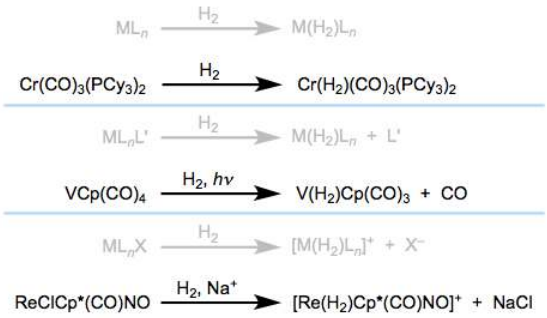


Dihydrogen bonding in metal hydrides: a sort of "interrupted protonation" of M–H.

Other kinds of σ complexes are known, but these are rarer than H–H complexes. One class that we’ve seen before involve agostic interactions of C–H bonds in alkyl ligands. σ Complexes of inorganic ligands like silanes and stannanes may involve complex bonding patterns, but we won’t concern ourselves with those here.

Synthesis

If a metal center with an open coordination site has the “Goldilocks combination” of electronic factors, simply treating it with dihydrogen gas is enough to form the σ complex. Metals that bear labile L- or X-type ligands can also yield σ complexes upon treatment with H2.



Methods for the synthesis of σ complexes from dihydrogen gas. Displacement of a labile ligand or occupation of a vacant site represent the essence of these methods.

An alternative synthetic method involves the protonation of a basic M–H bond…taking dihydrogen bonding to the extreme! This method is especially nice if a cationic complex is the goal; of course, the metal needs to be π basic to make protonation favorable.

Protonation of an M–H bond for the synthesis of dihydrogen σ complexes.

Reactions

Deprotonation of an L-type X–H ligand is probably the simplest reaction of this class of ligands. This process is just the reverse of the synthetic method described above. We can refer to it as heterolytic cleavage, since the X atom that stays bound to the metal holds on to the electrons of the X–H bond. The charge of the product complex is one less than that of the starting material. A variation on this theme involves intramolecular proton transfer.

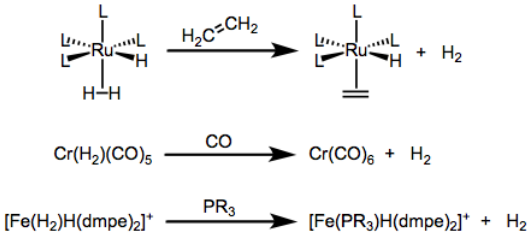
Deprotonation of dihydrogen complexes produces metal hydrides.

Homolytic cleavage of X–H is also possible, and it can happen in two ways. Intramolecular oxidative addition is the first, and we've seen it already. Since this process is intramolecular and little geometric reorganization is necessary, kinetic barriers tend to be low and the process may be reversible (unless the electronic circumstances of the metal are extreme). This sort of oxidative addition is important for many hydrogenation reactions, such as those employing Wilkinson's catalyst.

Oxidative addition of dihydrogen via a sigma complex. In some cases, this process is a finely balanced equilibrium.

And the second way? In theory at least, intermolecular homolytic cleavage is possible. This process corresponds to one-electron oxidation of two distinct metal centers. Contrast this pattern of electron exchange with intramolecular oxidative addition, which involves two-electron oxidation of a single metal center. This kind of reactivity is rare in practice.

Ligand substitutions with other L-type ligands— including CO, N2, phosphines, and unsaturated organics—are also known. In fact, this process has been implicated in catalytic cycles for some hydrogenation reactions.



Ligand substitution reactions of sigma complexes. Can you justify the favorability of these reactions?

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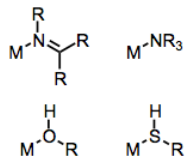
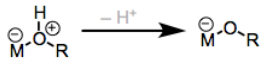
2.4: Dative Ligands of N, O, and S

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 → dσ 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.

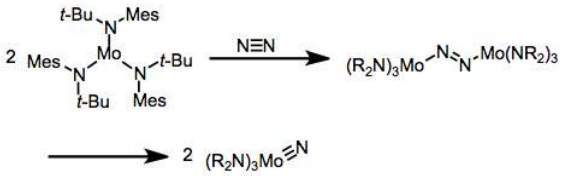


Coordination increases acidity.

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.

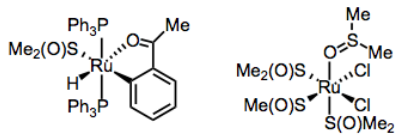
Although dinitrogen (N2) is isoelectronic with carbon monoxide, it's been a tough nut for organometallic chemists to crack. An electron-rich metal center lacking π-acidic ligands is an absolute must for dinitrogen-containing complexes, as the π*NN orbital does not easily participate in backbonding. What 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 N2 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 polarizeable than oxygen, sulfur binds to softer (low-valent) metals and oxygen to harder metal centers.

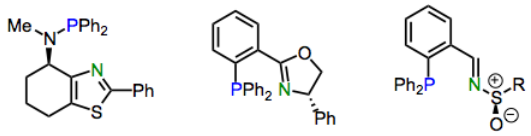


The soft Ru(II) center with hydrocarbyl ligands contains S-bound DMSO, while the harder Ru(II) with chloride ligands includes one O-bound DMSO.

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

Synthesis

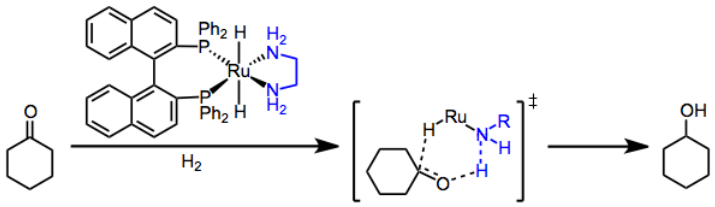
Ligand substitution reactions are most commonly used to load dative ligands of N, O, and S onto metal centers. In some cases, when the heteroatom bears a hydrogen atom, deprotonation can produce a covalent, X-type ligand. Usually, however, these types of ligands are incorporated into organic substrates 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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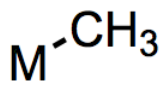
2.5: Metal Alkyls

Part 1:

With this post we finally reach the defining ligands of organometallic chemistry, alkyls. Metal alkyls feature a metal-carbon σ bond and are usually actor ligands, although some alkyl ligands behave as spectators. Our aim will be to understand the general dependence of the behavior of alkyl ligands on the metal center and the ligand's substituents. Using this knowledge, we can make meaningful comparisons between related metal alkyl complexes and educated predictions about their likely behavior. Because alkyl ligands are central to organometallic chemistry, I've decided to spread this discussion across multiple posts. We'll deal first with the general properties of metal alkyls.



In the Simplifying the Organometallic Complex series, we decomposed the M–C bond into a positively charged metal and negatively charged carbon. This deconstruction procedure is consistent with the relative electronegativities of carbon and the transition metals. It can be very useful for us to imagine metal alkyls essentially as stabilized carbanions—but it's also important to understand that M–C bonds run the gamut from extremely ionic and salt-like ($NaCH_3$) to essentially covalent ($[HgCH_3]^+$). The reactivity of the alkyl ligand is inversely related to the electronegativity of the metal center.

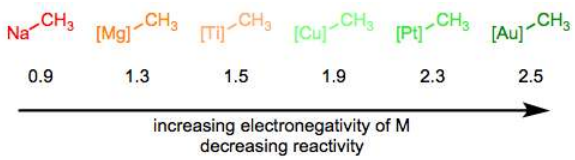


Figure 2.5.1: Reactivity decreases as the metal's electronegativity increases. Values given are Pauling electronegativities. (Michael Evans)

The hybridization of the carbon atom is also important, and the trend here follows the trend in nucleophilicity as a function of hybridization in organic chemistry. *sp*-Hybridized ligands are the least nucleophilic, followed by sp^2 and sp^3 ligands respectively.

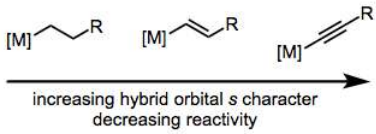


Figure 2.5.1: Note that this trend is similar to the nucleophilicity of carbanions as a function of hybridization. (Michael Evans)

The history of transition metal alkyls is an intriguing example of an incorrect scientific paradigm. After several unsuccessful attempts to isolate stable metal alkyls, organometallic chemists in the 1920s got the idea that metal-carbon bonds were weak in general. However, later studies showed that it was *kinetic instability*, not thermodynamic, that was to blame for our inability to isolate metal alkyls. In other words, most metal alkyls are susceptible to decomposition pathways with low activation barriers—the instability of the M–C bond *per se* is not to blame. Crabtree cites typical values of 30-65 kcal/mol for M–C bond strengths.

What are the major decomposition pathways of metal alkyl complexes? **β-hydride elimination** is the most common. Thermodynamically, the ubiquity of β-hydride elimination makes sense—M–C bonds run 30-65 kcal/mol, while M–H bonds tend to be stronger. The figure below summarizes the accepted mechanism and requirements of β-hydride elimination. We'll revisit this fundamental reaction of organometallic complexes in a future post.

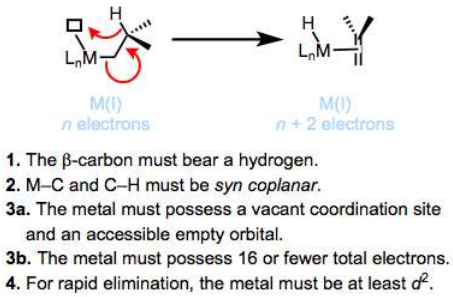


Figure 2.5.1: What kinds of metal alkyl complexes violate the requirements for beta-hydride elimination? (Copyright; author via source)

Kinetically stable metal alkyl complexes violate one of the requirements for β-hydride elimination. Methyl and neopentyl complexes lack β-hydrogens, violating requirement 1. Tightly binding, chelating ligands may be used to prevent the formation of an empty coordination site, violating requirements 3a and 3b. Titanium complexes are known that violate requirement 4 and eliminate only very slowly—back-donation from the metal to the $\sigma^*_{C–H}$ is required for rapid elimination (see below).

Reductive elimination is a second common decomposition pathway. The alkyl ligand hooks up with a second X-type ligand on the metal, and the metal is reduced by two units with a decrease in the total electron count by two units. I've omitted curved arrows here because different mechanisms of reductive elimination are known. We'll discuss the requirements of reductive elimination in detail in a future post; for now, it's important to note that the thermodynamic stability of C–X versus that of (M–X + M–C) is a critical driving force for the reaction.

Figure 2.5.1: The thermodynamics of reductive elimination can present problems for some alkyl complexes. (Copyright; author via source)

When X = H, reductive elimination is nearly always thermodynamically favorable; thus, isolable alkyl hydride complexes are rare. This behavior is a feature, not a bug, when we consider that hydrogenation chemistry depends on it! On the other hand, when X = halogen reductive elimination is usually disfavored. Reductive elimination of C–C (X = C) can be favored thermodynamically, but is usually slower than the corresponding C–H elimination.

Complexes that cannot undergo β-hydride elimination are sometimes susceptible to **α-elimination**, a mechanistically similar process that forms a metal carbene. This process is particularly facile when the α-position is activated by an adjacent electron donor (Fischer carbenes are the result).

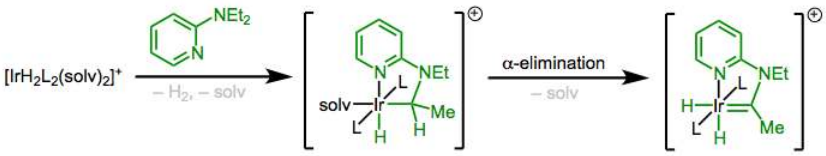


Figure 2.5.1: Oxidative addition followed by alpha-elimination, forming a Fischer carbene from an alkyl complex. (Copyright; author via source)

In some metal alkyl complexes, C–H bonds at the α, β, or even farther positions can serve as electron donors to the metal center. This idea is supported by crystallographic evidence and NMR chemical shifts (the donating hydrogens shift to high field). Such interactions are called **agostic interactions**, and they resemble an "interrupted" transition state for hydride elimination. Alkyl complexes that cannot undergo β-hydride elimination for electronic reasons (high oxidation state, d^0 metals) and vinyl complexes commonly exhibit this phenomenon. The fact that β-hydride elimination is slow for d^0 metals—agostic interactions are seen instead—suggests that back-donation from a filled metal orbital to the $\sigma^*_{C–H}$ is important for β-hydride elimination. Here's an interesting, recent-ish review of agostic interactions.

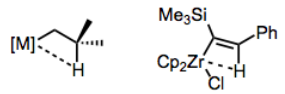


Figure 2.5.1: Copy and Paste Caption here. (Copyright; author via source)

In the next post in this series, we'll explore the synthesis of metal alkyl complexes in more detail, particularly clarifying the question: how can we conquer β-hydride elimination?

Part 2:

In this post, we'll explore the most common synthetic methods for the synthesis of alkyl complexes. In addition to enumerating the reactions that produce alkyl complexes, this post will also describe strategies for getting around β-hydride elimination when isolable alkyl complexes are the goal. Here we go!

Properties of Stable Alkyl Complexes

Stable alkyl complexes must be resistant to β-hydride elimination. In the last post we identified four key conditions necessary for elimination to occur:

1. The β-carbon must bear a hydrogen.
2. The M–C and C–H bonds must be able to achieve a *syn* coplanar orientation (pointing in the same direction in parallel planes).
3. The metal must bear 16 total electrons or fewer and possess an open coordination site.
4. The metal must be at least d^2.

Stable alkyl complexes must violate at least one of these conditions. For example, titanium(IV) complexes lacking *d* electrons β-eliminate very slowly. The complex below likely also benefits from chelation (see below).

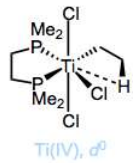


Figure 2.5.1: No d electrons here! (Michael Evans)

Complexes have been devised that are unable to achieve the *syn* coplanar orientation required for elimination, or that lack β-hydrogens outright. A few examples are provided below—one has to admire the cleverness of the researchers who devised these complexes. The metallacyclobutane is particularly striking!

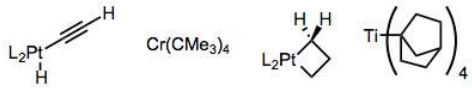


Figure 2.5.1: Complexes whose beta-C–H bonds cannot align in a syn coplanar manner with the M–C bond. (Copyright; author via source)

Using tightly binding, chelating ligands or a directing group on the substrate, the formation of 16-electron complexes susceptible to β-hydride elimination can be discouraged. Notice how the hyrdrogen-bonding L_2 ligands in the central complex below hold the metal center in a death grip.

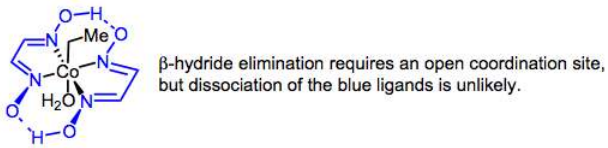


Figure 2.5.1: Tightly chelating ligands prevent the opening of a coordination site. (Copyright; author via source)

Finally, it's worth noting that complexes with an open coordination site—such as 16-electron, square-planar complexes of Ni, Pd, and Pt important for cross-coupling—are susceptible to reactions with solvent or other species at the open site. Bulky alkyl ligands help prevent these side reactions. In the example below, the methyl groups of the *o*-tolyl ligands extend into the space above and below the square plane, discouraging the approach of solvent molecules perpendicular to the plane.

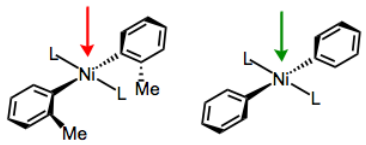


Figure 2.5.1: The approach of solvent perpendicular to the square plane is slowed by methyl groups on the aryl ligand. (Copyright; author via source)

Many transition metal complexes catalyze (*E*)/(*Z*) isomerization and the isomerization of terminal alkenes (α-olefins) to internal isomers via β-hydride elimination. This is a testament to the importance of this process for alkyl complexes. Of course, transient alkyl complexes may *appear* to be susceptible to β-hydride elimination, but if other processes are faster, elimination will not occur. Thus, the optimization of many reactions involving alkyl complexes as intermediates has involved speeding up other processes at the expense of β-hydride elimination—hydrocyanation is a good example.

Synthesis of Alkyl Complexes

The dominant synthetic methods for alkyl complexes are based on nucleophilic attack, electrophilic attack, oxidative addition, and migratory insertion. The first two methods should be intuitive to the organic chemist; the second two are based on more esoteric (but no less important) reactions of organometallic complexes.

Metals bearing good leaving groups are analogous to organic electrophiles, and are susceptible to **nucleophilic attack** by organolithiums, Grignard reagents, and other polarized organometallics. These reactions can be viewed as a kind of **transmetalation**, as the alkyl ligand moves from one metal to another. Electron-withdrawing X-type ligands like –Cl and –Br should jump out as good leaving groups. On the other hand, clean substitution of L-type ligands by anionic nucleophiles is much more rare (anionic complexes would result).

Figure 2.5.1: Simple and straightforward: nucleophile attacks electrophilic metal. (Copyright; author via source)

Many anionic metal complexes are nucleophilic enough to attack electrophilic sources of carbon such as alkyl and acyl halides in an **electrophilic attack** mode. An available lone pair on the metal and open coordination site are prerequisites for this chemistry. The charge on the complex increases by one unit (in effect, negative charge is transferred to the electrophile's leaving group). We can classify these as oxidative ligation reactions—notice that the oxidation state of the metal increases by two units.

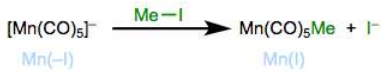


Figure 2.5.1: Oxidative ligation for the synthesis of alkyl complexes. Total electron count does not change. (Copyright; author via source)

Oxidative addition results in the cleavage of a W–Z bond and placement of two new X-type ligands (–W and –Z) on the metal center, with an increase in the oxidation state of the metal and the total electron count by two units. Organic halides are extremely common substrates for this reaction, the first step in the mechanism of cross-coupling reactions. The oxidized metal complex containing new alkyl and halide ligands is the final product. Notice that *two* open coordination sites are required (not necessarily simultaneously), the metal center must be amenable to two-electron oxidation, and the number of total electrons of the complex increases by two. In essence, the electrons of the W–Z bond join the complex's party. Take note that there are many known mechanisms for oxidative addition! We'll explore these different mechanisms in detail in a future post.

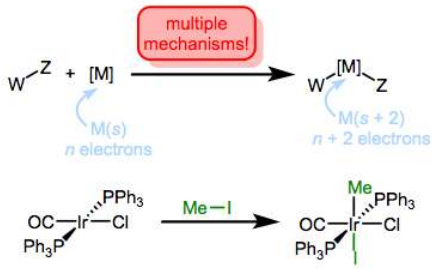


Figure 2.5.1: Oxidative addition, with a representative example, for the synthesis of metal alkyl complexes. (Copyright; author via source)

Finally, **migratory insertion** of unsaturated organic compounds is an important method for the synthesis of certain alkyl complexes, and an important step of organometallic reactions that result in addition across π bonds. Migratory insertion is the microscopic reverse of β-hydride elimination. The clever among you may notice that the use of migratory insertion to synthesize alkyl complexes seems inconsistent with our observation that its reverse is ubiquitous for metal alkyls—shouldn't equilibrium favor the olefin hydride complex? In many cases this is the case; however, there are some notable exceptions. For example, perfluoroalkyl complexes are exceptionally stable (why?), so the insertion of fluoroalkenes is often favored over elimination.

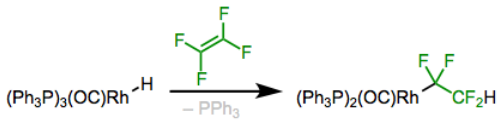


Figure 2.5.1: Why does this work? Thank fluorine! (Copyright; author via source)

As we noted above, we can still invoke kinetically stable alkyl complexes as *intermediates* in reactions provided subsequent steps are faster. In the next post, we'll examine the general classes of reactions in which alkyl complexes find themselves the major players, focusing on the specific mechanistic steps that involve the alkyl complex (reductive elimination, transmetalation, migratory insertion, and [naturally] β-hydride elimination).

Part 3:

In this last post on alkyl ligands, we'll explore the major modes of reactivity of metal alkyls. We've discussed β-hydride elimination in detail, but other fates of metal alkyls include reductive elimination, transmetallation, and migratory insertion into the M–C bond. In a similar manner to our studies of other ligands, we'd like to relate the steric and electronic properties of the metal alkyl complex to its propensity to undergo these reactions. This kind of thinking is particularly important when we're interested in controlling the relative rates and/or extents of two different, competing reaction pathways.

Reactions of Metal Alkyl Complexes

Recall that **β-hydride elimination** is an extremely common—and sometimes problematic—transformation of metal alkyls. Then again, there are reactions for which β-hydride elimination is desirable, such as the Heck reaction. Structural modifications that strengthen the M–H bond relative to the M–C bond encourage β-hydride elimination; the step can also be driven by trapping of the metal hydride product with a base (the Heck reaction uses this idea).

