

# CHEM 20200 (Inorganic Chemistry II) Notes

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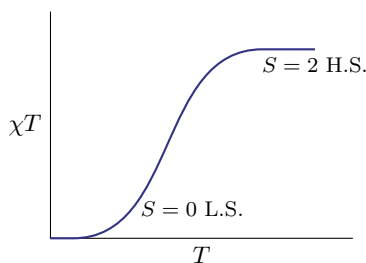
# Unit 1

## Electronic Phenomena

### 1.1 Lecture 1: Introduction/Key Trends

- 3/29:
- Largely asynchronous, but synchronous discussions, office hours, and tests.
    - Refer to the Canvas site for all information; it's the class hub.
  - To understand transition metal trends and properties, start with *atomic* properties and trends.
  - **Electronegativity:** The energy that an atom will gain when it gains an electron.
    - Fluorine really wants to gain an electron; thus, it has high electronegativity.
      - Do you mean electron affinity?
    - Increases across a row; decreases down a column.
      - Transition metals, in general, are an exception to this rule.
      - This is because of the **lanthanide contraction**.
    - Discontinuities in the transition metals (Mn and Ni) correspond to half-filled and filled *d* shells, respectively.
      - Extra stability means less of a desire to gain an electron.
  - **Ionization potential:** The energy required to remove an electron.
    - Varies with the identity of an element *and* its oxidation state.
    - Increases across a row; decreases down a column.
  - Size:
    - Many different definitions (depending on the specific thing you're interested in, one may be more useful than another). For example,
      - Atomic radius: Specific to an element.
      - Ionic radius: Specific to an oxidation state; as in salts and coordination complexes.
      - Covalent radius: Distance that one would expect for a bond; varies with bond order.
    - Decreases across a row; increases down a column (a notable exception to the latter trend follows from the lanthanide contraction).
    - Things that affect size:
      - Oxidation state.
      - Spin state (high spin [larger; this is because the  $e_g$  orbitals are antibonding, and antibonding electrons both push the bounds of the atom and weaken bonds, increasing the covalent radius] vs. low spin [smaller]).

- **Lanthanide contraction:** In the transition metals, there is a small/no increase in size between the second and third rows.
  - This is because the shell added in between contains the  $f$  orbitals, which are small, do not extend past the noble gas core, and do not provide good shielding.
  - $Z$  goes up a lot with little shielding, so the  $5d$  orbitals are contracted; thus,  $4d/5d$  orbitals are similar in size.
- **Oxidation state:** The number of electrons a metal center is below its valence.
  - Typically, the maximum oxidation state is defined by the  $d$ -count for the 0-valent metal.
- Having discussed four trends, how are they related?
  - As oxidation state increases, “electronegativity” and ionization potential will increase, and the radius will decrease.
    - This is because removing an electron  $\Rightarrow$  reduces shielding  $\Rightarrow$  higher positive charge  $\Rightarrow$  all orbitals decrease in energy  $\Rightarrow$  all orbitals decrease in size (hence radius decreases, too).
    - Watch out for discontinuities such as  $\text{Mn}^{2+}$ .
- **Magnetic properties:** Unique to the transition metals and the  $f$  block.
  - Consider  $\text{Fe}^{\text{II}}\text{L}_6^{2+}$  ( $d^6$ ).
  - Possible states: Low spin ( $S = 0$ ), intermediate spin ( $S = 1$ ; rare), and high spin ( $S = 2$ ).
  - We predict which state dominates by the:
    - **Pairing energy.**
    - **Ligand field stabilization energy.**
- **Pairing energy:** The energy cost of putting two electrons in the same orbital. *Also known as PE.*
  - Trends with orbital size/radius.
  - Decreases down a column.
- **Ligand field stabilization energy:** *Also known as LFSE.*
  - Can be thought of in terms of crystal field theory.
    - Extra thoughts on Figure VI.10 of Labalme (2021): Donating negative charge to a free metal ion in a spherically symmetric fashion uniformly raises the energy of the  $d$  orbitals by increasing repulsions and size.
    - Low-spin LFSE:  $6 \cdot -4 \text{ Dq} + 3 \text{ PE} = -24 \text{ Dq} + 3 \text{ PE}$ .
    - Intermediate-spin LFSE:  $5 \cdot -4 \text{ Dq} + 1 \cdot 6 \text{ Dq} + 2 \text{ PE} = -14 \text{ Dq} + 2 \text{ PE}$ .
    - High-spin LFSE:  $4 \cdot -4 \text{ Dq} + 2 \cdot 6 \text{ Dq} + 1 \text{ PE} = -4 \text{ Dq} + 1 \text{ PE}$ .
    - Thus, the energy difference between the low-spin and high-spin configurations is  $20 \text{ Dq} + 2 \text{ PE}$ . It follows that if  $10 \text{ Dq} > 1 \text{ PE}$ , then the complex will be low spin; and if  $10 \text{ Dq} < 1 \text{ PE}$ , then the complex will be high spin.
    - This also explains why the intermediate spin state is rare: if  $\Delta_o$  is large enough to make  $10 \text{ Dq} > 1 \text{ PE}$ , then it will likely take the complex all the way to a low-spin configuration (and vice versa for high spin).
    - Lastly, this means that  $\text{Fe}^{\text{II}}$  is a good **spin-crossover** ion.
- **Spin-crossover (ion):** An ion that can have both high- and low-spin states.
  - The graph of the magnetic moment  $\chi T$  of  $\text{Fe}^{\text{II}}$  vs. temperature  $T$  (see Figure 1.1) moves from  $S = 0$  at the bottom left to  $S = 2$  at the top right.
  - $d^2$  ions are never spin-crossover ions:  $-8 \text{ Dq} + 0 \text{ PE}$  for high spin vs.  $-8 \text{ Dq} + 1 \text{ PE}$  for low spin.

Figure 1.1: Magnetic moment vs. temperature for the  $\text{Fe}^{\text{II}}$  ion.

- Dq and PE values depend on:

- Ligand field strength.

- $\Delta O_h$  increases as  $\sigma$  donation increases.
- $\Delta O_h$  increases as  $\pi$  acceptance increases.
- $\Delta O_h$  decreases as  $\pi$  donation increases.
- To what extent do we need to have the spectrochemical series memorized?

- Metal center.

- Larger, more diffuse metals (i.e., second- and third-row transition metals) have better overlap with the ligands, giving rise to larger  $\Delta O_h$ .
- Note that pairing energy decreases in second- and third-row transition metals (due to the larger orbitals).
- These two factors imply that second- and third-row transition metals are almost always low spin.

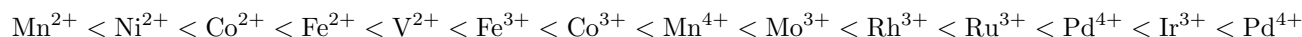
- Oxidation state.

- As oxidation state increases,  $\Delta O_h$  increases (due to better energy matching, higher “electronegativity,” the role of electrostatics, and the electron configuration [ $d^5$  is almost always high spin, and  $d^6$  is often low spin]).
- Why do  $d^5$  and  $d^6$  exhibit the above behavior? Shouldn’t the stabilized orbitals be split more?
- See the below spectrochemical series for metals.

- Geometry.

- In a  $\sigma$ -only sense, lower coordination numbers tend to have smaller LFSEs.
- $T_d < C_{4v} \approx D_{3h} < O_h < D_{4h}$ .
- $\Delta_{\text{sq. pl.}} \approx 1.74 \Delta O_h$ .

- Spectrochemical series for metals (not as precise as the one for ligands, but a decent approximation):



- Hard/soft acid-base theory:

- Common Lewis acids:

- Proton:  $\text{H}^+$ .
- Molecules with no octet:  $\text{AlCl}_3$ ,  $\text{BR}_3$  (boranes),  $\text{BeH}_2$ .
- Metal cations:  $\text{Na}^+$ ,  $\text{Ti}^{4+}$ .
- $\pi$  acids:  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{PR}_3$ .

- Common Lewis bases:

- Carbanions:  $\text{CR}_3$ .



- Hydrides:  $\text{KH}$ ,  $\text{NaH}$ ,  $\text{LiAlH}_4$ .
  - Amines, amides, and phosphines:  $\text{NH}_3$ ,  $\text{PR}_4$ ,  $\text{NH}_2^-$ .
  - $\text{OH}_2$ ,  $\text{SR}_2$ ,  $\text{OH}^-$ .
  - Halides:  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ .
  - Carbonyl:  $\text{CO}$  (means  $\text{CO}$  is amphoteric).
  - Olefins:  $\text{C}_2\text{H}_4$ .
- Distinguishes hard vs. soft<sup>[1]</sup>.

## 1.2 Office Hours (Whitmeyer)

- 3/30:
- Electron affinity, not electronegativity, for the periodic trend?
    - At higher levels, people don't really distinguish between the two.
  - To what extent do we need to have the spectrochemical series memorized?
    - You don't need to memorize them, but it's good to know some of them off the top (exams are open note, but there are time constraints).
  - In connection with oxidation state, Prof. Anderson mentioned that  $d^5$  is almost always high spin, and  $d^6$  is often low spin. Why? Shouldn't the stabilized orbitals be split more?
    - 5  $d$  electrons each in their own orbital minimizes the pairing energy.
    - 6  $d$  electrons all occupy the lower orbitals to minimize antibonding contributions.
  - Using the textbook:
    - The lectures are essential in this course, and if you don't understand something in the lecture, ask Sophie or John or read the textbook.
    - If it's in those chapters, it could be asked about, but it probably won't be if John doesn't talk about it.

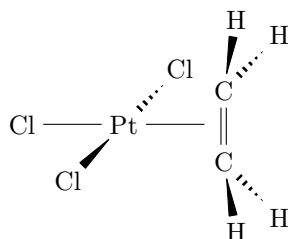
## 1.3 Chapter 1: An Overview of Organometallic Chemistry

*From Spessard and Miessler (2010).*

- 4/1:
- **Cluster compound:** A compound containing two or more metal-metal bonds.
  - **Sandwich compound:** A compound with a metal sandwiched between two ligand rings with cyclic delocalized  $\pi$  systems.
  - $\text{CO}$  is the most common of all ligands in organometallic chemistry.
  - **Carbide cluster:** A metal cluster encapsulating a carbon atom.
  - "Strictly speaking, the only compounds classified as organometallic are those that contain metal-carbon bonds, but in practice, complexes containing several other ligands similar to  $\text{CO}$  in their bonding, such as  $\text{NO}$  and  $\text{N}_2$ , are frequently included" (Spessard & Miessler, 2010, p. 4).
  - In the anionic component of Zeise's salt, the  $\pi$  electrons of ethene bond to a  $\text{PtCl}_3^-$  fragment (see Figure 1.2).
  - Complexes with chiral ligands can "catalyze the selective formation of specific enantiomers of chiral molecules. In some cases, the enantioselectivity of these reactions has even equaled that of enzymatic systems" (Spessard & Miessler, 2010, p. 7).

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<sup>1</sup>Hard vs. soft is the basis for the solubility rules!

Figure 1.2:  $\pi$  bonding in Zeise's salt.

## 1.4 Chapter 2: Fundamentals of Structure and Bonding

From Spessard and Miessler (2010).

- Review of the Schrödinger wave equation atomic orbitals, and molecular orbitals.
  - *Shell* and *subshell* are older terminology.
  - “In a bonding interaction, electrons are concentrated between the nuclei and tend to hold the nuclei together; in an antibonding interaction, electrons avoid the region of space between the nuclei and therefore expose the nuclei to each other’s positive charges, tending to cause the nuclei to repel each other” (Spessard & Miessler, 2010, p. 18).
- Discusses a bit of computational chemistry in the abstract.
  - Some of this stuff relates to what I talked about with Dr. Vázquez-Mayagoitia; I should reread this before I email him.
- There may be some stuff here that CHEM 20100 didn’t cover, but I’ll only come back if necessary.

## 1.5 Lecture 2: Electron Counting, $18e^-$ Rule

- 3/31:
- Organometallic chemistry: Strictly speaking, compounds containing metal-carbon bonds. More broadly, it’s homogeneous transition metal chemistry ([frequently diamagnetic] metals bonded to light atoms).
    - Deeply related to catalysis (both fine and bulk chemical synthesis, and biology).
  - Transition metal trends:
    1. Early transition metals tend to have higher oxidation states.
      - It’s easier to remove electrons from less electronegative elements (electronegativity increases across a period).
    2. Size: 1st row < 2nd row  $\approx$  3rd row.
    3. M–L bond strengths increase down a column.
      - Two reasons: Size (larger, more diffuse orbitals have better overlap) and electronegativity (increases down a column; this trend is unique to the transition metals).
    4. Higher coordination numbers are found for heavier metals.
    5. More high-spin species in the first row.
    6. First row transition metals prefer  $1e^-$  coupled.
      - Why?
    7. More difficult to reduce as you go down a triad (column).
  - Common structures:

– 4 coordinate:

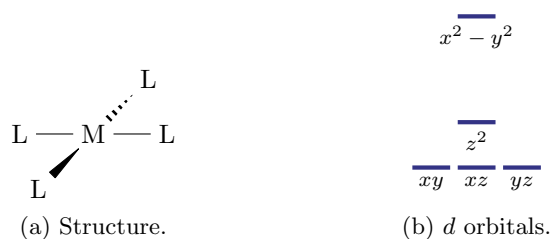


Figure 1.3: Square planar information.

- Square planar (note that the  $z^2$  orbital can swap with the three degenerate orbitals beneath it fairly easily; what's important is that  $x^2 - y^2$  is higher).



Figure 1.4: Tetrahedral information.

- Tetrahedral (much smaller splitting energy than some of the others).
- 5 coordinate:

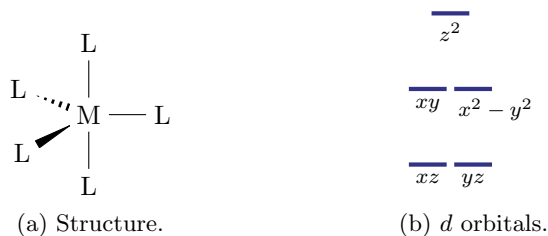


Figure 1.5: Trigonal bipyramidal information.

- Trigonal bipyramidal (the axial ligands push  $d_{z^2}$  high in energy,  $d_{xy, x^2-y^2}$  are degenerate by the threefold  $D_{3h}$  symmetry, and  $d_{xz, yz}$  are nonbonding and thus lowest in energy; note also that this geometry has **fluxional ligands**).

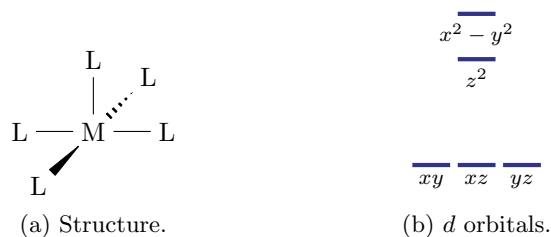


Figure 1.6: Square pyramidal information.

- Square pyramidal (think of it either as square planar with an axial ligand on top, or as octahedral missing one axial ligand on the bottom; thinking of it this way also rationalizes Figure 1.6b as the mean of Figures 1.3b and 1.7b).

- 6 coordinate.

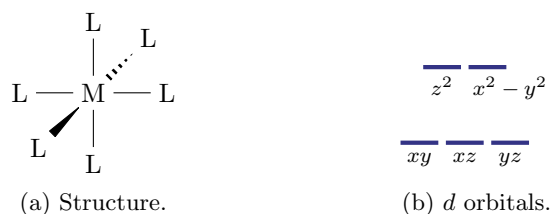


Figure 1.7: Octahedral information.

- Octahedral ( $d_{xy,xz,yz}$  are nonbonding in a  $\sigma$ -only framework, but can take on bonding character when  $\pi$  interactions are considered).

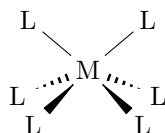


Figure 1.8: Trigonal bipyramidal information (structure).

- Trigonal bipyramidal (each pyramid is eclipsed, rather than staggered as in octahedral; Pfenig and Seppelt (1996) explores this geometry in greater depth).
- **Fluctional ligands:** A set of ligands that readily exchange positions around the molecular center via a **Berry pseudorotation**.
- Ligand types (see Labalme (2021, p. 93)).
- **X-type** (ligand): Typically anionic, covalent donors.
- **L-type** (ligand): Typically neutral. *Also known as dative donor*.
- **Z-type** (ligand): Typically neutral, but can be cationic (no electrons to donate; these are acceptors).
- Note that a carbonyl group can be both an L- and a Z-type ligand (L if it participates in  $\sigma$  donation, and Z if it participates in  $\pi$  acceptance).
  - Similar to how  $\text{Cl}^-$  can be both a  $\sigma$  and  $\pi$  donor.
- On hard/soft matching: remember that harder ligands will prefer harder metals, and vice versa.
- Electron counting:
- Organic chemistry concerns itself with an octet.
- But the octet rule is really a large HOMO-LUMO gap rule; filling stable orbitals and leaving the unstable orbitals empty.
  - In  $\text{CH}_4$  for example, we want to fill the  $\sigma$  and  $\pi$  MOs with all 8 electrons that they can hold, but leave  $\sigma^*$  and  $\pi^*$  unfilled (see Figure III.17 in Labalme (2021)).
  - However, in  $\text{ML}_6$  for example (considering only  $d$  orbital/ligand  $\sigma$  orbital interactions), we have nine  $\sigma$ /nonbonding orbitals that are ok to fill up and two  $\sigma^*$  orbitals that we should try to avoid filling up (see Figure 1.7b as well as Figure VI.2 from Labalme (2021) for a decent approximation).
- The nine orbitals that are ok to fill up in an  $\text{ML}_6$  compound can hold 18 electrons; this gives rise to the **18 electron rule**.

- **18 electron rule:** An octahedral  $ML_6$  transition metal complex with 18 electrons is fairly energetically favorable.
- Low-spin square planar:
  - 4  $\sigma$ /NB ligand orbitals plus 4 nonbonding metal  $d$  orbitals gives 8  $\sigma$ /NB orbitals that can hold 16 electrons in total (see Figure 1.3b).
  - Figure VI.13 of Labalme (2021) says that *two* metal orbitals form bonding/antibonding orbitals with the ligand orbitals, so why does Dr. Anderson assert that only *one* does? Is it because of what he said about  $d_{z^2}$  being practically interchangeable with the  $d_{xy,xz,yz}$  ligands in square planar complexes?
- **16 electron rule:** A square planar  $ML_4$  transition metal complex with 16 electrons is fairly energetically favorable.
- Note that the 18 and 16 electron rules respectively imply that octahedral complexes prefer  $d^6$  configurations and square planar complexes prefer  $d^8$  configurations.
- Note also that since the HOMOs in both 18-electron octahedral and 16-electron square planar complexes are nonbonding, the 18/16 electron rules are more of a suggestion.
  - In general, these numbers are more of a maximum; lower counts can still be stable.
  - However, there are cases of 19 and 20 electron systems.
- 2 schools of thought on electron counting: the **ionic method** and the **covalent method**.
  - Dr. Anderson prefers the covalent method; he's of the opinion that it's a bit more foolproof.
  - Proponents of the ionic method argue that it's nice because it gives you the oxidation state of the metal center throughout the process, but it can run into snags with certain ligands (in step 1 below, it is not always clear what splitting electronegativity dictates).

Ionic Method	Covalent Method
1. Break all M–L bonds according to electronegativity (or accordingly, to form the most stable fragments). Note that M–L bonds split homolytically.	1. Draw a legitimate Lewis structure (no half bonds or circles [as in benzene]). Don't forget lone pairs.
2. The charge on the metal after step 1 is its oxidation state.	2. Assign formal charges (in a dative bond, these belong to the ligand).
3. From 2, assign a $d$ -electron count.	3. The number of electrons that a given ligand donates is equal to its formal charge plus twice the number of dative bonds plus the number of covalent bonds.
4. The electron count equals the $d^n$ count plus the ligand donors (typically 2 electrons per ligand).	4. The electron count is that $d^n$ count for $M^0$ plus the sum of the ligand electron donations minus the charge on the complex.

- Gain familiarity with the  $d$  counts of common transition metals.
- A metal can actually have multiple oxidation states in resonance with each other, whereas the electron count is indisputable, i.e., the only number that you can definitively assign to a complex.
  - This is why it's better to use the covalent method; it goes straight to assigning the electron count, foregoing any possible issues with the oxidation state.
- If you apply each method correctly, they should both give the same answer.
- Examples (ligands):

- A phosphine  $\text{PR}_3$ .
  - The phosphine has a lone pair to donate to the metal center, forming a **dative bond**.
  - Alternatively, the formal charge on phosphorous in a  $\text{M}-\text{PR}_3$  situation is +1 and there is 1 covalent bond.
  - Either way, the phosphine is a 2-electron donor; this is further confirmed by the fact that phosphines are L-type ligands.
- CO.
  - We have multiple possible resonance structures for a  $\text{M}-\text{C}\equiv\text{O}$  bond, but we can robustly treat this with the covalent method.
  - $\text{M}-\text{C}\equiv\text{O}^{\oplus}$  has a +1 formal charge and 1 covalent bond, suggesting that CO is a 2-electron donor.
  - $\text{M}=\text{C}=\text{O}^{\cdot\cdot}$  has no formal charge and 2 covalent bonds, suggesting that CO is a 2-electron donor.
  - $\text{M}\equiv\text{C}-\text{O}^{\ominus}$  has a -1 formal charge and 3 covalent bonds, suggesting that CO is a 2-electron donor.
  - $\text{M}\leftarrow\text{C}\equiv\text{O}^{\oplus}$  has a net 0 formal charge and 1 dative bond, suggesting that CO is a 2-electron donor.
- NO.
  - If NO bonds linearly, it's a 3-electron donor (take  $\text{M}-\text{N}\equiv\text{O}^{\oplus}$  as a possible resonance structure).
  - If NO bonds bent, it's a 1-electron donor (take  $\text{M}-\ddot{\text{N}}=\text{O}^{\oplus}$  for example).
- **Dative bond:** A covalent bond between two atoms where one of the atoms provides both of the electrons that form the bond.
- Examples (metal complexes):
  - Ferrocene, a sandwich compound with an iron atom between two cyclopentadienyl (or Cp) groups (covalent method).
    - Each carbon atom forms a single covalent bond to iron. This gives each iron four covalent bonds (two to its neighbors in the ring, one to its hydrogen, and one to iron), so there are no formal charges.
    - Thus, each Cp ligand donates 5 electrons by the covalent method, and iron as a  $d^8$  compound donates 8 electrons.
    - Therefore, this is an 18 electron complex.
  - Ferrocene (ionic method):
    - The cyclopentadienyl anion has a 1- charge, making it a  $6\pi$ -electron aromatic system.
    - There are two of these anions, with a total charge of 2- between them, so iron must be in the  $\text{Fe}^{2+}$  oxidation state to compensate.
    - This makes iron  $d^6$ , which plays well with 18 electron systems.
  - Hexamethyl tungsten  $\text{W}(\text{CH}_3)_6$  (covalent method):
    - Each  $\text{CH}_3$  ligand forms a single covalent bond with W without formal charge; thus, each donates 1 electron.
    - W is  $d^6$ .
    - Thus, the  $d$  count is 12, making it a pretty reactive compound.
  - $\text{W}(\text{CH}_3)_6$  (ionic method):
    - For each ligand, we split to  $\text{W}^+$  and  $\text{CH}_3^-$ .
    - This makes the metal center oxidation state  $\text{W}^{\text{VI}}$ , with a resultant  $d^0$  configuration.

- $\text{W}(\text{CO})_6$  (covalent method).
  - From above, CO is a 2-electron donor. Thus, the 6 CO's donate 12 electrons. This combined with the fact that W is  $d^6$  makes this an 18 electron system, i.e., pretty stable.
- $\text{W}(\text{CO})_6$  (ionic method):
  - We split  $\text{W}-\text{CO}$  into  $\text{W}^0 + \text{CO}$ .
- $\text{Pt}(\text{Cl})_4^{2-}$  (covalent method):
  - Each chloride forms 1 covalent bond (donates 1 electron).
  - Platinum is  $d^{10}$  (because it's chemically bound, the 6s electrons fall to the d orbitals; what would the d count of copper or zinc be? 10 as well?).
  - The charge on the complex is 2–, so the electron count is  $4 \cdot 1 + 10 - (-2) = 16 e^-$ 's.
- $\text{Pt}(\text{Cl})_4^{2-}$  (ionic method):
  - $\text{Pt}-\text{Cl} \longrightarrow \text{Pt}^+ + \text{Cl}^-$ .
  - Thus, we have  $\text{Pt}^{4+}$ . But the charge is 2–, so we actually have  $\text{Pt}^{2+}$ , which is  $d^8$ , which plays well with the 16-electron system.
- An enzymatic cofactor (covalent method):

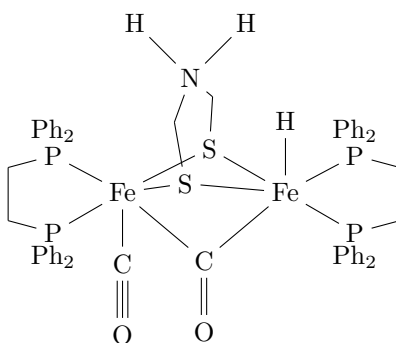
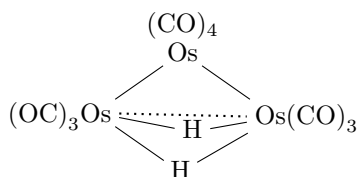


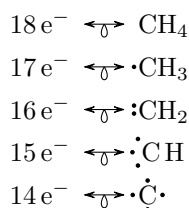
Figure 1.9: An enzymatic cofactor.