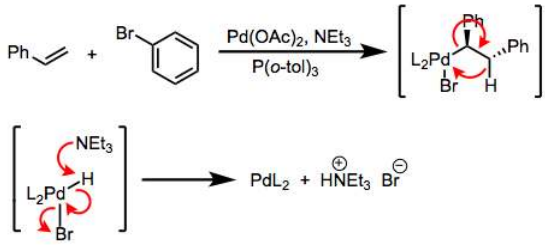


Figure 2.5.1: During the Heck reaction, beta-hydride elimination is driven by a base. (Copyright; author via source)

On the flip side, stabilization of the M–C bond discourages elimination and encourages its reverse: migratory insertion of olefins into M–H. Previously we saw the example of perfluoroalkyl ligands, which possess exceptionally stable M–C bonds. The fundamental idea here—that electron-withdrawing groups on the alkyl ligand stabilize the M–C bond—is quite general. Hartwig

describes an increase in the "ionic character" of the M–C bond upon the addition of electron-withdrawing groups to the alkyl ligand (thereby strengthening the M–C bond, since ionic bonds are stronger than covalent bonds). Bond energies from organic chemistry bear out this idea to an extent; for instance, see the relative BDEs of Me–Me, Me–Ph, and Me–CCH in this reference. I still find this explanation a little "hand-wavy," but it serves our purpose, I suppose.

Metal alkyls are subject to **reductive elimination**, the microscopic reverse of oxidative addition. The metal loses two covalent ligands, its formal oxidation state decreases by two units, total electron count decreases by two units, and an R–X bond forms. Reductive elimination is favorable when the R–X bond in the organic product is more stable than the M–R and M–X bonds in the starting complex (a thermodynamic issue). It should be noted, however, that the kinetics of reductive elimination depend substantially on the steric bulk of the eliminating ligands. Concerted reductive elimination of R–H usually possesses a lower activation energy than R–R elimination.

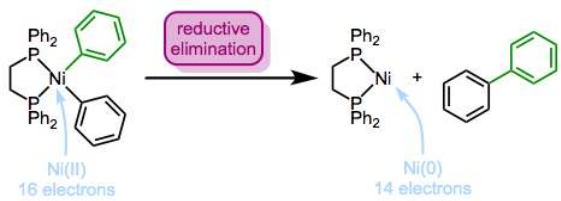


Figure 2.5.1: An example of reductive elimination. Intuitively, the electron density at the metal center increases as this step proceeds. (Copyright; author via source)

Transmetalation involves the transfer of an alkyl ligand from one metal to the other. An interesting problem concerns the relative reactivity of metal alkyls toward transmetalation. Assuming similar, uncomplicated ligand sets, which of two metal centers is more likely to hold on to an alkyl ligand? Consider the two situations below.

$$\mathrm{MR} + \mathrm{M'} \rightleftharpoons \mathrm{M} + \mathrm{M'R}$$

$$\mathrm{MR} + \mathrm{M'R'} \rightleftharpoons \mathrm{MR'} + \mathrm{M'R}$$

The first is a *bona fide* transmetalation; the second is really a double replacement reaction. The distinction is rarely drawn in practice, but it's important! The difference is that in the first case, a single-electron transfer of sorts must take place, while in the second case, no redox chemistry is necessary. Favorability in the first case is governed by the relative reduction potentials of M and M' (the reaction goes forward when M' is more easily oxidized than M); in the second case, the relative electropositivities of the metals is key, and other factors like lattice energies may be important. The distinction between transmetalation *per se* and double replacement explains the paradoxical synthetic sequence in the figure below. In practice, both are called "transmetalation." See these slides (page 6) for a summarizing reference.

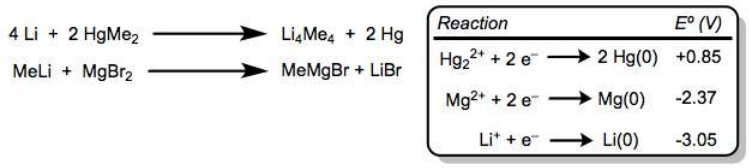


Figure 2.5.1: How are both of these reactions favorable? The first is a true transmetalation; the second is a double replacement. (Copyright; author via source)

This brings our extended look at metal alkyl complexes to a temporary close. Of course, metal alkyls are *everywhere* in organometallic chemistry…so seeing them again is pretty much inevitable! The next installment in the Epic Ligand Survey series concerns allyl, cyclopentadienyl, and other odd-membered pi systems. These L_nX-type ligands can, like arenes, pile as many as six electrons on the metal center at once.

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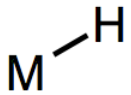
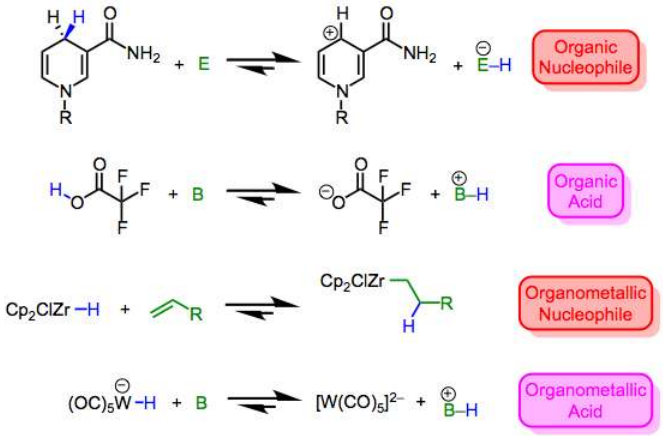
2.6: Metal Hydrides

Metal-hydrogen bonds, also known (misleadingly) as **metal hydrides**, are ubiquitous X-type ligands in organometallic chemistry. There is much more than meets the eye to most M-H bonds: although they're simple to draw, they vary enormously in polarization and pKa. They may be acidic or hydridic or both, depending on the nature of the metal center and the reaction conditions. In this post, we'll develop some heuristics for predicting the behavior of M-H bonds and discuss their major modes of reactivity (acidity, radical reactions, migratory insertion, etc.). We'll also touch on the most widely used synthetic methods to form metal hydrides.



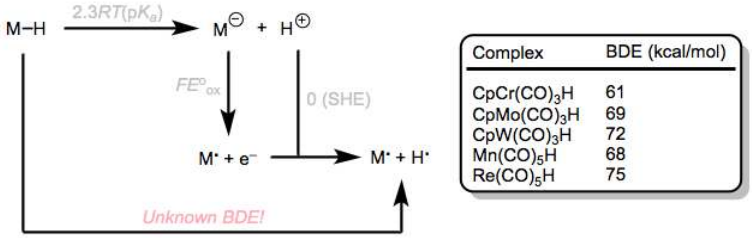
General Properties

Metal hydrides run the gamut from nucleophilic/basic to electrophilic/acidic. Then again, the same can be said of X–H bonds in organic chemistry, which may vary from mildly nucleophilic (consider Hantzsch esters and NADH) to extremely electrophilic (consider triflic acid). As hydrogen is what it is in both cases, it's clear that the nature of the X fragment—more specifically, the stability of the charged fragments X+ and X——dictate the character of the X–H bond. Compare the four equilibria outlined below—the stabilities of the ions dictate the position of each equilibrium. By now we shouldn't find it surprising that the highly π-acidic W(CO)5 fragment is good at stabilizing negative charge; for a similar reason, the ZrCp2Cl fragment can stabilize positive charge.*



Metal-hydrogen bonds may be either hydridic (nucleophilic) or acidic (electrophilic). The nature of other ligands and the reaction conditions are keys to making predictions.

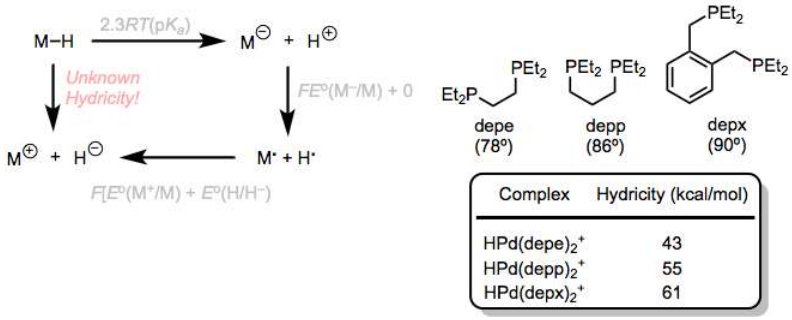
Let's turn our attention now to *homolytic* M–H bond strength. A convenient thermodynamic cycle allows us to use the acidity of M–H and the oxidation potential of its conjugate base in order to determine bond strength. This clever method, employed by Tilset and inspired by the inimitable Bordwell, uses the cycle in the figure below. BDE values for some complexes are provided as well. From the examples provided, we can see that bond strength increases down a group in the periodic table. This trend, and the idea that bridging hydrides have larger BDEs than terminal M–H bonds, are just about the only observable trends in M–H BDE.



A clever cycle for determining BDEs from other known quantities, with select BDE values. I've left out solvation terms from the thermodynamic cycle. For more details, see the Tilset link above.

Why is knowing M-H BDEs useful? For one thing, the relative BDEs of M-C and M-H bonds determine the thermodynamics of β-hydride elimination, which results in the replacement of a covalent M-C bond with an M-H bond. Secondly, complexes containing weak M-H bonds are often good hydrogen transfer agents and may react with organic radicals and double bonds, channeling stannane and silane reductants from organic chemistry.

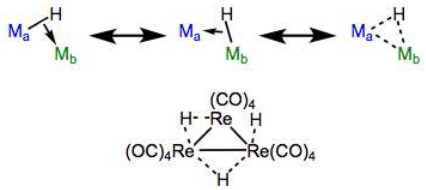
Hydricity refers to the tendency of a hydride ligand to depart as H–. A similar thermodynamic cycle relates the energetics of losing H– to the oxidation potentials of the conjugate base and the oxidized conjugate base; however, this method is complicated by the fact that hydride loss establishes an open coordination site. I've provided an abridged version of the cycle below. Hydricities are somewhat predictable from the electronic and steric properties of the metal center: inclusion of electron-donating ligands tends to increase hydricity, while electron-withdrawing or acidic ligands tend to decrease it. For five-coordinate hydrides that form 16-electron, square planar complexes upon loss of hydride, the bite angle of chelating phosphines plays an interesting role. As bite angle increases, hydricity does as well.



Complex	Hydricity (kcal/mol)
$HPd(depe)_2^+$	43
$HPd(depp)_2^+$	55
$HPd(depx)_2^+$	61

A thermodynamic cycle for hydricity, with some examples. Hydricity and bite angle are well correlated in five-coordinate palladium hydrides.

Bridging hydrides are an intriguing class of ligands. A question to ponder: how can a ligand associated with only two electrons possibly bridge two metal centers? How can two electrons hold three atoms together? Enter the magic of three-center, two-electron bonding. We can envision the M–H sigma bond as an electron donor itself! With this in mind, we can imagine that hydrides are able to bind end-on to one metal (like a standard X-type ligand) and side-on to another (like an L-type π system ligand, but using sigma electrons instead). Slick, no? We'll see more side-on bonding of sigma electrons in a future post on sigma complexes.



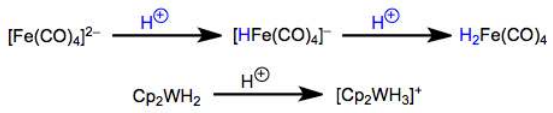
Resonance forms of bridging hydrides, with an example. Sigma complexes like these show up in other contexts, too!

Consistent with the idea that bridging is the result of "end-on + side-on" bonding, bond angles of bridging hydrides are never 180°.

Synthesis

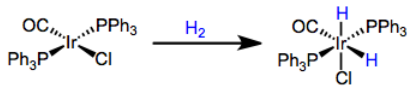
Here we'll discuss four ways to make hydrides: metal protonation, oxidative addition of H2, addition of nucleophilic main-group hydrides (borohydrides, aluminum hydrides, and silanes), and β-hydride elimination.

Just as in organic chemistry, the basicity of an organometallic complex is inversely related to the acidity of its conjugate base. Furthermore, charges have a predictable effect on the basicity of organometallic complexes: negatively charged complexes lacking π-acidic ligands are highly basic. Even neutral complexes containing strong donor ligands, like the tungsten complex below, can be protonated effectively. Notice that protonation is actually a kind of oxidative addition—the oxidation state of Fe in the first reaction below goes from -2 to 0 to +2! All coordination events of isolated electrophiles can also be viewed in this light. Reactions of this type are sometimes called **oxidative ligations** to distinguish them from oxidative addition reactions, which involve the addition of two ligands to the metal center with oxidation.



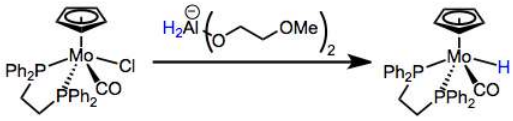
Metal protonation reactions involve the metal center as a base.

Contrast oxidative ligation with the **oxidative addition** of dihydrogen (H2), a second method for the synthesis of hydride complexes. A key requirement here is that the starting metal center is at least d2—two electrons are formally lost from the metal center, and metals can't possess a negative number of d electrons. An open coordination site on the starting material must also be present (or possible through ligand dissociation). The reaction below is a standard example of the addition of H2 to Vaska's complex, but there are some funky variations on this theme. These riffs include third-order homolytic cleavage of H2 by two metal radicals, and oxidative addition followed by deprotonation by the starting complex (apparent heterolytic cleavage).



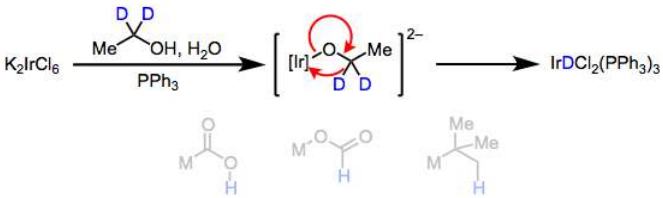
Oxidative addition of dihydrogen for the synthesis of metal hydrides.

Main-group hydrides like borohydrides and aluminum hydrides are great sources of H– for organometallic complexes. These reactions seem more natural than metal protonations, since we often think of metals as electropositive or electrophilic species. Indeed, the combination of main-group sources of nucleophilic hydride with complexes containing metal–leaving group bonds is a very general method for the synthesis of metal hydride complexes. Check out the reaction below—what's the most likely mechanism? Is associative or dissocative substitution more likely? Hint: count electrons!



Nucleophilic substitution with a hydride source. What's the most likely mechanism?

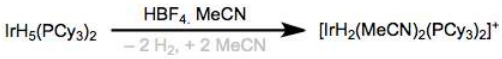
β-hydride elimination forms metal hydride complexes and double bonds within organic ligands. Alkoxide ligands are commonly used for this purpose—elimination to form the hydride complex and aldehyde is more favorable than the reverse, migratory insertion of C=O into the M–H bond. Since the unsaturated byproduct is thrown away, it's desirable to make it something small, cheap, and gaseous. Hydroxycarbonyl, formate, and tert-butyl ligands have been applied successfully with this goal in mind…what are the byproducts?



Beta-hydride elimination for the synthesis of metal hydrides.

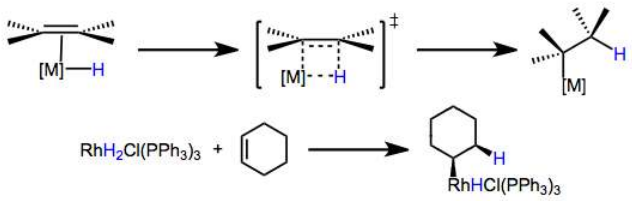
Reactions

Metal hydrides are characterized by nucleophilic, electrophilic, and radical behavior. The exact behavior of a given metal hydride complex depends on its electronic properties, its M–H bond dissociation energy, and the nature of the reacting partner. Basic metal hydrides react with acids to free up a coordination site on the metal center (file this reaction alongside photolytic M–CO cleavage and M–CO cleavage with amine oxides).



"Protonolysis" generates two open coordination sites with loss of hydrogen gas.

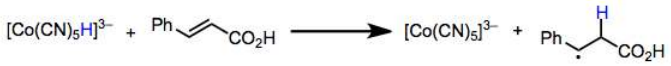
Migratory insertion reactions involving M–H bonds are extremely important in a practical sense (see hydrogenation and hydroformylation), and are conceptually related to nucleophilic hydride transfers from the metal center. We can think of insertions of π bonds into M–H as internal nucleophilic attack by the hydride ligand at one end of the π bond, with coordination of the metal center to the other. The figure below depicts the transition state for migratory insertion of an olefin into M–H and an example reaction. Notice the coplanarity of M, H, and the C=C bond in the transition state for insertion, which determines the cis configuration of the product. The same is required for the microscopic reverse (β-hydride elimination) but this essential geometry is easily overlooked for β-hydride elimination.



Migratory insertion of an olefin into M–H. Note the relative configuration of M–C and C–H!

It is important to note that insertions of CO into M–H bonds are rare, because such insertions are usually unfavorable thermodynamically.

Finally, the radical behavior of certain metal hydrides in the presence of olefins deserves a nod. The behavior of the cobalt hydride complex in the reaction below is typical of these types of reactions.



Hydrogen atom transfer to olefins. Radical reduction of carbon tetrachloride is a related process.

And there you have it: the properties, synthesis, and reactivity of metal hydrides in a nutshell. Like other ligands we've seen so far, the behavior of hydrides is controlled by the nature of the metal center and its accompanying ligands. However, it's interesting to note that the observed behavior of hydrides often depends on the nature of the reaction conditions, as well. Some complexes display "schizophrenic" behavior, so to speak, putting on their nucleophile hat in the presence of an electrophile and their electrophile hat in the presence of a nucleophile.

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2.7: N-heterocyclic Carbenes

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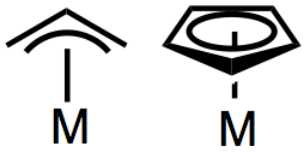
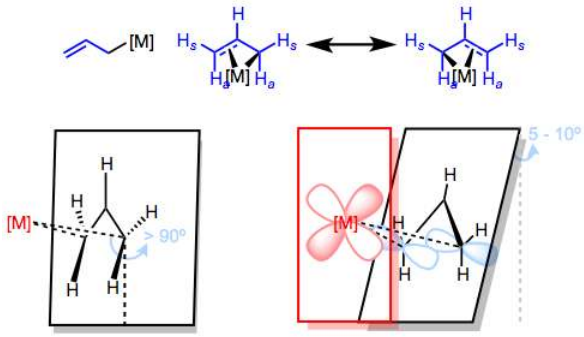
2.8: Odd-numbered π Systems

Odd-numbered π systems—most notably, the allyl and cyclopentadienyl ligands—are formally LnX-type ligands bound covalently through one atom (the “odd man out”) and datively through the others. This formal description is incomplete, however, as resonance structures reveal that multiple atoms within three- and five-atom π systems can be considered as covalently bound to the metal. To illustrate the plurality of equally important resonance structures for this class of ligands, we often just draw a curved line from one end of the π system to the other. Yet, even this form is not perfect, as it obscures the possibility that the datively bound atoms may dissociate from the metal center, forming σ-allyl or ring-slipped ligands. What do the odd-numbered π systems really look like, and how do they really behave?



General Properties

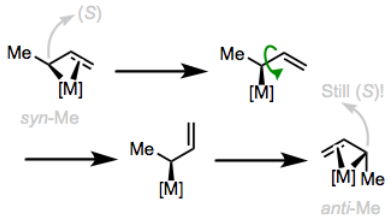
Allyls are often actor ligands, most famously in allylic substitution reactions. The allyl ligand is an interesting beast because it may bind to metals in two ways. When its double bond does not become involved in binding to the metal, allyl is a simple X-type ligand bound covalently through one carbon—basically, a monodentate alkyl! Alternatively, allyl can act as a bidentate LX-type ligand, bound to the metal through all three conjugated atoms. The LX or “trihapto” form can be represented using one of two resonance forms, or (more common) the “toilet-bowl” form seen in the general figure above. I don’t like the toilet-bowl form despite its ubiquity, as it tends to obscure the important dynamic possibilities of the allyl ligand.



Can we use FMO theory to explain the wonky geometry of the allyl ligand?

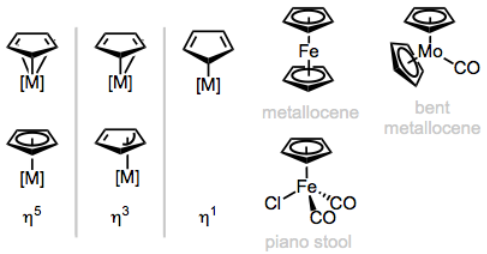
The lower half of the figure above illustrates the slightly weird character of the geometry of allyl ligands. In a previous post on even-numbered π systems, we investigated the orientation of the ligand with respect to the metal and came to some logical conclusions by invoking FMO theory and backbonding. A similar treatment of the allyl ligand leads us to similar conclusions: the plane of the allyl ligand should be parallel to the xy-plane of the metal center and normal to the z-axis. In reality, the allyl plane is slightly canted to optimize orbital overlap—but we can see at the right of the figure above that π2–dxy orbital overlap is key. Also note the rotation of the anti hydrogens (anti to the central C–H, that is) toward the metal center to improve orbital overlap.