- Each phosphine and each carbonyl is a 2-electron donor.
  - The hydride is an X-type ligand with a covalent bond, and thus a 1-electron donor.
  - Now for the big bulky center bridging ligand: The sulfurs each carry a +1 formal charge and form two covalent bonds to the metal centers, so they each contribute three electrons. The nitrogen has an additional +1 formal charge, so the ligand overall is a  $2 \cdot 3 + 1 = 7$ -electron donor.
  - Summing all of this gives us 20 electrons.
  - Now for the metal centers: Each iron is  $d^8$ .
  - Thus, that's 36 electrons in total, but divided over two iron centers.
  - Therefore, the electron count for each iron is 18.
- Metal-metal bonds:
    - Assume that each metal will want to get to an electron count of 18.
    - Thus, the number of M–M bonds you would expect is
 
$$\# \text{ of M-M bonds} = (18 e^- \cdot \# \text{ of metals} - \# \text{ of } e^- \text{'s from L's and M}^0 \text{'s}) / 2$$
    - Essentially, one M–M covalent bond contributes one electron to each M, or two electrons to the complex as a whole.

- As we can see, this number would be 0 for the enzymatic cofactor in Figure 1.9, which is why we'd expect no metal-metal bonding between the two iron centers.
- Bridging hydrides and halides:
  - We can treat this by putting a +1 formal charge on the bridging atom:  $M-\overset{\oplus}{X}-M$ .
  - Alternatively, we can recognize what the nature of the interaction is:  $M-\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}-M$ .
    - From the above picture, it is clear that there is one covalent and one dative bond at play, making the bridging X-type ligand a 3-electron donor.
- We are now prepared to treat one final example:

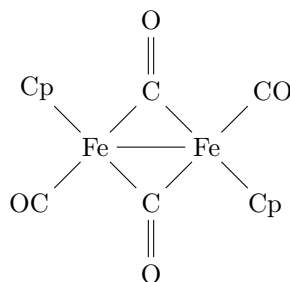
Figure 1.10: Electron counting for  $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-H})_2$ .

- Each carbonyl ligand is a 2-electron donor.
- Each bridging hydride is a 3-electron donor.
- Each Os–Os bond contributes 2 electrons.
- Thus, the ligands donate 30 electrons in total.
- Each osmium is  $d^8$ .
- Thus, the metal centers donate 24 electrons in total.
- Therefore, the number of Os–Os bonds is  $\frac{18 \cdot 3 - (30 + 24)}{2} = 0$ , i.e., there are no Os–Os bonds.
- Now this question could just be a relic of my previous understanding of bonding, and the answer may just be “MO theory,” but I’m still gonna ask: Where do the electrons in all of the bonds come from? It seems like if the osmiums are giving electrons to Os–Os and Os–H bonds, and we still count osmium as  $d^8$ , we are counting some electrons twice.
- Isolobal/isoelectronic analogy:
  - We can assume based on the fact that  $\text{Cr}(\text{CO})_6$  has 18 electrons and is stable that the isoelectronic compounds  $\text{V}(\text{CO})_6^-$  and  $\text{Mn}(\text{CO})_6^+$  have identical electron counts and similar properties.
    - Note that all of these compounds are both isoelectronic and isolobal. What does isolobal mean?
  - We can do the same thing between  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{NO})(\text{CO})_3$ , and  $\text{Fe}(\text{NO})_2(\text{CO})_2$ .
  - Also  $\text{Mn}(\text{CO})_5$ ,  $[\text{CpMn}(\text{CO})_2]^-$ , and  $\text{CpFe}(\text{CO})_2$  (these are isoelectronic, but not isolobal).
- We can also consider isolobal analogies between transition-metal-complex electron counts and organic fragments.
  - For example,





- We can also make analogies between other atoms/metal fragments:  $\cdot\dot{\text{P}} \cdot \leftrightarrow \cdot\dot{\text{C}}\text{H} \cdot \leftrightarrow (\text{CO})_3\text{Co}$ .
- Multiply bonded fragments can also work:  $\text{M}=\text{O} \leftrightarrow \text{M}=\text{N}-\text{R} \leftrightarrow \text{R}_2\text{C}=\text{O}$  for double bonds, and for triple bonds:  $\text{M}\equiv\text{O} \leftrightarrow \text{M}\equiv\text{N}-\text{R} \leftrightarrow [\text{R}-\text{C}\equiv\text{N}-\text{H}]^+$ .
- **Oxidation state:** The number of electrons a metal has given up or acquired.
- **Chemical valence:** The number of electrons from the metal that are engaged in bonding.
- In many cases, the valence and oxidation state are the same, but they can differ.
  - They notably differ when M–M bonds and Z-type ligands are in play.
- Consider the structure formed by two dimerized  $\text{Fp}^-$  (is this the right spelling? Does it have a charge by itself?) fragments (a  $\text{Fp}^-$  fragment is  $\text{CpFe}(\text{CO})_2^-$ ).

Figure 1.11: Two dimerized  $\text{Fp}^-$  fragments.

- The oxidation state of each iron is  $\text{Fe}^{\text{I}}$  (since Cp is the only electronegative ligand).
- The valence of each iron is  $\text{Fe}^{\text{II}}$  (since Cp takes 1 electron and the Fe–Fe bond takes another).
- Note that as this is an 18-electron complex, it makes sense that the bound “iron ion” should be  $d^6$  ( $\text{Fe}^{\text{II}}$ ), not  $d^7$  ( $\text{Fe}^{\text{I}}$ ).
- Does the iron have tetrahedral or square planar geometry and why?
- Now consider the compound  $[\text{CpFe}(\text{CO})_2\text{AlMe}_3]^-$ .
  - The oxidation state of the iron is  $\text{Fe}^{\text{II}}$ .
  - The valence of the iron is  $\text{Fe}^{\text{III}}$  (confirm this?).
  - Here, unlike the last example, the oxidation state is a better descriptor (we can think of the iron as donating two electrons to  $\text{AlMe}_3$ ).

## 1.6 Lecture 3: TM Magnetism

4/2:

- Magnetism is unique to the transition metals, and actually predominantly the lanthanides.
- Goes through the “Theoretical background for determining magnetic spins experimentally” derivation from Module 34.
  - $\kappa$  can also be denoted by  $\chi_V$ .
  - More on  $\chi_M$ : Copies Table VI.2 from Labalme (2021). Some differences?
- Diamagnetism:
  - Arises from the circulation of paired electrons.
  - These currents generate a field opposite of  $H$ , which implies that  $\chi_{\text{dia}}$  is negative.

- Contributions from atoms, bonds, and molecules (anything with paired electrons). These can just be summed for a given molecule (see Pascal's constants).

- Paramagnetism:

- Arises from the spin-orbit angular momentum of unpaired electrons.
- Note that  $\chi_{\text{para}} = \chi_{\text{measured}} - \chi_{\text{dia}}$ .
- We can consider a value called the magnetic moment  $\mu$  of the electron. We define

$$\mu = -g\beta\vec{s}$$

where  $g$  is the  $g$ -factor of the free electron (*also known as* the gyromagnetic ratio in Labalme (2021, p. 119)),  $\beta$  is the Bohr magneton, and  $\vec{s}$  is the spin angular momentum.

- The Hamiltonian  $\mathcal{H}$  describing the energy of the interaction of the magnetic field with the magnetic moment of the electron is as follows:

$$\mathcal{H} = -\vec{\mu} \cdot \vec{H} = g\beta\vec{s} \cdot \vec{H}$$

- We can visualize this with a Zeeman splitting diagram.

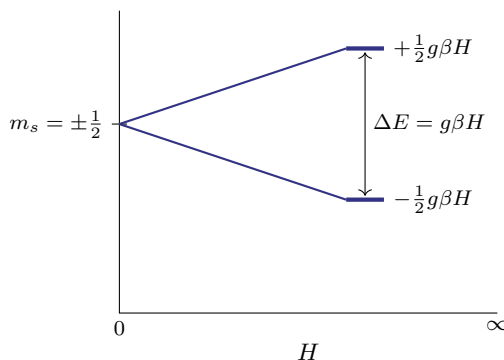


Figure 1.12: A Zeeman splitting diagram for a single electron.

- Consider a single electron.
- Under zero magnetic field ( $H = 0$ ), there will be no preference for spin-up or spin-down ( $M_s = \pm \frac{1}{2}$ ).
- However, as we apply a magnetic field of increasing strength, a preference develops (and the diagram splits). Indeed, under some nonzero magnetic field  $H$ , the system will be higher energy if the electron spin is  $+\frac{1}{2}$  and lower energy if the electron spin is  $-\frac{1}{2}$  (why these specific spins to higher and lower energy? Or is it arbitrary?). This effect is heightened by increasing  $H$ .
- The magnitude of  $\Delta E$  in Figure 1.12.
  - Let  $H = 25 \text{ kG} = 2.5 \text{ T}$ . We know that  $g = 2.0023$ . Thus,  $\Delta E = 2.3 \text{ cm}^{-1}$  (which is very small).
  - What is a Boltzmann population?
  - When we sum the magnetic contributions from all possible spin states, we find that the magnetization constant can be written as

$$M = \frac{N g^2 \beta^2}{4 k_B T} H$$

where  $N$  is Avogadro's number,  $k_B$  is the Boltzmann constant, and  $T$  is temperature.

- But since  $\chi_M = \frac{M}{H}$ , this implies that

$$\chi_M = \frac{Ng^2\beta^2}{4k_B} \cdot \frac{1}{T} = C \cdot \frac{1}{T}$$

where  $C = \frac{Ng^2\beta^2}{4k_B}$  is the Curie constant. How does this relate to Curie's law from last quarter?

- The above relationship is useful because it tells us that we can get a linear relationship through the origin between magnetic susceptibility and  $\frac{1}{T}$ . Additionally, it tells us that as temperature increases, magnetic susceptibility decreases (inversely proportionally).
- Ferromagnetism and antiferromagnetism:
  - Temperature's influences on these types of magnetism vary from their effects on paramagnetism.

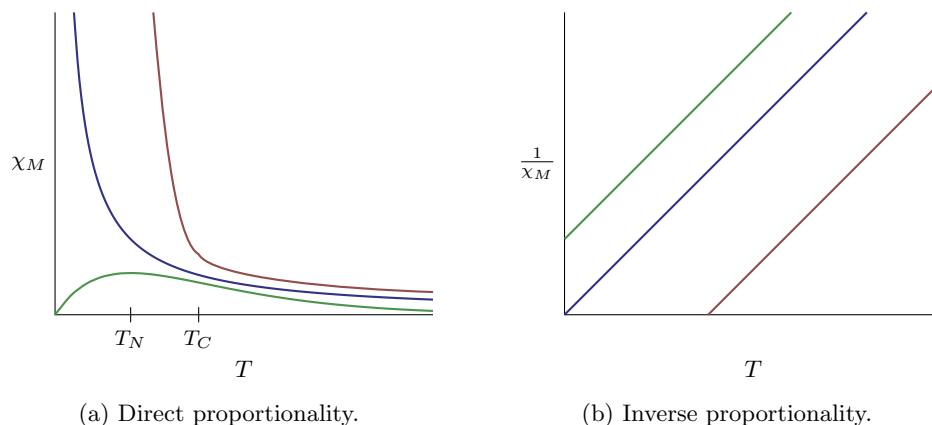


Figure 1.13: Temperature vs. magnetic susceptibility in different magnets.

- The blue lines correspond to paramagnetism, the red lines correspond to ferromagnetism (which, under direct proportionality, have an abrupt inflection point at the Curie temperature  $T_C$ ), and the green lines correspond to antiferromagnetism (which, under direct proportionality, have a maximum at the Neel temperature  $T_N$ ).

- **Curie-Weiss law:** The relationship

$$\chi_M = \frac{C}{T - \theta}$$

where  $\theta$  is the Weiss temperature.  $\theta > 0$  for a ferromagnet and  $\theta < 0$  for an antiferromagnet.

- Measuring and observing magnetism:

- Goes through the  $\mu_S$  derivation on Labalme (2021, p. 119).
- Arrives at the following important equations (defining our observables  $\chi T$  and  $\mu_{\text{eff}}$ ):

$$\mu_{\text{eff}} = g\sqrt{S(S+1)} \qquad \chi T = \frac{g^2}{8}(S(S+1))$$

- Allows us to experimentally determine if a complex is high- or low-spin.
- However, experimental values actually deviate substantially from the spin-only predicted values.

- This is because of **spin-orbit coupling**.

- **Spin-orbit coupling:** A phenomenon where a single electron hops between degenerate orbitals, generating a ring current that either reinforces or opposes the applied magnetic field. *Also known as S.O.C.*

- To account for S.O.C., we need a new Hamiltonian with  $L, S$ .

$$\mathcal{H} = \lambda L \cdot S$$

- In the above equation,  $\lambda$  is the S.O.C. constant.
- Because the equation contains the product of  $L$  and  $S$ ,  $L$  and  $S$  are no longer good quantum numbers. Thus, we need a new quantum number, namely  $J$ .
- Adding  $J$  into our new Hamiltonian gives us

$$\mathcal{H} = \lambda L \cdot S + \beta(L + g_e S) \cdot H$$

where  $g_e$  is the free-electron  $g$  value and  $H$  is the applied magnetic field.

- Let's break the above Hamiltonian down.
  - It tells us that the energy  $E$  that we get from an applied magnetic field is

$$E = \vec{B} \cdot \vec{m} = \mu \vec{m} \cdot \vec{H}$$

where  $\vec{B}$  is the induced magnetic field and  $\vec{m}$  is the magnetization.

- Additionally, we have that  $\chi = \frac{m}{H}$ , so

$$\Delta m = -\frac{dE_i}{dH} = -E_i^1 - 2w_i^2 \cdot H$$

- Thus, the total energy  $E_{\text{total}}$  is given by

$$E_{\text{total}} = E_i^0 + H E_i^1 + H^2 E_i^2$$

where  $H E_i^1$  is the first-order term, and  $H^2 E_i^2$  is the second-order term.

- We can break this down even further.

- We find that

$$m_i = \frac{d}{dH} (E_i^0 + E_i^1 H + E_i^2 H^2 + \dots) = -E_i^1 + 2E_i^2 H$$

- Additionally, we know that  $\chi = \frac{m_i}{H}$ , so

$$\chi_i = \left( -\frac{dE_i}{dH} \right) \frac{1}{H}$$

- The final result above tells us that the magnetic susceptibility depends on the magnetic field. This is rooted in the fact that there are different Boltzmann populations in different ligand field states.
- Now we can account for all of the Boltzmann populations and math that back to the observed  $\chi$ .
- To begin,

$$\chi = \frac{N}{H} = \frac{\sum_i [-E_i^1 - 2E_i^2 H] \exp\left(-\frac{E_i}{k_B T}\right)}{\sum_i \exp\left(\frac{E_i}{k_B T}\right)}$$

where  $N$  is the number of atoms (if it's molar,  $N$  is Avogadro's number).

- Additionally, we know that

$$\begin{aligned} e^{-E_i/k_B T} &= 1 - \frac{E_i}{k_B T} \\ &= e^{-(E_i^0 + E_i^1 H + E_i^2 H^2 + \dots)/k_B T} \\ &= e^{-E_i/k_B T} \left( 1 - \frac{E_i^1 H}{k_B T} \right) \left( 1 - \frac{E_i^2 H^2}{k_B T} \right) (\dots) \end{aligned}$$

- Note that if  $E_i^1 \ll k_B T$ , then  $e^{-x} = 1 - x$  for small  $x$ . This is what allows us to get from the second to the third line above.
- Combining the above two equations, we have

$$\chi = \frac{N}{H} \cdot \frac{(-E_i^1 - 2E_i^2 H) e^{-E_i/k_B T} \left(1 - \frac{E_i^1 H}{k_B T}\right) \left(1 - \frac{E_i^2 H^2}{k_B T}\right)}{\sum_i e^{-E_i^0/k_B T} \left(1 - \frac{E_i^1 H}{k_B T}\right) \left(1 - \frac{E_i^2 H^2}{k_B T}\right)}$$

- If we measure at a constant field, we can simplify the above to

$$\chi = \frac{N\beta^2}{3k_B T} \mu_{\text{eff}}^2$$

- This implies that

$$\mu_{\text{eff}} = \sqrt{\frac{8 + \left(\frac{3\lambda}{k_B T} - 8\right) \left(\exp\left(\frac{-3\lambda}{2k_B T}\right)\right)}{\frac{\lambda}{k_B T} \left[2 + \exp\left(\frac{-3\lambda}{k_B T}\right)\right]}} \cdot \beta^2$$

- **Van Vleck equation:** The above equation<sup>[2]</sup>.
  - It is only valid for  $S = \frac{1}{2}$  (single electron terms).
    - Multi-electron terms are too complicated to do by hand and must be handled by computer modeling.
  - You can explicitly account for S.O.C. with a known  $\lambda$ .
    - For  $\text{Ti}^{3+}$  for example,  $\lambda = 154 \text{ cm}^{-1}$ .
    - For  $\text{Zr}^{3+}$  for example,  $\lambda = 500 \text{ cm}^{-1}$ .
- S.O.C. constants increase for heavier elements. Elements with large relativistic effects have large S.O.C. constants.
- Intuitive insight into the conditions surrounding a large degree of spin-orbit coupling:
  - An applied magnetic field causes the electron to rotate through the  $d$ -orbitals.
    - If an electron hops between  $d_{x^2-y^2}$  and  $d_{xy}$  for instance, this creates rotation (and a ring current).
  - The ring current will create a magnetic field  $B$  around the  $z$  axis that opposes  $H$ .
  - This opposing magnetic field gives a lower magnetic moment than spin-only calculations would predict.
  - Note that rotation of a single electron in a  $d^1$  complex lowers the magnetic moment, but rotation of a single “hole” (positive charge) in a  $d^9$  complex raises the magnetic moment.
    - In  $d^5$  (and technically  $d^{10}$ ), no electrons can move without violating the Pauli exclusion principle, so we would expect the observed moment to be close to the spin-only value. (Quantum mechanical explanation: The electronic symmetry of a totally symmetric state precludes any mixing of the orbital angular momentum with the spin angular momentum.)
- A first approximation of S.O.C.:
  - For a less than half-filled set of orbitals, expect  $\mu_{\text{eff}} / \chi T$  to be lower than the spin-only value, i.e.,  $g < 2$ .
    - Typically  $\mu_{\text{eff}} / \chi T$  is close to the spin-only value.

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<sup>2</sup>Having seen this equation is all that is required for this course (it's good to have seen it). The derivation will never come up again.

- For a greater than half-filled set of orbitals, expect  $\mu_{\text{eff}} / \chi T$  to be larger than the spin-only value, i.e.,  $g > 2$ .
  - $\mu_{\text{eff}} / \chi T$  can be much larger.
- For a half-filled set of orbitals, we expect little to no S.O.C. Thus,  $\mu_{\text{eff}} / \chi T$  should be roughly equal to the spin-only value, i.e.,  $g \approx 2$ .
- The magnitude of S.O.C.: The key is orbital degeneracy.
  - For example, if we have a  $d^3 \text{Cr}^{3+}$  complex, we would predict more S.O.C. in the tetrahedral state (Figure 1.4b) than in the octahedral state (Figure 1.7b).
    - This is because in the tetrahedral orbitals, there is only one electron in the upper orbitals; thus, we have a set of degenerate orbitals with a non-degenerate electron configuration, which promotes S.O.C. Note that  $d^3$  octahedral is totally degenerate by contrast.
  - Note that this is totally dependent on the ligand field: Stronger ligand fields increasingly break degeneracy, thus quenching S.O.C.
- S.O.C. trends:
  1. Heavy elements have larger S.O.C.
  2. Lanthanides have larger S.O.C. from larger  $\lambda$ 's.
    - Lanthanides in general also just have very large S.O.C. effects; this effect arises from the degenerate  $f$  set.
      - Since the  $f$  orbitals do not extend beyond the noble gas core to engage in bonding, they do not split; thus, they are totally degenerate; thus, there is large S.O.C.
    - Note that neodymium magnets are strong because they combine a lanthanide that contributes massive S.O.C. effects, lots of electrons, and anisotropy (neodymium) and a transition metal that effectively couples with orbitals that aren't as buried as neodymium's  $f$  orbitals (iron).

## 1.7 Office Hours (Anderson)

- 4/5:
- Electron counting for a metal center bonded to a  $\pi$  bond?
    - As in PSet 1 Questions 1.2 and 1.6.
    - Example:  $\text{Ni}^0$ -ethene.
      - The  $\pi$  electron density can donate to the nickel atom in a dative fashion.
      - We can also think of two covalent bonds to the nickel; one from each carbon.
    - Example:  $\text{Ni}(\text{COD})_2$ .
      - Electron count: 18 (8 from the ligands [2 from each of 4  $\pi$  bonds] and 10 from the  $d^{10}$  nickel atom).
  - Electron counting for a metal center bonded to a  $\sigma$  bond?
    - Also donates two electrons datively, as in PSet 1 Question 1.9.
  - M–M bonds and oxidation states?
    - Reviews the discussion surrounding Figure 1.11.
  - The binding of a Z-type ligand does not affect the electron count of a compound at all.
  - The formal charges on the molecules in the PSet are the charges of the molecules as a whole, not any one part.
  - **Metal-organic frameworks** or MOFs.

## 1.8 Office Hours (Whitmeyer)

- 4/6:
- Transition metal trends: Why do first row transition metals prefer to have  $1e^-$  coupled?
    - Referring to reactivity? B/c higher oxidation states are more stable for early row transition metals.
  - Figure VI.13 of Labalme (2021) says that *two* metal orbitals form bonding/antibonding orbitals with the ligand orbitals, so why does Dr. Anderson assert that only *one* does? Is it because of what he said about  $d_{z^2}$  being practically interchangeable with the  $d_{xy,xz,yz}$  ligands in square planar complexes?
    - Yes it is.
  - Now this question could just be a relic of my previous understanding of bonding, and the answer may just be “MO theory,” but I’m still gonna ask: Where do the electrons in all of the bonds come from? It seems like if the osmiums are giving electrons to Os–Os and Os–H bonds, and we still count osmium as  $d^8$ , we are counting some electrons twice.
    - It’s fine to count them twice. The electron count is a computational tool, not a count of electrons.
    - Does the electron count have physical meaning?
      - Guides you toward what compounds are more reactive. And other chemical properties.
  - What does isolobal mean?
  - The fic fragment: Right spelling/charge?
  - Does the iron in Figure 1.11 have tetrahedral or square planar geometry and why?
  - Copies Table VI.2 from Labalme (2021). Some differences?
  - Why these specific spins to higher and lower energy (Figure 1.12)? Or is it arbitrary?
  - What is a Boltzmann population?
  - Differences in Curie’s Law from last quarter?
  - How do you define  $d$  count? Green (1995) defines it as  $d^n - x$  where  $d^n$  is the ground state configuration and  $x$  is the number of X-functions.
    - The  $d^n$  count should reflect the oxidation state.
  - Charges on compounds affect the oxidation state of the metal.
  - Where do the extra electrons come from in the CO resonance structures (the ones that are bonded to the metal)?
    - All M–C bonds are 2-electron? The IR stretching frequency just changes in some resonance structures so we call this a multiple M–C bond even though it isn’t.
  - How do we handle ligands with preexisting charges (i.e.,  $\text{NO}^+$ ,  $\text{SO}_4^{2-}$ ,  $\eta^3\text{-C}_3\text{H}_5^+$ , etc.)

## 1.9 Discussion Section

- No discussion or office hours on the April 20; instead, there will be a special 2-hour exam review on April 15, 16, 17 (she will send a When2Meet poll). There will be 3 lectures per week, of 2-3 videos on Panopto. Office hours (one for Dr. Anderson and one for Sophie) will be one time per week. Please come to discussion: this is your question venue! Feel free to send along things you want discussed to Sophie in advance. Sophie can answer things much more thoroughly in discussion.
- Difference between L- and X-type ligands:

- Draw out lone pairs. Break bonds (pushing electrons back onto ligands). If the ligand is neutral, it's L-type. If it's negatively charged, it's X-type.
  - So if you have an oxygen as a singly bonded ligand and break the bond, oxygen will be negative. If you do the same thing with nitrogen, it will be neutral. *draw a picture*
- When dealing with *f*-block compounds, be careful about the periodic placement (different periodic tables place lanthanum and actinium in different places).
- Why *f*-block electrons for the electron count?
  - The lanthanides and actinides don't follow the 18 electron rule.
  - This is a very active area of research (at the forefront of bonding actually), but the growing consensus is that...
    - The lanthanides do not engage in covalent bonding; they're purely ionic.
    - The actinides can engage in limited covalent bonding with their *f* block because their larger *f* block extends a little bit further.
- We can do isolobal analogies with bridging ligands, too!
- One should never *assume* that there's a M–M bond, but one should always *wonder* if there's one.
- Potentially you can invoke  $\pi$  donation from a ligand to get a compound to 18 electrons.
- **Hapticity**: The number of carbons in the  $\pi$  system. *Also known as  $\eta$ .*



## Unit 2

# Intro to Reactions and Ligands

### 2.1 Lecture 4: Substitution Reactions

4/5:

- Association/dissociation reactions.
- Fairly related to organic  $S_N2$  and  $S_N1$  reactions, respectively.
- General form:



- We investigate the position of the equilibrium with the three main characteristics that determine reactivity.
  1. Sterics.
    - Related to the metal coordination number.
      - C.N.  $> 6$  is typically disfavored.
      - C.N.  $< 6$  is possible.
    - The size of  $L'$  is also important: If  $L' = PPh_3$  for example, this is hard to get to C.N.  $> 4$ .
  2. Ligand character.
    - In nonpolar media, dissociation of charged groups (e.g.,  $Cl^-$ ) will be disfavored. However, the opposite is true in polar media.
      - This is because of the issue of making charge/ionizing.
    - The match between M and L (e.g., hard/soft, electron rich/poor) is also important.
      - For example,  $Fe^0$  will bind CO strongly since  $Fe^0$  is electron rich and CO is a  $\pi$  acceptor.
      - However,  $Fe^{IV}$  will not (as a hard, electron-poor metal center).
  3. Electronic structure of the metal center (whether or not the metal is electronically saturated [has 18 electrons]).
    - $18e^-$ : it will not want to coordinate an additional  $L'$ .
    - $20e^-$ : it will want to dissociate.
    - $16e^-$ : it *can* associate.
      - However, it may not want to given that  $16e^-$  square-planar complexes are fairly stable.
      - The associated state may be a transition state in a square-planar ligand substitution or otherwise not a ground state.
- Ligand substitution reactions terms: **Kinetic** and **thermodynamic**.
- **Kinetic** (considerations): Elements are inert (slow) or labile (fast).
- **Thermodynamic** (considerations): Which side of an equilibrium will be favored. Elements are stable or reactive.