Exchange of the syn and anti substituents can occur through σ,π-isomerization followed by bond rotation and formation of the isomerized trihapto form. Notice that the configuration of the stereocenter bearing the methyl group is unaffected by the isomerization! It should be noted that 1,3-disubstituted allyl complexes almost exclusively adopt a syn,syn configuration without danger of isomerization.



The methylene and central C–H simply change places!

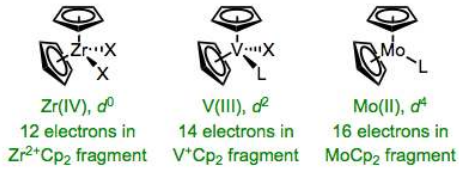
Upon deconstruction, the cyclopentadienyl (Cp) ligand yields the aromatic cyclopentadienyl anion, an L2X-type ligand. Cp is normally an η5-ligand, but η3 (LX) and η1 (X) forms are known in cases where the other ligands on the metal center are tightly bound. η1-Cyclopentadienyl ligands can sometimes be fluxional—the metal has the ability to "jump" from atom to atom. Variations on the Cp theme include Cp* (C5Me5) and the monomethyl version (C5H4Me). Cp may be found as a loner alongside other ligands (in "half-sandwich" or "piano-stool" complexes), or paired up with a second Cp ligand in metallocenes. The piano-stool and bent metallocene complexes are most interesting for us, since these have potential for open coordination sites—plain vanilla metallocenes tend to be relatively stable and boring.



Binding modes of Cp and general classes of Cp complexes.

Research for this post has made me appreciate the remarkable electron-donating ability of the cyclopentadienyl (Cp) ligand, which renders its associated metal center electron rich. The LUMO of Cp is high in energy, so the ligand is a weak π-acid and is, first and foremost, a σ-donor. This effect is apparent in the strong backbonding displayed by Cp carbonyl complexes. Despite its strong donating ability, Cp is rarely an actor ligand unless another ligand shakes things up—check out the nucleophilic reactivity of doubly jazzed-up ferrocene for a nice example.

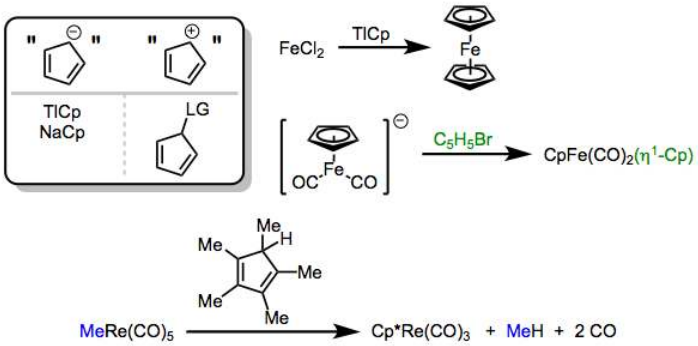
It's critical to recognize that η5-Cp is a six-electron ligand (!). Because Cp piles on electrons, the numbers of ligands bound to the metal in Cp complexes tend to be lower than we might be used to, especially in bent metallocenes containing two Cp's. Still, the number of ligands we'd expect on the metal center in these complexes is perfectly predictable. We just need to keep in mind that the resulting complexes are likely to contain 16 or 18 total electrons.



By considering the MCp2 fragment, we can predict the nature of ancillary ligands in bent metallocenes.

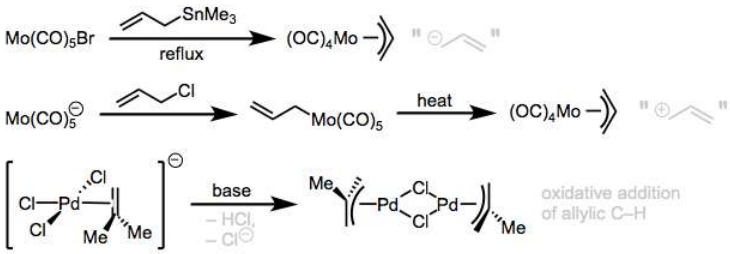
Synthesis

Crabtree cleanly divides methods for the synthesis of Cp complexes into those employing Cp+ equivalents, Cp– equivalents, and the neutral diene. Naturally, the first class of reagents are appropriate for electron-rich, nucleophilic complexes, while the second class are best used in conjunction with electron-poor, electrophilic complexes. The figure below provides a few examples.



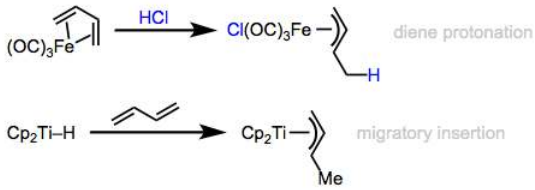
Methods for the synthesis of Cp complexes. The possibilities are exhausted by anionic, cationic, and neutral Cp equivalents!

Methods for synthesizing allyl complexes can also be classified according to whether the allyl donor is a cationic, anionic, or neutral allyl equivalent. In metal-catalyzed allylic substitution reactions, the allyl donor is usually a good electrophile bearing a leaving group displaced by the metal (an allyl cation equivalent). However, similar complexes may be obtained through oxidative addition of an allylic C–H bond to the metal, as in the synthesis of methallyl palladium chloride dimer below. Transmetalation of nucleophilic allyls from one metal to another, which we can imagine as nucleophilic attacks of an anionic allyl group, are useful when the metal is electron-poor.



Nucleophilic, electrophilic, and neutral allyl donors.

Complexes containing conjugated dienes are also viable precursors to allyl complexes. Migratory insertion of a diene into the M–H bond is a nice route to methyl-substituted allyl complexes, for example. Interestingly, analogous insertions of fulvenes do not appear to lead to Cp complexes, but some funky reductive couplings that yield ansa-metallocenes are known. External electrophilic attack (e.g., protonation) and nucleophilic attack on coordinated dienes also result in allyl complexes. In essence, one double bond of the diene becomes a part of the allyl ligand in the product; the other is used as a “handle” to establish the key covalent bond to the allyl ligand.

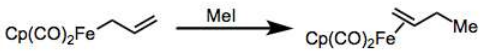


Dienes: brave crusaders in the quest for allyl complexes.

Reactions

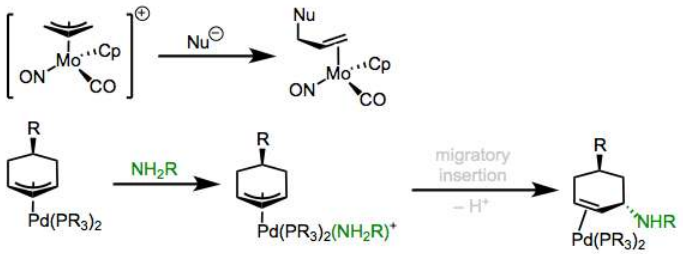
Since the Cp ligand is typically a spectator, we’ll focus in this section on the reactivity of allyl ligands. As usual, the behavior of the allyl ligand depends profoundly on the nature of its coordinated metal center, which depends in turn on the metal’s ancillary ligands. Avoid “tunnel vision” as you study the examples below—depending on the issue at hand, the ancillary ligands may be as important as (or more important than) the actor ligand.

Nucleophilic allyl complexes react with electrophiles like H+, MeI, X+, and acylium ions to yield cationic alkene complexes.



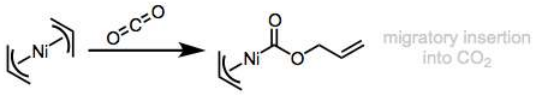
Attack of electrophiles on nucleophilic allyl complexes. Notice the donating Cp ligand!

In a conceptually related process, nucleophiles can attack allyl ligands bound to electrophilic metals. This process is key in allylic substitution reactions. In some cases, the nucleophile is known to bind to the metal first, then transfer to the allyl ligand through reductive elimination. Alternatively, direct attack on the allyl ligand may occur on the face opposite the metal. The figure below illustrates both possibilities.



External and internal attack of nucleophiles on coordinated allyl ligands.

Migratory insertion of allyl ligands is known, and is analogous to insertions involving alkyl ligands (see the figure below). Movement of the allyl ligand toward the coordination site of the dative ligand is assumed. Of course if oxidative addition to form allyl complexes is possible, reductive elimination of allyl ligands with other X-type ligands is also possible. We'll hit on these process in more detail in their dedicated posts.



Like alkyl ligands, allyls can migrate onto dative ligands like CO and π bonds.

One final post on σ-complexes will bring this series to a temporary close. In the next post, we'll look at ligands that, rather surprisingly, bind through their σ-electrons. These "non-classical" ligands behave like other dative ligands we've seen before, but are important for many reactions that involve main-group single bonds, such as oxidative addition. Before their discovery, the relevance of σ-ligands for reaction mechanisms went unappreciated by organometallic chemists.

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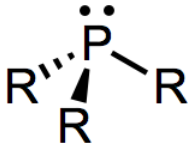
2.9: Phosphines

The epic ligand survey continues with tertiary phosphines, PR_3. Phosphines are most notable for their remarkable electronic and steric tunability and their "innocence"—they tend to avoid participating directly in organometallic reactions, but have the ability to profoundly modulate the electronic properties of the metal center to which they're bound. Furthermore, because the energy barrier to umbrella flipping of phosphines is quite high, "chiral-at-phosphorus" ligands can be isolated in enantioenriched form and introduced to metal centers, bringing asymmetry just about as close to the metal as it can get in chiral complexes. Phosphorus NMR is a technique that Just Works (thanks, nature). Soft phosphines match up very well with the soft low-valent transition metals. Electron-poor phosphines are even good π-acids!

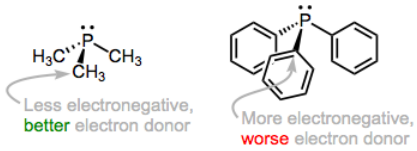


General Properties

Like CO, phosphines are dative, L-type ligands that formally contribute two electrons to the metal center. Unlike CO, most phosphines are not small enough to form more than four bonds to a single metal center (and for large R, the number is even smaller). Steric hindrance becomes a problem when five or more PR_3 ligands try to make their way into the space around the metal. An interesting consequence of this fact is that many phosphine-containing complexes do not possess 18 valence electrons. Examples include $Pt(PCy_3)_2$, $Pd[P(t\text{-}Bu)_3]_2$, and $[Rh(PPh_3)_3]^+$. Doesn't that just drive you crazy? It drives the complexes crazy as well—and most of these coordinatively unsaturated compounds are wonderful catalysts.

Bridging by phosphines is extremely rare, but ligands containing multiple phosphine donors that bind in an L_n (n > 1) fashion to a single metal center are all over the place. These ligands are called chelating or polydentate to indicate that they latch on to metal centers through multiple binding sites. For entropic reasons, chelating ligands bind to a single metal center at multiple points if possible, instead of attaching to two different metal centers (the aptly named chelate effect). An important characteristic of chelating phosphines is bite angle, defined as the predominant P–M–P angle in known complexes of the ligand. We'll get into the interesting effects of bite angle later, but for now, we might imagine how "unhappy" a ligand with a preferred bite angle of 120° would be in the square planar geometry. It would much rather prefer to be part of a trigonal bipyramidal complex, for instance.

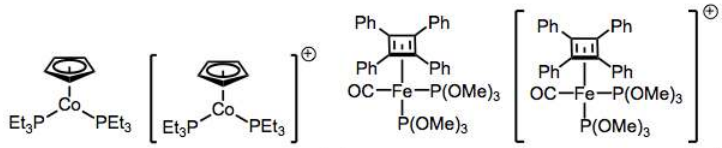
The predominant orbital interaction contributing to phosphine binding is the one we expect, a lone pair on phosphorus interacting with an empty metallic d orbital. The electronic nature of the R groups influences the electron-donating ability of the phosphorus atom. For instance, alkylphosphines, which possess P–Csp^3 bonds, tend to be better electron donors than arylphosphines, which possess P–Csp^2 bonds. The rationale here is the greater electronegativity of the sp^2 hybrid orbital versus the sp3 hybrid, which causes the phosphorus atom to hold more tightly to its lone pair when bound to an sp^2 carbon. The same idea applies when electron-withdrawing and -donating groups are incorporated into R: the electron density on P is low when R contains electron-withdrawing groups and high when R contains electron-donating groups. Ligands (and associated metals) in the former class are called electron poor, while those in the latter class are electron rich.



As we add electronegative R groups, the phosphorus atom (and the metal to which it's bound) become more electron poor.

Like CO, phosphines participate in backbonding to a certain degree; however, the phenomenon here is of a fundamentally different nature than CO backbonding. For one thing, phosphines lack a π* orbital. In the days of yore, chemists attributed backbonding in phosphine complexes to an interaction between a metallic dπ orbital and an empty 3d orbital on phosphorus. However, this idea has elegantly been proven bogus, and a much more organicker-friendly explanation has taken its place (no d orbitals on P required!). In an illuminating series of experiments, M–P and P–R bond lengths were measured via crystallography for several redox pairs of

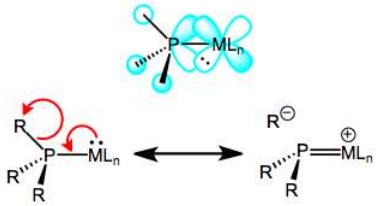
complexes. I've chosen two illustrative examples, although the linked reference is chock full of other pairs. The question is: how do we explain the changes in bond length upon oxidation?



M–P	2.218 Å	2.230 Å	**M–P**	2.146 Å	2.261 Å
P–R	1.846 Å	1.829 Å	**P–R**	1.598 Å	1.578 Å

Upon oxidation, M–P bond lengths increase and and P–R bond lengths decrease. Why?

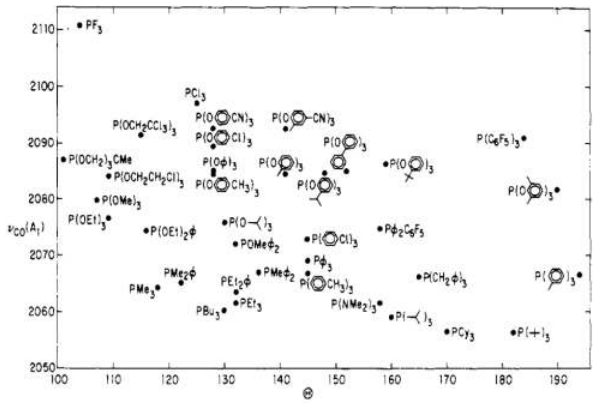
Oxidation decreases the ability of the metal to backbond, because it removes electron density from the metal. This explains the increases in M–P bond length—just imagine a decrease the M–P bond order due to worse backbonding. And the decrease in P–R bond length? It's important to see that invoking only the phosphorus 3d orbitals would not explain changes in the P–R bond lengths, as the 3d atomic orbitals are most definitely localized on phosphorus. Instead, we must invoke the participation of σ*P–R orbitals in phosphine backbonding to account for the P–R length decreases. When all is said and done, the LUMO of the free phosphine has mostly P–R antibonding character, with some 3d thrown into the mix. The figure below depicts one of the interactions involved in M–P backbonding, a dπ → σ* interaction (an orthogonal dπ → σ* interaction also plays a role). As with CO, a resonance structure depicting an M=P double bond is a useful heuristic! Naturally, R groups that are better able to stabilize negative charge—that is, electron-withdrawing groups—facilitate backbonding in phosphines. Electron-rich metals help too.



Backbonding in phosphines, a sigma-bond-breaking affair.

The steric and electronic properties of phosphines vary enormously. Tolman devised some intriguing parameters that characterize the steric and electronic properties of this class of ligands. To address sterics, he developed the idea of cone angle—the apex angle of a cone formed by a point 2.28 Å from the phosphorus atom (an idealized M–P bond length), and the outermost edges of atoms in the R groups, when the R groups are folded back as much as possible. Wider cone angles, Tolman reasoned, indicate greater steric congestion around the phosphorus atom. To address electronics, Tolman used a not-so-old friend of ours—the CO stretching frequency (νCO) of mixed phosphine-carbonyl complexes. Specifically, he used Ni(CO)3L complexes, where L is a tertiary phosphine, as his standard. Can you anticipate Tolman's logic? How should νCO change as the electron-donating ability of the phosphine ligands increases?

Tolman's logic went as follows: more strongly electron-donating phosphines are associated with more electron-rich metals, which are better at CO backbonding (due fundamentally to higher orbital energies). Better CO backbonding corresponds to a lower νCO due to decreased C–O bond order. Thus, better donor ligands should be associated with lower νCO values (and vice versa for electron-withdrawing ligands). Was he correct? Exhibit A…

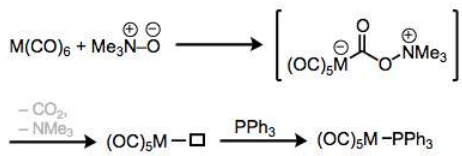


Tolman's map of the steric and electronic properties of phosphine ligands.

Notice the poor ligand trifluorophosphine stuck in the “very small, very withdrawing” corner, and its utter opposite, the gargantuan tri(tert-butyl)phosphine in the “extremely bulky, very donating” corner. Intriguing! One can learn a great deal just by studying this chart.

Synthesis

Phosphine complexes are most commonly made through ligand substitution processes—the exchange of one ligand for another on a metal center. One interesting method utilizes tertiary N-oxides to essentially “oxidize off” a CO ligand, leaving behind an open coordination site that may be filled by a phosphine. Notice that the carbon of CO is behaving as an electrophile in this process. Shi and Basolo masterfully demonstrate that an intermediate amine complex cannot be involved in this mechanism. Irradiation by ultraviolet light is an alternative method to coax the CO ligand off of metal carbonyl complexes.



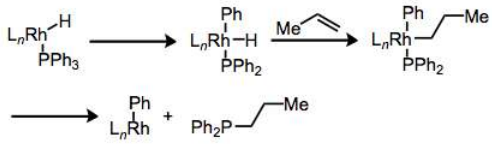
Ligand substitution with the help of trimethylamine oxide.

Methods for synthesizing the phosphine ligands themselves are somewhat beyond our scope, but electrophilic phosphorus chemistry is common, particularly when arylphosphines are the target.

Reactions

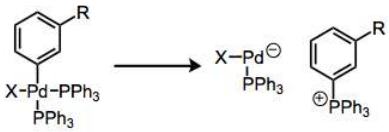
Phosphines are most often spectator ligands, meaning that they don’t participate in reactions, but hang on for the ride. There are, however, some important exceptions to this rule. First of all, dissociation of a phosphine ligand is often required to generate a site of coordinative unsaturation before catalytic reactions can begin. Good examples are cross-couplings employing the saturated $Pd(PPh_3)_4$. This complex is actually just a precatalyst that must lose phosphine ligands to enter the catalytic cycle of cross-coupling. Phosphine association is also an important step of many catalytic reactions.

What decomposition pathways are available to phosphine ligands? P–C bond cleavage is a surprisingly common process. In general, the idea is that the metal center can insert into the P–C bond via concerted oxidative addition, then reductively eliminate to establish a new P–C bond. Reductive elimination can even occur after some intermediate steps, as in the example below.



P–C bond cleavage: also known as the "R group shuffle."

Phosphonium salt formation from arylphosphine complexes is a related process. Here, the complex essentially just falls apart after P–C reductive elimination.



Reductive elimination to form phosphonium salts.

Phosphine ligands are everywhere, and we'll definitely see more of this fascinating class of ligands in the future. They are particularly powerful as the bearers of asymmetry in chiral metal complexes, which are used to prepare enantioenriched organic products.

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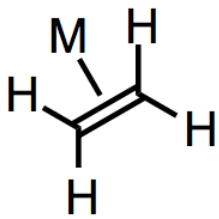
2.10: π Systems

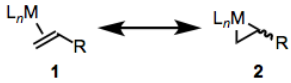
With this post, we finally reach our first class of dative **actor** ligands, **π systems**. In contrast to the **spectator** L-type ligands we've seen so far, π systems most often play an important role in the reactivity of the OM complexes of which they are a part (since they act in reactions, they're 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

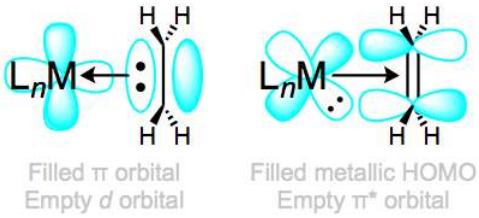
The π bonding orbitals of alkenes, alkynes, carbonyls, and other unsaturated compounds may overlap with dσ orbitals on metal centers. This is the classic ligand HOMO → metal LUMO interaction that we've beaten into the ground over the last few posts. Because of this electron donation from the π system 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.



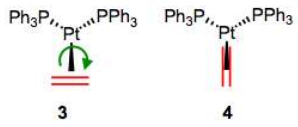
Resonance forms of alkene ligands.

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?