- In ligand substitution reactions, there are two limiting regimes:

1. Associative substitution.

- See the related discussion in Labalme (2021).
- This is the most general reaction type, even for coordinatively saturated complexes.
- Rate law:

$$\frac{d[\text{ML}_5\text{L}']}{dt} = k_{\text{obs}}[\text{ML}_6][\text{L}']$$

2. Dissociative mechanism.

- See the related discussion in Labalme (2021).
- There are many things that look dissociative that are associative (e.g., instead of forming a 5-coordinate species, you could just have a molecule of the solvent displace a ligand).
- This mechanism is rare and hard to prove.
- Rate law:

$$\frac{d[\text{ML}_5\text{L}']}{dt} = \frac{k_2 k_1 [\text{ML}_6][\text{L}]}{k_{-1}[\text{L}] + k_2[\text{L}']}$$

- Experimentally, we swamp the reaction with L' so that [L'] >>> than all other reagents. This makes it so that the rate is just  $k_{\text{obs}}[\text{ML}_6]$ , i.e., pseudo-first order conditions.

- Unfortunately, much like in orgo, very few cases are at these extremes and we can have hybrids called. . .

3. Interchange mechanisms.

- See the related discussion in Labalme (2021).
- Within this category, we can have  $I_a$  (associative interchange) and  $I_d$  (dissociative interchange).
- In the transition state, we have L' coming in and L leaving at the same time.

- Kinetics and rates of these mechanisms.

- Several categories (measure with water exchange rates; see Labalme (2021)):

- I) Very fast.

- Alkali metals (species that primarily engage in ionic bonding; little covalent character).
- $1 \times 10^8 \text{ s}^{-1}$ ; close to the diffusion limit.

- II) Fast.

- Higher valent ions; often  $\text{M}^{3+}$  such as  $\text{Al}^{3+}$ .
  - Higher charge  $\Rightarrow$  higher ligand affinity  $\Rightarrow$  slightly slower but still pretty fast.
- $1 \times 10^3$ - $1 \times 10^8 \text{ s}^{-1}$ .

- III) Slower.

- Getting into the transition metals:  $\text{Fe}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Ti}^{3+}$ .
  - $d$ -orbital splitting + covalency  $\Rightarrow$  stronger bonding  $\Rightarrow$  slower exchange rate.
- $1 \times 10^1$ - $1 \times 10^4 \text{ s}^{-1}$ .

- IV) Inert.

- $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pt}^{2+}$ , and  $\text{Fe}^{2+}(\text{L.S.})$ .
- $1 \times 10^{-8}$ - $1 \times 10^{-4} \text{ s}^{-1}$ .

- The overlap between the rates reflects the fact that there is no hard and fast cut off between categories.

- The identity of L' also influences rates.

- Reaction rates increase with the ligand field strength of L'<sup>[1]</sup>.

---

<sup>1</sup>Goes over Table IX.1 from Labalme (2021).

- Characteristics of the metal that control the observed rates.
  - Ranking L.S. metal centers (slowest to fastest):  $\text{Co}^{\text{III}} < \text{Cr}^{\text{III}} < \text{Mn}^{\text{III}} < \text{Fe}^{\text{III}} < \text{Ti}^{\text{III}} < \text{V}^{\text{III}}$ .
  - Considering the  $d$  counts, we have  $d^6 < d^3 < d^4 < d^5 < d^1 < d^2$ .
  - Now think of this in terms of the  $d$ -orbitals splitting diagram (Figure 1.7b).
    - As the antibonding orbitals get filled,  $\sigma$  bonds will weaken, promoting a faster exchange.
    - Full and half-full  $t_{2g}$  also provides stability.
- Thus, we list the following configurations as inert and labile (see the related discussion in Labalme (2021)):
  - Inert:  $d^3$ , L.S.  $d^{4,5,6}$ , and square planar  $d^8$ .
  - Labile:  $d^0$ ,  $d^1$ ,  $d^2$ , H.S.  $d^{4,5,6}$ ,  $d^7$ ,  $d^9$ ,  $d^{10}$ .
- Other important kinetic factors:
  1. Oxidation state.
    - As oxidation state increases, exchange rate decreases (becomes more inert).
  2. Size.
    - Smaller ions are more inert.
    - However, first row ions are almost always labile (because they more readily populate higher spin states).
  3. Chelate effect.
    - Reviews some info from Labalme (2021).
    - Chelating ligands form a ring or a **metallacycle** (this is why 4,5-membered ligands are stable; because 5,6-membered rings are favorable).
    - Binding of a chelating ligand is typically favored, primarily due to entropic reasons (effective concentration is secondary).
    - Example: Gives actual  $\Delta G = \Delta H - T\Delta S$  thermodynamic data for the formation reaction of  $\text{Cu}(\text{MeNH}_2)_4^{2+}$  vs.  $\text{Cu}(\text{en})_2^{2+}$  to emphasize the importance of entropy (see the related discussion in the notes on Chapter 10 in Labalme (2021)).
    - EDTA is a hexadentate ligand that is commonly used in biology to pull all metal centers out of solution.
      - For  $\text{Fe}^{3+}$  for example,  $K_f = 1 \times 10^{25} \text{ mol}^{-1}$ . What is  $\text{mol}^{-1}$  and why is it here?
      - Siderophores and eubacterin are biology's own chelators ( $K_f = 1 \times 10^{52} \text{ mol}^{-1}$ ).
      - These chelators involved because if bacteria are going to invade a host, they need to scavenge iron, but iron is pretty tightly regulated. Thus, there has been an arms race of molecules that can scavenge iron or prevent iron from being scavenged.
    - Chelation therapy: If exposed to a heavy metal, you will be given chelating agents that will bind to metal ions and cause them to be excreted from the body.
  4. Trans effect.
    - Reviews some info from Labalme (2021).
    - Helps predict the **regiochemistry** of where a given ligand will substitute.
    - Cis-platin reaction mechanism:  $\text{cis-Pt}(\text{NH}_3)_2(\text{Cl})_2 \longrightarrow \text{cis-Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2$  in the body, which binds to DNA on the *cis*-water side, causing a kink, stopping transcription, and initiating apoptosis.
      - Cis-platin is quite toxic (people are trying to develop formulations that are less so), but highly effective at stopping cancer.
      - Can't have *trans* because it doesn't have the *cis*-water side. Thus, this synthesis mechanism doesn't work:  $[\text{PtCl}_4]^{2-} \xrightarrow{2\text{NH}_3} \text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$ .

- Therefore, we synthesize it as follows.



- Note that we start from tetrachloroplatinate because it is the most common form of platinum.
- Also note that XS stands for “excess.”
- Trans-effect order listed.
- The trans-effect is kinetic; concerned with rates of exchange.
  - Stronger *trans*-directors **labelize** the ligands opposite them.
- The trans influence is thermodynamic.
  - It influences the ground state structure, causing lengthening of bonds *trans* to a strong-field ligand (think of this in terms of competition for electrons on the central atom; a strong-field ligand will attract more of these, making the other bond weaker).
- Note that intramolecular reactions (such as a second binding of a bidentate chelating ligand) are highly favored.

## 2.2 Lecture 5: Electron Transfer Reactions

- 4/7:
- More unique to inorganic chemistry since metal atoms have access to many more electrons than common organic atoms.

- General form:



- The forward reaction is known as **oxidation** (metal oxidation state increases), while the reverse is known as **reduction** (metal oxidation state decreases).
- This is different than the oxidation/reduction reactions of organic chemistry, which involve removing or adding, respectively, a hydrogen.
- This redox chemistry is important because many transition metals have access to multiple oxidation states.
- Two Nobel prizes in this area:
  - Henry Taube (1983): Electron transfer in metals.
  - Rudy Marcus (1992): Marcus theory of electron transfer.
- 2 general flavors of electron transfer reactions: **inner sphere** and **outer sphere**.
- **Inner sphere**: Bonds are formed.
- **Outer sphere**: No bonds are formed.
- Example:
  - Consider the reaction  $\text{Fe}(\text{CN})_6^{4-} + \text{Mo}(\text{CN})_8^{3-} \longrightarrow \text{Fe}(\text{CN})_6^{3-} + \text{Mo}(\text{CN})_8^{4-}$  (electron transfer from iron to molybdenum).
  - The energies at play:  $\text{A}^{(n+1)} + \text{B}^n \longrightarrow [\text{A}^{(n+1)} + \text{B}^n] \longrightarrow [\text{A}^n + \text{B}^{(n+1)}]^* \longrightarrow \text{A}^n + \text{B}^{(n+1)}$ .
  - Reactants  $\rightarrow$  encounter complex  $\rightarrow$  electron transfer state (an excited state)  $\rightarrow$  products.

- Energies:



Figure 2.1: Electron transfer reaction energies.

## 1. Thermodynamic:

- The difference in the potentials of  $A^{n+1}$  and  $A^n$ , and  $B^{n+1}$  and  $B^n$ .
  - These can be measured electrochemically.
  - We can measure the electrochemical driving force for these processes (i.e., the change in free energy during the reaction) with cyclic voltammetry.
- In a cyclic voltammetry experiment...
  - As we increase the potential to the point where the redox reaction will occur, we will see an increase as oxidation occurs.
  - Then as we decrease the potential again to where the redox reaction will occur in the reverse direction, we will see a decrease as reduction occurs.
- The midpoint  $E_{1/2}$  is the thermodynamic potential (where redox is at equilibrium and you have equal amounts of both species). Is this  $\Delta G$ ? What is going on here? Why are the equilibria misaligned?

## 2. Kinetics:

- $\Delta G = E_{1/2A} - E_{1/2B}$  where  $E_{1/2X}$  is the thermodynamic potential of substance X.
  - $\Delta G$  is the thermodynamic contribution.
- $\Delta G^\ddagger$  is the kinetic barrier, or activation energy.

- The role of  $\Delta G^\ddagger$  in an electron transfer.

- Electrons move very quickly and are highly delocalized with respect to the nuclei, so what dictates kinetics in these processes is nuclear motion (recall reorganization energy).
- In a simplistic sense, the key is the  $[A^n + B^{(n+1)}]^*$  encounter complex.
- Electron transfer changes bond length.
  - There is a kinetic barrier to the electron transfer because the thermodynamic energy is based on minimizing the energy in the reduced and oxidized forms.
- Bond lengths change upon redox, so the solvent and counteranions have to reorganize.
- This **reorganization energy** leads to a kinetic barrier (i.e.,  $\Delta G^\ddagger$ ).
- You can see evidence of the reorganization energy in Figure 2.1a.
  - You must go past the thermodynamic potential to observe the maximum/minimum current and attain complete oxidation/reduction.

- Measuring the reorganization energy.
  - We do a self-exchange reaction with radiolabeled metal centers (see Labalme (2021)).
  - Think of the energy scale on Figure IX.1 in Labalme (2021)) as discrete. To get over  $\Delta G^\ddagger$ , we must change vibrational states.
    - Indeed, the short- and long-bond iron complexes have two vibrational states, but their combined transition state with medium bonds has a new vibrational state.
  - With electronic coupling, the two parabolas split into an upper loop and a lower loop with a bump.
  - To treat this, we use the equation  $\Delta G^\ddagger = \Delta G_t^\ddagger + \Delta G_v^\ddagger + \Delta G_0^\ddagger$ .
    - $\Delta G_t^\ddagger$  is the translational energy, which is moving the two species together.
    - $\Delta G_v^\ddagger$  is vibrational, which is concerned with the bond lengths of the irons' matching structures.
    - $\Delta G_0^\ddagger$  is the solvent, dipole, counterion, etc. This can be large (so one of the greatest contributors is the environment in which the system lies).
- Example:
  - $\text{Co}(\text{NH}_3)_6^{2+} / \text{Co}(\text{NH}_3)_6^{3+}$  is H.S.  $d^7$  / L.S.  $d^6$ .
  - Self-exchange is slow because nuclear reorganization is large (0.2 Å difference in bond length, which is significant).
    - Note that this arises from the different electronic configurations.
  - The ion is getting smaller *and* going low-spin during reorganization.
- Another example:
  - $\text{Ru}(\text{NH}_3)_6^{2+} / \text{Ru}(\text{NH}_3)_6^{3+}$ .
  - $k_{\text{exch}}$  is eight orders of magnitude faster than the previous example.
  - This is because ruthenium is low-spin throughout ( $\Delta(\text{Ru}-\text{N}) \approx 0.04 \text{ \AA}$  which is much smaller, so there is a smaller reorganization energy).
- Key take aways:
  - Electrons move fast, so what actually induces a kinetic barrier is the movement of the nuclei which have to reorganize in order to accommodate the electron popping between the two atoms.
  - Can be accelerated by electron coupling, as in inner sphere mechanisms.
- Inner sphere electron transfer: Some bonds are involved in the electron transfer.
  - Accelerated by electron coupling, but hindered by greater nuclear reorganization energy (a bridging bond must be formed).
- Example:
  - Consider the reaction
 
$$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} + \text{Cr}(\text{H}_2\text{O})_5^{2+} \longrightarrow \text{Co}(\text{NH}_3)_5^{2+} + \text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$$

$$\xrightarrow{\text{H}_2\text{O}} \text{Co}(\text{H}_2\text{O})_6^{2+} + \text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$$
  - The intermediates are  $[(\text{H}_3\text{N})_5\text{Co}^{\text{III}}-\text{Cl}-\text{Cr}^{\text{II}}(\text{OH}_2)_5]^{4+} \longrightarrow [(\text{H}_3\text{N})_5\text{Co}^{\text{II}}-\text{Cl}-\text{Cr}^{\text{III}}(\text{OH}_2)_5]^{4+}$ .
  - The rate is reasonably fast ( $6 \times 10^5 \text{ mol}^{-1} \text{ s}^{-1}$ ).
  - How does this vary as a function of  $\text{X}^-$ ?
    - As ligand size (more diffuse; better at bridging) and charge (more electrostatic influences) increase, so does rate ( $\text{Br}^- > \text{Cl}^- > \text{F}^- > \text{H}_2\text{O} > \text{NH}_3$ ).

- Inner-sphere electron transfer: Mixed valency.
- Consider the Creutz-Taube ion.



Figure 2.2: The Creutz-Taube ion.

- The bridging ligand is a pyrazole.
- The electron transfer is very fast; thus, the oxidation state is approximately  $\text{Ru}_2^{2.5}$ .
- Such electron transfers are measured with Near-IR spectroscopy, which can see inter-valence charge transfer bands (IVCT), which include bonds.
  - This very low energy form of spectroscopy observes the energy that it takes to excite an electron between the two ruthenium centers.
- Robin-Day classification:
  - I) Completely localized.
    - Regardless of the spectroscopic technique used, a difference between  $\text{Ru}^{\text{II}}$  and  $\text{Ru}^{\text{III}}$  can be observed.
  - II) Evidence of some delocalization.
    - Most common.
  - III) Completely delocalized.
- If you go fast enough (ultrafast spectroscopy; femtosecond lasers), almost any system looks localized.
- Marcus theory:
  - Built off of the Bell-Evans-Polanyi Relationship.
  - See Figure IX.2 and the related discussion in Labalme (2021).
  - Two big insights:
    - When  $\Delta G = -\lambda$ ,  $\Delta G^\ddagger = 0$ .
    - When  $\Delta G < -\lambda$ ,  $\Delta G^\ddagger > 0$ .
  - The case where  $\Delta G^\circ < -\lambda$  is called the **Marcus inverted region**.
  - **Marcus equation:**

$$k_{\text{ET}} = \nu_N k_e e^{-\Delta G^\ddagger / RT}$$

where  $\nu_N$  is the nuclear frequency (how accessible vibrational excited states are; related to the width of the parabolas in Figure IX.2 of Labalme (2021)) and  $k_e$  is the electronic factor (related to overlap, probability of transfer, etc.; usually set to 1).

- More importantly, Marcus discovered that

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G)^2}{4\lambda}$$

which implies that as  $\lambda \rightarrow -\Delta G$ ,  $\Delta G^\ddagger \rightarrow 0$ . Furthermore, as  $\lambda$  passes  $-\Delta G$ ,  $\Delta G^\ddagger$  increases.

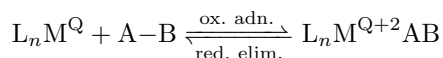
- This has important implications in biology, catalysis, etc. For example, if you want to slow down an undesirable side reaction and speed up your main reaction, provide more driving force. This accelerates your main reaction and moves your side reaction into the inverted region.

## 2.3 Lecture 6: Oxidative Addition and Reductive Elimination

4/9:

- Even further detached from organic chemistry (but scientists are looking for this reactivity in phosphorous and other *p*-block main group elements).

- General form:



- Changes at the metal center during these two reactions (generically).
  - Oxidative addition: Oxidation state, electron count, and coordination number increase by 2.
  - Vice versa for reductive elimination.
- Some notes on this reactivity:
  1. Concerted reductive elimination must occur from a *cis*-arrangement of ligands.
    - Not true if it's stepwise.
  2. Reductive elimination is favored by bulky ligands.
    - Naturally: The more sterically crowded it is, the faster it will want to go.
  3. Reductive elimination is disfavored for early metals.
    - Since the early metals are very electropositive and don't want to access their lower oxidation states.
  4.  $H^-$  as a reductive-elimination ligand is faster than other ligands.
    - Due to it's spherically symmetric electron density.
    - Hydrides kinetically (not thermodynamically) tend to react faster.
  5. Oxidative addition can occur to give *cis* or *trans* products.
    - The relative distribution of the stereochemistries gives us mechanistic information.
- Classic studies: On Vaska's complex.

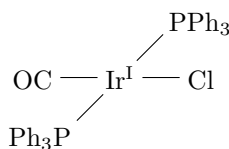


Figure 2.3: Vaska's complex.

- Characteristics of the reactant:  $d^8$ ,  $16e^-$ , canary yellow color.
- Characteristics of the product (after reacting with MeI,  $H_2$ , or  $O_2$ ):  $d^6$ ,  $18e^-$ .
- MeI bonds *trans*,  $H_2$  bonds *cis*, and  $O_2$  forms a peroxide.
- $Ir^{III}$  is inert, so we observe the kinetic products. These give us mechanistic information.
- Mechanistics can vary from  $S_N2$ , to radical, to concerted, and so on.
  - Classifying this reaction can get blurry. For instance, is  $M^Q + H^+ \longrightarrow M^{Q+2}-H^+$  an oxidative addition?
- Types of mechanisms:



## 1. Concerted.



Figure 2.4: The concerted mechanism for oxidative addition.

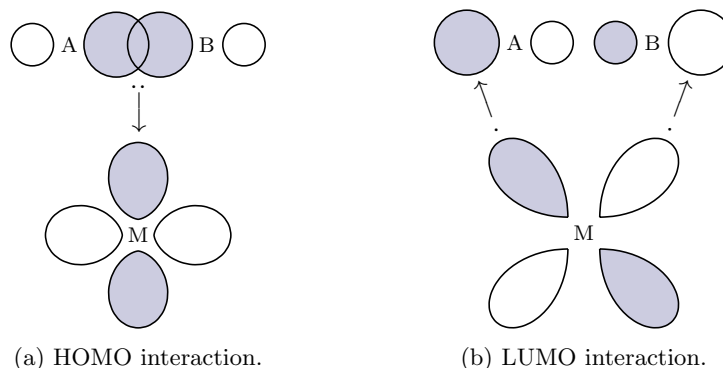


Figure 2.5: Orbital interactions in concerted oxidative addition.

- *cis* products.
  - If you see a *trans* product, this is not the mechanism.
- HOMO interaction: The A–B  $\sigma$ -bonding orbital donates to an empty metal  $d_{x^2-y^2}$ -symmetry orbital.
- LUMO interaction: The metal  $d_{xy}$  orbital backbonds into the A–B  $\sigma^*$  antibonding orbital. It is these electrons that depopulate the  $\sigma$  bond and allow the A–B bond to split.

2.  $S_N2$ .

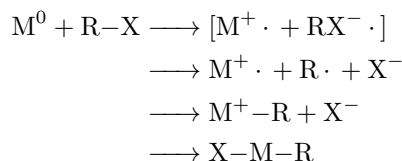
- *cis* or *trans*; no clear preference.
- One signature of this reactivity is a steric preference where primary > secondary > tertiary.
  - Some of the trends of organic reactions can appear in inorganic reactions!

## 3. Radical chain.



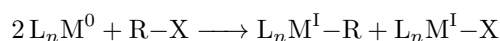
- We begin with a metal and an initiator (denoted In).
  - These react to form the adduct  $M\text{In}\cdot$ , which is a radical.
  - This radical grabs an X from R–X to form InM–X (this product is worthless and the final step of initiation). A  $R\cdot$  is also generated in this step (this is the radical to be propagated).
  - The  $R\cdot$  reacts with another equivalent of the metal to create an  $R-M\cdot$  radical which can then grab a halide, generating an R–M–X and an  $R\cdot$ , the former of which is the desired product and the latter of which can continue propagating.
- Pretty common.

## 4. Electron transfer.

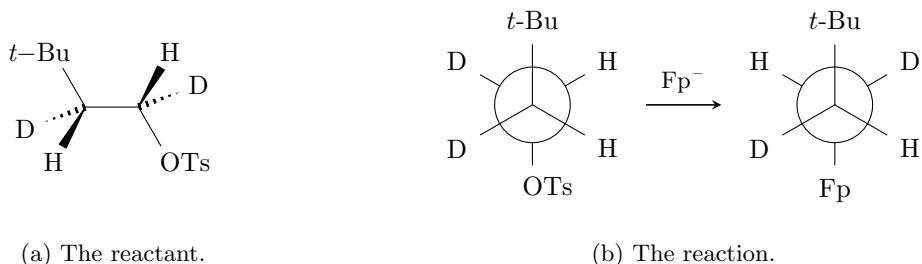


- Related to  $S_N2$  again.
- This is not a radical chain process (no propagation); it's just an electron transfer followed by fragmentation and recombination.
- Jack Halpern of UChicago writes Chock and Halpern (1966).
  - Studies  $L_2IrClCo \xrightarrow{MeX} L_2IrClCoMeX$ , specifically the reaction rates as a function of X.
  - Determines that  $I^- > Br^- \gg Cl^-$ , and that  $Rate = k[CH_3X][Ir]$ .
  - $\Delta S^\ddagger = -43$  e.u. (where an e.u. is an entropy unit).
  - Solvent effects are also consistent with an ionic mechanism.
  - There is a 5-coordinate intermediate, and the two new ligands end up adding *trans*.
  - If you use EtI, this reaction proceeds through a radical mechanism.
    - You have mechanistic switching based on the identity of the substrate.

## • Bimolecular oxidative addition:



- Jack Halpern again writes Halpern and Maher (1965).
  - Studies the reaction  $2 Co^{II}(CN)_5^{3-} + MeI \longrightarrow Co^{III}(CN)_5Me^{3-} + Co^{III}(CN)_5I^{3-}$ .
  - Follows some transition metal trends:
    - Heavier metals (such as iridium above) do 2-electron chemistry.
    - Lighter metals (such as this one) do 1-electron chemistry.
  - We can also see radical-type reactivity.
- Another parallel example:  $2 L_n M + 2 RX \longrightarrow 2 L_n M-X + R-R$ .
  - For example,  $Cp_2^*Yb(OEt_2) + CH_2Cl_2 \longrightarrow 2 Cp_2^*Yb-Cl + ClCH_2-CH_2Cl$ .
  - This can also occur through a radical mechanism. We form an  $R \cdot$  radical that can recombine to form  $R-R$  or make  $M-R$ .
- Stereochemistry of  $S_N2$  type reactivity.
- George Whitesides writes Bock et al. (1974).

Figure 2.6:  $S_N2$  stereochemistry.

- Observes inversion (by looking at  $J_{\text{H-H}}$  coupling by NMR) of H and D at a single stereocenter.
- React the compound in Figure 2.6a with a  $\text{Fp}^-$  fragment.
- Observe inversion, as in Figure 2.6b, so it's  $\text{S}_{\text{N}}2$ .

- Another synthesis:



Figure 2.7: An additional way of probing  $\text{S}_{\text{N}}2$  addition/elimination.

- This one shows us that palladium causes an inversion once again, but reductive elimination does not.
- Radical mechanisms.
  - We probe these with **radical clocks**.
  - The unzipping of the methylcyclopropane radical ring happens so fast that it will necessarily be faster than any recombination with  $\text{M-Cl}$ .
  - Since iodides are easier to reduce than bromides, bromomethylcyclopropane will react in a straightforward manner with  $\text{Fp}^-$ , but iodomethylcyclopropane and  $\text{Fp}^-$  will pursue a radical mechanism to a competitive degree. Why does the reduction potential of iodides and bromides matter?
- **Radical clock:** A reagent such that if a radical is generated on it, it will undergo a rapid isomerization or redistribution to generate different product(s).
- A few notes.
  1. Similar rules to those in orgo apply.
    - For example,  $\text{I}^-$  is a better leaving group than  $\text{Cl}^-$ .
    - However, there are exceptions, too:  $\text{CN}$  is a terrible leaving group in inorganic chemistry, whereas you can sometimes kick it out in orgo.
  2. Sterics matter.
    - Oxidative addition is slower for sterically encumbered substrates.
    - If you want to favor a radical reaction over a concerted or nucleophilic mechanism, make the compound bulky. This will disfavor the two undesired mechanisms but not an electron transfer step.
  3. First row metals will be faster than second and third row metals.
    - This is because they're much more reactive. However, they will also go down competitive side paths more readily (can be good or bad).
    - Because of this, second and third row metals are more often used. Plus, you can just heat them up a bit to speed up the reaction.

## 2.4 Lecture 7: Insertion/Deinsertion and Kinetics

4/12:

- Migratory insertion/deinsertion.
- Also pretty unique to the transition metals.