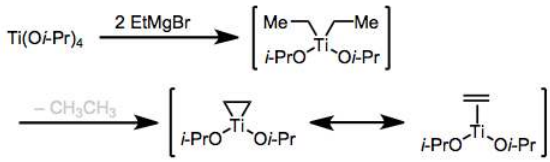
Two limiting cases for alkene orientation in a trigonal planar complex.

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 dxy and dx2–y2 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).



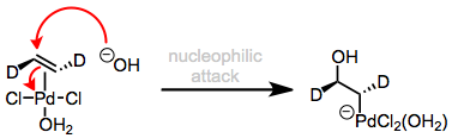
Kulinkovich synthesis of alkene complexes. A remarkable loss of ethane!

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…

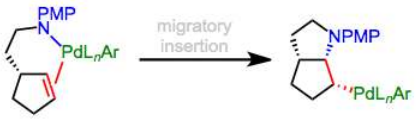
- Which atom gets the nucleophile/migrating group?
- Which atom gets the metal?
- What is the relative orientation of the nucleophile/migrating group and the metal (cis or trans)?

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.

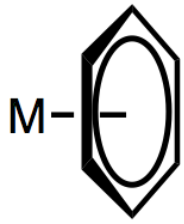


cis-Aminopalladation via migratory insertion. Two new bonds are established with stereospecificity!

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!

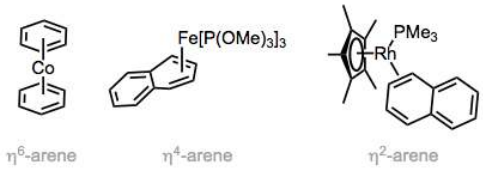
Arene or **aromatic ligands** are the subject of this post, the second in our series on π-system ligands. Arenes are dative, L-type ligands that may serve either as actors or spectators. Arenes commonly bind to metals through more than two atoms, although η2-arene ligands are known. Structurally, most 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.



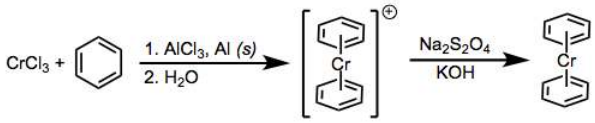
Arene ligands exhibit multiple coordination modes.

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

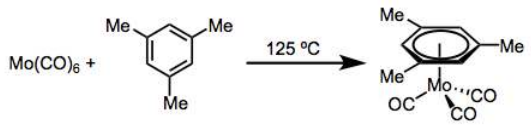
There are two common methods for the stoichiometric synthesis of arene "sandwich" complexes, in which a metal is squished between two arenes. Starting from a metal halide, treatment with a Lewis acid and mild reductant rips off the halogen atoms and replaces them with arene ligands. The scope of this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

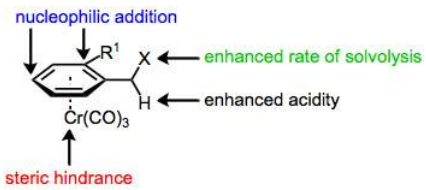
Syntheses of metal arene carbonyl complexes take advantage of the fact that arenes are strongly binding, “chelating” ligands. Infrared spectroscopic studies have shown that a single benzene ligand is a stronger electron donor than three CO ligands—C–O stretching frequencies are lower in metal arene carbonyls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

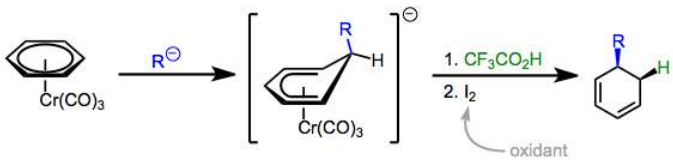
It’s important here to distinguish aromatic X-type ligands from the topic of this post, Ln-type arenes bound only through their π systems. The figure below nicely summarizes the typical behavior of arene ligands coordinated through their π clouds. Although the figure is for chromium carbonyls specifically, 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.

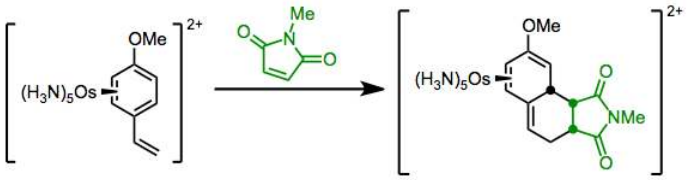
Since the coordination of arenes to metals depletes electron density on the arene, it makes sense that metal-arene complexes should be susceptible to nucleophilic aromatic substitution (NAS). In fact, NAS on metal-coordinated arene ligands has been extensively developed for several different metals. 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 η_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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CHAPTER OVERVIEW

3: Structural Fundamentals

3.1: Ligand Field Theory and Frontier Molecular Orbital Theory
3.2: Open Coordination Site
3.3: Periodic Trends of the Transition Metals
3.4: Predicting the Geometry of Organometallic Complexes
3.5: Simplifying the Organometallic Complex (Part 1)
3.6: Simplifying the Organometallic Complex (Part 2)
3.7: Simplifying the Organometallic Complex (Part 3)

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3.1: Ligand Field Theory and Frontier Molecular Orbital Theory

In this post, we'll begin to explore the molecular orbital theory of organometallic complexes. Some background in molecular orbital theory will be beneficial; an understanding of organic frontier molecular orbital theory is particularly helpful. Check out Fukui's Nobel Prize lecture for an introduction to FMO theory. The theories described here try to address how the approach of ligands to a transition metal center modifies the electronics of the metal and ligands. The last post on geometry touched on these ideas a little, but we'll dig a little deeper here. Notably, we need to address the often forgotten influence of the metal on the ligands—how might a metal modify the reactivity of organic ligands?

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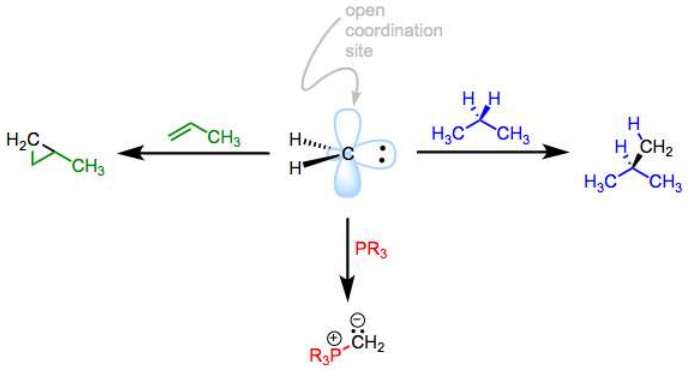
3.2: Open Coordination Site

The concept of coordinative unsaturation can be confusing for the student of organometallic chemistry, but recognizing open coordination sites in OM complexes is a critical skill.

Introduction

Let's begin with a famous example of coordinative unsaturation from organic chemistry.



An analogy from organic chemistry. The reactivity of the carbene flows from its open coordination site.

Carbenes are both nucleophilic and electrophilic, but the essence of their electrophilicity comes from the fact that they don't have their fair share of electrons (8). They have not been saturated with electrons—carbenes want more! To achieve saturation, carbenes may inherit a pair of electrons from a σ bond (σ-bond insertion), π bond (cyclopropanation), or lone pair (ylide formation). Notice that, simply by spotting coordinative unsaturation, we've been able to fully describe the carbene's reactivity! We can do the same with organometallic complexes—open coordination sites suggest specific reactivity patterns. That's why understanding coordinative unsaturation and recognizing its telltale sign (the open coordination site) are essential skills for the organometallic chemist.

Coordinative unsaturation is not just the possession of a coordination number less than 6, or an apparent space in which a ligand might be able to approach. Sixteen or fewer total electrons on the metal center are a second necessity—just as, in the organic case, 6 or fewer electrons on the unsaturated atom are essential. Sixteen or fewer total electrons and coordination number less than 6 add up to a more fundamental synonym for an open coordination site: an empty metal-centered orbital!

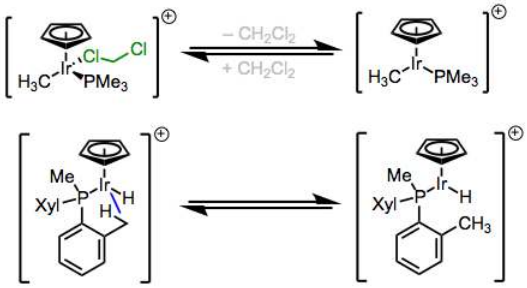
(<= 16 total electrons on M) + (< 6 coordination number on M) = empty d orbital on M

The lesson here is that we can't just look to the geometry of a complex to determine whether it bears an open coordination site—electron counting is essential too.

Like carbenes and carbocations, metal complexes containing open coordination sites don't just hang around. They react rapidly with all kinds of electron sources. Furthermore, you won't see them in stable starting materials or products. Thus, recognizing when a complex has the potential for an open site is important. What are some structural signs that point to the possibility of an open coordination site?

1. Weakly coordinating ligands

Ligand dissociation from an 18-electron complex produces an open coordination site. Solvent ligands and side-on σ ligands—both of which bind relatively weakly to metals—often engage in this process. Try counting electrons in the two pairs of cationic iridium complexes below.



Dissociation of weakly bound ligands reveals open coordination sites.

Dissociation of a π-system ligand may also reveal an open coordination site.

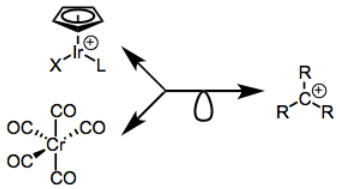
2. Reaction conditions encouraging dissociation

In this category, we might file away photochemical and amine-oxide-mediated dissociations of CO. Conditions like these encourage the loss of a ligand and subsequent replacement with something else, àla S_N1 substitution.

3. Potential for reductive elimination

Reductive elimination is the open coordination site's dream come true: two (sites) for the price of one (step)! Factors affecting the favorability of reductive elimination are beyond the scope of this post, but we can mention a couple here: steric crowding and an electron-poor metal.

Finally, it's important to note that open coordination sites often show up in fragments of OM complexes examined for one reason or another. We can relate these fragments to organic or main-group intermediates using isolobal analogies, powerful conceptual tools that we'll explore in detail in another post. For example, the fragment $(CO)_5Cr$ is isolobal with the organic carbocation—the two sets of frontier MOs are analogous, and both structures have an open coordination site.



All three of these analogous fragments bear an open coordination site.

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3.3: Periodic Trends of the Transition Metals

Periodic trends play a huge role in organic chemistry. Regular changes in electronegativity, atomic size, ionization energy, and other variables across the periodic table allow us to make systematic predictions about the behavior of similar compounds. Of course, the same is true for organometallic complexes! With a firm grip on the periodic trends of the transition metals, we can begin to make comparisons between complexes we're familiar with and those we've never seen before. Periodic trends essentially provide an exponential increase in predictive power. In this post, we'll hit on the major periodic trends of the transition metals and discuss a few examples for which these trends can be handy.

Before beginning, a couple of caveats are in order. First of all, many of the trends across the transition series are not perfectly regular. Hartwig wisely advises that one should consider the transition series in blocks instead of as a whole when considering periodic trends. For instance, general increases in a quantity may be punctuated by sudden decreases; in such a case, we may say that the quantity increases generally, but definite conclusions are only possible when the metals under comparison are close to one another in the periodic table (and we need to be careful about unexpected jumps). Secondly, periodic trends are significantly affected by the identity of ligands and the oxidation state of the metal center, so comparisons need to be appropriately controlled. Using periodic trends to compare a Pd(II) complex and a Ru(III) complex is largely an exercise in futility, but comparing Pt(II) and Pd(II) complexes with similar ligand sets is reasonable. Keep these ideas in mind to avoid spinning your wheels unnecessarily! Alright, let's dive in…

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3.4: Predicting the Geometry of Organometallic Complexes

An important issue that we've glossed over until now concerns what organometallic complexes actually look like: what are their typical geometries? Can we use any of the "bookkeeping metrics" we've explored so far to reliably predict geometry? The answer to the latter questions is a refreshing but qualified "yes." In this post, we'll explore the possibilities for complex geometry and develop some general guidelines for predicting geometry. In the process we'll enlist the aid of a powerful theoretical ally, crystal field theory (CFT), which provides some intuitive explanations for geometry the geometry of organometallic complexes.

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3.5: Simplifying the Organometallic Complex (Part 1)

Organometallic complexes, which consist of centrally located metals and peripheral organic compounds called ligands, are the workhorses of organometallic chemistry. Just like organic intermediates, understanding something about the structure of these molecules tells us a great deal about their expected reactivity. Some we would expect to be stable, and others definitely not! A big part of our early explorations will involve describing, systematically, the principles that govern the stability of organometallic complexes. From the outset, I will say that these principles are not set in stone and are best applied to well controlled comparisons. Nonetheless the principles are definitely worth talking about, because they form the foundation of everything else we'll discuss. Let's begin by exploring the general characteristics of organometallic complexes and identifying three key classes of organic ligands.

When we think of metals we usually think of electropositive atoms or even positively charged ions, and many of the metals of OM chemistry fit this mold. In general, it is useful to imagine organic ligands as electron donors and metals as electron acceptors. When looking at a pair of electrons shared between a transition metal and main-group atom (or hydrogen), I imagine the cationic metal center and anionic main-group atom racing toward one another from oblivion like star-crossed lovers. In the opposite direction (with an important caveat that we'll address soon), we can imagine ripping apart metal–R covalent bonds and giving both electrons of the bond to the organic atom. This heterolytic bond cleavage method reproduces the starting charges on the metal and ligand. Unsurprisingly, the metal is positive and the ligand negative.

FYI, you might see the blue bipyridine referred to as an L2 ligand elsewhere; this just means that a single bipyridine molecule possesses two L-type binding points. Ligands with multiple binding points are also known as chelating or polydentate ligands. Chelating ligands may feature mixed binding modes; for instance, the allyl ligand is of the LX-type. Chelating ligands can also bind to two different metal centers; when they act in this way, they're called bridging ligands. But don't let all this jargon throw you! Deconstruct complexes one binding point at a time, and you cannot go wrong.

Next, we'll take a closer look at the metal center and expand on the purpose of the deconstruction process described here.

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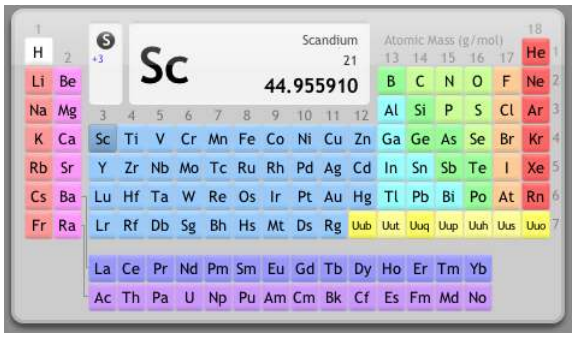
3.6: Simplifying the Organometallic Complex (Part 2)

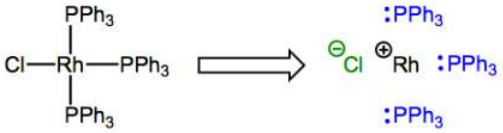
Now it's time to turn our attention to the metal center, and focus on what the deconstruction process can tell us about the nature of the metal in organometallic complexes. We'll hold off on a description of periodic trends of the transition series, but now is a good time to introduce the general characteristics of the transition metals. Check out groups 3-12 in the table below.



The transition metals are colored dark blue in this table.

The transition metals occupy the d-block of the periodic table, meaning that, as we move from left to right across the transition series, electrons are added to the d atomic orbitals. Just like organic elements, the transition metals form bonds using only their valence electrons. But when working with the transition metals, we need to concern ourselves only with the d atomic orbitals, as none of the other valence subshells contain any electrons. Although the periodic table may lead you to believe that the transition metals possess filled s subshells, we imagine metals in organometallic complexes as possessing valence electrons in d orbitals only! The reason for this is somewhat complicated, but has to do with the partial positive charge of complexed metals. Neutral transition metal atoms do, in fact, possess filled s subshells. Why, then, is it important to remember that the valence electrons of complexed metal centers are all d electrons? We will see that the number of d electrons possessed by a complexed metal is in many ways a useful concept. If you find that your counts are off by two, this common mistake is probably the culprit!

Let's turn our attention now to a new complex. I've gone ahead and deconstructed it for us.



Say hello to rhodium (Rh)! Don't fret; it's just a group 9 element.

The complex possesses one X-type and three L-type ligands, so the rhodium atom ends up with a formal charge of +1. The formal charge on the metal center after deconstruction has a very special name that you will definitely want to commit to memory: it's called the oxidation state. It's usually indicated with a roman numeral next to the atomic symbol of the metal (the "+" is implied). In the complex shown above, rhodium is in the Rh(I) or +1 oxidation state. Oxidation state is most useful because changes in oxidation state indicate changes in electron density at the metal center, and this can be a favorable or unfavorable occurrence depending on the other ligands around. We will see this principle in action many, many times! Get used to changes in oxidation state as everyday events in organometallic reaction mechanisms. Unlike carbon (with the exception of carbene…what's its oxidation state?!) and other second-row elements, the transition metals commonly exhibit multiple different oxidation states. More on that later, though. For now, training yourself to rapidly identify the oxidation state of a complexed metal is most important. Please note that when a complex possesses an overall charge, the oxidation state is affected by this charge!

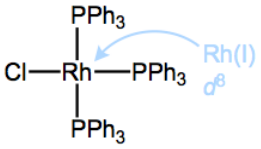
oxidation state = number of X-type ligands bound to metal + overall charge of complex

What of this number of d electrons concept? A very useful way to think about "number of d electrons" is as the "number of non-bonding electrons on the metal center," and you're probably familiar with identifying non-bonding electrons from organic chemistry. The numbers of valence electrons of each organic element are set in stone: carbon has four, nitrogen has five, et cetera. Furthermore, using this knowledge, it's straightforward to determine the number of lone pair electrons associated with an atom by

subtracting its number of covalent bonds from its total number of valence electrons. E.g., for a neutral nitrogen atom in an amine NR3, 5 – 3 = 2 lone pair electrons, typically. The extension to organometallic chemistry is natural! We can analyze complexed metal centers in the same way, but they tend to have a lot more non-bonding electrons than organic atoms, and the number depends on the metal's oxidation state. For instance, the deconstructed rhodium atom in the figure above has 8 d electrons: 9 valence electrons minus 1 used for bonding to Cl. Dative bonds don't affect d electron count since both electrons in the bond come from the ligand.

number of non-bonding electrons = number of d electrons = metal's group number – oxidation state

Drawing all the non-bonding d electrons out as lone pairs would clutter things up, so they are never drawn…but we must remember that they're around! Why? Because the number of d electrons profoundly affects a complex's geometry. We will return to this soon, but the key idea is that the ligands muck up the energies of the d orbitals as they approach the metal (recall the "star-crossed lovers" idea), and the most favorable way to do so depends on the number of non-bonding electrons on the metal center.



Oxidation state and d electron count: two tools the OM chemist can't live without!

This post introduced us to two important bookkeeping tools, oxidation state and number of d electrons. In the final installment of the "Simplifying the Organometallic Complex" series, we'll bring everything together and discuss total electron count. We'll see that total electron count may be used to draw a variety of insightful conclusions about organometallic complexes.

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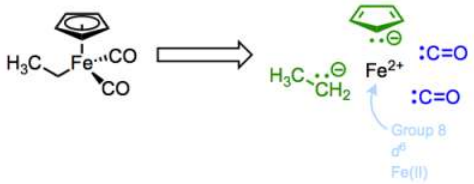
3.7: Simplifying the Organometallic Complex (Part 3)

So far, we've seen how deconstruction can reveal useful "bookkeeping" properties of organometallic complexes: number of electrons donated by ligands, coordination number, oxidation state, and d electron count (to name a few). Now, let's bring everything together and discuss total electron count, the sum of non-bonding and bonding electrons associated with the metal center. Like oxidation state, total electron count can reveal the likely reactivity of OM complexes—in fact, it is often more powerful than oxidation state for making predictions. We'll see that there is a definite norm for total electron count, and when a complex deviates from that norm, reactions are likely to happen.

Let's begin with yet another new complex. This molecule features the common and important cyclopentadienyl and carbon monoxide ligands, along with an X-type ethyl ligand.



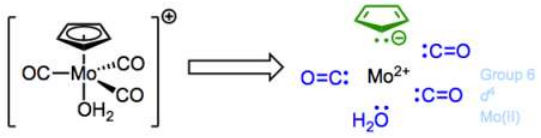
What is the total electron count of this Fe(II) complex?

The Cp or cyclopentadienyl ligand is a polydentate, six-electron L2X ligand. The two pi bonds of the free anion are dative, L-type ligands, which we'll see again in a future post on ligands bound through pi bonds. Think of the electrons of the pi bond as the source of a dative bond to the metal. Since both electrons come from the ligand, the pi bonds are L-type binders. The anionic carbon in Cp is a fairly standard, anionic X-type binder. The carbon monoxide ligands are interesting examples of two-electron L-type ligands—notice that the free ligands are neutral, so these are considered L-type! Carbon monoxide is an intriguing ligand that can teach us a great deal about metal-ligand bonding in OM complexes…but more on that later.