- General form:

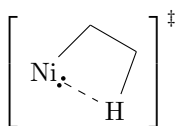


- In the course of this reaction, the L is converted into an X-type ligand.
- Characteristics of insertion: Electron count decreases by 2, coordination number decreases by 1, and the oxidation state does not change.
- Examples:
  - 1,1-insertion:  $\text{Me}-M-\text{CO} \rightleftharpoons M-\text{C}(=\text{O})-\text{Me}$ .
    - So named because the metal and the migrating group end up at the same position on the carbonyl ligand (the 1 position).
  - 1,2-migration:  $\text{Cp}_2\text{Zr}(-||)\text{Me} \rightleftharpoons \text{Cp}_2\text{ZrPr}$ .
    - So named because the metal ends up on the 1 position of the ethylene olefin and the migrating group ends up on the 2 position of the ethylene olefin (remember that we number substituents from the metal center outwards).
- More groups than methyl can migrate; it's just that methyl commonly migrates.
- Insertions into M–C bonds are common.
  - Insertions into M–H bonds are common for olefins, but uncommon for CO because metal carbonyl species are unstable.
  - You can also insert into M–O bonds (note that dppe stands for diphenylphosphinoethane):



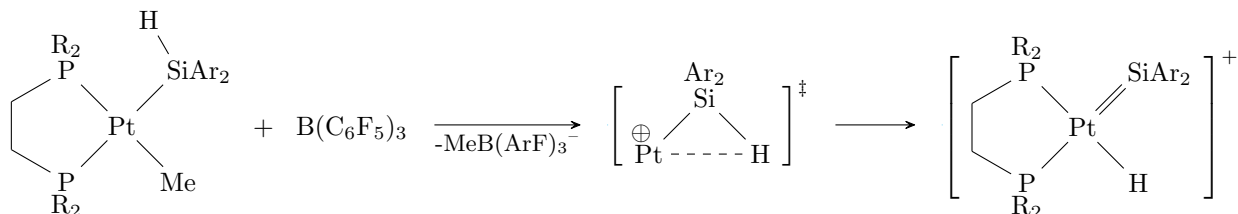
Figure 2.8: Insertion into an M–O bond.

- A note on the mechanism:
  - We can either take the perspective that the X group migrates or that the L group inserts itself into the M–X bond.
  - Thus, either the  $\sigma$  bond of the migrating ligand attacks the site to which it bonds or the L group moves into the  $\sigma$  bond.
  - We call this a migratory insertion, but there are two possible mechanisms (it's hard to know what is migrating and what is staying put).
  - Answer: The X-type ligand is migrating. We can test this by radiolabeling one of the carbonyls in  $\text{Mn}(\text{CO})_5\text{Me}$ ?
- $\beta$ -H elimination:  $\text{L}_2\text{NiEt} \rightleftharpoons \text{L}_2\text{Ni}(-||)\text{H}$ .

Figure 2.9: The transition state in a  $\beta$ -H elimination.

- The transition state (see Figure 2.9) shows an **agostic interaction**.

- $\alpha$ -elimination<sup>[2]</sup>.

Figure 2.10: An example of  $\alpha$ -elimination.

- External attack at a ligand.

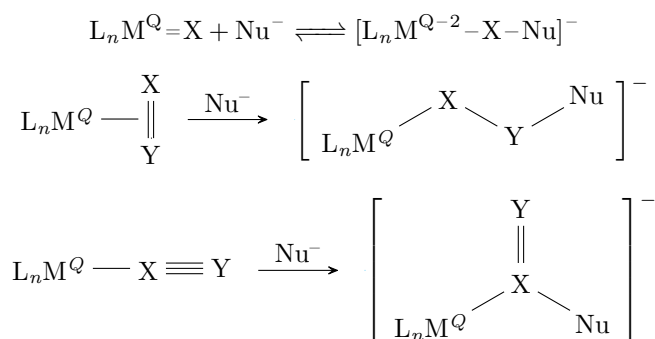


Figure 2.11: Types of external attack at a ligand.

- Somewhat more related to organic chemistry.
- Lists some examples.
- Tp is trispyrazolylborate.
  - It's a Cp analogue, meaning that it has the same electron count and similar sterics.
- Be aware of Fischer carbenes.
- There could be a radical process.
  - Crevier and Mayer (1998) tells us that an osmium-nitrido external attack at a ligand must be a 2-electron process, not a radical mechanism.
- Electrophilic attack on a ligand.
- Example:  $Ir^{II}(PPh_3)_2HCl(NO) \xrightarrow{HCl} Ir^{III}(PPh_3)_2HCl_2(N(=O)H)$ .
  - The reactant is a  $16e^-$  species.
  - The nitrogen-containing ligand is a nitroxyl ligand.
- Gives some other examples.
- $Tp^*$  is a Tp group where each pyrazole is 3,5-dimethyl substituted.
- Sometimes we create a positive metal cation. This can be accomplished either via a direct electrophilic attack on an attached R group or via an attack at the metal followed by reductive elimination.

<sup>2</sup>Note that Ar stands for an aryl group.

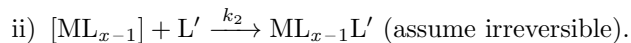
- $\sigma$ -bond metathesis:  $L_nM^Q-X + Y-Z \rightleftharpoons L_nM^Q-Y + X-Z$ .
  - Usually observed for  $d^0$  systems.
- Example:  $Zr^{IV}(N(SiR_3)H)_3Me \longrightarrow Zr(N(SiR_3)H)_2(=N-SiR_3) + CH_4$ .
  - C–H activation is a big thing in synthetic chemistry, and a lot of the pathways go through  $d^0$ , early, reactive transition metals.
- More on  $\sigma$ -bond metathesis:
  1. Most common for early metals.
    - Especially  $d^0$  metals.
  2. Thought to go through a 4-membered transition state.
  3. There is likely a continuum between “pure”  $\sigma$ -bond metathesis and oxidative addition/reductive elimination.
  4. This still requires an open coordination site and  $\leq 16 e^-$ .
    - Because the first step is coordination, usually to form some kind of  $\sigma$ -adduct.
- Kinetics of associative substitution.

$$\text{rate} = -\frac{d[ML_x]}{dt} = \frac{d[ML_{x-1}L']}{dt} = k[ML_x][L']$$



Figure 2.12: Kinetics of associative substitution.

- Experimentally, we can use a large  $[L']$  to get to pseudo-first order conditions.
- This gives us  $\text{rate} = k_{\text{obs}}[ML_x]$  where  $k_{\text{obs}} = k[L']$ .
- In Figure 2.12a,  $t_{1/2}$  is a midpoint, and the rate gets faster (steeper slope) with more  $[L']$  and slower (more gradual slope) with less  $[L']$ .
- There is a discrepancy between theory and experiment in Figure 2.12b.
  - This is because of the presence of a solvent-assisted mechanism.
  - $L_xM + \text{solv} \xrightleftharpoons{k_s} L_{x-1}ML(\text{solv}) \xrightarrow[\text{fast}]{L'} L_{x-1}ML' + \text{solv} + L$ .
  - Note that  $k_s$  is the rate of solvent association.
- The solvent-assisted mechanism dominates at low  $[L']$ , and vice versa for the normal mechanism.
- Kinetics of dissociative substitutions.



– There are now two cases:

a) Fast pre-equilibrium, i.e.,  $k_1, k_{-1} \gg k_2$ . This gives us

$$\text{rate} = k_1 k_2 \cdot \frac{[\text{ML}_x][\text{L}']}{[\text{L}]}$$

b) Steady state approximation:  $d[\text{ML}_{x-1}]/dt = 0 = k_1[\text{ML}_x] - k_{-1}[\text{ML}_{x-1}] - k_2[\text{ML}_{x-1}][\text{L}']$ . If we solve the above for  $[\text{ML}_{x-1}]$ , then we get

$$\text{rate} = \frac{k_1 k_2 [\text{ML}_x][\text{L}']}{k_{-1}[\text{L}] + k_2[\text{L}']}$$

If we now assume that  $k_2[\text{L}']$  is large, then we get  $\text{rate} = k_1[\text{ML}_x]$ .

■ The steady state approximation is a good assumption to make because if you see a buildup of the dissociative intermediate, you can measure the rates. Alternatively, if you don't see it, you can assume that  $[\text{ML}_{x-1}] = 0$ .

– To do this experimentally, we add a large concentration of  $[\text{L}']$ , or  $[\text{L}]$  in some cases.

■ This gives us  $\text{rate} = k_{\text{obs}}[\text{ML}_x]$  where  $k_{\text{obs}}$  denotes the mess from the above equation.



Figure 2.13: The effect of  $[\text{L}']$  on rate.

– If we plot  $k_{\text{obs}}$  vs.  $[\text{L}']$ , we get Figure 2.13.

■ In the second order region,  $\text{ML}_x \xrightleftharpoons[\text{fast}]{k_1} \text{ML}_{x-1}$  many times before product formation.

■ In the first order region, every time  $\text{ML}_{x-1}$  forms, it goes on to become a product.

– In other words,  $k_{\text{obs}}$  should approach  $k_1$  when  $k_2[\text{L}'] \gg k_{-1}[\text{L}]$ .

– Importantly, as  $\text{L}'$  is varied with different ligands,  $k_1$  should stay constant (assuming the mechanism doesn't change).

– A double reciprocal plot can be used to obtain still more information about the reaction.

■ If you plot  $\frac{1}{k_{\text{obs}}}$  vs.  $\frac{[\text{L}]}{[\text{L}]}$  and run a linear regression, the slope will be  $\frac{k_{-1}}{k_1 k_2}$  and the  $y$ -intercept will be  $\frac{1}{k_1}$ .

• Transition state theory basics:

– In 1887, Arrhenius comes up with the Arrhenius equation  $k = Ae^{-E_A/RT}$ , which can be algebraically manipulated into

$$\ln k = \ln A - \frac{E_A}{RT}$$

where  $E_A$  is the activation energy,  $R$  is the gas constant, and  $T$  is temperature.

- This allows us to create a linear  $\ln k$  vs.  $\frac{1}{T}$  plot from which we can pull out important information.
- In the 1930s, Eyring comes up with the Eyring equation

$$\ln \left( \frac{k}{T} \right) = \frac{-\Delta H^\ddagger}{RT} + \ln \left( \frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R}$$

where we can calculate that  $\ln(k_B/h) \approx 23.76$ .

- This allows us to create a linear  $\ln(k/T)$  vs.  $\frac{1}{T}$  plot from which we can pull out additional important information.

## 2.5 Office Hours (Anderson)

- Explain cyclic voltammetry.
    - SOP for CV in the modules explains cyclic voltammetry.
    - You have a working and a reference electrode, as well as an auxiliary platinum wire. All of these are submerged in the same solution (of a polar solvent and your compound).
    - You apply a voltage across the working and auxiliary electrodes.
    - With nothing in your solution, you have pseudo-capacitance/polar something-or-other. It's basically just a loop with spikes on the end ( $D_{2h}$  symmetry) in your voltage vs. current graph.
    - However, if we have a compound, we pass some current in the forward and reverse directions at the thermodynamic potential point (the free energy of the reduction/oxidation vs. some other reduction/oxidation process; we can convert to  $\Delta G$  with the Nernst equation); the spikes aren't entirely superimposable because we must push the equilibrium a bit past to get something to happen.
  - How do you handle ligands with charges? Like  $\text{SO}_4^{2-}$  in question 8 of the last homework or the allyl group in 1.16. Where do the electrons come from?
    - 1.16:
      - Redraw as a legitimate Lewis structure.
- 
- Allyl is 1 covalent, 1 dative; the other two ligands are each dative donors.
    - Thus, palladium's oxidation state is  $\text{Pd}^{2+}$ .
    - The synthetic route by which we get to this compound has no bearing on its properties (electron count, oxidation state, etc.).
    - In one reaction mechanism, it's  $\text{C}_3\text{H}_5^+$  before, and then it's  $\text{C}_3\text{H}_5^-$  after splitting.
  - 8:
    - 8b: Solve with electron counts?  $\text{MoL}_2\text{X}_4$  is  $14e^-$ , whereas  $\text{MoL}_4\text{X}_2$  is  $16e^-$ .
    - 8d: Donates the same number of electrons in each case! They're just different resonance structures!!
    - 8e: Cp is an  $\text{L}_2\text{X}$ -type ligand with L.B.N. = 3, for example.
    - 8f: Ligand domains are useful, but not every inorganic chemist uses them.
- Intuition for reductive elimination?
  - Yes, it is the reverse of oxidative addition.



- Generally, you break the M–B bond and then the M–A bond.
- You could also break M–B and A–B, and then have  $B^-$  nucleophilically attack  $[M-A]^+$ .
- You could also do this radical-wise:  $M-A\cdot + \cdot B \longrightarrow M + A-B$ .
- Could be thought of as concerted, but probably best not to.
- To do one-electron chemistry, you have to stabilize radicals.
  - You have more one-electron chemistry in high-spin first-row transition metals.
- There is a synthesis question on the Homework 2, so start looking at that sooner as opposed to later.

## 2.6 Office Hours (Whitmeyer)

- 4/13:
- The fic fragment: Right spelling/charge?
  - Does the iron in Figure 1.11 have tetrahedral or square planar geometry and why?
  - Copies Table VI.2 from Labalme (2021). Some differences?
  - Why these specific spins to higher and lower energy (Figure 1.12)? Or is it arbitrary?
    - Convention that negative is lower.
  - What is a Boltzmann population?
    - A Boltzmann distribution is a mathematical distribution much like the normal distribution.
    - There is an ideal bond distance, and some atoms bond closer or farther.
  - Differences in Curie's Law from last quarter?
  - In this course, we include units for equilibrium constants, derived from the mass-action expression.
  - HW2 4a:
    - First row compounds are less likely to delocalize?
    - LFSE is larger for second, third row.
    - First row complexes are more likely to have higher spin states.
    - Bigger orbitals with more overlap are better at electron transfer.

## 2.7 Discussion Section

- HW2 due 4/19 at 12 PM CT.
- Midterm 1: 4/22 from 6pm-8pm CT (proctored by Dr. Anderson).
- No discussion section or office hour on 4/20; there will however be a 2 hour exam review and office hour session on 4/17 from 11:30-1:30 CT.
- Sophie will not be available at all Midterm week.
- I can send discussion topics ahead of time or post in the Discussion on Canvas.
- More information will be forthcoming on where Sophie took off points on our homework.
- Zirconium is quasi-stable at  $16e^-$ .

## 2.8 Lecture 8: Alkyls, Aryls, and Multiple Bonds

4/14:

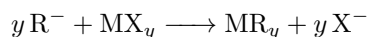
- Done with reactions; we're now onto ligand types.
- Alkyls and aryls are the quintessential organometallic ligands.
- **Alkyl**: An  $M-CR_3$  ligand where the carbon is  $sp^3$  hybridized.
- Historically, the stability of these compounds has hindered their isolation.
- The first alkyl compound to be characterized was  $ZnEt_2$ , synthesized in 1847 by E. Franklin at Imperial College.
  - He reacted  $Zn^0 + EtI \longrightarrow ZnEt_2(l)$ .
  - $ZnEt_2$  is extremely flammable, can be distilled, and is a good alkylating agent.

- 50 years later, Victor Grignard reacts



- The equilibrium between the solvate and  $MgR_2 + MgX_2$  is called the **Schlenk equilibrium**. It can be pushed one way or the other with certain reagents.
- For example, adding dioxane precipitates out the magnesium halides, leaving you with only the desired alkyl halide Grignard reagent in solution.
- Note that dioxane is a six-membered single-bonded ring with para-oxygens in the ring. It has the formula  $C_4H_8O_2$ .
- You can have lithium, sodium, potassium, thallium, aluminum, etc. alkyls.
- Transition metal alkyls:
  - $\beta$ -H elimination is a problem (this is why TM alkyls were only discovered later).
    - An electronically and coordinatively unsaturated metal ethyl complex reacts in a way that heavily favors the ethylene olefin product.
    - Note, however, that this reaction is less favored for  $d^0$  metals.
  - First characterized in the early 1900s.
    - $I_xPt-Me_{4-x}^{2-}$  and  $IPt-Me_3^{2-}$  were partially characterized.
  - First quasi-stable example:  $FeCp(CO)_2Et$  has  $18e^-$ . Over time, however, UV light causes it to lose a carbonyl group and form an ethylene olefin hydride (as from a reverse 1,2-migration).
  - They began to use alkyl ligands with no  $\beta$ -hydrogens or unreactive  $\beta$ -hydrogens.
    - They made compounds such as  $W(CH_3)_6$ ,  $M-CH_2-Ph$ ,  $M-CH_2-t-Bu$ , and  $M-CH_2-TMS^{[3]}$ .
    - 1-adamantyl, norbornyl have  $\beta$ -hydrogens, but elimination is disfavored by ring strain.
    - Fluoroalkyls and metallacycles were also attractive. A fluoroalkyl will not undergo hydride elimination [obviously], but halide elimination is a possible issue. Metallacycles cannot adopt a syn-coplanar arrangement to eliminate.
    - $M-C\equiv C-H$  as well (the  $\beta$ -hydrogen is once again in the wrong position).
- Types of synthesis of transition metal alkyls.

1. Nucleophilic attack on M:

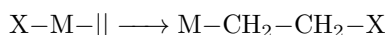


- For example,  $WCl_6 + 6 MeLi \longrightarrow WMe_6 + 6 LiCl$ .
- Electron transfer can also be an issue (alkyl lithium agents can be strongly reducing).

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<sup>3</sup>TMS is trimethylsilyl, a ligand of the structure  $SiMe_3$ .

- There is also the possibility of productive radical mechanisms, but there is lots of side reactivity in radical mechanisms, too. We can limit side reactions with a less reducing nucleophile.
- 2. Electrophilic attack on M.
  - For example,  $\text{Mn}(\text{CO})_5^- + \text{MeI} \longrightarrow \text{MnMe}(\text{CO})_5 + \text{I}^-$ .
  - Also,  $\text{Fp}^- + \text{Ph}_2\text{I}^+ \longrightarrow \text{CpFe}(\text{CO})_2\text{Ph} + \text{IPh}$ . Note that  $\text{Ph}_2\text{I}^+$  is an **aryllating reagent**.
- 3. Oxidative addition.
  - Vaska's complex and MeI.
  - Also C–H activation:  $\text{M} + \text{H}-\text{CR}_3 \longrightarrow \text{H}-\text{M}-\text{CR}_3$ .
    - This is much more difficult than oxidative addition to alkyl halides and is a big area of interest to organic chemistry.
- 4. Insertion of olefins or alkynes.



- X can be an alkyl or a hydride.
- $(\text{Et}_3\text{P})_2\text{Pt}^{\text{II}}\text{ClH} \xrightarrow{\text{||}} (\text{Et}_3\text{P})_2\text{PtClEt}$ .
- $(\text{Et}_3\text{P})_2\text{Pt}^{\text{II}}\text{ClH} \xrightarrow{\text{|||}} (\text{Et}_3\text{P})_2\text{PtClVinyl}$ .
  - Insertion almost always happens with a *trans* disposition to the metal so the H that was originally attached to the metal ends up on the vinylic group *cis* to the metal.
- Also,  $\text{Cp}(\text{CO})_3\text{MoH} \xrightarrow{\text{N}_2\text{CH}_2} \text{Cp}(\text{CO})_3\text{Mo}-\text{CH}_3$  (note that the compound above the arrow is diazomethane, a common  $\text{CR}_2$  transfer reagent).
- All of these require an open coordination site.
- 5. External nucleophilic attack on an olefin.



- **Aryl**: Similar to an alkyl group, but no  $\beta$ -H's to eliminate.
- M–C multiple bonds.
- Three types of compounds: Carbenes/alkylidenes ( $\text{M}=\text{CR}_2$ ), carbynes/alkylidyne, and carbides.
  - We will focus on carbenes today.
- Two limiting regimes (for carbenes):

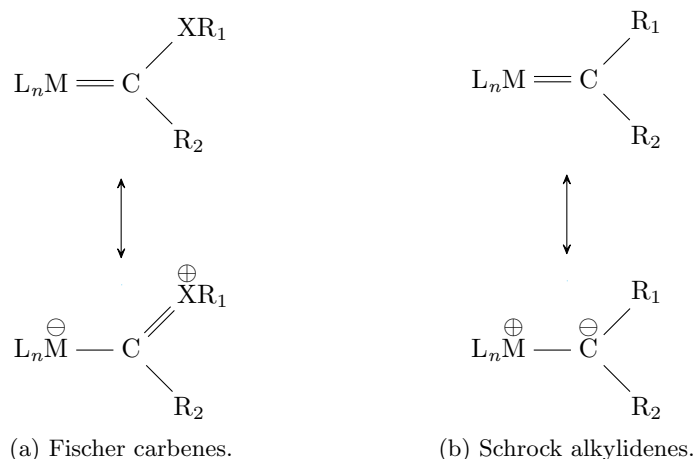


Figure 2.14: Carbene regime resonance structures.

1. Fischer carbenes:  $L_nM=C(XR_1)(R_2)$ .
  - Electrophilic at C.
  - $X = O, NR, S$ .
  - Lower valent metals from the middle-late transition metals.
  - $\pi$ -acceptors, L-type ligands.
2. Schrock alkylidenes:  $L_nM=C(R_1)(R_2)$ .
  - Nucleophilic at C.
  - High valent metals from the early-middle transition metals.
  - $\pi$ -donors,  $X_2$ -type ligand.
  - $R_1, R_2$  are typically alkyls or aryls.
- Both are two electron donors.
- Synthesis of carbenes:
  - Fischer carbenes were made first historically.
  - For example,  $W(CO)_6 + MeLi \longrightarrow Li^+[(CO)_5W-C(=O)(Me)]^- \xrightarrow{Me_3O^+BF_4^-} (CO)_5W=C(OMe)(Me)$ .
  - Also,  $W(CO)_6 + MeLi \xrightarrow[-CO]{2KC_8} K_2[W(CO)_5] \xrightarrow[R-X]{Cl-C(=O)-OR} (CO)_5W=C(OMe)(Me)$ .
    - Note that a carbonyl group is lost after the first step to maintain an electron count of 18, instead of forcing one of 20. Is this method of reducing a compound to remove ligands common?
  - Also,  $W(CO)_6 + MeLi \xrightarrow[-CO]{2KC_8} K_2[W(CO)_5] \xrightarrow{R_1-C(=O)-NR_2} (CO)_5W-C(O-)(R_1)(NR_2) \xrightarrow{TMSCl} (CO)_5W=C(NR_2)(R_1)$ .
  - More syntheses listed.
- Classic alkylidenes:
  - $TaCl_5 + \frac{3}{2}Np_2Zn \longrightarrow (Np)_3TaCl_2 \xrightarrow{2NpLi} Np_3Ta=C(t-Bu)(H)^{[4]}$ .
  - $TaCl_5 + Np_2Zn \longrightarrow Np_2TaCl_3 \xrightarrow{2L} Ta(=C(t-Bu)(H))Cl_3L_2$ .
  - More syntheses listed.
  - Essentially, in every synthesis, you make a transiently saturated penta- or hexa-coordinated tantalum center and then do an alkyl elimination to give you the desired alkylidene.
  - These syntheses were discovered in Dick Schrock's attempts to synthesize  $TaMe_5$ , which actually can't be done because it's so unstable (because of its tendency to participate in bimolecular elimination).
- Olefin metathesis (see Figure 2.15).
  - We'll talk about what this is later.
  - Done with tungsten and molybdenum in Dick Schrock's lab as well.
  - The second step contains an alkylidyne that is very resilient throughout the rest of the mechanism.
- Grubbs type alkylidenes are synthetically much more useful and ruthenium based.

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<sup>4</sup>Note that we are using Np to denote a neopentyl group.

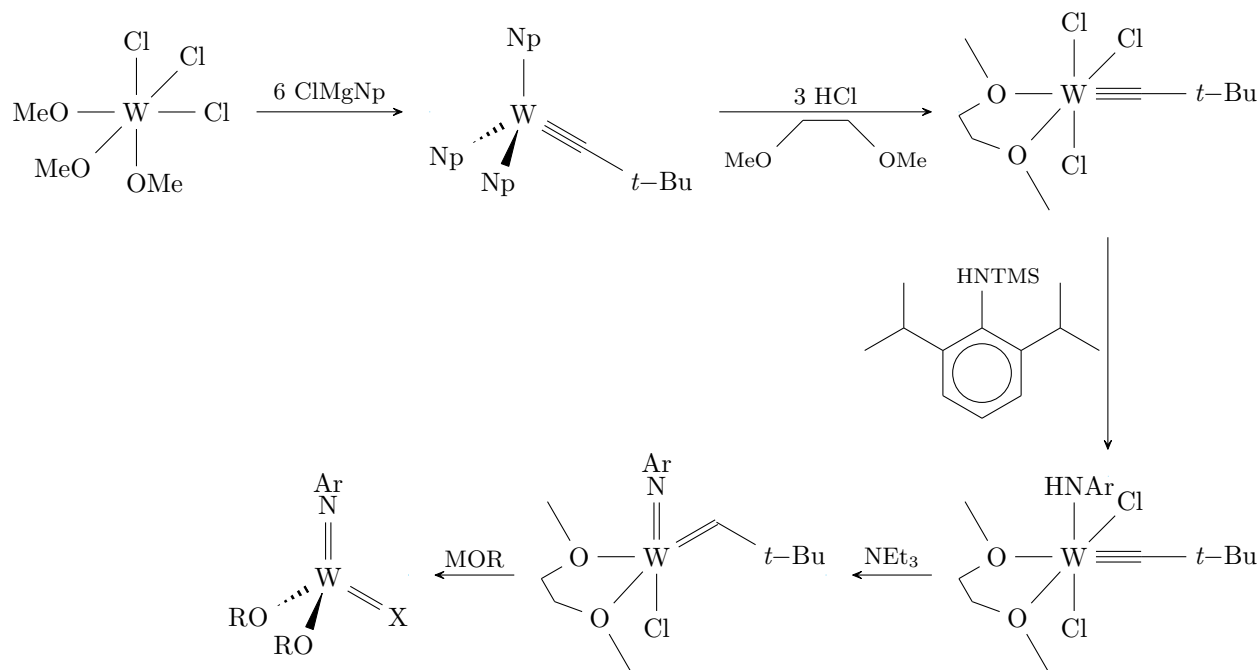


Figure 2.15: Tungsten olefin metathesis.

- Tebbe's reagents:

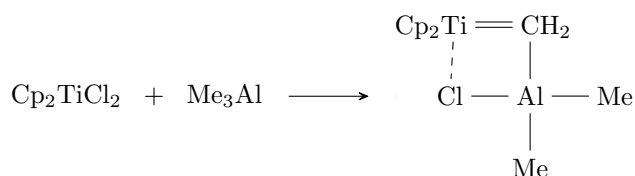


Figure 2.16: Tebbe's reagents.

- If you treat a Tebbe's reagent with an olefin in the presence of DMAP, you can form a 4-membered ring.
- N-heterocyclic carbenes (NHC complexes).
  - Neutral L-type ligands that are very strong  $\sigma$ -donors (much stronger than phosphines), but very weak  $\pi$ -acceptors.
- Reactivity:
  - 2 + 2 addition: The defining reactivity of carbenes.
    - React a carbene with an olefin to make a metallacycle, which can then collapse into olefin metathesis.
    - It allows us to swap the two  $\text{CR}_2$  fragments, which is pretty useful.
  - Cyclopropanation: Occurs through electrophilic, Fischer carbenes.
    - Allows us to create a cyclopropane compound with both of the carbene R groups attached to one of the cyclopropane carbons.
- Carbide: A terminal carbon atom; a  $\text{C}^{4-}$  ligand.

## 2.9 Lecture 9: Olefins, Carbonyls, and Phosphines

- 4/16:
- Top  $\pi$ -acceptors: CO,  $\text{NO}^+$ , and  $\text{PF}_3$ .
    - CO is also a decent  $\sigma$  donor.
  - CO provides a great IR handle, enabling characterization.
    - $\nu_{\text{CO}}$  is a measure of the electron density on the metal center.
  - We generally consider CO in the resonance structure  $\text{:}\overset{\ominus}{\text{C}}\equiv\overset{\oplus}{\text{O}}\text{:}$ .
    - Each atom in CO has four  $\pi^*$  lobes in the plane perpendicular to the bond axis and slightly oriented away from those on the other atom (note that the lobes on the carbon are significantly larger than those on the oxygen). Additionally, there is a nonbonding  $\sigma$  orbital originating from atomic  $p$  orbitals that runs along the bond axis.
    - Recall the CO resonance structures.
  - Free CO has a stretching frequency of  $\nu_{\text{CO}} = 2143\text{ cm}^{-1}$ .
    - This is also a range of the spectrum with little else going on, making these peaks easily identifiable.
    - CO has a large dipole (about  $\mu = 4.80\text{ D}$ ). This also really helps it stick to transition metals.
  - In  $\text{Mn}(\text{CO})_5\text{Me}$ , the Mn–Me bond is  $2.18\text{ \AA}$  and the Mn–CO bonds are  $1.86\text{ \AA}$ , so these latter bonds clearly have some multiple bond character.
    - The trans effect is also partially at play.
  - Synthesis:
    - In 1890, the Mond process is discovered:  $\text{NH}_3 + \text{NaCl} + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{NH}_4\text{Cl}$ .
      - After a year however, the plant built to run this process was trashed! The nickel in the steel pipes was reacting with CO to form  $\text{Ni}(\text{CO})_4$ , a volatile compound.
      - Leaching the nickel weakened the pipes, causing them to fall apart.
      - Take away: metal-carbonyl complexes can be pretty easy to form (as a general synthetic scheme, just add CO and apply pressure, as in the following mechanisms).
    - Pressurized CO:
      - $\text{Co} + \text{CO} \xrightarrow[\text{RT}]{35\text{ atm}} \text{Co}_2(\text{CO})_8^{[5]}$ .
      - $\text{Fe} + \text{CO} \xrightarrow[300^\circ\text{C}]{300\text{ atm}} \text{Fe}(\text{CO})_5$ .
    - Reduce with CO:
      - $\text{Re}_2\text{O}_7 \xrightarrow{\text{CO}} \text{Re}_2(\text{CO})_{10} + \text{CO}_2$ .  $\text{CO}_2$  is given off by reductive elimination from an intermediate.
      - More syntheses listed.
  - We predict stoichiometry (i.e., constitutional isomerism) with the  $18\text{ e}^-$  rule (except for square planar).
    - Group 9:  $\text{M}_4(\text{CO})_{12}$  is common.
    - Group 8:  $\text{M}_3(\text{CO})_{12}$  is common.
  - IR signatures.
    - Ketones are usually  $1750\text{--}1720\text{ cm}^{-1}$ .
    - $\text{R}_3\text{COH}$  compounds are usually  $1100\text{ cm}^{-1}$ .

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<sup>5</sup>RT is short for room temperature.

- $\nu_{\text{CO}}$  will increase if there is no backbonding, and will decrease if there is strong backbonding.
- Influences on backbonding:
  - Primarily the metal oxidation state and electronegativity.
  - Electron count does not matter as much, aside from  $d^0$  (obviously no backbonding can occur in this case).
  - Second and third row metals tend to backbond more strongly (stems from their larger orbital radius).
- Thus, we can predict that low-valent, early metals are strong backbonders, and high-valent, late metals are weak backbonders.
- “Extreme” carbonyls (those with a high degree of backbonding, resulting from a very reduced/comparably early metal center):

- $\text{Fe}(\text{CO})_5 \xrightarrow[-\text{CO}]{2\text{Na}/\text{THF}} \text{Na}_2\text{Fe}(\text{CO})_4^{2-}$ .
- $\text{M}(\text{CO})_n \xrightarrow[-\text{CO}]{2\text{Na}} \text{Na}_2\text{M}(\text{CO})_{n-1}^{2-}$ .
- $\text{Re}_2(\text{CO})_{10} \xrightarrow{\text{Na}} \text{Na}^+\text{Re}(\text{CO})_5^-$ .
- $\text{Re}_2(\text{CO})_{10} \xrightarrow[-2\text{CO}]{6\text{Na}/\text{HMPA}} \text{Na}_3\text{Re}(\text{CO})_4^{3-}$ .
- $\text{Mo}(\text{CO})_6 \xrightarrow{2\text{Na}} \text{Mo}(\text{CO})_5^{2-}$ .
- $\text{Mo}(\text{CO})_6 \xrightarrow{\Delta, \text{TMEDA}} (\text{CO})_4\text{Mo}(\text{EDA}) \xrightarrow{4\text{NaNH}_3} \text{Na}_4\text{Mo}(\text{CO})_4^{4-}$ .
  - This is  $d^{10}$  and thus  $\nu_{\text{CO}} \lll 2000\text{ cm}^{-1}$ .
  - TMEDA is tetramethylethylenediamine.

- We can also go the other direction to find carbonyls with a very low degree of backbonding.

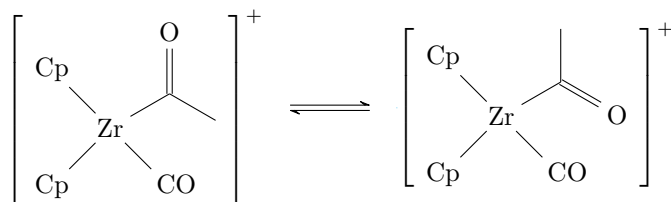


Figure 2.17: Low backbonding carbonyl complexes.

- The reactant has  $\nu_{\text{CO}} = 2123\text{ cm}^{-1}$ , which is slightly lower than that of free CO due to some  $\sigma$  donation from the acetyl ligand.
  - The product has  $\nu_{\text{CO}} = 2176\text{ cm}^{-1}$ , which is slightly higher because the acetyl's oxygen is pushing more electron density off of the CO ligand.
- Higher  $d$  counts can also lead to higher stretching frequencies.
  - It may seem counterintuitive that compounds with more electrons backbond less, but backbonding is actually dictated by reduction potentials, electronegativity, and oxidation states.
  - Indeed, both *cis*- and *trans*- $\text{PtCl}_2(\text{CO})_2$  exhibit CO stretching frequencies that are very similar to that of free CO.
- More extreme:  $2\text{IrF}_6 + 15\text{CO} + \text{HSbF}_5 \xrightarrow[60^\circ\text{C}, 12\text{ h}]{\text{SbF}_5} 2[\text{Ir}(\text{CO})_6]^{3+}$ .
  - This gives us  $\nu_{\text{CO}} = 2254\text{ cm}^{-1}$ .
  - We also have  $\text{Au}(\text{CO})_2^+$  at  $2217\text{ cm}^{-1}$ .

- Reducing extreme:
  - $\text{Zr}(\text{CO})_6^{2-}$  is  $1\,757\text{ cm}^{-1}$ .
  - $\text{W}(\text{CO})_6$  is  $1\,983\text{ cm}^{-1}$ .
- Neutral L-type olefins:  $\text{M}-||$ .
- Dewar-Chat-Duncanson model: Very related to Figure 2.5.
  - Thus, the ethylene is both a  $\sigma$  donor and  $\pi$  acceptor.
    - This relates it to CO as a ligand. Of course, CO is  $C_{\infty v}$  and CO has 2  $\pi$ -accepting orbitals instead of just one, but there is a relation nonetheless.
- Use ionization potential to measure the magnitude of  $\sigma$  donation:
  - Ethylene:  $10.5\text{ eV}$ .
  - CO:  $14\text{ eV}$ .
- Thus, ethylene is a better  $\sigma$  donor but worse  $\pi$  acceptor.
- Comparing C=C bond length in Zeise's salt (see Figure 1.2),  $(\text{Ph}_3\text{P})_2\text{Pt}-||$ , and  $\text{C}_2\text{H}_4$ .
  - Bond length is significantly elongated (close to a C–C single bond) for  $(\text{Ph}_3\text{P})_2\text{Pt}-||$  but similar for the other two.
  - We can also see that the C–H bonds are bent back by  $15^\circ$  in  $(\text{Ph}_3\text{P})_2\text{Pt}-||$ , which is consistent with  $sp^3$  hybridization.
- There are two resonance structures for an olefin: An olefin adduct and a metallacyclopropane.
  - The olefin adduct is an L-type ligand and the metallacyclopropane is an  $\text{X}_2$ -type ligand, but by convention we almost always treat olefins as L-type ligands.
  - Both are  $2e^-$  donors.
- Polyolefins.
- Example: Butadiene.



Figure 2.18: Butadiene.

- We have four bonding modes:  $\sigma$ ,  $\pi$ ,  $\pi^*$ , and  $\delta^*$ .
  - Each corresponds to a different orientation of the  $p_z$  orbitals at each carbon and has a different number of nodes.
- $\pi$  and  $\pi^*$  orbitals are the major contributors.
  - The metal  $d$  orbitals will project toward butadiene in a  $\pi$ -symmetry fashion, and the  $s$  orbitals (which would bond with the butadiene  $\sigma$  orbital) are more secondary for a transition metal.
  - $\sigma$  contributions are reduced because of symmetry.
- $\sigma$  and  $\pi$  orbitals are  $\sigma$  donors;  $\pi^*$  engages in backbonding.
- Lowering the energy of the  $\pi$  orbital and populating the  $\pi^*$  orbital favors new resonance structures that distort the bonds in butadiene (why to the resonance structure shown?).
  - Originally, the bonds are distorted. However, after bonding, all bonds in butadiene are the same length.



- Review of insertion, nucleophilic attacks, and electrophilic attacks.
- $M\equiv C-OE$  where E is an electrophile is a Fischer carbyne.
- The relative backbonding plays a crucial role in determining reactivity.
- Olefin limiting cases: Metallacyclop propane and direct  $\pi$ -bonding.
  - Different resonance structures are more suitable for different kinds of attacks.
  - The stronger the backbonding, the easier it is to get the ligands to play nice with electrophiles.
- Orbitals in bridging CO.
  - A bridging CO is a  $\sigma$  donor, and donates into  $d_{xy}$  metal orbitals.
  - It's also a  $\pi$  acceptor, and accepts electrons from  $d_{x^2-y^2}$  orbitals.
  - Bridging is typically much more activated (in terms of CO stretching frequencies).
- CO activation.
  - All renewables technology boils down to finding ways to reduce CO into multiple carbon products.
  - C–O BDE = 1 075 kJ/mol<sup>[6]</sup>.
    - This is an even higher BDE than that of the  $N\equiv N$  triple bond.
    - CO is easier to activate due to the dipole (more on this on Canvas).
  - There is a lot of interest in deoxygenating CO and forming C–C bonds from the products. The classic way to do this used highly reduced transition metal centers:
 
$$Ta^{III}(OSi(t-Bu)_3)_3 \xrightarrow{2CO} 2 R_3SiO_3Ta^V=O + (R_3SiO)_3Ta=C=C-Ta(OSiR_3)_3$$
    - The latter product exhibits significant variation in its double bond lengths (the C=C one is much shorter than the two Ta=C ones).
- Lists a few more syntheses.
- Don't worry about memorizing all these reactions; just know the general types and reagents.

## 2.10 Midterm 1 Review

- 4/17:
- Up through what lecture is covered on the midterm?
    - Up through lecture 11.
  - For problem 7: Do you want us to count an olefin as having coordination number 1 or 2? Is it ok to treat the olefin as if it's ethylene.
    - An olefin has coordination number 2.
  - Are alkyl groups more stable?
  - Synthesis questions.
    - Try to stay under  $18e^-$ .
      - Don't include the electron counts as part of the synthesis but think about them for yourself.
      - $ZrCl_4$  has  $8e^-$ ? We describe metal chlorides as simply as possible, but it's probably in a chain or something in real life so each Zr gets more electrons.
    - CO just comes off (it's a gas).

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<sup>6</sup>Note that BDE is short for bond dissociation energy.

- You can just say “add a CpMe” group and some COs will come off.
- We can do  $-\text{CO}$  as needed.
- Keep in mind which metal centers are more labile based on their oxidation state.
- We don’t have to draw structures; we can just use formulas.
- Difference in oxidation state of the zirconiums means we need to add a reductant at some point. We can choose to reduce first or add Cp’s first. We’ll add Cp’s first because adding the Cp’s might make it more stable before we reduce it.
- It’s generally lithium or sodium, not potassium.
- As reductants, we can use  $\text{KC}_8$  (potassium graphite),  $\text{Na}^0$  (sodium metal), or  $\text{NaNaph}$  (sodium naphthalenide), but not hydride reductants like in orgo.
  - In the lab, you don’t want to use too strong a reductant.
  - However, in this theoretical case, it’s ok to use these real hammers.
  - Some mild reductants:  $\text{CoCp}_2$  (cobaltocene) and  $\text{CoCp}^*$ .
- We reduce before adding COs because if we added two COs right now, we’d get a  $20e^-$  species.
- *In situ* means in the situation. Anything you do in the same mixture is something you’ve done *in situ*.
- Oxidants:
  - $\text{AgPF}_6$ :  $\text{Ag}^0$  is super stable?
  - Bromine can be an oxidant? Look back at orgo notes for dinuclear oxidative addition.
- Review the powerpoint on carbonyls.
- Midterm tips:
  - CO is a really important ligand to understand: Know its MO diagram, resonance structures, IR stretch influences.
  - Know phosphines: Tolman parameter and cone angle, donor properties, orbitals, etc.
  - Know some about olefins, too.
  - Synthesis is very important. Use your electron counting skills, understanding of lability, and redox reactions.
  - Be able to draw the carbenes and various binding modes of the different ligands we’ve discussed, including resonance.
  - Know lability abilities and how to predict orbital splitting and spin state.
  - Know the two equations from magnetism.
  - Different types of insertion and their final stereochemistry.
  - If there’s a drawing in the notes, ask yourself if you know how to draw it.
- Homework 2 should be a pretty good review for Midterm 1.
- Question 11:
  - For favorability, talk about hard/soft.
- Question 13:
  - Part a: Draw the starting compound and the products of the  $\text{MeI}$  and  $\text{H}_2$  reactions.
  - Part c: The compounds with each type of X (i.e., all of the halogens).

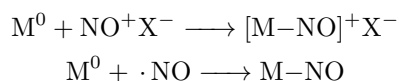
## 2.11 Lecture 10: Nitrosyls, Allyls, and More

4/19:

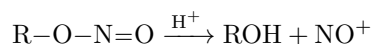
- First off, a survey of other  $\pi$  acceptors.
  - Many of these are analogous to CO.
- $\text{C}\equiv\text{S}$  (carbon sulfide).
  - $2\text{e}^-$  L-type donor.
  - Not stable unless it's ligated to a metal (will decompose as a free gas).
  - Due to the weak C–S binding, it can be more of a  $\pi$  acceptor than CO even though the polarization is a bit off.
- $[\text{C}\equiv\text{N}]^-$  (cyanide).
  - $1\text{e}^-$  X-type.
  - Much better  $\sigma$  donor, but a much weaker  $\pi$  acceptor.
- $\text{C}\equiv\text{N}-\text{R}$  (isocyanides).
  - Quite similar to CO (via the isolobal/isoelectronic analogy).
  - Slightly stronger  $\sigma$  donor, but a slightly weaker  $\pi$  acid.
- $\text{PR}_3$  (phosphines).
  - Good  $\sigma$  donors (better than CO), and ok  $\pi$  acceptors.
  - $\pi$  acceptance occurs through the  $\sigma^*$  orbitals.
    - More polarized the P–R bond  $\Rightarrow$  more  $\pi^*$  character on the phosphorous  $\Rightarrow$  better  $\pi$  acceptor  $\text{PR}_3$  will be.
    - Phosphines with strong electron-donating R groups will be better  $\sigma$  donors but worse  $\pi$  acceptors.
  - Know  $\text{P}(\text{OR})_3$  ligands (phosphites).
    - Very good  $\pi$  acceptors.
  - $\text{PF}_3$  is almost as good as CO in terms of its  $\pi$ -acceptance.
- $[\text{N}\equiv\text{O}]^+$  (nitrosyls).
  - Isoelectronic/isolobal to CO, so it engages in the same types of interactions.
  - Probably the strongest  $\pi$  acceptor known.
  - Two main modes of binding (linear and bent).
  - Bioinorganic chemistry of  $\text{NO}^+$ : An important signaling molecule; a potent vasodilator (i.e., a molecule that when released in the bloodstream causes blood vessels to expand); important in blood pressure.

Linear	Bent
$\text{M}-\text{N}\equiv\text{O}^{\oplus}$ LX-type. $3\text{e}^-$ donor. 3 CO's provide similar stability to 2 NO's (in terms of electron counting). Oxidation state: Formally $\text{NO}^+$ but this is not a good description (it would imply $\text{M}^-$ ).	$\text{M}-\ddot{\text{N}}=\text{O}^{\oplus}$ X-type. $1\text{e}^-$ donor.  Oxidation state: Formally anionic, so $\text{M}^+$ .

- Oxidation state debates led to the development of **Enemark-Feltham notation**.
- **Enemark-Feltham notation:** Considers the  $d$  count of the metal center and any extra electrons beyond  $\text{NO}^+$  that the NO brings.
- Consider heme centers.
  - Hemes bind to porphyrins.
    - Porphyrins are the macrocyclic aromatic ligands that bind iron and magnesium in a fashion hemoglobin and chlorophyll, respectively.
    - Porphyrins are very common in biology in general, too.
  - Formally a square-planar binding ligand with a  $2^-$  charge when deprotonated.
  - Thus, heme iron is  $2+$ , i.e.,  $d^6$ .
  - If heme  $\text{FeNO}$  is neutral,  $\cdot\text{NO}$  bound as a radical:  $\{\text{FeNO}\}^7$ .
  - If heme  $\text{FeNO}^-$  is anionic,  $\text{NO}^-$  bound as an anion:  $\{\text{FeNO}\}^8$ .
  - If heme  $\text{FeNO}^+$  is cationic,  $\text{NO}^+$  bound as a cation:  $\{\text{FeNO}\}^6$ .
- Nitrosyl geometry (linear vs. bent) is sensitive to the  $d$  count of the metal.
  - If the metal wants to get an extra  $3e^-$ ,  $\text{NO}^+$  will be linear. Otherwise,  $\text{NO}^+$  will be bent.
  - An example of a limiting case: When bonding to benzene,  $\text{NO}^+$  will be bent because there is no possible  $\pi$  bonding.
- Synthesis of nitrosyls:
  - Two main routes:



- In the first case, we react a reduced metal center with a nitrosonium salt to in-situ oxidize the metal center to make a metal-nitrosyl cation with the  $\text{X}^-$  as a counteranion.
  - In the second case, we react a metal center with  $\text{NO} \cdot$  gas, which is a radical and pretty nasty.
- One less common route:



- An analogous reaction with metals is  $\text{M}-\text{N}(=\text{O})-\text{O} \xrightarrow{\text{PR}_3} \text{M}-\text{NO} + \text{R}_3\text{PO}$ .
- Note that in general, because NO and CO are both such strong  $\pi$  acceptors, they do not go *trans* to each other.
  - One notable exception:  $\text{V}(\text{CO})_5(\text{NO})$ .
- Allys:

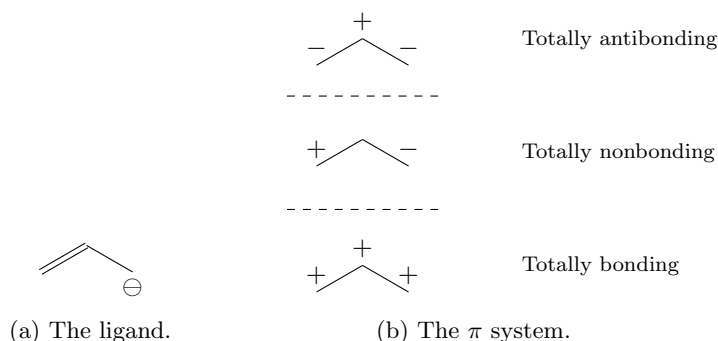
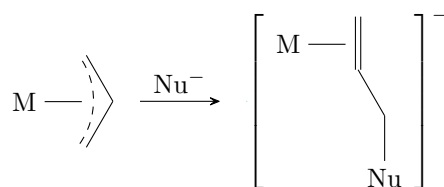
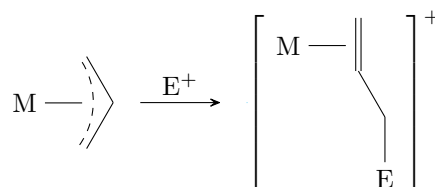


Figure 2.19: The allyl ligand.

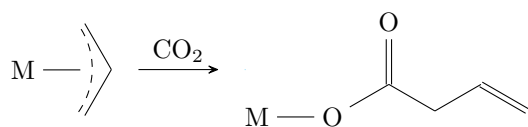
- $3e^-$  LX-type donor.
- Barry Trost's palladium allyls: Changing side-on vinyl ethers into allyls (structures shown).
- Synthesis of allyls:
  - We can synthesize allyls (from olefins) that bind to their metal center from above and below the molecular plane.
  - We can synthesize allyls by oxidizing a butadiene with acid.
  - There also exist allyls in the form of isobutane with conjugated electron systems between each carbon. This bonds to metal centers from above.
  - More syntheses listed.
- Note: Sodium is a possible reductant ( $\text{Mn}_2(\text{CO})_{10} \xrightarrow{\text{Na}} 2\text{Mn}(\text{CO})_5^-$ ).
- Allyl reactivity:



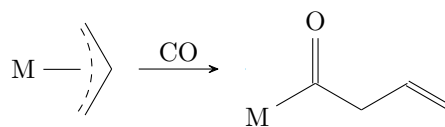
(a) Nucleophilic attack.



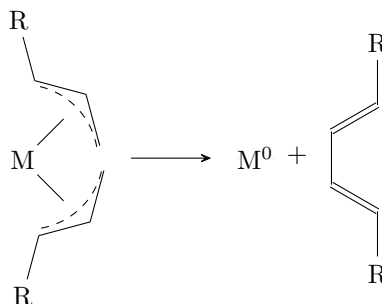
(b) Electrophilic attack.



(c) Insertion (1).



(d) Insertion (2).



(e) Coupling/reductive elimination.

Figure 2.20: Allyl reactivity.

- Other extended  $\pi$  systems.
- Cyclopentadienyl (Cp).

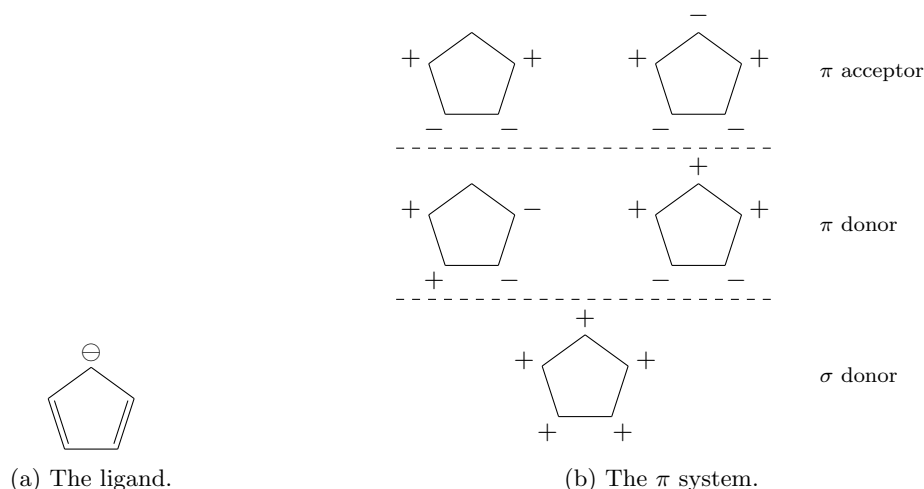


Figure 2.21: The cyclopentadienyl ligand.