After deconstruction, we see that the Fe(II) center possesses 6 non-bonding d electrons. The total electron count is just the d electron count plus the number of electrons donated by the ligands. Since the d electron count already takes overall charge into account, we need not worry about it as long as we've followed the deconstruction procedure correctly.

total electron count = number of d electrons + electrons donated by ligands

For the Fe(II) complex above, the total electron count is thus 6 + (6 + 2 + 2 + 2) = 18. Let's work through another example: the complex below features an overall charge of +1. Water is a dative ligand—that "2″ is very important!

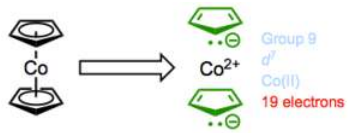


Note that the overall charge is lumped into the oxidation state and d electron count of Mo.

The oxidation state of molybdenum is +2 here…remember that the overall charge factors in to that. When everything is said and done, the total electron count is 4 + (6 + 2 + 2 + 2 + 2) = 18.

What's up with 18?! As it turns out, 18 electrons is a very common number for stable organometallic complexes. So common that the number got its own rule—the 18-electron rule—which states that stable transition-metal complexes possess 18 or fewer electrons. The rule is analogous to organic chemistry's octet rule. The typical explanation for the 18-electron rule points out that there are 9 valence orbitals (1 s, 3 p, 5 d) available to metals, and using all of these for bonding seems to produce the most stable complexes. Of course, as soon as the rule left the lips of some order-craving chemist, researchers set out to find counterexamples to it, and a number of counterexamples are known. Hartwig describes the rule as an "empirical guideline" with little theoretical support. In fact, theoretical studies have shown that the participation of p orbitals in complex MOs is unlikely. I know that's not what you want to hear—but hang with me! The 18-electron rule is still a very useful guideline. It's most interesting, in fact, when it is not satisfied.

One last example…how would you expect the complex below to react?



Cobaltocene: jonesing for chemical change.

If we assume that the 18-electron rule is true, then cobaltocene has a real problem. It possesses 7 + (6 + 6) = 19 total valence electrons! Yet, we can also reason that this complex will probably react to relieve the strain of not having 18 electrons by giving up an electron. Guess what? In practice, cobaltocene is a great one-electron reducing agent, and can be used to prepare anionic complexes through electron transfer.

$$CoCp_2 + ML_n \rightarrow [CoCp_2] + [ML_n]^- \tag{3.7.1}$$

This post described how to calculate total electron count and introduced the power of the 18-electron rule for predicting whether a complex will donate or accept electrons. We will definitely see these ideas again! But what happens when the electron counts of two complexes we're interested in comparing are the same? We'll need more information. In the next post, we'll explore the periodic trends of the transition series. Our goal will be to make meaningful comparisons between complexes of different metals.

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CHAPTER OVERVIEW

4: Fundamentals of Organometallic Chemistry

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4.2: Associative Ligand Substitution
4.3: Dissociative Ligand Substitution Reactions
4.4: Ligand substitution
4.5: Migratory Insertion- 1,2-Insertions
4.6: Migratory Insertion- Introduction and CO Insertions
4.7: Oxidative Addition- General Ideas
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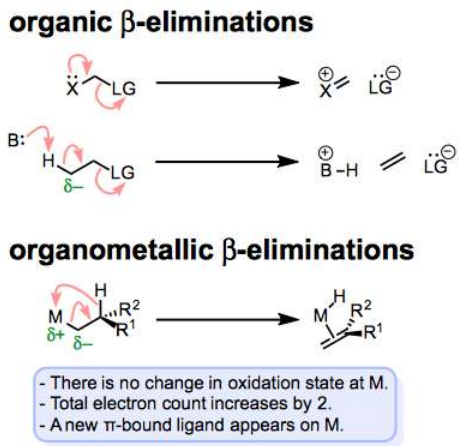
4.1: β-Elimination Reactions

In organic chemistry class, one learns that elimination reactions involve the cleavage of a σ bond and formation of a π bond. A nucleophilic pair of electrons (either from another bond or a lone pair) heads into a new π bond as a leaving group departs. This process is called β-elimination because the bond β to the nucleophilic pair of electrons breaks. Transition metal complexes can participate in their own version of β-elimination, and metal alkyl complexes famously do so. Almost by definition, metal alkyls contain a nucleophilic bond—the M–C bond! This bond can be so polarized toward carbon, in fact, that it can promote the elimination of some of the world's worst leaving groups, like –H and –CH3. Unlike the organic case, however, the leaving group is not lost completely in organometallic β-eliminations. As the metal donates electrons, it receives electrons from the departing leaving group. When the reaction is complete, the metal has picked up a new π-bound ligand and exchanged one X-type ligand for another.



Comparing organic and organometallic β-eliminations. A nucleophilic bond or lone pair promotes loss or migration of a leaving group.

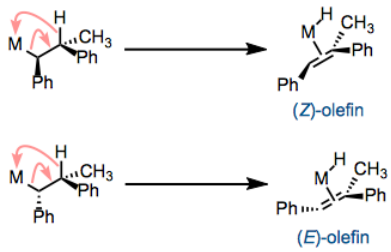
In this post, we'll flesh out the mechanism of β-elimination reactions by looking at the conditions required for their occurrence and their reactivity trends. Many of the trends associated with β-eliminations are the opposite of analogous trends in 1,2-insertion reactions. A future post will address other types of elimination reactions.

β-Hydride Elimination

The most famous and ubiquitous type of β-elimination is **β-hydride elimination**, which involves the formation of a π bond and an M–H bond. Metal alkyls that contain β-hydrogens experience rapid elimination of these hydrogens, provided a few other conditions are met.

The complex must have an open coordination site and an accessible, empty orbital on the metal center. The leaving group (–H) needs a place to land. Notice that after β-elimination, the metal has picked up one more ligand—it needs an empty spot for that ligand for elimination to occur. We can envision hydride "attacking" the empty orbital on the metal center as an important orbital interaction in this process.

The M–C_α and C_β–H bonds must have the ability to align in a syn coplanar arrangement. By "syn coplanar" we mean that all four atoms are in a plane and that the M–C_α and C_β–H bonds are on the same side of the C_α–C_β bond (a dihedral angle of 0°). You can see that conformation in the figure above. In the syn coplanar arrangement, the C–H bond departing from the ligand is optimally lined up with the empty orbital on the metal center. Hindered or cyclic complexes that cannot achieve this conformation do not undergo β-hydride elimination. The need for a syn coplanar conformation has important implications for eliminations that may establish diastereomeric olefins: β-elimination is stereospecific. One diastereomer leads to the (E)-olefin, and the other leads to the (Z)-olefin.



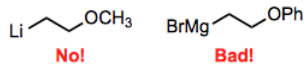
β-elimination is stereospecific. One diastereomer of reactant leads to the (Z)-olefin and the other to the (E)-olefin.

The complex must possess 16 or fewer total electrons. Examine the first figure one more time—notice that the total electron count of the complex increases by 2 during β-hydride elimination. Complexes with 18 total electrons don't undergo β-elimination because the product would end up with 20 total electrons. Of course, dissociation of a loose ligand can produce a 16-electron complex pretty easily, so watch out for ligand dissociation when considering the possibility of β-elimination in a complex. Ligand dissociation may be reversible, but β-Hydride elimination is almost always irreversible.

The metal must bear at least 2 d electrons. Now this seems a bit strange, as the metal has served as nothing but an empty bin for electrons in our discussion so far. Why would the metal center need electrons for β-hydride elimination to occur? The answer lies in an old friend: backbonding. The $\sigma_{C–H} \rightarrow M$ orbital interaction mentioned above is not enough to promote elimination on its own; an $M \rightarrow \sigma^*_{C–H}$ interaction is also required! I've said it before, and I'll say it again: backbonding is everywhere in organometallic chemistry. If you can understand and articulate it, you'll blow your instructor's mind.

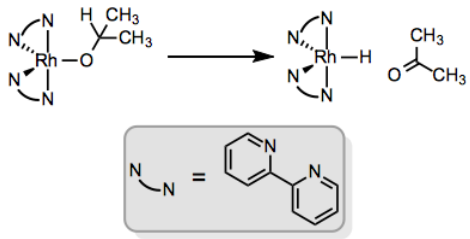
Other β-Elimination Reactions

The leaving group does not need to be hydrogen, of course, and a number of more electronegative groups come to mind as better candidates for leaving groups. β-Alkoxy and β-amino eliminations are usually thermodynamically favored thanks to the formation of strong M–O and M–N bonds, respectively. These reactions are so favored in β-alkoxyalkyl "complexes" of alkali and alkaline earth metals (R–Li, R–MgBr, etc.) that using these as σ-nucleophiles at carbon is untenable. Such compounds eliminate immediately upon their formation. I had an organic synthesis professor in undergrad who was obsessed with this—using a β-alkoxyalkyl lithium or β-alkoxyalkyl Grignard reagent in a synthesis was a recipe for red ink. β-Haloalkyls were naturally off limits too.



Watch out…these are not stable compounds!

The atom bound to the metal doesn't have to be carbon. β-Elimination of alkoxy ligands affords ketones or aldehydes bound at oxygen or through the C=O π bond (this step is important in many transfer hydrogenations, and an analogous process occurs in the Oppenauer oxidation). Amido ligands can undergo β-elimination to afford complexes of imines; however, this process tends to be slower than β-alkoxy elimination.



β-Elimination helps transfer the elements of dihydrogen from one organic compound to another.

Incidentally, I haven't seen any examples in which the β atom is not carbon, but would be interested if anyone knows of an example!

Applications of β-Eliminations

As with many concepts in organometallic chemistry, there are two ways to think about applications of β-elimination. One can take either the “inorganic” perspective, which focuses on the metal center, or the “organic” perspective, which focuses on the ligands.

With the metal center in focus, we can recognize that β-hydride elimination has the wonderful side effect of establishing an M–H bond—a feat generally difficult to achieve in a selective manner via oxidative addition of X–H. If the ligand from which the hydrogen came displaced something more electronegative, the whole process represents reduction at the metal center. For example, imagine rhodium(III) chloride is mixed with sodium isopropoxide, $NaOCH(CH_3)_2$. The isopropoxide easily displaces chloride, and subsequent β-hydride elimination affords a rhodium hydride, formally reduced with respect to the chloride starting material. See p. 236 of this review for more.

With the ligand in focus, we see that the organic ligand is oxidized in the course of β-hydride elimination. Notice that the metal is reduced and the ligand oxidized! A π bond replaces a σ bond in the ligand, and if the conditions are right, this represents a bona fide oxidation (as opposed to a mere elimination). For example, oxidative addition into a C–H bond followed by β-hydride elimination at a C–H bond next door sets up an alkene where two adjacent C–H bonds existed before, an oxidation process. These dehydrogenation reactions are incredibly appealing in a theoretical sense, but still at an early stage when it comes to scope and practicality.

Summary

We already encountered β-hydride elimination in an earlier series of posts on metal alkyl complexes, where we noted that it’s a very common decomposition pathway for metal alkyls. β-Hydride elimination isn’t all bad, however, as it can be an important step in catalytic reactions that result in the oxidation of organic substrates (dehydrogenations and transfer hydrogenations) and in reactions that reduce metal halides to metal hydrides. The general idea of β-elimination involves the transfer of a leaving group from a ligand to the metal center with simultaneous formation of a π bond in the ligand. β-Elimination requires an open coordination site and at least two d electrons on the metal center, and eliminations of chiral complexes are stereospecific. The leaving group is commonly hydrogen, but need not be—the more electronegative the leaving group, the more favorable the elimination. Stronger π bonds in the product also encourage β-elimination, so eliminations that form carbonyl compounds or imines are common.

In the next post, we’ll explore other types of organometallic elimination reactions, which establish π bonds at different positions in metal alkyl or other complexes. α-Eliminations, for example, establish metal-carbon, -oxygen, or -nitrogen multiple bonds, which are generally difficult to forge through other means

Contributors and Attributions

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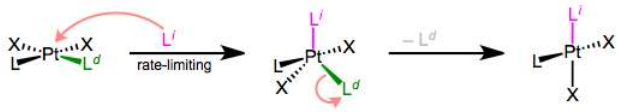
4.2: Associative Ligand Substitution

Despite the sanctity of the 18-electron rule to many students of organometallic chemistry, a wide variety of stable complexes possess fewer than 18 total electrons at the metal center. Perhaps the most famous examples of these complexes are 14- and 16-electron complexes of group 10 metals involved in cross-coupling reactions.

Ligand substitution in complexes of this class typically occurs via an associative mechanism, involving approach of the incoming ligand to the complex before departure of the leaving group. If we keep this principle in mind, it seems easy enough to predict when ligand substitution is likely to be associative. But how can we spot an associative mechanism in experimental data, and what are some of the consequences of this mechanism?



The prototypical mechanism of associative ligand substitution. The first step is rate-determining. A typical mechanism for associative ligand substitution is shown above. It should be noted that square pyramidal geometry is also possible for the intermediate, but is less common. Let's begin with the kinetics of the reaction.

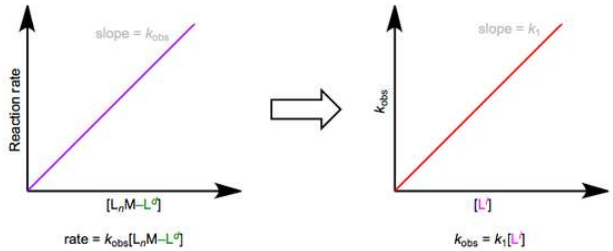
Reaction Kinetics

Reaction kinetics are commonly used to elucidate organometallic reaction mechanisms, and ligand substitution is no exception. Different mechanisms of substitution may follow different rate laws, so plotting the dependence of reaction rate on concentration often allows us to distinguish mechanisms. Associative substitution's rate law is analogous to that of the S_N2 reaction—rate depends on the concentrations of both starting materials.

$$L_nM\text{–}L^d + L_i \rightarrow L_nM\text{–}L_i + L^d \tag{4.2.1}$$

$$\frac{d[L_nM\text{–}L^i]}{dt} = rate = k_1[L_nM\text{–}L^d][L^i] \tag{4.2.2}$$

The easiest way to determine this rate law is to use pseudo-first-order conditions. Although the rate law is second order overall, if we could somehow render the concentration of the incoming ligand unchanging, the reaction would appear first order. The observed rate constant under these conditions reflects the constancy of the incoming ligand's concentration ($k_{obs} = k_1[L^i]$, where both k_1 and $[Li]$ are constants). How can we make the concentration of the incoming ligand invariant, you ask? We can drown the reaction in ligand to achieve this. The teensy weensy bit actually used up in the reaction has a negligible effect on the concentration of the "sea" of starting ligand we began with. The observed rate is equal to $k_{obs}[L_nM\text{–}L^d]$, as shown by the purple trace below. By determining k_{obs} at a variety of $[L^i]$ values, we can finally isolate k_1, the rate constant for the slow step. The red trace below at right shows the idea.



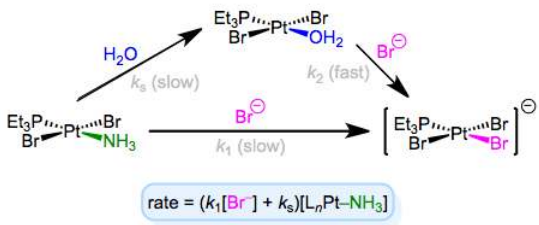
Associative substitution under pseudo-first-order conditions. The reaction is "swamped out" with incoming ligand.

In many cases, the red trace ends up with a non-zero y-intercept…curious, if we limit ourselves to the simple mechanism shown in the first figure of this post. A non-zero intercept suggests a more complex mechanism. We need to add a new term (called k_s for reasons to become clear shortly) to our first set of equations:

$$rate = (k_1[L_i] + k_s)[L_nM\text{–}L^d] \tag{4.2.3}$$

$$k_{obs} = k_1[L_i] + k_s \tag{4.2.4}$$

The full rate law suggests that some other step (with rate ks[LnM–Ld]) independent of incoming ligand is involved in the mechanism. To explain this observation, we can invoke the solvent as a reactant. Solvent can associate with the complex first in a slow step, then incoming ligand can displace the solvent in a fast step. Solvent concentration doesn't enter the rate law because, well, it's drowning the reactants and its concentration undergoes negligible change! An example of this mechanism in the context of Pt(II) chemistry is shown below.

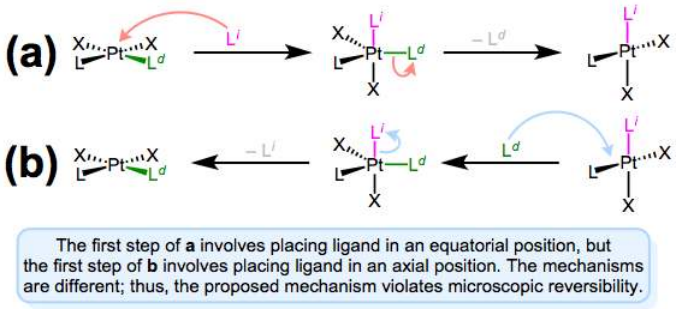


Associative substitution with solvent participation—a head-scratching mechanism for many an organometallic grad student!

As an aside, it's worth mentioning that the entropy of activation of associative substitution is typically negative. Entropy decreases as the incoming ligand and complex come together in the rate-determining step. Dissociative substitution shows the opposite behavior: loss of the departing ligand in the RDS increases entropy, resulting in positive entropy of activation.

Stereochemistry of Substitution

As we saw in discussions of the trans effect, the entering and departing ligands both occupy equatorial positions in the trigonal bipyramidal intermediate. Microscopic reversibility is to blame: the mechanism of the forward substitution (displacement of the leaving by the incoming ligand) must be the same as the mechanism of the reverse reaction (displacement of the incoming by the leaving ligand). This can be a confusing point, so let's examine an alternative mechanism that violates microscopic reversibility.

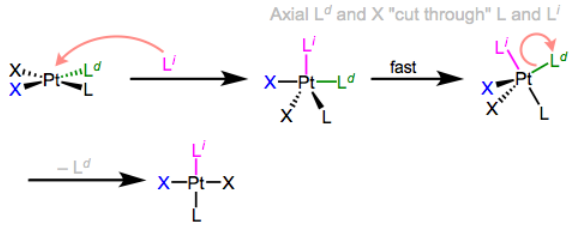


A mechanism involving approach to an axial position and departure from an equatorial position violates microscopic reversibility. Forward and reverse reactions a and b differ!

The figure above shows why a mechanism involving axial approach and equatorial departure (or vice versa) is not possible. The forward and reverse reactions differ, in fact, in both steps. In forward mechanism a, the incoming ligand enters an axial site. But in the reverse reaction, the incoming ligand (viz., the departing ligand in mechanism a) sits on an equatorial site. The second steps of each mechanism differ too—a involves loss of an equatorial ligand, while b involves loss of an axial ligand. Long story short, this mechanism violates microscopic reversibility. And what about a mechanism involving axial approach and axial departure? Such a mechanism is unlikely on electronic grounds. The equatorial sites are more electron rich than the axial sites, and σ bonding to the axial d_{z^2} orbital is expected to be strong. Intuitively, then, loss of ligand from an axial site is less favorable than loss from an equatorial site.

I know what you're thinking: what the heck does all of this have to do with stereochemistry? Notice that, in the equatorial-equatorial mechanism (first figure of this post), the axial ligands don't move at all. The configuration of the starting complex is thus retained in the product. Although retention is "normal," complications often arise because five-coordinate TBP complexes—like other odd-coordinate organometallic complexes—are often fluxional. Axial and equatorial ligands can rapidly exchange through a

process called Berry pseudorotation, which resembles the axial ligands “cutting through” a pair of equatorial ligands like scissors (animation!). Fluxionality means that all stereochemical bets are off, since any ligand can feasibly occupy an equatorial site. In the example below, the departing ligand starts out cis to L, but the incoming ligand ends up trans to L.



Berry pseudorotation in the midst of associative ligand substitution.

Associative Substitution in 18-electron Complexes?

Associative substitution can occur in 18-electron complexes if it’s preceded by the dissociation of a ligand. For example, changes in the hapticity of cyclopentadienyl or indenyl ligands may open up a coordination site, which can be occupied by a new ligand to kick off associative substitution. An allyl ligand may convert from its π to σ form, leaving an open coordination site where the π bond left. A particularly interesting case is the **nitrosyl ligand**—conversion from its linear to bent form opens up a site for coordination of an external ligand.

Summary

Associative ligand substitution is common for complexes with 16 total electrons or fewer. The reaction is characterized by a second-order rate law, the possibility of solvent participation, and a trigonal bipyramidal intermediate that is often fluxional. An open coordination site is essential for associative substitution, but such sites are often hidden in the dynamism of 18-electron complexes with labile ligands.

Dr. Michael Evans (Georgia Tech)

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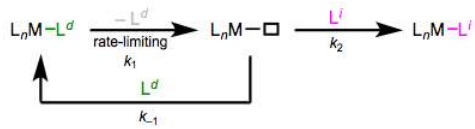
4.3: Dissociative Ligand Substitution Reactions

Associative substitution is unlikely for saturated, 18-electron complexes—coordination of another ligand would produce a 20-electron intermediate. For 18-electron complexes, dissociative substitution mechanisms involving 16-electron intermediates are more likely. In a slow step with positive entropy of activation, the departing ligand leaves, generating a coordinatively unsaturated intermediate. The incoming ligand then enters the coordination sphere of the metal to generate the product. For the remainder of this post, we'll focus on the kinetics of the reaction and the nature of the unsaturated intermediate (which influences the stereochemistry of the reaction). The reverse of the first step, re-coordination of the departing ligand (rate constant k–1), is often competitive with dissociation.



A general scheme for dissociative ligand substitution. There's more to the intermediate than meets the eye!

Reaction Kinetics

Let's begin with the general situation in which k_1 and k_{-1} are similar in magnitude. Since k_1 is rate limiting, k_2 is assumed to be much larger than k_1 and k_{-1}. Most importantly, we need to assume that variation in the concentration of the unsaturated intermediate is essentially zero. This is called the steady state approximation, and it allows us to set up an equation that relates reaction rate to observable concentrations Hold onto that for a second; first, we can use step 2 to establish a preliminary rate expression.

$$\text{rate} = k_2[L_nM–\Diamond][Li] \tag{1}$$

Of course, the unsaturated complex is present in very small concentration and is unmeasurable, so this equation doesn't help us much. We need to remove the concentration of the unmeasurable intermediate from (1), and the steady state approximation helps us do this. We can express variation in the concentration of the unsaturated intermediate as (processes that make it) minus (processes that destroy it), multiplying by an arbitrary time length to make the units work out. All of that equals zero, according to the SS approximation. The painful math is almost over! Since Δt must not be zero, the other factor, the collection of terms, must equal zero.

$$\Delta[LnM–\Diamond] = 0 = (k1[LnM–L^d]–k–1[LnM–\Diamond][L^d]–k_2[LnM–\Diamond][Li])\Delta t \tag{2}$$

$$0 = k_1[LnM–Ld]–k_{-1}[LnM–\Diamond][Ld]–k_2[LnM–\Diamond][Li] \tag{3}$$

Rearranging to solve for [LnM–◊], we arrive at the following.

$$[LnM–\Diamond] = k_1\frac{[LnM–L_d]}{(k_{-1}[L_d] + k_2[Li]} \tag{4}$$

Finally, substituting into equation (1) we reach a verifiable rate equation.

$$\text{rate} = k_2k_1\frac{[LnM–Ld][Li]}{(k_{-1}[L_d] + k_2[Li]} \tag{5}$$

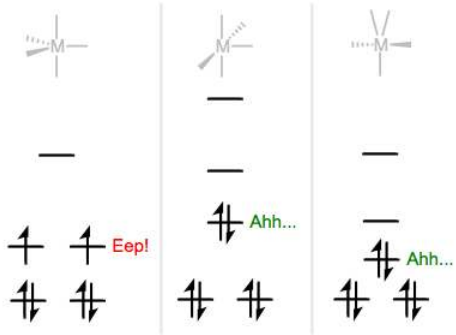
When k_{-1} is negligibly small, (5) reduces to the familiar equation (6), typical of dissociative reactions like S_N1.

$$\text{rate} = k_1[LnM–L_d] \tag{6}$$

Unlike the associative rate law, this rate does not depend on the concentration of incoming ligand. For reactions that are better described by (5), we can drown the reaction in incoming ligand to make $k_2[Li]$ far greater than $k_{-1}[Ld]$, essentially forcing the reaction to fit equation (6).

The Unsaturated Intermediate & Stereochemistry

Dissociation of a ligand from an octahedral complex generates an usaturated ML5 intermediate. When all five of the remaining ligands are L-type, as in Cr(CO)5, the metal has 6 d electrons for a total electron count of 16. The trigonal bipyramidal geometry presents electronic problems (unpaired electrons) for 6 d electrons, as the figure below shows. The orbital energy levels come from crystal field theory. Distortion to a square pyramid or a distorted TBP geometry removes the electronic issue, and so five-coordinate d6 complexes typically have square pyramidal or distorted TBP geometries. This is just the geometry prediction process in action!



TBP geometry is electronically disfavored for d6 metals. Distorted TBP and SP geometries are favored.

When the intermediate adopts square pyramidal geometry (favored for good π-acceptors and σ-donors…why?), the incoming ligand can simply approach where the departing ligand left, resulting in retention of stereochemistry. Inversion is more likely when the intermediate is a distorted trigonal bipyramid (favored for good π-donors). As we've already seen for associative substitution, fluxionality in the five-coordinate intermediate can complicate the stereochemistry of the reaction.

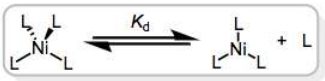
Encouraging Dissocative Substitution

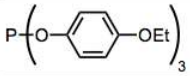
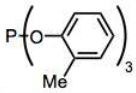
In general, introducing structural features that either stabilize the unsaturated intermediate or destabilize the starting complex can encourage dissociative substitution. Both of these strategies lower the activation barrier for the reaction. Other, quirky ways to encourage dissociation include photochemical methods, oxidation/reduction, and ligand abstraction.

Let's begin with features that stabilize the unsaturated intermediate. Electronically, the intermediate loves it when its d electron count is nicely matched to its crystal field orbitals. As you study organometallic chemistry, you'll learn that there are certain "natural" d electron counts for particular geometries that fit well with the metal-centered orbitals predicted by crystal field theory. Octahedral geometry is great for six d electrons, for example, and square planar geometry loves eight d electrons. Complexes with "natural" d electron counts—but bearing one extra ligand—are ripe for dissociative substitution. The classic examples are d8 TBP complexes, which become d8 square planar complexes (think Pt(II) and Pd(II)) upon dissociation. Similar factors actually stabilize starting 18-electron complexes, making them less reactive in dissociative substitution reactions. d6 octahedral complexes are particularly happy, and react most slowly in dissociative substitutions. The three most common types of 18-electron complexes, from fastest to slowest at dissociative substitution, are:

d8 TBP > d10 tetrahedral > d6 octahedral

Destabilization of the starting complex is commonly accomplished by adding steric bulk to its ligands. Naturally, dissociation relieves steric congestion in the starting complex. Chelation has the opposite effect, and tends to steel the starting complex against dissociation.



L	Cone Angle	K_d
$P(OEt)_3$	109	$< 10^{-10}$
	128	$6 * 10^{-10}$
$P(Oi\text{-}Pr)_3$	130	$2.7 * 10^{-5}$
	141	$4 * 10^{-2}$
PPh_3	145	huge

As steric bulk on the ligand increases, dissociation becomes more favorable.

I plan to cover the "quirky" methods in a post of their own, but these include strategies like N-oxides for CO removal, photochemical cleavage of the metal–departing ligand bond, and the use of silver cation to abstract halide ligands. Oxidation and reduction can also be used to encourage substitution: 17- and 19-electron complexes are much more reactive toward substitution than their 18-electron analogues.

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4.4: Ligand substitution

Ligand substitution is the first reaction one typically encounters in an organometallic chemistry course. In general, ligand substitution involves the exchange of one ligand for another, with no change in oxidation state at the metal center. The incoming and outgoing ligands may be L- or X-type, but the charge of the complex changes if the ligand type changes. Keep charge conservation in mind when writing out ligand substitutions.

How do we know when a ligand substitution reaction is favorable? The thermodynamics of the reaction depend on the relative strength of the two metal-ligand bonds, and the stability of the departing and incoming ligands (or salt sof the ligand, if they're X type). It's often useful to think of X-for-X substitutions like acid-base reactions, with the metal and spectator ligands serving as a "glorified proton." Like acid-base equilibria in organic chemistry, we look to the relative stability of the two charged species (the free ligands) to draw conclusions. Of course, we don't necessarily need to rely just on primal thermodynamics to drive ligand substitution reactions. Photochemistry, neighboring-group participation, and other tools can facilitate otherwise difficult substitutions.

Ligand substitution is characterized by a continuum of mechanisms bound by associative (A) and dissociative (D) extremes. At the associative extreme, the incoming ligand first forms a bond to the metal, then the departing ligand takes its lone pair and leaves. At the dissociative extreme, the order of events is opposite—the departing ligand leaves, then the incoming ligand comes in. Associative substitution is common for 16-electron complexes (like d8 complexes of Ni, Pd, and Pt), while dissociative substitution is the norm for 18-electron complexes. Then again, reality is often more complicated than these extremes. In some cases, evidence is available for simultaneous dissociation and association, and this mechanism has been given the name interchange (IA or ID).

Over the next few posts, we'll explore ligand substitution reactions and mechanisms in detail. We'd like to be able to (a) predict whether a mechanism is likely to be associative or dissociative; (b) propose a reasonable mechanism from given experimental data; and (c) describe the results we'd expect given a particular mechanism. Keep these goals in mind as you learn the theoretical and experimental nuts and bolts of substitution reactions.

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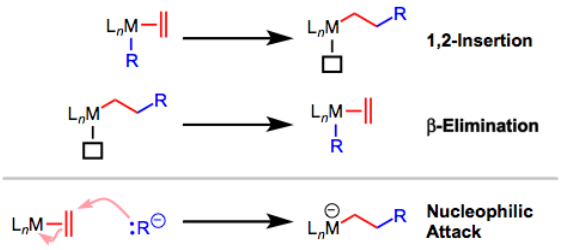
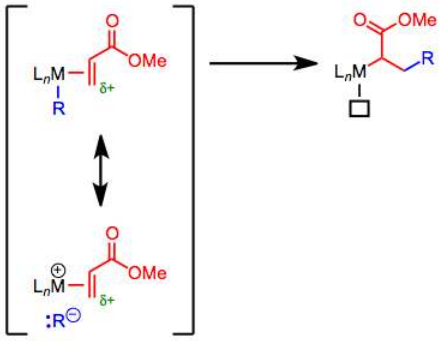
4.5: Migratory Insertion- 1,2-Insertions

Insertions of π systems into M-X bonds are appealing in the sense that they establish two new σ bonds in one step, in a stereocontrolled manner. As we saw in the last post, however, we should take care to distinguish these fully intramolecular migratory insertions from intermolecular attack of a nucleophile or electrophile on a coordinated π-system ligand. The reverse reaction of migratory insertion, β-elimination, is not the same as the reverse of nucleophilic or electrophilic attack on a coordinated π system.



1,2-Insertion is distinct from nucleophilic/electrophilic attack on coordinated ligands.

Like 1,1-insertions, 1,2-insertions generate a vacant site on the metal, which is usually filled by external ligand. For unsymmetrical alkenes, it's important to think about site selectivity: which atom of the alkene will end up bound to metal, and which to the other ligand? To make predictions about site selectivity we can appeal to the classic picture of the M–X bond as M+X–. Asymmetric, polarized π ligands contain one atom with excess partial charge; this atom hooks up with the complementary atom in the M–R bond during insertion. Resonance is our best friend here!



The site selectivity of 1,2-insertion can be predicted using resonance forms and partial charges.

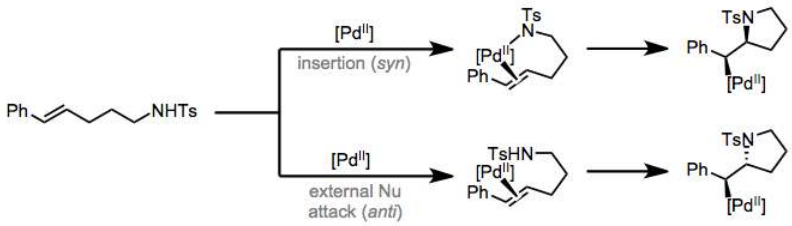
A nice study by Yu and Spencer illustrates these effects in homogeneous palladium- and rhodium-catalyzed hydrogenation reactions. Unactivated alkenes generally exhibit lower site selectivity than activated ones, although steric differences between the two ends of the double bond can promote selectivity.

Reactivity Trends in 1,2-Insertions

The thermodynamics of 1,2-insertions of alkenes depend strongly on the alkene, but we can gain great insight by examining the structure of the product alkyl. Coordinated alkenes that give strong metal-alkyl bonds after migratory insertion tend to undergo the process. Hence, electron-withdrawing groups, such as carbonyls and fluorine atoms, tend to encourage migratory insertion—remember that alkyl complexes bearing these groups tend to have stable M–C bonds.

Insertions of alkenes into both M–H and M–R (R = alkyl) are favored thermodynamically, but the kinetics of M–R insertion are much slower. This observation reflects a pervasive trend in organometallic chemistry: M–H bonds react more rapidly than M–R bonds. The same is true of the reverse, β-elimination. Even in cases when both hydride and alkyl elimination are thermodynamically favored, β-hydride elimination is much faster. Although insertion into M–R is relatively slow, this elementary step is critical for olefin polymerizations that form polyalkenes (Ziegler-Natta polymerization). This reaction deserves a post all its own!

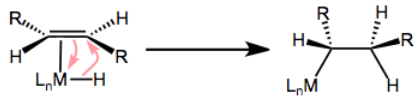
As the strength of the M–X bond increases, the likelihood that an L-type π ligand will insert into the bond goes down. Hence, while insertions into M–H and M–C are relatively common, insertions into M–N and M–O bonds are more rare. Lanthanides and palladium are known to promote insertion into M–N in some cases, but products with identical connectivity can come from external attack of nitrogen on a coordinated π ligand. The diastereoselectivity of these reactions provides mechanistic insight—since migratory insertion is syn (see below), a syn relationship between Pd and N is to be expected in the products of migratory insertion. An anti relationship indicates external attack by nitrogen or oxygen.



The diastereoselectivity of formal insertions provides insight about their mechanisms.

Stereochemistry of 1,2-Insertions

1,2-Insertion may establish two stereocenters at once, so the stereochemistry of the process is critical! Furthermore, 1,2-insertions and β-eliminations are bound by important stereoelectronic requirements. An analogy can be made to the E2 elimination of organic chemistry, which also has strict stereoelectronic demands. For migratory insertion to proceed, the alkene and X-type ligand must be syncoplanar during insertion; as a consequence of this alignment, X and MLn end up on the same face of the alkene after insertion. In other words, insertions into alkenes take place in a syn fashion. Complexes that have difficulty achieving a coplanar arrangement of C=C and M–X undergo insertion very slowly, if at all.

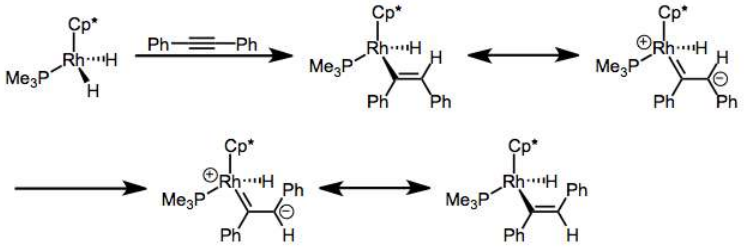


1,2-Insertions take place in a syn fashion. The metal and X end up bound to the same face of the alkene.

This observation has important implications for β-elimination, too—the eliminating X and the metal must have the ability to align syn.

Insertions of Other π Systems

To close this post, let's examine insertions into π ligands other than alkenes briefly. Insertions of alkynes into metal-hydride bonds are known, and are sometimes involved in reactions that I refer to collectively as "hydrostuffylation": hydrosilylation, hydroesterification, hydrogenation, and other net H–X additions across the π bond. Strangely, some insertions of alkynes yield trans products, even though cis products are to be expected from syn addition of M–X. The mechanisms of these processes involve initial syn addition followed by isomerization to the trans complex via an interesting resonance form. The cis complex is the kinetic product, but it isomerizes over time to the more thermodynamically stable trans complex.



Migratory insertions of alkynes into M–H produce alkenyl complexes, which have been known to isomerize.

The strongly donating Cp* ligand supports the legitimacy of the zwitterionic resonance form—and suggests that the C=C bond may be weaker than it first appears!

Polyenes can participate in migratory insertion, and insertions of polyenes are usually quite favored because stabilized π-allyl complexes result. In one mind-bending case, a coordinated arene inserts into an M–Me bond in a syn fashion!

Have you ever stopped to consider that the addition of methyllithium to an aldehyde is a formal insertion of the carbonyl group into the Li–Me bond? It's true! We can think of these as (very) early-metal "insertion" reactions. Despite this precedent, migratory insertion reactions of carbonyls and imines into late-metal hydride and alkyl bonds are surprisingly hard to come by. Rhodium is the most famous metal that can make this happen—rhodium has been used in complexes for arylation and vinylation, for example. Insertion of X=C into the M–R bond is usually followed by β-hydride elimination, which has the nifty effect of replacing H in aldehydes and aldimines with an aryl or vinyl group.

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4.6: Migratory Insertion- Introduction and CO Insertions

Introduction

We've seen that the metal-ligand bond is generally polarized toward the ligand, making it nucleophilic. When a nucleophilic, X-type ligand is positioned *cis* to an unsaturated ligand in an organometallic complex, an interesting process that looks a bit like nucleophilic addition can occur.

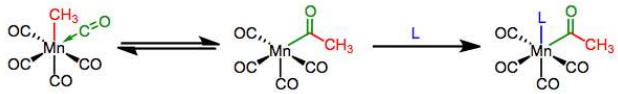

Figure 4.6.1: Migratory insertion into a metal-carbon bond. (Michael Evans)

On the whole, the unsaturated ligand appears to insert itself into the M–X bond; hence, the process is called **migratory insertion**. An open coordination site shows up in the complex, and is typically filled by an added ligand. The open site may appear where the unsaturated ligand was *or* where the X-type ligand was, depending on which group actually moved (see below). There is no change in oxidation state at the metal (unless the ligand is an alkylidene/alkylidyne), but the total electron count of the complex decreases by two during the actual insertion event—notice in the above example that the complex goes from 18 to 16 total electrons after insertion. A dative ligand comes in to fill that empty coordination site, but stay flexible here: L could be a totally different ligand or a Lewis base in the X-type ligand. L can even be the carbonyl oxygen itself!

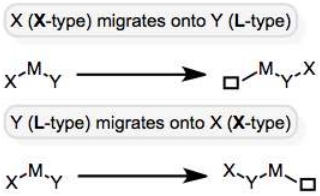

Figure 4.6.2: X can migrate onto unsaturated ligand Y, or Y onto X. The former is more common for CO insertions. (Michael Evans)

We can distinguish between two types of insertions, which differ in the number of atoms in the unsaturated ligand involved in the step. Insertions of CO, carbenes, and other η^1 unsaturated ligands are called **1,1-insertions** because the X-type ligand moves from its current location on the metal to one spot over, on the atom bound to the metal. η^2 ligands like alkenes and alkynes can also participate in migratory insertion; these reactions are called **1,2-insertions** because the X-type ligand slides two atoms over, from the metal to the distal atom of the unsaturated ligand.

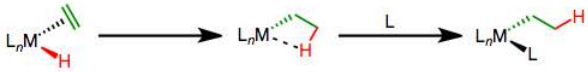

Figure 4.6.3: 1,2-insertion of an alkene and hydride. In some cases, an agostic interaction has been observed in the unsaturated intermediate. (Michael Evans)

This is really starting to look like the addition of M and X across a π bond! However, we should take care to distinguish this completely intramolecular process from the attack of a nucleophile or electrophile on a coordinated π system, which is a different beast altogether. Confusingly, chemists often jumble up all of these processes using words like "hydrometalation," "carbometalation," "aminometalation," etc. Another case of big words being used to obscure ignorance! We'll look at nucleophilic and electrophilic attack on coordinated ligands in separate posts.

Reactivity Trends in CO Insertions

Certain conditions *must* be met for migratory insertion to occur: the two ligands undergoing the process must be *cis*, and the complex must be stable with two fewer total electrons. Thermodynamically, the formed Y–X and covalent M–Y bonds must be more stable than the broken M–X and dative M–Y bonds for insertion to be favored. When the opposite is true, the microscopic reverse (**elimination** or **deinsertion**) will occur spontaneously.

Migratory aptitudes for insertion into CO have been studied extensively, and the general conclusion here is “it’s complicated.” A few ligands characterized by remarkably stable metal-ligand bonds don’t undergo insertion for thermodynamic reasons—the M–X bond is just too darn strong. Perfluoroalkyl complexes and metal hydrides are two notable examples. Electron-withdrawing groups on the X-type ligand, which strengthen the M–X bond, slow down insertion (likely for thermodynamic reasons though… Hammond’s postulate in action).

What factors affect the relative speed (kinetics) of favorable insertions? Sterics is one important variable. Both 1,1- and 1,2-insertions can relieve steric strain at the metal center by spreading out the ligands involved in the step. In 1,2-insertions, the X-type ligand removes itself completely from the metal! Unsurprisingly, then, bulky ligands undergo insertions more rapidly than smaller ligands. Complexes of the first-row metals tend to react more rapidly than analogous second-row metal complexes, and second-row metal complexes react faster than third-row metal complexes. This trend fits in nicely with the typical trend in M–C bond strengths: first row < second row < third row. Lewis acids help accelerate insertions into CO by coordinating to CO and making the carbonyl carbon more electrophilic. For a similar reason, CO ligands bound to electron-poor metal centers undergo insertion more rapidly than CO’s bound to electron-rich metals. Finally, for reasons that are still unclear, one-electron oxidation often increases the rate of CO insertion substantially.