- Strong field ligand.
- $5e^-$   $L_2X$ -type donor.
- Ferrocene is a classic example of a Cp-containing compound.
- In 1951, Pauson (very respected, famous chemist) showed that a  $Cp-MgBr$  Grignard (a Cp anion source) becomes a radical when treated with an oxidant and then dimerizes. This product when heated would lose  $H_2$  and become a fulvalene.
  - However, if you use  $FeCl_3$  as the oxidant, you get a compound with the formula  $(C_5H_5)_2Fe$  (as determined by elemental analysis, or EA).
  - This compound had a number of interesting properties, all demonstrating that it was very stable.
    - Orange solid.
    - Air stable.
    - Temperature stable.
    - Base stable (at 10% NaOH).
    - Melting point of  $173^\circ C$  (thus, a clean melting point transition).
    - Stable up to  $500^\circ C$ .
    - Water stable.
  - To characterize it as a sandwich compound, scientists used the fact that it has 1  $\nu_{C-H}$  stretch in the IR spectrum, 1 peak in  $^1H$  (proton) NMR, and no Diels-Alder reactivity.
  - Pauson missed this in his initial analysis. Woodward and E. O. Fischer proposed the real structure, which was later confirmed by X-ray diffraction (XRD) crystallography.
- There are tons of Cp complexes.
- However, almost any  $\pi$  system can bond to a metal center in a face-on fashion. For example, there are...
  - Benzene and tropylium (cycloheptatrienyl cation) aromatic adducts.
  - Butadiene and borazine nonaromatic adducts.

- **Ring-slipping:** When an aromatically bonded ring redistributes its electron density to localize it and only bind through some of its ring.
  - For example,  $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)_2 \longrightarrow \text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_6)$ . The driving force is a  $20e^-$  to  $18e^-$  transition.
- Triple bonds:
  - $\sigma$  donation, (weak)  $\pi$  donation, and  $\pi$  acceptance (same idea, orbitally, as answer to Homework 2, problem 11a).
  - Upon binding, we see lengthening of the  $\text{C}\equiv\text{C}$  bond and the  $\text{C-H}$  bonds bending backwards away from the metal center.
- Phosphines (and derivatives):
  - $\text{PR}_3$ : Bulky, soft, good donors, strong field ligands.
  - $\text{P(OR)}_3$ : Harder (due to the oxygens), weaker donors, stronger acceptors.
  - Compares basicity in a number of phosphines (phosphines with a greater ability to delocalize the electron pair on the phosphorous are weaker bases [i.e.,  $\text{PPh}_3$  is weak while  $\text{PMe}_3$  is strong]).
- **Tolman electronic parameter:** The  $\nu_{\text{CO}}$  value for  $(\text{CO})_3\text{NiL}$  where L is some ligand.
  - Allows us to gauge the  $\pi$ -accepting character of different ligands: Stronger  $\pi$  acceptors will invoke a higher  $\nu_{\text{CO}}$  value.
  - Weakly basic ligands do not do much  $\sigma$  or  $\pi$  donation and thus do a lot of  $\pi$  acceptance. It follows that these ligands will have a higher Tolman electronic parameter.
  - There is a good Wikipedia page for this.
  - Judges  $\sigma/\pi$  donation/acceptance properties all together (i.e., their ratio), not each individually.
    - For example, a ligand that is a strong  $\sigma$  donor and a strong  $\pi$  acceptor will have a middling Tolman electronic parameter, whereas a ligand that is a weak  $\sigma$  donor and a strong  $\pi$  acceptor will have a high Tolman electronic parameter.
- $\pi$ -accepting character of various ligands:
 
$$\text{NMe}_2 < \text{NH}_3 \ll \text{py} < \text{PR}_3 < \text{P(OR)}_3 \ll \text{PF}_3 < \text{PCl}_3 \ll \text{CO}$$
  - Ranked on a scale of 0-100 where the  $\pi$ -accepting character of CO is defined to equal 100.
- **Tolman cone angle:** The angle for the cone that encapsulates all of the R groups.
 
$$\text{PMe}_3 < \text{P(Ph)}_3 < \text{P}(t\text{-Bu})_3$$
  - Describes the sterics of the phosphine.
  - Lists the cone angles of several common phosphines.
- $\text{AsR}_3$  (arsenes):
  - Isoelectronic/isolobal to phosphines.
  - Not as common, but typically better  $\pi$  acceptors.
- N-heterocyclic carbenes:

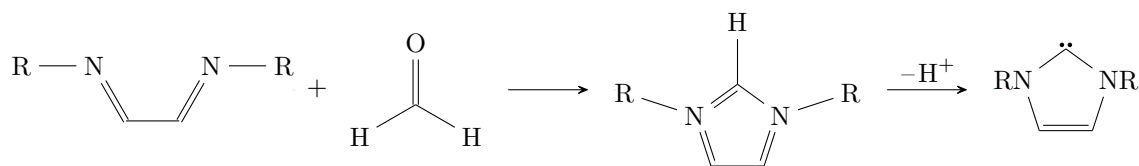
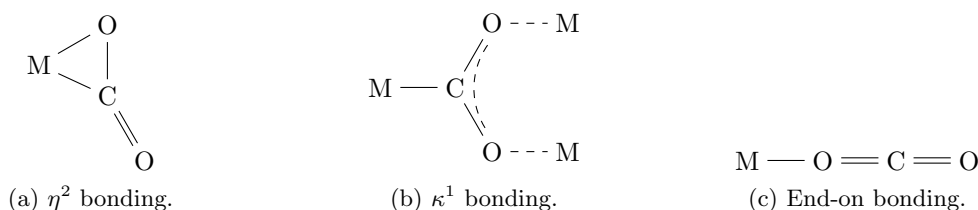


Figure 2.22: Synthesis of N-heterocyclic carbenes.

- A new class of ligands that are extremely strong donors.
- Many resonance structures.
- A very strong  $\sigma$  donor and a very weak  $\pi$  acceptor. Essentially pure  $\sigma$  donors.
  - $\sigma$  donor properties: Originate from the lone pair on the carbon.
  - $\pi$  acceptor properties: These exist in principle since the carbon has an empty  $p$  orbital, but in practice, it's  $\pi$  acceptor abilities are very weak since the carbon  $p$  orbital is donated into by the lone pairs on the neighboring nitrogens. Thus, N-heterocyclic carbenes aren't really  $\pi$  acceptors.
  - $\pi$  donor properties: Nonexistent.
- Stronger  $\sigma$  donors than phosphines.
- Other  $\pi$ -bound ligands.
- $\text{CO}_2$  /  $\text{CS}_2$ .

Figure 2.23: Bonding of  $\text{CO}_2$  to metal centers.

- There's a lot of interest in bonding  $\text{CO}_2$  to transition metals in terms of catalytic reduction/functionalization of  $\text{CO}_2$ .
- What is  $\kappa^1$  bonding?
- Aldehydes / ketones.
  - Binding  $\eta^2$  and end-on through the oxygen.

## 2.12 Lecture 11: Hydrides and Silyls

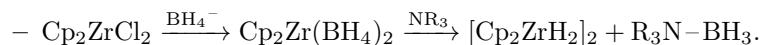
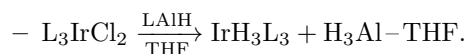
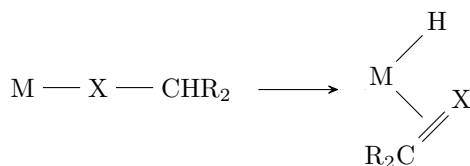
- 4/21:
- $\text{M-SiR}_3$  (silyl).
    - $1\text{e}^-$  X-type donor.
    - Closely related to alkyls, but with some important differences (esp. with regard to synthesis and properties).
    - Important role in a number of catalytic processes (esp. hydrosilylations).
    - First synthesis reported by Wilkinson in 1956.
      - He reacted  $\text{Fp}^- \xrightarrow{\text{TMSCl}} \text{CpFe}(\text{CO})_2(\text{SiMe}_3)$ .
    - The bonding is more covalent than with carbon since silicon is more electropositive.
  - Synthesis of silyls:
    1. Electrophilic:
      - Mid to late TM's.
      - Note that  $\beta$ -H elimination is not a problem typically as  $\text{Si}=\text{CR}_2$  bonds are not stable (unless you add a lot of steric bulk).
        - Thus,  $\text{SiMe}_3$  does not undergo  $\beta$ -H elimination.



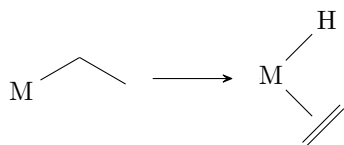
2. Oxidative addition:  $L_nM^0 + HSiR_3 \rightleftharpoons L_nMH(SiR_3)$ .
  - Almost always occurs through Si–H bonds.
  - C–H addition can be quite hard, but Si–H addition can be quite easy.
    - Thus, for example,  $HSiR_2Cl$  will add through the Si–H bond, not the Si–Cl bond since the latter are thermodynamically strong.
  - Si–H bonds form and break in a mobile and dynamic equilibrium.
    - The larger orbital radius of silicon helps form the  $\sigma$  adducts.
3. Nucleophilic:  $SiR_3^-$  is very rare, so this is uncommon.
  - There are some examples, though.
    - You can make  $LiSiMePh_2$  in-situ.
    - You can also make  $(THF)_3LiSi(TMS)_3$  and then crystalize it for storage (this compound is known as super silyl).
    - Lastly,  $Cp_2ZrCl_2 + LiSi(TMS)_3 \longrightarrow Cp_2ZrCl(Si(TMS)_3)$ .
- M–H (hydrides and  $H_2$  adducts).
  - Pure (and strong)  $\sigma$  donors and strong field ligands.
  - Important intermediates in
    - a) Olefin/alkyne hydrogenations.
    - b) Isomerizations/polymerizations of olefins.
    - c) Hydroformylations.
    - d) Decarbonylations.
    - e) Hydrogen/deuterium (H/D) exchange.
  - Many important structures:
    - For example, there are hydrides supported by phosphine ligands, *trans* to carbonyls, *cis* to carbonyls, Cp metal hydrides, and binary hydrides such as  $ReH_9^{2-}$  (which is face capped trigonal prismatic).
    - Bridging hydrides: M–H–M,  $MHM_2$ , and interstitial hydrides (which is a hydrogen surrounded octahedrally by metals in a solid). Interstitial hydrides are important in solid state hydrogenation catalysts (such as Pd /  $H_2$ ).
- Bond properties of hydrides:
  - Hydrides are small compared to typical ligands.
    - Thus, for example,  $ML_4H$  will not be trigonal bipyramidal but almost tetrahedral, with the equatorial ligands bending downwards toward the hydride.
    - The distance between the equatorial ligand plane in  $ML_5$  and  $ML_4H$  is denoted by  $d$ .
  - Jim Ibers (emeritus professor at Northwestern) studied various compounds and their  $d$  values vs. the *trans* ligand.
    - Several examples are listed.
    - What he found is that bigger ligands make more tetrahedral structures.
  - The most tetrahedral structures show up as  $T_d$  without the hydride in X-ray diffraction since X-rays scatter off of electrons and hydrides have basically none.
    - Thus, you need neutron diffraction (which requires really big solid state crystals).
- Electronegativity trends in hydrides:
  - In general:  $M^{\oplus} - H^{\ominus}$
  - Early metal hydrides are very polar and anionic; late transition metal hydrides are more covalent.
  - Hydrides can react like  $H^+$ ,  $H^\cdot$ , and  $H^-$ .

- Electronegativity trends can influence reactivity.
  - Hydrides acting as acids:
    - $\text{HCo(CO)}_4 \rightleftharpoons \text{H}^+ + \text{Co(CO)}_4^-$ ,  $\text{p}K_{\text{a}} < 0$  (favorable).
    - $\text{HCo(CN)}_5^{3-} \rightleftharpoons \text{H}^+ + \text{Co(CN)}_5^{4-}$ ,  $\text{p}K_{\text{a}} > 20$  (unfavorable).
    - Think about the electronegativity and how electron rich or poor a metal center to determine whether or not it will want to ionize.
  - Hydrides acting as classic hydrides:
    - $\text{Cp}_2^*\text{ZrH}_2 \xrightarrow{\text{HCl}} \text{H}_2 + \text{Cp}_2^*\text{ZrHCl}$ .
    - $\text{Cp}_2^*\text{ZrH}_2 \xrightarrow{2\text{O}=\text{CH}_2} \text{Cp}_2^*\text{Zr(OCH}_3)_2$ .
  - Hydrides acting somewhere in-between these two extremes (actin acidic and hydritic):
    - $\text{Cp}_2\text{MoH}_2 \xrightarrow{\text{LDA}} [\text{Cp}_2\text{MoH}^- \text{Li}]_4$ .
    - Note that LDA is a strong base.
    - $\text{Cp}_2\text{MoH}_2 \xrightleftharpoons{\text{H}^+} \text{Cp}_2\text{MoH}_3^+$ .
    - Note that  $\text{H}^+$  is just a generic acid, and the product is an  $\text{H}_2$  adduct.
  - Radical:
    - $\text{M-H} \longrightarrow \text{M}\cdot + \text{H}\cdot$ .
    - The classic example of this is  $(\text{CO})_5\text{Mn-H}$  which can homolyze pretty easily.
- Synthesis of hydrides (the first four are fundamental reactions, but the latter ones are also important):
1.  $\text{H}_2$  directly:
    - $\text{CoS} + [\text{CO} + \text{H}_2] \xrightarrow[\text{Cu} / 200^\circ\text{C}]{200 \text{ atm}} \text{HCo(CO)}_4 + \text{CuS}$ .
      - $[\text{CO} + \text{H}_2]$  is a mixture of the two gasses known as Syn gas.
      - The key to making this reaction proceed is just temperature and pressure. Catalysts can also help.
    - $\text{FeI}_2 + \text{PF}_3 + \text{H}_2 \xrightarrow[\text{Zn} / 250^\circ\text{C}]{100 \text{ atm}} \text{H}_2\text{Fe(PF}_3)_4 + \text{ZnI}_2$ .
      - Zinc serves as a reductant here.
    - Other examples exist, but no more are shown.
  2. Protonation of metal anions:
    - $\text{Ru(CO)}_5 \xrightarrow[-\text{CO}]{\text{Na}} \text{Na}_2\text{Ru(CO)}_4 \xrightarrow{\text{HA}} \text{H}_2\text{Ru(CO)}_4$ .
    - Similar chemistry exists with Os and Fe.
  3. Oxidative addition across a M–M bond.
    - $\text{Cp(CO)}_3\text{Cr-Cr(CO)}_3\text{Cp} \xrightarrow{\text{H}_2} 2 \text{CpCr(CO)}_3\text{H}$ .
    - $\text{Os}_3(\text{CO})_{12} \xrightarrow[80 \text{ atm}]{\text{H}_2} \text{H}_2\text{Os(CO)}_4$ .
  4. Oxidative addition to a single metal center.
    - $\text{IrCl(CO)(PPh}_3)_2 \xrightarrow{\text{H}_2} \text{IrClH}_2(\text{CO})(\text{PPh}_3)_2$ .
    - $\text{HCo(N}_2)(\text{PPh}_3)_3 \xrightarrow[\text{H}_2]{-\text{N}_2} \text{H}_3\text{Co}^{\text{III}}(\text{PPh}_3)_3$
  5. Hydrogenations of M–L bonds with  $\text{H}_2$ .
    - $\text{M-R} + \text{H}_2 \longrightarrow [\text{MRH}_2]^\ddagger \longrightarrow \text{M-H} + \text{R-H}$ .
    - $\text{M-OR} + \text{H}_2 \longrightarrow \text{M-H} + \text{HOR}$ .
      - Much harder to do since the M–O bond is typically more ionic, and thus stronger.
    - Example:  $\text{Cp}_2^*\text{Ta(CH}_3)_4 \xrightarrow{\text{H}_2} \text{Cp}_2^*\text{TaH}_4 + 4 \text{CH}_4$ .
      - This reaction must proceed through  $\sigma$ -bond metathesis.

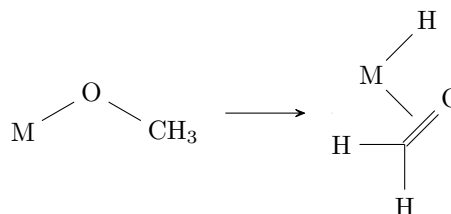
## 6. Electrophilic metal centers with hydride reagents.

7.  $\beta$ -H elimination.

(a) General case.



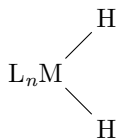
(b) Simplest case.



(c) Alternate case.

Figure 2.24:  $\beta$ -H elimination synthesis of metal hydrides.

- The relative direction of the equilibrium depends on the system, but this can definitely happen.
- Goes over how to isolate osmium from osmium ore.
- Non-classical and paramagnetic hydrides.



(a) General dihydride.

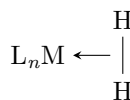
(b) General  $\text{H}_2$  adduct.

Figure 2.25: Non-classical hydrides.

- $\text{L}_n\text{MH}_2$  could be a dihydride or an  $\text{H}_2$  adduct (or some resonance structure in between). The latter is a non-classical hydride.
- We distinguish between the two with NMR spectroscopy since  $^1\text{H}$  hydrides are usually upfield ( $-1$  to  $-15$  ppm).
- A  $T_1$  relaxation also provides the H-H distance.
- Lastly,  $\text{H}_1\text{D}$  isotopologues give you a H-D coupling constant, which can be correlated to bond distances.
- If you have paramagnetic complexes, this is much harder, so you have to use special techniques such as ENDOR spectroscopy.

## Unit 3

# Intro to Catalysis

### 3.1 Lecture 12: Intro to Catalysis

- 4/26:
- We're now moving from theoretical chemistry to some applications (namely catalysis) of the theory we've been learning.
  - History of defining catalysts:
    - Berzelius (in 1836) becomes interested in this behavior.
    - Ostwald (in 1894) defines a **catalyst**.
  - **Catalyst**: A substance that increases the rate of a chemical reaction without being consumed.
  - Energetically, this must happen by altering the transition state (this is a simplistic explanation).
    - The thermodynamics ( $\Delta G$ ,  $\Delta S$ , and  $\Delta H$ ) are unaffected.
    - The kinetics ( $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\Delta H^\ddagger$ ) are reduced.
  - More realistically, a catalyst often substantially changes the reaction coordinate (one big hump in the energy diagram to many small humps).
    - The general set of intermediates during the reaction is the starting material plus the catalyst ( $S + C$ ), the starting material-catalyst complex ( $S \cdot C$ ), the product-catalyst complex ( $P \cdot C$ ), and the product plus the catalyst ( $P + C$ ).
    - Note that  $\Delta G^\ddagger$  is the activation energy for the highest barrier step, as measured against the free energy of the reactants. This notably implies that  $\Delta G^\ddagger$  is not necessarily the  $E_A$  of the *first* step; only the biggest. See Figure 3.2b.
    - Even though there are more steps, the rate increases because  $\Delta G^\ddagger$  decreases.
  - If you get stuck at a low energy intermediate, this can reduce reaction rate, and the process is no longer being catalyzed.
    - Indeed, if your catalyst is a different structure at the end of the reaction, it's not a catalyst but a reagent.
    - Excessively stabilizing the starting materials can create a higher energy barrier to the products.
  - Example:

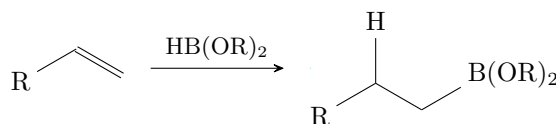


Figure 3.1: A process to be catalyzed.

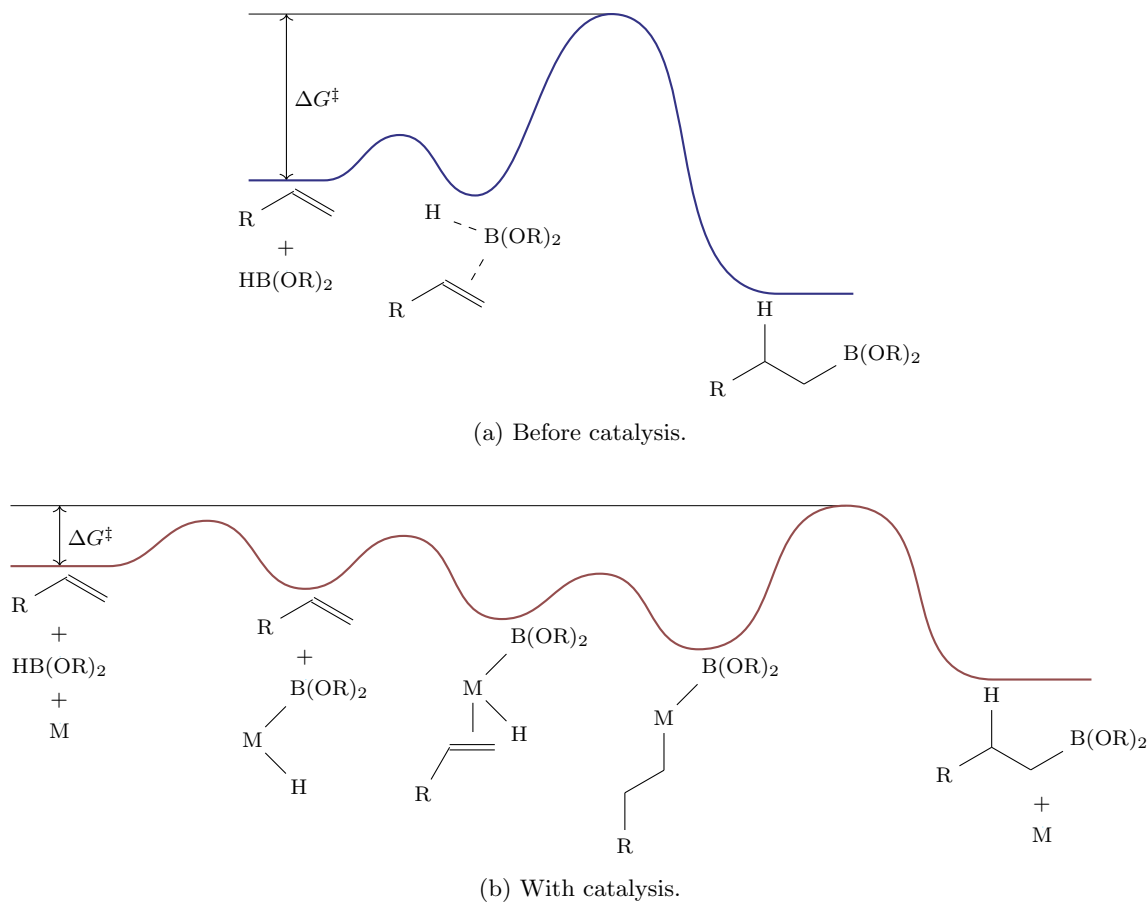


Figure 3.2: Catalysis energy diagrams.

- With transition metal catalysts, we have many more steps but potentially a lower  $\Delta G^\ddagger$ .
- Anatomy/terminology of a catalytic cycle.

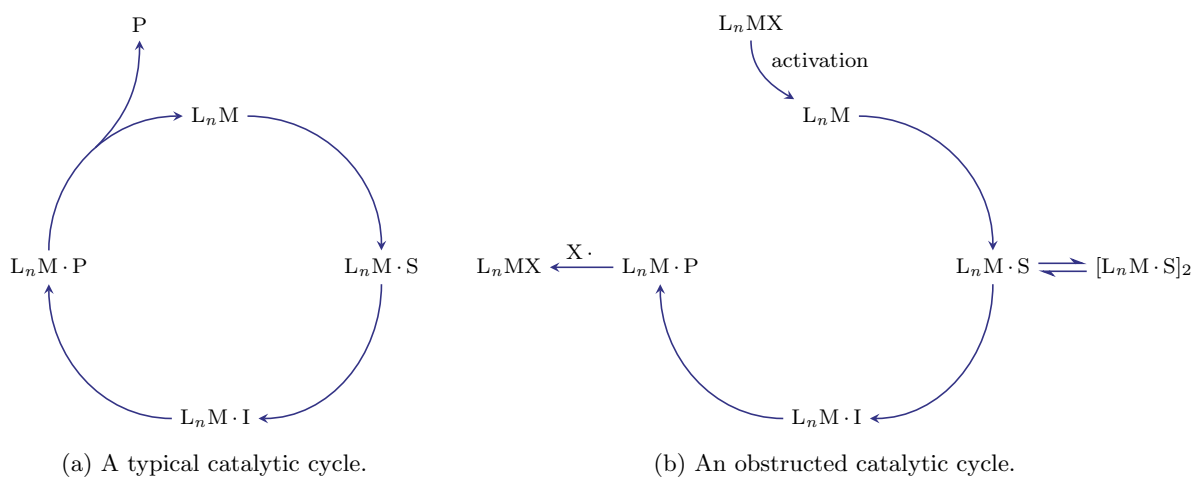


Figure 3.3: The anatomy of catalytic cycles.

- Simplistically, a catalytic cycle occurs as in Figure 3.3a.

- However, catalytic cycles can be complicated by **catalyst precursors**, **inactive off-cycles**, and **inactive poisoned states**.
- **Catalyst precursor:** A complex that must go through an activation step before it can be used as a catalyst.
  - See the reactant that becomes  $L_nM$  in Figure 3.3b.
- **Inactive off-cycle:** A reversible reaction that an intermediate participates in that is different from the intended reaction.
  - See the alternate pathway that  $L_nM \cdot S$  participates in in Figure 3.3b.
- **Inactive poisoned state:** When an intermediate follows an alternate nonreversible reaction pathway.
  - See the alternate pathway that  $L_nM \cdot P$  participates in in Figure 3.3b.
- Gives two examples of activating a catalyst (just a chemical reaction where one product is the catalyst).
  - A  $Pd^{2+}$  precursor must often be activated into a  $Pd^0$  catalyst.
- **Turnover number:** The quotient of the moles of product and the moles of catalyst. *Also known as TON.*
- **Turnover frequency:** The quotient of the TON and time. *Also known as TOF.*
- Kinetics:
  - The rate constant for individual steps can vary, but at a steady state (where the catalyst is transforming the substrate as fast as possible), the rates must be identical.
- **Catalyst resting state:** The highest concentration form of the catalyst.
  - Can also be off-cycle or dormant.
  - The rate constant after it (i.e., the rate constant of the **turnover limiting step**) is the smallest among all rate constants for steps.
- **Turnover limiting step:** The step which proceeds from the catalyst resting state. *Also known as rate-determining step.*
- Heterogeneous vs. homogeneous catalysis:

Heterogeneous	Homogeneous
Solid state (2 phases).	Solution phase.
Robust (high pressures and temperatures are ok).	Selective.
Low-cost.	Tunable.
Easy separation.	Easy to study (comparatively).