Although the thermodynamics of alkene 1,2-insertion are more favorable for metal-carbon than metal-hydrogen bonds, M–H bonds react *much* more rapidly than M–C bonds in 1,2-insertions. This fact has been exploited for olefin hydrogenation, which would be much less useful if it had to complete with olefin polymerization (the result of repeated insertion of C=C into M–C) in the same reaction flask! More on that in the next post.

Stereochemistry in CO Insertions

Migratory insertion steps are full of stereochemistry! Configuration at the migrating alkyl group is retainedduring insertion—a nice piece of evidence supporting a concerted, intramolecular mechanism of migration.

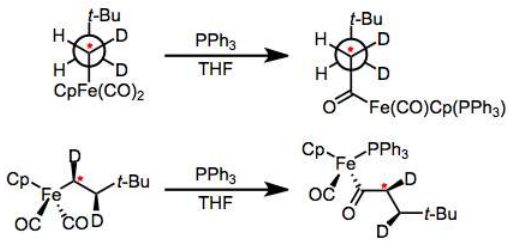

Figure 4.6.4: Migratory insertion occurs with retention of configuration at the migrating alkyl group. Two different views of the same reaction are shown here. (Michael Evans)

What about stereochemistry at the metal center? Migratory insertion may create a stereogenic center at the metal—see the iron example above. Whether the X-type ligand moves onto the unsaturated ligand or *vice versa* will impact the configuration of the product complex. Calderazzo’s study of this issue is one of my favorite experiments in all of organometallic chemistry! He took the simple labeled substrate in the figure below and treated it with dative ligand, encouraging insertion. Four products of insertion are possible, corresponding to reaction of the four CO ligands *cis* to the methyl ligand. Try drawing a few curved arrows to wrap your mind around the four possibilities, and consider both CO migration and Me migration as possible at this point.

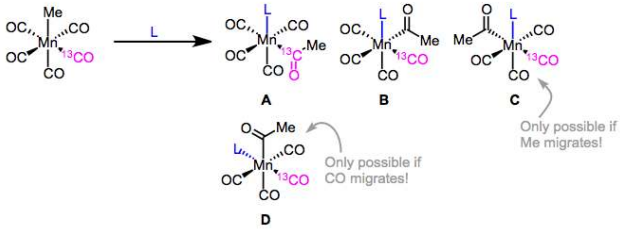

Figure 4.6.5: Insertion of the labeled complex shown could produce four products. Calderazzo did not observe product **D**, supporting a mechanism involving Me migration to CO. (Michael Evans)

Note that product **D** is impossible if we only allow the Me group to migrate—the spot *trans* to the labeled CO is another CO ligand, so that spot can only pick up L if CO migrates (not if Me migrates). On the other hand, product **C** must have come from the

migration of Me, since the Me group has moved from a *cis* to a *trans*position relative to the labeled CO in product **C**. Calderazzo observed products **A**, **B**, and **C**, but not **D**, supporting a mechanism involving Me migration. Other experiments since support the idea that most of the time, the alkyl group migrates onto CO. Slick, huh?

I won't address insertions into alkylidenes, alkylidynes, and other one-atom unsaturated ligands in this post, as insertions into CO are by far the most popular 1,1 insertions in organometallic chemistry. In the next post, we'll dig more deeply into 1,2-insertions of alkenes and alkynes. Thanks for reading!

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4.7: Oxidative Addition- General Ideas

A critical difference between the transition metals and the organic elements is the ability of the former to exist in multiple oxidation states. In fact, the redox flexibility of the transition metals and the redox obstinacy of the organic elements work wonderfully together. Why? Imagine the transition metal as a kind of matchmaker for the organic elements. Transition metals can take on additional covalent bonds (oxidation), switch out ligands (substitution), then release new covalent bonds (reduction). The resulting organic products remain unfazed by the metal's redox insanity. Talk about a match made in heaven!

The following series of posts will deal with the first step of this process, oxidation. More specifically, we'll discuss the oxidation of transition metals via formal insertion into covalent bonds, also known as **oxidative addition (OA)**. Although we often think of oxidative addition as an elementary reaction of organometallic chemistry, it is *not* an elementary mechanistic *step*. In fact, oxidative addition can proceed through a variety of mechanisms. Furthermore, any old change in oxidation state does not an oxidative addition make (that almost rhymes…). Formally, the attachment of an electrophile to a metal center (e.g., protonation) represents oxidation, but we shouldn't call this oxidative addition, since two ligands aren't entering the fray. Instead, we call this **oxidative ligation (OL)**.

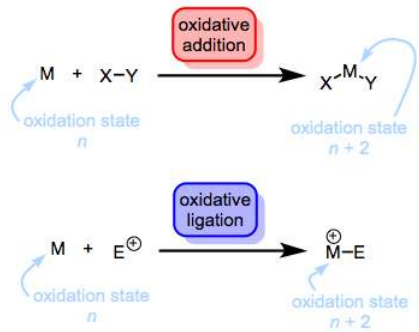

Figure 4.7.1: Oxidative addition involves formal bond insertion and the introduction of two new ligands to the metal. Oxidative ligation, OTOH, involves the coordination of only one new ligand, an electrophile. (Michael Evans)

Protonation is (formally) a kind of oxidation. Who knew?! S_N2 reactions with the metal as nucleophile are also oxidative ligations. Of course, if the leaving group comes back and forms a new bond to the metal, we're back to oxidative addition. Both reactions lead to an increase in the oxidation state of the metal by two units and a decrease in the *d* electron count of the metal by two electrons. However, note how the total electron count changes in each case. The total electron count does not change during an oxidative ligation. Think of it this way: the new ligand brings no electrons with it to the complex. On the other hand, the total electron count of the complex actually *increases* by two electrons during oxidative addition. As a result, *eighteen-electron complexes do not undergo oxidative addition*. Carve that sucker on a stone tablet. Seventeen-electron complexes can undergo oxidative addition via bimolecular OA reactions, which leave X on one metal center and Y on another.

What are the mechanisms of oxidative addition, anyway? Let's begin with the "concerted" mechanism, which can be thought of as σ-complex formation followed by insertion. The metal first sidles up to the X–Y bond and a σ complex forms (ligand dissociation may be required first). As we've seen, σ complexes $M(X_2)$ are tautomeric with their $M(X)_2$ forms. When back donation from the metal is strong enough, the σ complex disappears and $M(X)_2$ is all that remains. The metal has been formally oxidized: oxidative addition!

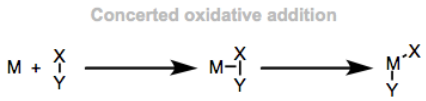

Figure 4.7.2: Copy and Paste Caption here. (Copyright; author via source)

There are several variations on this theme. When X and Y are different, the σ complex is skewed and approach to the metal "asynchronous." When the metal isn't a great nucleophile, the reaction may stop at the σ-complex stage.

Other mechanisms of oxidative addition require multiple steps and the formation of polar or radical intermediates. An important two-step, polar mechanism involves S_N2 attack of a nucleophilic metal on an electrophile, followed by coordination of the leaving

group to the metal center. What we might call S_N1-type mechanisms, involving dissociation of the electrophile before nucleophilic attack by the metal, also occur (HCl and other strong acids operate like this). Finally, both non-chain and chain radical mechanisms are possible in reactions of metal complexes with alkyl halides. We'll dive into these mechanisms in more detail in upcoming posts.

Hopefully from this general discussion, you've gleaned a few trends. The metal *must* have a stable oxidation state two units higher than its current OS for oxidative addition to occur. For the reaction to work well, the metal typically needs to be electron rich (and in a relatively low oxidation state) and the organic compound needs to be electron poor. To see why, consider that during oxidative addition, the metal formally loses two *d*electrons. Furthermore, the main-group atoms X and Y gain electron density, since the new M–X and M–Y bonds are likely polarized toward X and Y. The metal needs to bear *two* open coordination sites (not necessarily at the same time) for oxidative addition to occur, because two new ligands enter the metal's coordination sphere. Since the new ligands need space, steric hindrance tends to discourage oxidative addition. Oftentimes ligand dissociation is required before oxidative addition can occur; in many of these cases, the rate of dissociation influences the overall rate of the reaction.

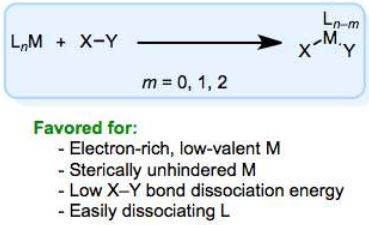

Figure 4.7.3: Factors affecting the kinetics and thermodynamics of oxidative addition. (Michael Evans)

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4.8: Oxidative Addition of Non-polar Reagents

How important are oxidative additions of non-polar reagents? *Very*. The addition of dihydrogen (H_2) is an important step in catalytic hydrogenation reactions. Organometallic C–H activations depend on oxidative additions of C–H bonds. In a fundamental sense, oxidative additions of non-polar organic compounds are commonly used to establish critical metal-carbon bonds. Non-polar oxidative additions get the ball rolling in all kinds of catalytic organometallic reactions. In this post, we'll examine the mechanisms and important trends associated with non-polar oxidative additions.

Oxidative Additions of H_2

Electron-rich metal centers with open coordination sites (or the ability to form them) undergo oxidative additions with dihydrogen gas. The actual addition step is concerted, as we might expect from the dull H_2molecule! However, before the addition step, some interesting gymnastics are going on. The status of the σ complex that forms prior to H–H insertion is an open question—for some reactions it is a transition state, others a discrete intermediate. In either case, the two new hydride ligands end up *cis* to one another. Subsequent isomerization may occur to give a *trans* dihydride.

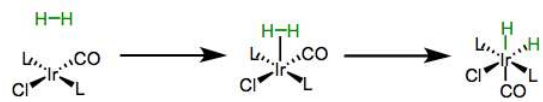

Figure 4.8.1: Oxidative addition of dihydrogen to Vaska's complex. Note the *cis*arrangement of the hydride ligands. (Michael Evans)

There's more to this little reaction than meets the eye. For starters, either pair of *trans* ligands in the starting complex (L/L or Cl/CO) may "fold back" to form the final octahedral complex. As in associative ligand substitution, the transition state for folding back is basically trigonal bipyramidal. As we saw before, π-acidic ligands love the equatorial sites of the TBP geometry, which are rich in electrons capable of π bonding. As a consequence, π-acidic ligands get folded back preferentially, and tend to end up *cis* to their *trans* partners in the starting complex.

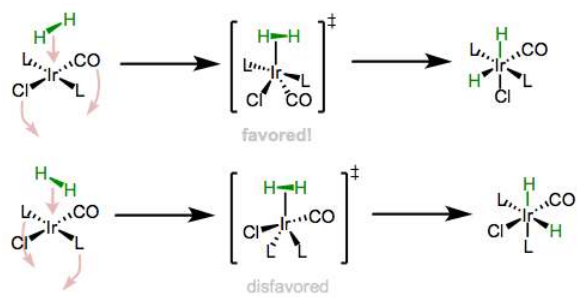

Figure 4.8.2: Dihydrogen may approach along two distinct trajectories. Placing π-acidic ligands in the equatorial plane of the TBP transition state is favored. (Michael Evans)

Termolecular oxidative additions of H_2, in which the two H atoms find their way to two different metal centers, are also known, but these suffer from entropic issues, since H_2 is jammed between two metal complexes in the transition state of the (concerted) mechanism.

Oxidative Additions of Silanes (H–Si)

Silanes bearing Si–H bonds may react with organometallic complexes in oxidative addition reactions. Spectroscopic experiments support the intermediacy of a silyl σ complex before insertion. Since the mechanism is concerted, oxidative addition occurs with retention of configuration at Si. The usual pair of forward bonding ($\sigma_{Si–H} \rightarrow d_\sigma$) and backbonding ($d_\pi \rightarrow \sigma^*_{Si–H}$) orbital interactions are at play here. File this reaction away as a great method for the synthesis of silyl complexes.

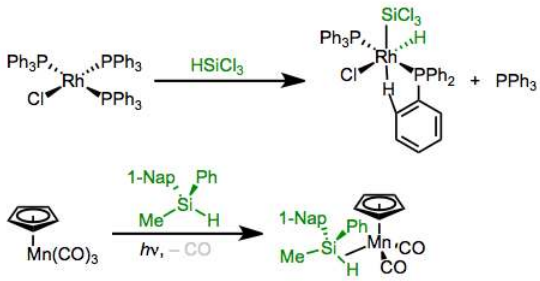

Figure 4.8.3: Si–H bonds undergo oxidative addition to electron-rich metal complexes. Electron-poor complexes may stop at the σ complex stage. (Michael Evans)

Oxidative Additions of C–H Bonds

Needless to say, oxidative addition reactions of C–H bonds are highly prized among organometallic chemists. As simple as it is to make silyl complexes through oxidative addition, analogous reactions of C–H bonds that yield alkyl hydride complexes are harder to come by.

The thermodynamics of C–H oxidative addition tell us whether it's favorable, and depend heavily on the nature of the organometallic complex. The sum of the bond energies of the new M–C and M–H bonds must exceed the sum of the energies of the C–H bond and any M–L bonds broken during the reaction (plus, OA is entropically disfavored). For many complexes, the balance is not in favor of oxidative addition. For example, the square planar Vaska's complex (L_2(CO)IrCl; L = PPh_3) seems like a great candidate for oxidative addition of methane—at least to the extent that the product will be six-coordinate and octahedral. However, thermodynamics is a problem:

$$104\ (C–H) – [60\ (Ir–H) + 35\ (Ir–Me)] + 9\ kcal/mol\ (entropy) = 18\ kcal/mol$$

18 kcal/mol is prohibitively high in energy, and playing with the temperature to adjust the entropy factor can't "save" the reaction.

More electron-rich complexes exhibit favorable thermodynamics for insertions of C–H bonds. The example below is so favorable (104 – [75 + 55] + 9 = –17 kcal/mol) that the product is a rock!

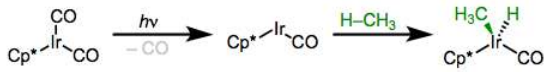

Figure 4.8.4: This thermodynamically favorable C–H oxidative addition is helped by the electron-donating Cp* ligand. (Michael Evans)

Arenes undergo C–H oxidative addition faster (and more favorably) than alkanes for several reasons. It seems likely that an intermediate arene π complex and/or C–H σ complex precede insertion, and these complexes ought to be more stable than alkyl σ complexes. In addition, metal-aryl bonds tend to be stronger than metal-alkyl bonds.

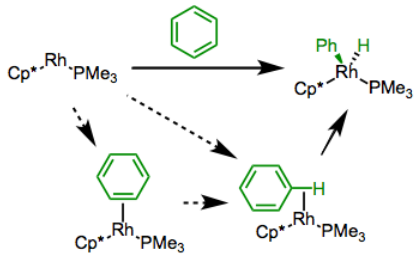

Figure 4.8.5: Mechanistic possibilities for the oxidative addition of arene C–H bonds. (Michael Evans)

Your average organic compound is covered in C–H bonds. Thus, for C–H oxidative addition to be synthetically useful, we need to understand how to control the selectivity of the reaction. In most early studies, selectivity for insertion into primary C–H bonds was observed. It became apparent that primary alkyl complexes (*viz.*, the observed products) are generally much more stable than secondary alkyl complexes, even though the corresponding primary and secondary σ complexes are comparable in energy. Steric factors are a likely culprit!

Naturally, other strategies for controlling selectivity in C–H “activations” have appeared; however, be aware that these may not involve oxidative addition. Lewis basic directing groups have been used with success to direct oxidative addition to a nearby C–H bond—but these reactions are aided by base and do not involve oxidation. Metal carbenoid insertions into C–H bonds also do not involve oxidation at the metal center. The lesson of these reactions: *be careful*, and don’t assume that all alkyl complexes are the result of C–H oxidative addition!

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4.9: Oxidative Addition of Polar Reagents

Organometallic chemistry has vastly expanded the practicing organic chemist's notion of what makes a good nucleophile or electrophile. Pre-cross-coupling, for example, using unactivated aryl halides as electrophiles was largely a pipe dream (or possible only under certain specific circumstances). Enter the oxidative addition of polarized bonds: all of a sudden, compounds like bromobenzene started looking a *lot* more attractive as starting materials. **Cross-coupling reactions** involving sp^2– and *sp*-hybridized C–X bonds beautifully complement the "classical" substitution reactions at sp^3 electrophilic carbons. Oxidative addition of the C–X bond is the step that kicks off the magic of these methods. In this post, we'll explore the mechanisms and favorability trends of oxidative additions of polar reagents. The landscape of mechanistic possibilities for polarized bonds is much more rich than in the non-polar case—concerted, ionic, and radical mechanisms have all been observed.

Concerted Mechanisms

Oxidative additions of aryl and alkenyl C_{sp^2}–X bonds, where X is a halogen or sulfonate, proceed through **concerted** mechanisms analogous to oxidative additions of dihydrogen. Reactions of N–H and O–H bonds in amines, alcohols, and water also appear to be concerted. A π complex involving η^2-coordination is an intermediate in the mechanism of insertion into aryl halides at least, and probably vinyl halides too. As two open coordination sites are necessary for concerted oxidative addition, loss of a ligand from a saturated metal complex commonly precedes the actual oxidative addition event.

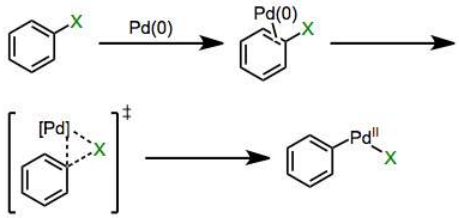

Figure 4.9.1: Concerted oxidative addition of aryl halides and sulfonates. (Copyright; author via source)

Trends in the reactivity of alkyl and aryl (pseudo)halides toward oxidative addition are some of the most famous in organometallic chemistry. Aryl iodides are most reactive, followed by bromides, tosylates, and chlorides. To counter the lower electrophilicity of aryl chlorides, electron-rich alkyl phosphine ligands may be used to accelerate reactions of aryl chlorides. These "hot" ligands increase electron density at the metal center, facilitating oxidative addition. Because they tend to be bulkier than aryl phosphines, though, complexes of alkyl phosphines sometimes operate through slightly different mechanisms than aryl phosphine complexes. Although the exact species undergoing oxidative addition may differ (see below), all of the actual oxidative addition events are thought to be concerted.

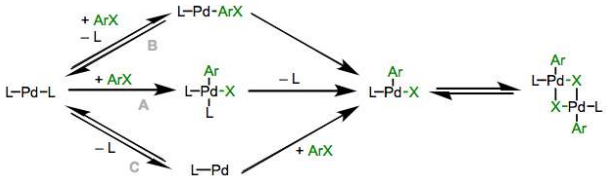

Figure 4.9.2: Mechanisms of oxidative addition to palladium(0) phosphine complexes. Much depends on the nature of L. (Copyright; author via source)

Here, as we've seen before, electron-rich organohalides react more slowly than electron-poor compounds. Oxidative addition depletes electron density from the metal center and increases electron density in the organic ligands, so this trend makes sense!

S_N2 and Ionic Mechanisms

Very electrophilic halides often react through ionic mechanisms in which oxidative addition *per se*takes place over multiple steps. As strange as it may be to imagine a metal center as a nucleophile, this exact reactivity is central to the S_N2 and ionic mechanisms of oxidative addition. In a slow step, the metal center attacks the electrophilic atom, displacing halide. Rapid recombination of the positively charged metal complex and negative halide ion yields the product of oxidative addition. In essence, this mechanism involves oxidative ligation followed by association of oppositely charged ions. Loss of a dative ligand is sometimes necessary as an intermediate step, if the metal complex is saturated after the S_N2 step.

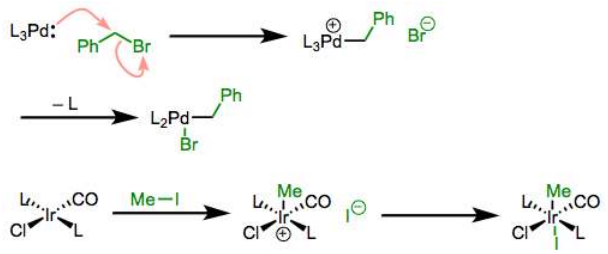

Figure 4.9.3: SN2 mechanisms of oxidative addition: oxidative ligation followed by ligand substitution or simple coordination. (Copyright; author via source)

An extremely solid analogy can be drawn between these reactions and classical S_N2 reactions from "sophomore organic" chemistry. Primary halides react most quickly, followed by secondary and tertiary halides. Inversion at carbon is observable in these reactions, and entropy of activation is negative (suggesting an associated transition state). Negatively charged metal complexes kick butt in these reactions, and as electron-withdrawing ligands are added to the metal center, reactivity decreases. Added halide anions can actually accelerate S_N2 oxidative additions—the anion coordinates to the metal center, making it negative and increasing its electron-donating power.

A nice analogy can also be drawn between S_N2-type oxidative additions and oxidative additions of strong acids, which occur basically through the same mechanism (with replacement of hydrogen for carbon). During these so-called "ionic mechanisms," protonation of the metal center usually occurs first, followed by ligand substitution or simple coordination of the conjugate base. In rarer circumstances and for less nucleophilic metal complexes, coordination of the conjugate base can actually occur first, followed by protonation!

Radical Mechanisms

Radicals are sometimes thought of as the bucking broncos of the chemistry world, and as such, radical mechanisms for oxidative additions are more difficult to control and less appealing. For example, one must be careful to use solvents that don't react with the intermediate radicals. Still, a considerable amount of effort has been directed at "taming the wild beast." In some ways, radical reactions offer complementary selectivity to ionic and concerted mechanisms.

Non-chain radical mechanisms involve single-electron transfer from the metal complex to the organohalide, followed by recomination of the resulting radicals. The metallic and organic radicals, when stable, can even be isolated from the reaction as products.

$PtL_2 + RX \rightarrow PtL_2X^{\cdot} + R^{\cdot} +$

$PtL_2X^{\cdot} + R^{\cdot} \rightarrow PtL_2XR$

Reactivity trends here depend on the stability of the intermediate radical species. Tertiary halides react most rapidly, followed by secondary and primary halides. More electron-rich metal centers react more rapidly (are you sick of this trend yet?), since they can more easily donate an electron to the organohalide.

Chain radical mechanisms involve reactions between radical intermediates and even-electron starting materials, resulting in the continuous regeneration of radicals as products form. I like to imagine the radical intermediates as Tom Hanks in *Cast Away*, floating in an ocean of even-electron starting material. A nice example of this reactivity was explored by Hill and Puddephatt in the mid-1980s.

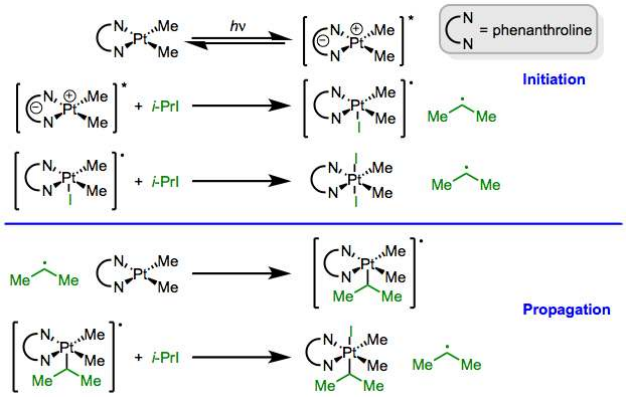

Figure 4.9.4: Organometallic complexes can carry out radical chain mechanisms too! Here, isopropyl radical is the propagating radical. (Copyright; author via source)

Excitation of the Pt(II) complex yields a charge-transfer complex that can abstract iodine from isopropyl iodide. A second abstraction event completes the initiation phase. During propagation, isopropyl radical couples with the (unexcited) Pt(II) complex, and the resulting organometallic radical abstracts iodine from the starting organohalide. Free radical scavengers kill the reaction, but interestingly, only the isopropyl radical reacts with radical traps.

Lastly, I'll just mention briefly that **binuclear oxidative additions**, which involve two metal centers "tugging" on the organohalide in concert, often involve radicals and/or one-electron transfers. Here's one example involving chromium, and here's a somewhat more famous example involving cobalt (by Budzelaar!).

Summing up, oxidative additions of polar reagents are critical steps in many organometallic reactions. We've only just barely scratched the surface of this important class of reactions, but a few powerful trends have emerged. In general, more electron-rich OM complexes and more electron-poor polar organics react more rapidly in oxidative additions. Steric hindrance in the metal complex can also play an interesting role, either by changing the actual species that undergoes oxidative addition or by discouraging oxidative addition altogether. Next up, we'll take a brief look at the microscopic reverse of oxidative addition, **reductive elimination**. Most of the trends and mechanisms associated with reductive elimination are simply the opposite of those for oxidative addition, so our discussions of reductive elimination will be fairly short.

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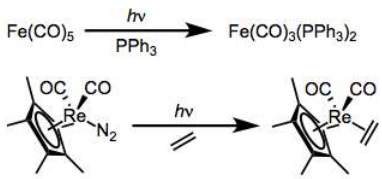
4.10: Quirky Ligand Substitutions

Over the years, a variety of “quirky” substitution methods have been developed. All of these have the common goal of facilitating substitution in complexes that would otherwise be inert. It’s an age-old challenge: how can we turn a stable complex into something unstable enough to react? Photochemical excitation, oxidation/reduction, and radical chains all do the job, and have all been well studied. We’ll look at a few examples in this post—remember these methods when simple associative or dissociative substitution won’t get the job done.

Photochemical Substitution

Substitution reactions of dative ligands—most famously, CO—may be facilitated by photochemical excitation. Two examples are shown below. The first reaction yields only monosubstituted product without ultraviolet light, even in the presence of a strongly donating phosphine.

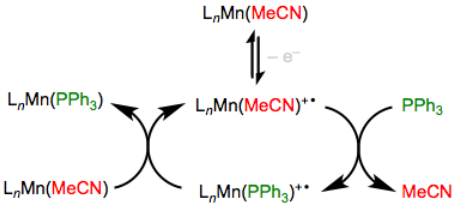


Dissociative photochemical substitutions of CO and dinitrogen.

All signs point to dissociative mechanisms for these reactions (the starting complexes have 18 total electrons each). Excitation, then, must increase the M–L antibonding character of the complex’s electrons; exactly how this increase in antibonding character happens has been a matter of some debate. Originally, the prevailing explanation was that the LUMO bears M–L antibonding character, and excitation kicks an electron up from the HOMO to the LUMO, encouraging cleavage of the M–L bond. A more recent, more subtle explanation backed by calculations supports the involvement of a metal-to-ligand charge-transfer state along with the “classical” ligand-field excited state.

Oxidation/Reduction

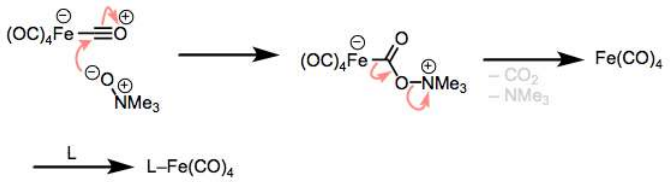
Imagine a screaming baby without her pacifier—that’s a nice analogy for an odd-electron organometallic complex. Complexes bearing 17 and 19 total electrons are much more reactive toward substitution than their even-electron counterparts. Single-electron oxidation and reduction (“popping out the pacifier,” if you will) can thus be used to efficiently turn on substitution. As you might expect, oxidation and reduction work best on electron-rich and electron-poor complexes, respectively. The Mn complex in the oxidative example below, for instance, includes a strongly donating MeCp group (not shown).



Oxidation accelerates substitution in electron-rich complexes through a chain process.

Reduction works well for electron-poor metal carbonyl complexes, which are happy to accept an additional electron.

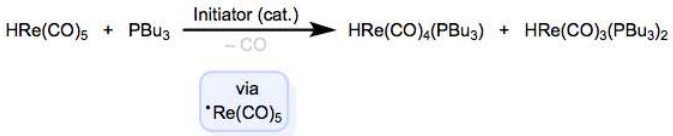
There is a two-electron oxidation method that’s also worth knowing: the oxidation of CO with amine oxides. This nifty little method releases carbon dioxide, amine, and an unsaturated complex that may be quenched by a ligand hanging around. The trick is addition to the CO ligand followed by elimination of the unsaturated complex. As the oxidized CO2 and reduced amine float away, the metal complex finds another ligand.



Oxidation of CO with amine oxides. A fun method for dissociative substitution of metal carbonyls!

Radical Chain Processes

Atom abstraction from 18-electron complexes produces neutral 17-electron intermediates, which are susceptible to ligand substitution via radical chain mechanisms. The fact that the intermediates are neutral distinguishes these methods from oxidation-based methods. First-row metal hydrides are great for these reactions, owing to their relatively weak M–H bonds. One example is shown below.



Radical-chain substitution involving atom abstraction.

After abstraction of the hydrogen atom by initiator, substitution is rapid and may occur multiple times. Propagation begins anew when the substituted radical abstracts hydrogen from the starting material to regenerate the propagating radical and form the product. These quirky methods are nice to have in your back pocket when you're backed into a synthetic corner—sometimes, conventional associative and dissociative substitution just won't do the job. In the next post, we'll press on to oxidative addition.

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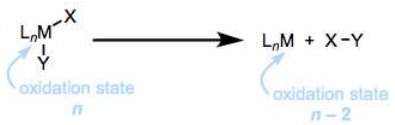
4.11: Reductive Elimination- General Ideas

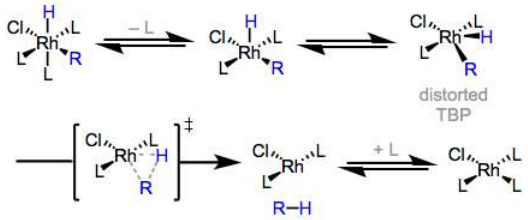
Reductive elimination is the microscopic reverse of oxidative addition. It is literally oxidative addition run in reverse—oxidative addition backwards in time! My favorite analogy for **microscopic reversibility** is the video game Braid, in which "resurrection is the microscopic reverse of death." The player can reverse time to "undo" death; viewed from the forward direction, "undoing death" is better called "resurrection." Chemically, reductive elimination and oxidative addition share the same reaction coordinate. The only difference between their reaction coordinate diagrams relates to what we call "reactants" and "products." Thus, their mechanisms depend on one another, and trends in the speed and extent of oxidative additions correspond to opposite trends in reductive eliminations. In this post, we'll address reductive elimination in a general sense, as we did for oxidative addition.



A general reductive elimination. The oxidation state of the metal decreases by two units, and open coordination sites become available.

During reductive elimination, the electrons in the M–X bond head toward ligand Y, and the electrons in M–Y head to the metal. The eliminating ligands are always X-type! On the whole, the oxidation state of the metal decreases by two units, two new open coordination sites become available, and an X–Y bond forms. What does the change in oxidation state suggest about changes in electron density at the metal? As suggested by the name "reductive," the metal gains electrons. The ligands lose electrons as the new X–Y bond cannot possibly be polarized to both X and Y, as the original M–X and M–Y bonds were. Using these ideas, you may already be thinking about reactivity trends in reductive elimination…hold that thought.

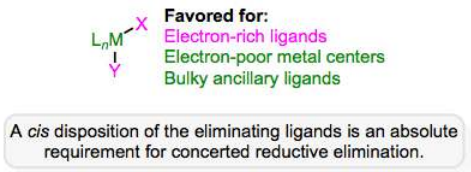
It's been observed in a number of cases that a ligand dissociates from octahedral complexes before concerted reductive elimination occurs. Presumably, dissociation to form a distorted TBP geometry brings the eliminating groups closer to one another to facilitate elimination.



Reductive elimination is faster from five-coordinate than six-coordinate complexes.

Square planar complexes may either take on an additional fifth ligand or lose a ligand to form an odd-coordinate complex before reductive elimination. Direct reductive elimination without dissociation or association is possible, too.

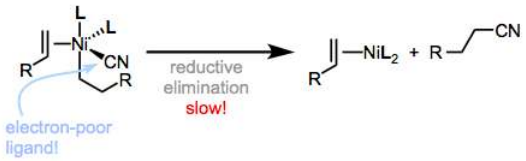
Reactivity trends in reductive elimination are opposite those of oxidative addition. More electron-rich ligands bearing electron-donating groups react more rapidly, since the ligands lose electron density as the reaction proceeds. More electron-poor metal centers—bearing π-acidic ligands and/or ligands with electron-withdrawing groups—react more rapidly, since the metal center gains electrons. Sterically bulky ancillary ligands promote reductive elimination since the release of X and Y can "ease" steric strain in the starting complex. Steric hindrance helps explain, for example, why coordination of a fifth ligand to a square planar complex promotes reductive elimination even though coordination increases electron density at the metal center. A second example: trends in rates of reductive eliminations of alkanes parallel the steric demands of the eliminating ligands: C–C > C–H > H–H.



Reactivity trends for reductive eliminations.

Mechanistic trends for reductive elimination actually parallel trends in mechanisms of oxidative addition, since these two reactions are the microscopic reverse of one another. Non-polar and moderately polar ligands react by concerted or radical mechanisms; highly polarized ligands and/or very electrophilic metal complexes react by ionic (S_N2) mechanisms. The thermodynamics of reductive elimination must be favorable in order for it to occur! Most carbon–halogen reductive eliminations, for example, are thermodynamically unfavorable (this has turned out to be a good thing, especially for cross-coupling reactions).

Reductive elimination is an important step in many catalytic cycles—it usually comes near the "end" of catalytic mechanisms, just before product formation. For some catalytic cycles it's the turnover-limiting step, making it very important to consider! Hydrocyanation is a classic example; in the mechanism of this reaction, reductive elimination of C–CN is the slow step. Electron-poor alkyl ligands, derived from electron-poor olefins like unsaturated ketones, are bad enough at reductive elimination to prevent turnover altogether! Of course, the electronegative CN ligand is not helping things either…how would you design the ancillary ligands L to speed up this step?



Reductive elimination is the turnover-limiting step of hydrocyanation. How would you design L to speed it up?

Contributors and Attributions

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4.12: The trans/cis Effects and Influences

The trans effect is an ancient but venerable observation. First noted by Chernyaev in 1926, the trans effect and its conceptual siblings (the trans influence, cis influence, and cis effect) are easy enough to comprehend. That is, it's simple enough to know what they are. To understand why they are, on the other hand, is much more difficult.

Definitions & Examples

Let's begin with definitions: what is the trans effect? There's some confusion on this point, so we need to be careful. The trans effect proper, which is often called the kinetic trans effect, refers to the observation that certain ligands increase the rate of ligand substitution when positioned trans to the departing ligand. The key word in that last sentence is "rate"—the trans effect proper is a kinetic effect. The trans influence refers to the impact of a ligand on the length of the bond trans to it in the ground state of a complex. The key phrase there is "ground state"—this is a thermodynamic effect, so it's sometimes called the thermodynamic trans effect. Adding to the insanity, cis effects and cis influences have also been observed. Evidently, ligands may also influence the kinetics or thermodynamics of their cis neighbors. All of these phenomena are independent of the metal center, but do depend profoundly on the geometry of the metal (more on that shortly).

Kinetic trans and cis effects are shown in the figure below. In both cases, we see that X1 exhibits a stronger effect than X2. The geometries shown are those for which each effect is most commonly observed. The metals and oxidation states shown are prototypical.

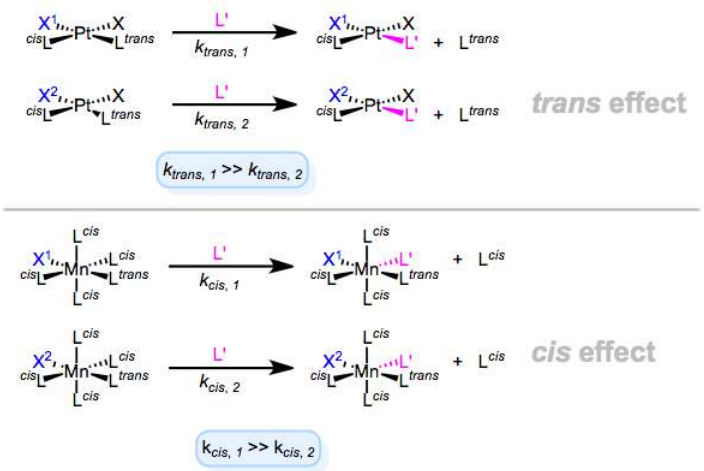

Figure 4.12.1: The kinetic trans and cis effects in action. X^1 is the stronger (trans/cis)-effect ligand in these examples.

On to the influences, which are simpler to illustrate since they're concerned with ground states, not reactions. The lengthened bonds below are exaggerated.

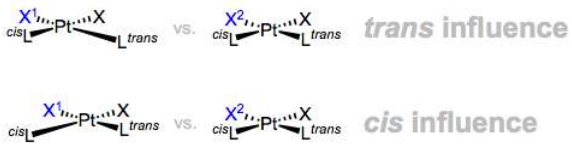

Figure 4.12.2: The trans and cis influences in action. Note the elongated bond lengths.

And there we have it folks, the thermodynamic and kinetic cis/trans effects. It's worth keeping in mind that the kinetic trans effect is most common for d8 square planar complexes, and the kinetic cis effect is most common for d6 octahedral complexes (particularly when the departing L is CO). But a lingering question remains: what makes for a strong trans effect ligand?

Origins of Effects & Influences

The trans effect and its cousins are all electronic, not steric effects. So, the electronic properties of the ligand dictate the strength of its trans effect. Let's finally dig into the trans effect series:

(weak) F^-, HO^-, H_2O <NH_3 < py < Cl^- < Br– < I–, SCN^-, NO_2^-, $SC(NH_2)_2$, Ph^- < SO_3^{2-} < PR_3 < AsR_3, SR_2, H_3C^- < H^-, NO, CO, NC^-, C_2H_4 (strong)

What's the electronic progression here? It's clear that electronegativity decreases across the series: F^- < Cl^- < Br^- < I^- < H_3C^-. From a bonding perspective, we can say that ligands with strong trans effects are strong σ-donors (or σ-bases). Yet σ-donation doesn't tell the whole story. What about ethylene and carbon monoxide, which both appear at the top of the heap? Neither of these ligands are strong σ-donors, but their π systems do interact with the metal center through backbonding. Consider the following sub-series: S=C=N– < PR_3 < CO. Backbonding increases across this series, along with the strength of the trans effect. Strong backbonders—better known as π-acceptors or π-acids—exhibit strong trans effects.

Strong trans effect = strong σ-donor + strong π-acceptor

Wonderful! Using these ideas we can identify ligands with strong trans effects. But we can dive deeper down the rabbit hole: why does this particular combination of electronic factors lead to a strong trans effect? To understand this, we need to know the mechanism of the ligand substitution reaction that's sped up by strong trans effect ligands. For 16-electron Pt(II) complexes, associative substitution is par for the course. The incoming ligand binds to the metal first, forming an 18-electron complex (yay!), which jettisons a ligand to yield a new 16-electron product. The mechanism in all its glory is shown in the figure below.

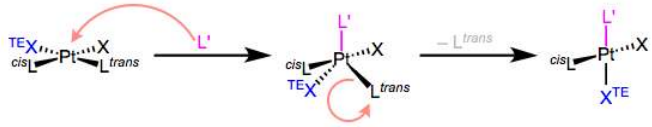

Figure 4.12.3: The mechanism of associative ligand substitution of Pt(II) complexes.

Some very important points about this mechanism:

- The incoming ligand always sits at an equatorial site in the trigonal bipyramidal intermediate. More on this another day, but I think of this result as governed by the principle of least motion. Consider the molecular gymnastics that would have to happen to place the incoming ligand in an axial position.
- Two ligands in the square plane are "pushed down" and become the other two equatorial ligands.
- Owing to microscopic reversibility, the leaving group must be one of the equatorial ligands.

The third point reveals that once L' has "pushed down" XTE and Ltrans, Ltrans has no choice but to leave (assuming XTE stays put). Thus, the trans effect has nothing to do with the second step of the mechanism, which is not rate determining anyway. The key is the first step—in particular, the "pushing down" event. Apparently, ligands with strong trans effects like to be pushed down. They like to occupy the equatorial plane of the TBP intermediate. Now here's the kicker: the equatorial sites of the TBP geometry are more π basic than the axial sites. The equatorial plane is just the xy-plane of the metal center, and the d orbitals in that plane (when occupied) are great electron sources for π-acidic ligands. Thus, π-acidic ligands want to occupy those equatorial sites, to receive the benefits of strong backbonding! Boom; strong π-acids encourage loss of the ligand trans to themselves.

Figure 4.12.4: The equatorial sites of TBP metals are rich in electrons that can π bond.

What about those pesky σ donors? Well, we can imagine that in a square planar complex, a ligand and its trans partner are competing for donation into the same d orbital. Strong σ donation from a ligand should thus weaken the bond trans to it. Although this is the thermodynamic trans effect (trans influence) in action, the resulting destabilization of the ground state relative to the transition state is a kinetic effect. On the whole, the barrier to substitution of the trans ligand goes down as σ-donating strength goes up.

This idea of "competition for the metal center" is a nice heuristic to use when thinking about the trans and cis influences. The type of metallic orbital involved in M–L bonding determines the strength of L's trans and cis influences on neighboring ligands that also need that metallic orbital for bonding. For example: both influences are large if the metal's s orbital is a significant contributor to M–L bonding, since it's non-directional; the trans influence is much greater than the cis influence when metallic p orbitals are primarily involved in M–L. For a deeper explanation of these ideas, see this paper.

Summing up

Perhaps the most valuable lesson from a study of the trans effect is that many concepts from organometallic chemistry involve more than meets the eye. Geometric effects and influences are real icebergs, in the sense that the observations and trends are easy to grasp, but difficult to explain. We had to dig all the way into the mechanism of associative ligand substitution before a satisfactory explanation emerged!

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