- We distinguish between the two with **transmission-electron microscopy**, kinetics, a **filtration test**, a **mercury drop test**, and/or a **three-phase test**.
- **Transmission-electron microscopy:** Looks for nanoparticles. *Also known as TEM.*
- Kinetics: We need to observe soluble intermediates and show that they are **kinetically competent**.
- **Kinetically competent:** The step from the soluble intermediates to the products under another reagent must be at least as fast as the overall rate of catalysis.

- **Filtration test:** For heterogeneous catalysts. Do the reaction over the heterogeneous catalyst, filter out the solid heterogeneous catalyst, add in more substrate and see if the mother liquor or supernatant still catalyzes the reaction. If so, then something is leaching out of the catalyst.
- **Mercury drop test:** Mercury can typically block the pores of high-surface area catalysts or poison the cycle by forming TM alloys. *Also known as Hg-drop test.*
- **Three-phase test:** Attach a substrate to an insoluble support. If the catalyst is solid state, we see no reaction (poor phase mixing).
  - The gold standard.
- Asymmetric catalysis:
  - Propene is pro-chiral (it has a Re and a Si face) at the central carbon.
- **Dynamic kinetic resolution:** When a racemic mixture goes to an enantioenriched product.
  - Occurs when an achiral intermediate is accessed and selectively filtered into an enantioenriched product.
- **Kinetic resolution.** When a racemic mixture goes to an enantioenriched starting material and enantioenriched product.
  - Arises from selective reaction with one enantiomer over another.
- **Enantiomeric excess:** The quantity given by the following formula. *Also known as ee.*

$$\frac{[\text{major en.}] - [\text{minor en.}]}{[\text{major en.}] + [\text{minor en.}]} \times 100\%$$

- Enantiomeric ratio:

$$\frac{[\text{major en.}]}{[\text{minor en.}]} = e^{-\Delta\Delta G^\ddagger/RT}$$

- Note that  $\Delta\Delta G^\ddagger$  is the difference in the  $\Delta G^\ddagger$  values for the major and minor enantiomers.

- Ee is dependent on  $\Delta\Delta G^\ddagger$  and  $T$ :

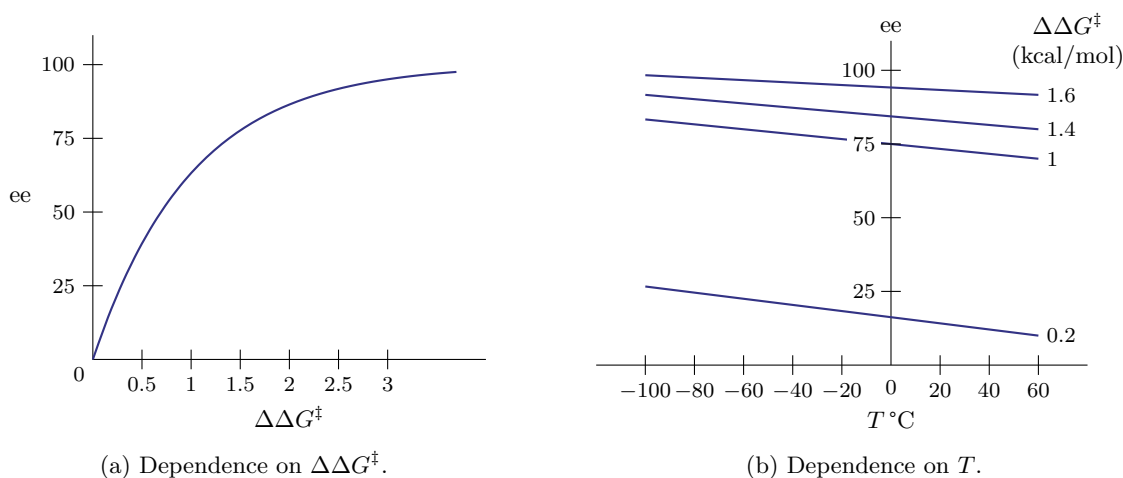


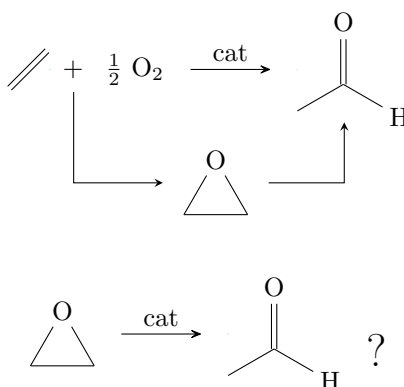
Figure 3.4: Dependence of ee on  $\Delta\Delta G^\ddagger$  and  $T$ .

- Some enantiomers have differing catalytic properties.

- Furthermore, chirality is not necessarily set at the RDS.
- If A and B are two enantiomers, then it is possible that  $\Delta G^\ddagger$  will differ for the formation of  $M \cdot A + B$  vs.  $M \cdot B + A$  (remember that this difference is  $\Delta\Delta G^\ddagger$ ).
- If the activation energy required to form  $M \cdot A + B$  (for example) is greater than that required to get from  $M \cdot A + B$  to the products, formation of the  $M \cdot A + B$  intermediate will be irreversible.
  - In this case, the kinetic product will be favored.
- If the activation energy required to form  $M \cdot A + B$  (for example) is less than that required to get from  $M \cdot A + B$  to the products, formation of the  $M \cdot A + B$  intermediate will be reversible.
  - In this case, the thermodynamic product will be favored (we may see more of the intermediate that forms quickly, but in time, more of the other product will be formed because formation of the other product is irreversible<sup>[1]</sup>).

### 3.2 Office Hours (Anderson)

- What does kinetically competent mean?



- Consider the reaction of ethylene and  $\frac{1}{2} O_2$  with a catalyst to make acetaldehyde.
  - We propose that the intermediate is an epoxide.
  - To test this hypothesis, we take ethylene oxide and react it with the catalyst to see if it makes acetaldehyde.
  - If it does, that's a good first step. If it reacts with a rate at least as fast or faster than the overall catalyzed reaction, then we know that this intermediate *is* an intermediate in a catalytic cycle.
  - Essentially, this test confirms that an intermediate is one. If the rate of epoxide to product is at least as fast as the overall rate, then we're good.
- What do all of those tests test for? I.e., if we find nanoparticles with TEM, what does this mean?
    - We need all of these tests because none of them are definitive.
    - You can never prove a mechanism; you can only disprove it.
    - If you see nanoparticles with TEM, it might make you ask if a heterogeneous pathway is present.
    - You go through these experiments to try to determine that it's *not* homogeneous or *not* heterogeneous.
  - Resources for synthesis?
    - Inorganic is not like organic where we're pushing electrons and stuff.

<sup>1</sup>Think the Mrs. Meer pens example.



- Don't worry about step efficiency.
- Don't worry about reactive fragments.
- For syntheses, completely ignore mechanism. Just balance the reaction.
  - Balance in terms of electrons and atoms.
  - Just focus on stoichiometry to start.
  - 99% of the time, this will get you to the right conclusion.
- If you have methyl iodide and you want to methylate the metal center, you want to make the metal nucleophilic and then react it.
- If you want to be really lazy, just show the reagents that will give you the products and be done.
  - You'll probs lose a few points for this, but that's ok.
  - Try and show the intermediates.
- Time crunch?
  - Skip a question.
  - Go through the easiest questions first.
  - You can probably get 80% of the points on the first question without writing a single synthesis.
  - Do the easy things fast and then move on.
  - View it as a scavenger hunt for points.

### 3.3 Discussion Section

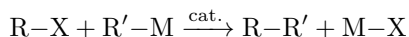
- 4/27:
- There may be a midterm key.
  - HW3 will be due Monday 5/3/2021 at 5:00 PM; HW4 will be due Monday 5/10/2021 at 12:00 PM (the usual time, no changes).
  - Notes on cross coupling:
    - Mizoroki-Heck cross couplings are characterized by a migratory insertion into an olefin in place of transmetalation.
    - In transmetalation, we typically use Grignards, boronic acids (Negishi), tin reagents (Stille), or silylethers.
    - $\alpha$  and  $\beta$  elimination (commonly hydride) can give competing reactions with the  $\beta$ -hydrogens especially.
  - Alkyls (such as ethyl groups) are more electron-rich than aryls (such as phenyl groups).
    - Think Homework 2, Problem 12.
  - Goes over the arrow pushing from a ring-closing and ring-opening metathesis (very similar to Figure 3.19).
  - Note the use of a Grignard in the basic cross coupling mechanism.

### 3.4 Lecture 13: Cross Coupling

- 4/28:
- Probably the single most-employed catalytic reaction in synthetic chemistry.
    - More important in pharmaceuticals and fine chemical synthesis, not industrial processes.
    - Nobel prize (2010) to Heck, Negishi, and Suzuki for aryl-type couplings.

- Dominated by Pd<sup>0</sup> / Pd<sup>II</sup> (“God’s Metal” - John Bercaw).
  - There are also examples with Ni, Rh, Ir, and Cu.
  - These metals are so good because the reactivity is often based in oxidative addition and reductive elimination, but radical reactions are also useful (particularly with nickel).

- General form:



- Basically a nucleophilic attack.
  - But since substrates like ArI don’t have very good reactivity for nucleophilic aromatic substitutions (despite the fact that iodide is a great leaving group), we need this mechanism.
- R, R’ are typically carbon-based, but carbon-heteroatom (where the heteroatom is N, O, S, or something else) couplings are also advancing.
- History:
  - Kumada and Corriu report  $\text{ArBr} + \text{RMgX} \xrightarrow[\text{substance}]{\text{Et}_2\text{O}, 25^\circ\text{C}} \text{Ph}-\text{C}=\text{C}-\text{R} + \text{R}'-\text{C}=\text{C}-\text{R}^{[2]}$ .
    - The *substance* is Ni(acac)<sub>2</sub>, dppe, NiCl<sub>2</sub>, FeCl<sub>3</sub>, CoCl<sub>2</sub>, or CrCl<sub>2</sub>.
    - Note that the aryl group can be phenyl, but it can also be vinylic or allylic (basically any *sp*<sup>2</sup>-hybridized carbon).
- There are many named reactions (usually defined by the nucleophile).

- This is a con of this field.
- Negishi: RZnX.
- Stille: RSnR<sub>3</sub>'.
- Hiyama: RSiMe<sub>2</sub>F.
- Suzuki: RB(OH)<sub>2</sub> or RBF<sub>3</sub><sup>−</sup>.
- Mizoroki/Heck:  $\text{Ph}-\text{Br} + \text{C}=\text{C}-\text{R} \xrightarrow[\text{base}]{\text{cat.}} \text{Ph}-\text{C}=\text{C}-\text{R}$ .

- Alkynes can also be coupled.
- Enolates can also be used as nucleophiles.
- Most cross coupling reactions involve aryl nucleophiles, but we can also use aliphatic ones.
- Aliphatic couplings:

- Alkyl electrophiles:  $\text{CRR}'\text{X} + \text{Ar}-\text{M} \xrightarrow{\text{Ni or Pd}} \text{CRR}'\text{Ar}$ .
  - These frequently go through a radical mechanism.
  - β-H can be a problem.

- Cyanide couplings:

- $\text{Ph}-\text{X} + \text{M}(\text{CN})_n$  or  $\text{CMe}_2(\text{CN})(\text{OH})$  can react with a palladium catalyst to form  $\text{Ph}-\text{CN}$ .
  - Note that M = K, Zn, K<sub>4</sub>Fe(CN)<sub>6</sub>.

- Enantioselective cross couplings:

- The nucleophile racemizes quickly.
- 93% ee with nickel.
- 99% ee with palladium.

---

<sup>2</sup>Note that Anderson often uses ∅ instead of Ph to denote a phenyl group.

- Homo-couplings:
  - An alkyl/aryl halide plus that same substance but as a Grignard forming a “dimer” at the place where the Grignard is attached.
  - Use nickel as a catalyst here.

- Heteroarene coupling partners:

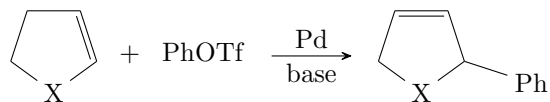


Figure 3.5: Heteroarene coupling partners.

- Note that TfO is triflate, an abbreviation of trifluoromethanesulfonate, which is an excellent leaving group.
- Also with enolates.

- Mechanism:

- Basic (see Figure 3.6a):
  - We must first activate our palladium catalyst by causing it to lose a ligand, thus becoming lower-coordinate.
  - Our aryl hydride will now oxidatively add to the activated catalyst.
  - Next, we have transmetalation (the most complicated step of the cycle). There are two possible paths by which we can introduce our nucleophile into the system and remove an X (to make space for it). First, we can use a hydride of the nucleophile which will do what we want and then form an acid with  $X^-$ ; this acid can then be neutralized by the base. Alternatively, we can bond a metal to the nucleophile and simply have the metal swap  $Nu^-$  for  $X^-$  with the palladium center, forming a metal salt as a byproduct.
  - The last step is reductive elimination, which (re)generates our product and starting material.
- Homocoupling (see Figure 3.6b):
  - Once again, we first oxidatively add our aryl hydride.
  - Then we transmetallate. Note that to regenerate our transmetallating nucleophile, we must treat it with some reductant (typically zinc metal); it can then oxidatively add  $Ar-X$ .
  - Finally, we reductively eliminate again.
- Mizoroki-Heck (see Figure 3.6c):
  - As in the basic cycle, we must activate our palladium catalyst.
  - Next, we oxidatively add  $Ar-X$  once again.
  - This time, however, we use an olefin as our electrophile. Note that  $R = H, CN$ , a ketone, etc. Additionally, note that we show in Figure 3.6c that we dissociate a ligand  $L$  at this point, but we could also dissociate an  $X^-$  and carry that through. Overall, this step is a ligand substitution.
  - A 1,2-migration follows. However, different types of migratory insertion can also occur as dictated by sterics.
  - After this, we do a  $\beta$ -H elimination to kick out our product (note that the product doesn't have to be *trans* but it typically is) and bring us closer to regenerating the catalyst.
  - Lastly, we can regenerate our initial catalyst with the reductive elimination of an acid (which will then be neutralized by an added base) as triggered by the addition of a ligand. Alternatively, the base can deprotonate the  $L_{n-2}XH$  intermediate before pulling off the  $X^-$ .
  - Note that this reaction must be carried out in basic media.

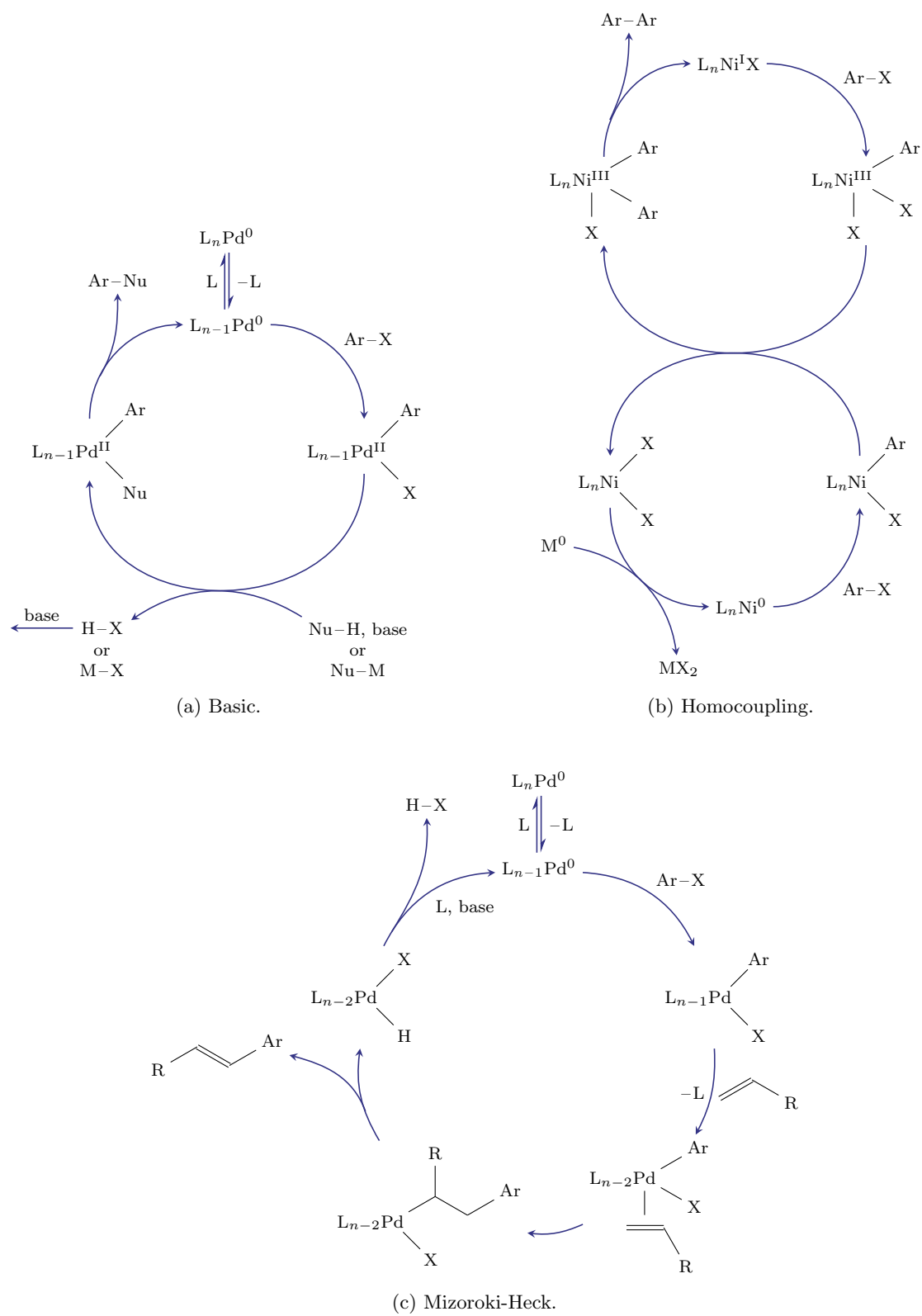
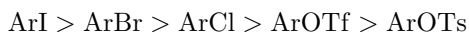


Figure 3.6: Cross coupling mechanisms.

- Oxidative addition:

- Occurs from a coordinatively and electronically unsaturated metal center
- Thus, we usually use either a monoligated or diligated neutral palladium center.
- Large, bulky monodentate ligands (e.g., phosphines) are good.
  - More steric hindrance enhances oxidative addition because we need easy dissociation later.
- Influence of the electrophile on the speed of oxidative addition:



- This shows that electron poor substrates are faster.
  - Note that this makes sense because in an oxidative addition, the substrate is reduced, and more electron poor substrates will want to be reduced more.
- Ni is generally faster than Pd.

- Transmetalation:

- By far the most complicated step in cross coupling mechanisms. The least is known about it and it exhibits great variability. Thus, the following is just a couple notes; there's not necessarily anything definite that you should take away.
- General form:

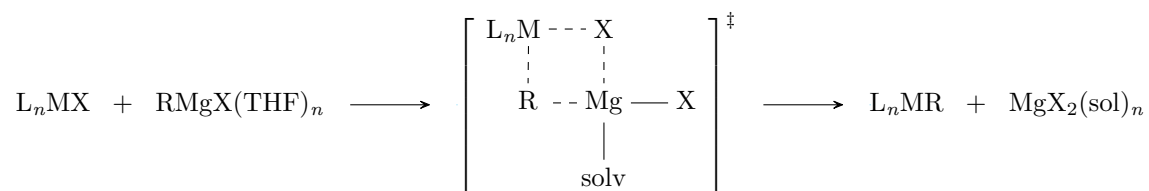


Figure 3.7: The general form of transmetalation.

- Some examples listed.
- On the subject of boronic acids, Negishi proposes the following:  $\text{L}_2\text{PhPdBr} \xrightarrow{\text{KOH}} [\text{LPhPd}(\mu\text{-OH})]_2 \xrightarrow{\text{Ar(BOH)}_2} \text{Ar-Ph}$ , 70%.
  - Negishi's conclusion: You typically need a base/nucleophile (such as hydroxide, water, or fluoride) to do the transfer of aryl boronic acids.
- Stille (Sn): Requires either a closed (such as in Figure 3.7) or open (as from a standard nucleophilic attack) transition state.
- Reductive elimination:
  - Steric pressure favors reductive elimination, yet it typically occurs from a less stable 3-coordinate intermediate.
  - Such an intermediate can be generated after ligand dissociation.
  - The two groups that reductively eliminate must be *cis*.
  - Aryl and vinyl groups are typically faster than alkyls.
- Ligands:
  - A huge number.
    - These are typically phosphines, though.
  - Tri(*tert*-butyl)phosphine is also known as tri(chicken foot)phosphine!

- Each ligand has very specific properties (better for one cross coupling than another).
- Very bulky phosphines tend to be good for these reactions, but chelating phosphines can be good, too.
- The reaction of a butyl Grignard in a cross coupling reaction gives us a couple of products (i.e., 1-Rbutane, 2-Rbutane).
  - Yields are poor with phosphines as L ligands.
  - Yields are much better with dppf.
- Dppf is ferrocene with a  $\text{PPh}_2$  off of each Cp group. It's a chelating ligand (through the phosphines) with a very wide bite angle.
- Dppf is better because...
  - With phosphines, during the reductive elimination step of the basic cycle (Figure 3.6a), we have interference from  $\beta$ -H elimination (and sometimes ensuing migratory insertion of the eliminated hydride).
  - $\beta$ -H elimination occurs with phosphine ligands because C.N. = 3, so there are open axial coordination sites to which the hydride can migrate.
  - However, with the bidentate dppf ligand, we essentially have a square-planar palladium species, which is very stable and will not easily form a 5-coordinate intermediate.
- Note that because dppf yields a 4-coordinate species, reductive elimination will be a bit slower, but we'll happily sacrifice speed for the much greater yield.
  - However, the large bite angle of dppf forces the aryl and R groups attached to the metal closer together, which promotes reductive elimination.
  - Thus, the decrease in speed is not that significant.
- Alternative schemes for cross coupling: Heteroatoms.
  - With nitrogen, we can do this with  $\text{HNR}_2$ ,  $\text{H}_2\text{NR}$ ,  $\text{NH}_3$ , imines, hydrosomes, etc.
  - Heterocycles, azoles, carbonates, sulfoximines, amides, etc.
  - Note that as  $\text{N}^-$  becomes less donating, reductive elimination slows down.
    - There's not really a transmetallation step here.
    - The issue is that these nucleophiles are not as basic as carbon-based ones.
  - We still need to worry about  $\beta$ -H elimination.
- Alternate mechanisms: Radicals.
  - Happens more with first-row transition metals (they're better at 1-electron redox chemistry).
  - Ullmann coupling (often with copper, but sometimes with nickel, too):  $2 \text{Ph-X} \xrightarrow[\text{> } 200^\circ\text{C}]{\text{Cu}} \text{Ph}_2 \text{Cu}$  salts, diamines, diols.
    - The temperature can be lowered with an appropriate ligand.
  - More flexibility in terms of the coupling partner.
    - We can do C-O, C-S, and C-N coupling in addition to C-C coupling.
  - Possible mechanisms (note that  $\text{Y} = \text{Ar}, \text{R}$ ):
    - $\text{Ar-X} + \text{Cu}^{\text{I}}\text{Y} \longrightarrow \text{YCu}^{\text{III}}\text{XAr} \xrightarrow{\text{red. elim.}} \text{Ar-Y} + \text{CuX}.$
    - $\text{Ar-X} + \text{Cu}^{\text{I}}\text{Y} \longrightarrow \text{Cu}^{\text{II}}\text{Y}(\text{XAr}\cdot) \longrightarrow \text{Cu}^{\text{II}}\text{XY} + \text{Ar}\cdot \longrightarrow \text{Ar-Y} + \text{CuX}$  (most likely).
    - $\text{Ar-X} + \text{Cu}^{\text{I}}\text{Y} \longrightarrow \text{Cu}^{\text{II}}\text{Y}(\text{XAr}\cdot) \longrightarrow \text{Cu}^{\text{II}}\text{ArY}^- + \text{X}\cdot \longrightarrow \text{Ar-Y} + \text{CuX}.$
  - Ullmann couplings can be photoactivated (suggests a radical mechanism).
  - $\text{Cu}^{\text{III}}$  is uncommon (suggests a radical mechanism).
  - Radical mechanisms can enable  $sp^3$ - $sp^3$  couplings, even bulky ones (outer sphere radical attacks aren't as affected by steric bulk).

### 3.5 Lecture 14: Olefin Metathesis

4/30:

- Applies to both alkenes and alkynes.
  - Metal carbene, alkylidene, and alkylidyne complexes are also important for their catalytic applications to olefin metathesis.
- Nobel prize (2005) to Richard Schrock, Bob Grubbs, and Yves Chauvin.
- General form:

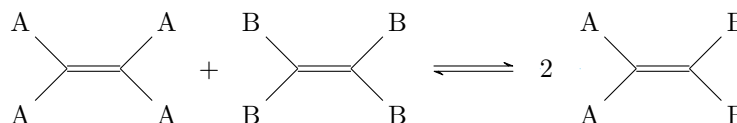


Figure 3.8: The general form of olefin metathesis.

- The olefins are not always tetrasubstituted, but we draw it as in Figure 3.8 to illustrate the point.
- Alkyne metathesis is symmetric; just with disubstituted alkynes.
- Equilibrium reaction (we need a thermodynamic driving force to favor specific products).
  - Can be limiting, but there are simple workarounds in the reaction types we are going to discuss.
- Not as widely used as cross coupling, but still important.
- Six basic classes of reactions:
  1. Distribution.

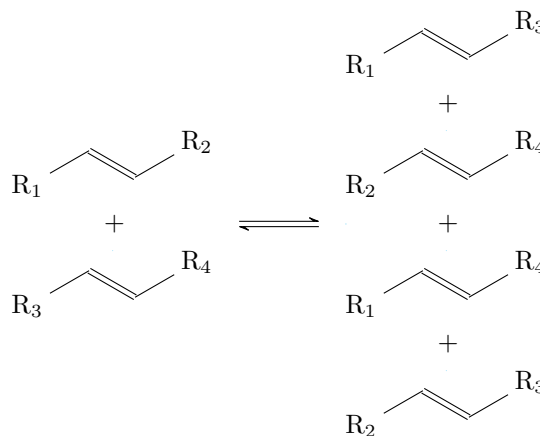


Figure 3.9: Olefin metathesis classes: Distribution.

- Two reactants form all possible permutations of the carbene fragments.
- Not often useful, but...
- Useful applications:
  - 2 propylenes make 2-butene and ethene, the latter of which is volatile and can be distilled off. Thus, distribution allows us to selectively make 2-butene from propylene, a widely available, mass-produced compound.
  - Shell higher olefin process (SHOP): Used to selectively make higher-mass olefins and distill off lighter ones.

## 2. Ring Opening Metathesis Polymerization (ROMP).

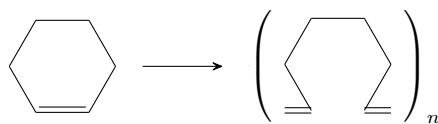


Figure 3.10: Olefin metathesis classes: ROMP.

- A ring with one double bond opens and polymerizes at the double bond.
- Note that this reaction can proceed with rings containing any number of carbons.
- Driving force: Release of ring strain.

## 3. Addition Metathesis Polymerization (ADMET).

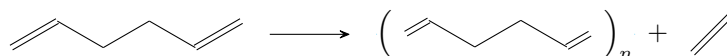


Figure 3.11: Olefin metathesis classes: ADMET.

- A diolefin (under metathesis conditions) breaks off ethylene at both ends and polymerizes.
- Not as broadly useful as ROMP due to competitive ring-closing metathesis.

## 4. Ring-closing metathesis.

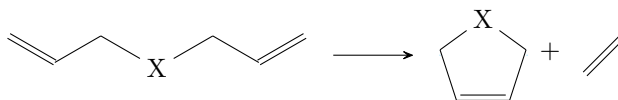


Figure 3.12: Olefin metathesis classes: Ring-closing metathesis.

- A diolefin (under metathesis conditions) makes a cyclic heterocycle and ethylene.
- Driving force: Release of a gas (ethene).
- Has utility in natural product synthesis (as a last step to close macrocyclic rings).

## 5. Cross metathesis.

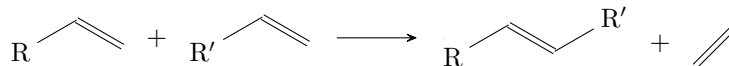


Figure 3.13: Olefin metathesis classes: Cross metathesis.

- Two terminal olefins break off their end carbons (which combine to form ethene) and then combine, themselves, as carbene fragments to form an internal olefin.
- An equilibrium process; must compete with homometathesis (forming R–R and R'–R').
- Driving force: Release of a gas (ethene).

## 6. Enyne metathesis.

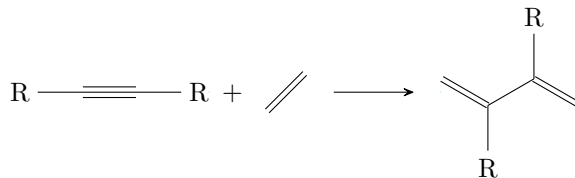


Figure 3.14: Olefin metathesis classes: Enyne metathesis.

- An alkyne and ethylene makes a diene.



- Alkyne metathesis polymerization.

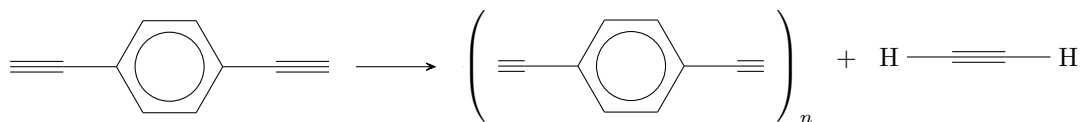


Figure 3.15: Alkyne metathesis polymerization.

- A dialkyne makes a polymer and acetylene.
- Very similar to ADMET.
- Ring-closing alkyne metathesis exists as well.
- Catalysts:

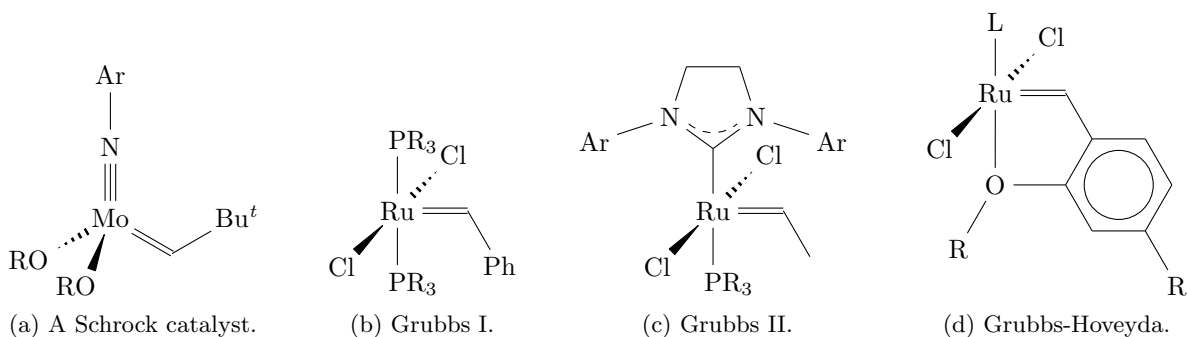


Figure 3.16: Olefin metathesis catalysts.

- Schrock catalysts (general form of Figure 3.16a).
    - Many of these exist.
      - The metal center, as well as the amido and alkoxide ligands can be varied.
      - Note that any X-type ligand can be substituted for the alkoxides.
    - Molybdenum or tungsten based (molybdenum is more active).
    - Since molybdenum is an early transition metal, the catalyst is very electropositive. Thus, it's an alkylidene with strong nucleophilic character at the carbon.
    - Extremely reactive. This is...
      - Good for hard reactions.
      - Bad because they're air sensitive and don't have a lot of functional group tolerance.
  - Grubbs catalysts (Figures 3.16b, 3.16c, and 3.16d).
    - Ruthenium based.
    - Less active, but more tolerant of air and water.
    - Note that the top ligand on Grubbs II (Figure 3.16c) is called an NHC ligand, and that it is the same ligand that is typically present where "L" is written on Grubbs-Hoveyda (Figure 3.16d).
    - Note also that the big bidentate ligand on the the Grubbs-Hoveyda catalyst (Figure 3.16d) is a tethered alkylidene.
    - There has probably been a lot more utility in these since they're initially less reactive.
- General rule in inorganic chemistry: You can often make things more reactive (e.g., by heating them up), but rarely less (cooling things down can make the chemistry less reliable).

- Two mechanisms that were proposed early-on (related to Figure 3.18b):
  1. Metal-diolefin adduct to  $\eta^4$ -cyclobutadiene adduct, then refragmentation.
  2. Metal-diolefin adduct reductively couples into a 5-membered metallacycle, then to a metallacyclobutane alkylidene, then rearrangement and separation.
- Actual mechanism:

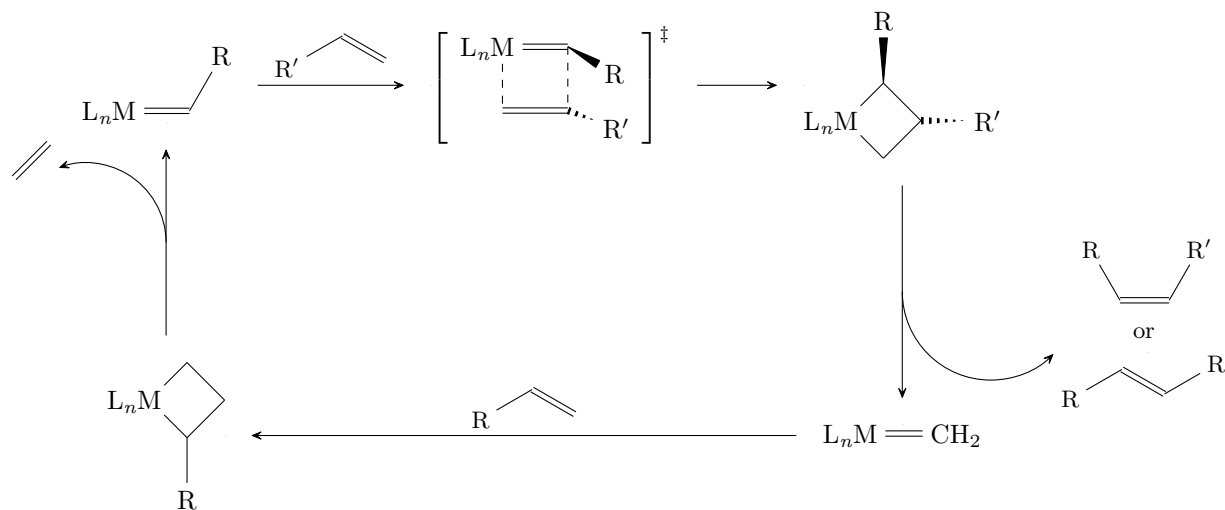


Figure 3.17: Olefin metathesis mechanism.

- Chauvin proposes this; Schrock and Grubbs prove it.
- Every step is an equilibrium reaction, but Figure 3.17 has monodirectional arrows for simplicity.
- On the transition state of the first step.
  - A 2 + 2 cycloaddition.
  - Forbidden in organic chemistry, but allowed in inorganic because of the symmetry of the  $d$  orbitals.
- The first intermediate is a metallacyclobutane, which is a very important intermediate.
- The second intermediate is a terminal methyldene, which is highly reactive.
- Note that the mechanism drawn in Figure 3.17 is technically that of cross metathesis.
- There is frequently an activation step involving the loss of a ligand to free up a coordination site.
- There is also a degenerate pathway.
  - This starts with the formation of a *trans* metallacyclobutane in step 1. Thus, this pathway is actually favored sterically.
  - This metallacyclobutane can then collapse back down to an olefin and a metal alkylidene, possibly with  $R'$  on the metal alkylidene instead of  $R$ .
  - This does indeed happen quite often, but it's clearly pretty harmless (also because this pathway is an equilibrium one, too).
  - If we have a means of siphoning off ethylene, we can favor the primary pathway.
- Mechanistic probes (things that indicated the actual mechanism over the other proposed ones):
  - Take a diphenyl compound with two styrenyl ligands (one with hydrogens; one with deuteriums).
  - The products are a cyclized olefin and distribution products.
  - A statistical mixture of  $CR_2$  fragments is observed; this is only possible with the mechanism in Figure 3.17.

- Decomposition:
  - Where the catalysis can go wrong (and how to shut down these alternate pathways).
  - Primarily caused by the electrophilic methylenes.
  - What happens is a nucleophilic attack by a phosphine on the electrophilic alkylidenes.
- Notes on stereochemistry.
  - Monoalkoxide pyridine (MAP) catalysts (recently reported by Schrock).
    - Chiral at Mo.
    - Can resolve enantiomers.
    - 100 times more active than bis-alkoxides (owing to the pyridine ligand, which can coordinate face-on with a Cp and do some other odd things).
  - *trans* metallacyclobutanes (which lead to *trans* products) are preferred, but *cis* metallacyclobutanes can be favored with sterics.
    - For example, with respect to a Schrock catalyst (Figure 3.16a), making the alkoxides large and the nitrido small can force both R groups above the plane of the metallacyclobutane.
- Alkyne metathesis.
  - Again, largely developed by Schrock.
- $\text{RC}\equiv\text{Mo}(\text{OR})_3$  is the active catalyst.
  - The method of generating this catalyst is shown.
- Mechanisms:

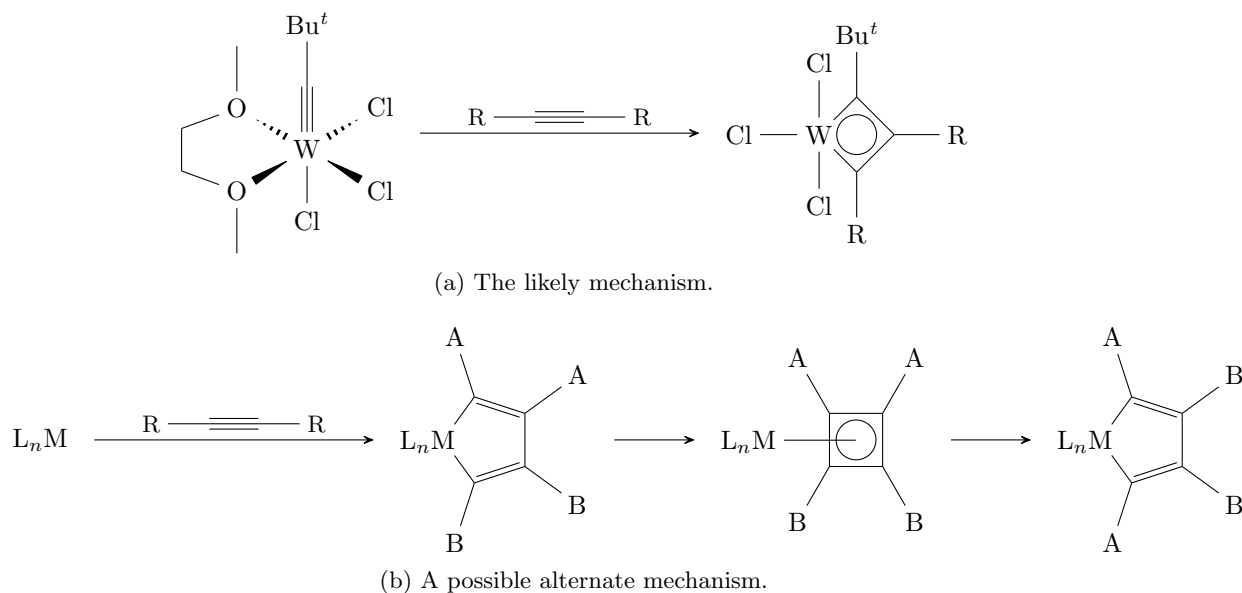
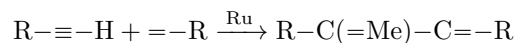


Figure 3.18: Alkyne metathesis mechanisms.

- By Schrock.
- In Figure 3.18a, a tungsten alkylidyne reacts with an alkyne to generate an isolable metallacyclobutadiene in a pathway quite similar to Figure 3.17.
- However, the pathway in Figure 3.18b has also been observed, although not yet in a mechanistically, kinetically competent manner.

- Note that alkyne metathesis polymerization is a really interesting area being worked on by Adam Veige.
- Enyne metathesis.
- General form (related to Figure 3.14):



– This chemistry is once again dominated by ruthenium.

- Mechanism.

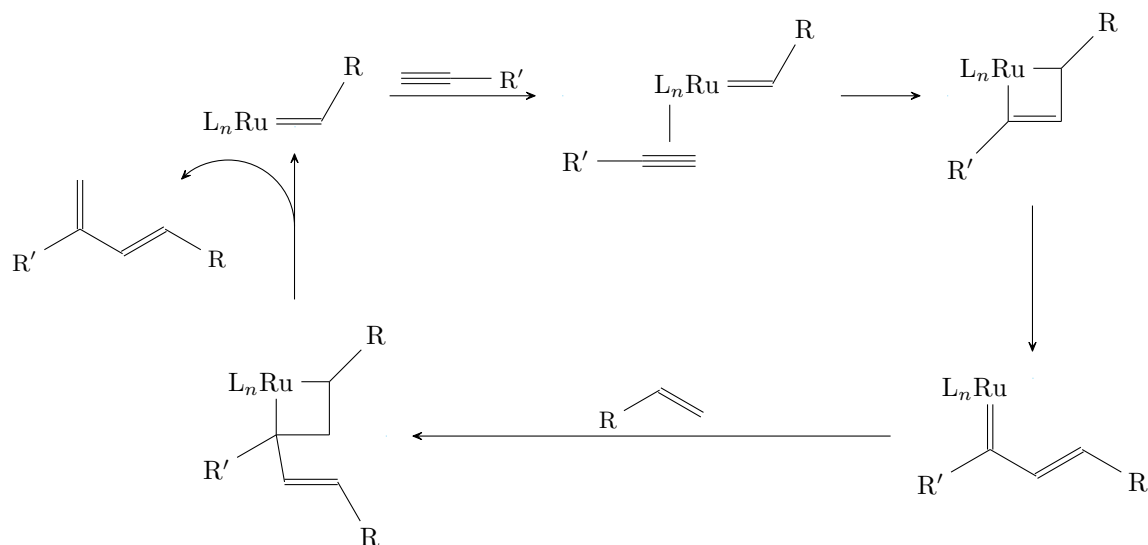


Figure 3.19: Enyne metathesis mechanism.

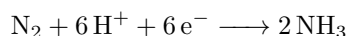
- The second step is a 2 + 2 cycloaddition, and yields a metallacyclobutene.
  - For the reaction to proceed, we must have a 1,3-regioisomer, as shown.
- The third step sees the double bond electrons push up and to the right, and the electrons from the top bond in the ring push down and to the left.
- The final step occurs partially because of the instability of the tertiary carbon.
- The product is often *trans* (as shown), but can be *cis*.

## Unit 4

# More Catalytic Processes

### 4.1 Lecture 15: Nitrogen Fixation

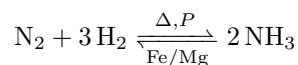
- 5/3: • General form:



- Alternatively, it could be  $\text{N}_2 + 3 \text{H}_2 \longrightarrow 2 \text{NH}_3$ .
- A simple reaction on paper, but in practice and mechanistically, very difficult.
- Nitrogen is one of the essential elements for life (CHNOPS), but we can't absorb it from the air in its elemental form as  $\text{N}\equiv\text{N}$  gas. Indeed, we need it to be **fixed** before we can incorporate it (i.e., through food sources).
- Main pathways:
  - Lightning.



- 4-10 million tons per year.
- Nitrate can be used by organisms; converted into useful nitrogen.
- Natural enzymatic fixation.
  - 100-300 million tons per year (probably closer to the 100 side).
  - 40/60 ocean/land ratio.
  - Done by the enzyme nitrogenase, with  $\text{FeMoCO}^{[1]}$  as a cofactor.
- Mankind.
  - About 190 million tons per year.
  - Thus, mankind is currently fixing more nitrogen than all natural sources combined by a fair amount right now. This is what allows us to feed the planet at its current population.
  - Accomplished by the **Haber-Bosch process**.
- **Haber-Bosch process**: Humanity's primary method of fixing nitrogen.

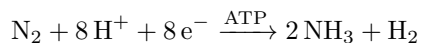


- $-92 \text{ kcal/mol}$  (thermodynamically favored but kinetically difficult).
- 200 atm of pressure (pushes the equilibrium to the right via Le Châtelier's principle).

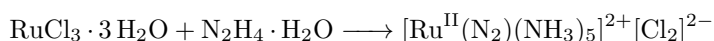
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<sup>1</sup>Literally pronounced as its written, i.e., “fih-MOH-koh.”

- 400 °C (required for the rate).
- Potassium is an activator.
- 2 Nobel prizes for this: Fritz Haber (1918) and Carl Bosch (1931).
  - Controversial at the time because the process facilitated the explosives industry and Haber was a Nazi.
  - World War I and II would not have been sustainable for Germany without this process.
- Mechanism:
  - On the surface of the iron catalyst, the pressure binds H<sub>2</sub> gas as hydrides and N<sub>2</sub> gas as bridging nitrides (between various iron atoms at the surface). It follows in a statistical and thermodynamic manner that amine ligands will be formed on the surface attached to the iron. These can then break off into ammonia gas.
  - A solid state heterogeneous process.
  - Nobel Prize (2007) to Gerhard Ertl for this mechanism.
- This process is highly efficient, but very energy intensive as well.
  - As such, there is a race to find a less energy-intensive catalytic alternative.
- Molecular systems: The nitrogenase enzyme.

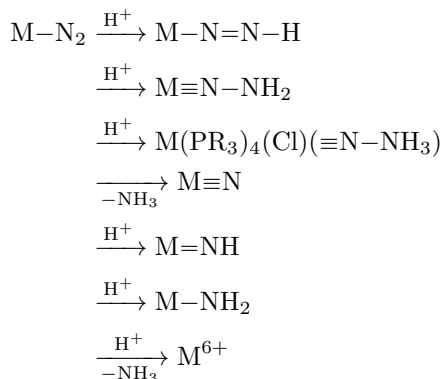


- Other extant cofactors include FeVCO and FeFeCO, but they are less common.
- Since ATP is used, this is still a very energy-intensive process.
- N<sub>2</sub> bonds to metal centers in many ways:
  - Linear, bent, side-on, bridging linear, bridging side-on, multi-metal center bridging, etc.
- N<sub>2</sub> complexes are much less common than CO complexes since N<sub>2</sub> is a terrible ligand.
  - The HOMO in N<sub>2</sub> makes it a  $\sigma$  donor, but CO's negative formal charge on the carbon makes it a better  $\sigma$  donor.
  - Additionally, CO is a much better  $\pi$  acid due to its polarization.
- Allen and Senoff (in 1965) reported the first dinitrogen complex.



- N<sub>2</sub>H<sub>4</sub> is hydrazine (rocket fuel), and is much more stable as a hydrate.
- The product is  $d^6$  with 18 e<sup>−</sup> and has  $\mu_{\text{N}_2} = 2170\text{--}2115 \text{ cm}^{-1}$  (the range depends on the anion).
- For reference, free N<sub>2</sub> has a stretching frequency of  $2331 \text{ cm}^{-1}$ .
- Yamamoto gives the first example of a dinitrogen complex formed from free N<sub>2</sub> (HCo(PPh<sub>3</sub>)<sub>3</sub>(N<sub>2</sub>)).
- Joe Chatt, George Leigh, and Dilworth in Sussex (of the British/American camp), and Hidai and Nishibayashi (of the Japanese camp) became interested in nitrogen fixation following Yamamoto's work.
  - Second and third row Group 6 complexes such as molybdenum were the focus.
  - Example:  $\text{MoX}_4\text{L}_2 \xrightarrow[\text{Na/Hg}]{\text{N}_2, \text{L}} \text{Mo}(\text{N}_2)_2\text{L}_4$ .
    - L is typically a phosphine.
    - With various phosphine ligands, you can get different geometries.

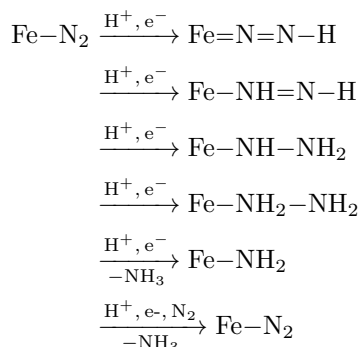
- Another example:  $\text{cis-W(N}_2)_2(\text{PMe}_2\text{Ph})_4 \xrightarrow[\text{MeOH}]{\text{H}_2\text{SO}_4} 2\text{NH}_3 + \text{N}_2 + \text{W}^{\text{VI}}(\text{oxo})$ .
  - Works with molybdenum, too, but tungsten gives a better yield.
  - The overall reaction is  $\text{W}^0 + 6\text{H}^+ + \text{N}_2 \longrightarrow 2\text{NH}_3 + \text{W}^{\text{VI}}$ .
  - Some important subreactions/steps are  $\text{N}_2 + 4\text{e}^- \longrightarrow \text{N}_2\text{H}_4$  and  $\text{N}_2 + 2\text{e}^- \longrightarrow \text{N}_2\text{H}_2$ .
- Mechanism (by Chatt):



- Very few compounds in the form of the first intermediate (diazene) are known. These compounds are very susceptible to  $\beta$ -H elimination from water, though.
- The second intermediate has a hydrazido ligand.
- The fourth intermediate has a nitride.
- The fifth intermediate has an imide.
- The sixth intermediate has an amide ligand.
- Hidai uses silanes:  $\text{M(N}_2)_2(\text{PR}_3)_4 \xrightarrow{\text{TMSI}} \text{TMS-N=N-MI(PR}_3)_4 \xrightarrow[\text{N}_2]{\text{Na, THF}} \text{M(N}_2)_2(\text{PR}_3)_4 + \text{NH(TMS)}_2 + \text{NH}_3 + \text{NaNH}_2 + \text{NaNH(TMS)}$ , etc.
- Yandulov and Schrock (2003) creates a well-defined catalyst for nitrogen fixation.
  - The catalyst is molybdenum bound to dinitrogen and a tridentate TREN scaffold anion (with hexa-iso-propyl-terphenyl (HIPT) aryl groups).
  - They add eight equivalents of cobaltocene ( $\text{CoCp}_2$ ), seven equivalents of lutidinium (a pyridinium acid), and the bulky, noncoordinating counteranion  $[\text{BAr}^{\text{F}}_4]^-$ .
  - They fish out  $\text{Mo-NH}_3 + \text{NH}_3$ . Reducing the former product gives  $\text{Mo}^{\text{III}}(\text{N}_2)$  with a weak reductant.
    - If you use a slightly stronger reductant (decamethylchromocene;  $\text{CrCp}_2^*$ ) and a slow addition of acid, you get approximately 8 turnovers.
  - This is not a great yield, but the important part is that it exists and they can observe all of the intermediates.
    - Observing said intermediates verified the mechanism proposed by Chatt and Hidai.
  - To reiterate, this is the Chatt/Distal<sup>[2]</sup> cycle they observed:  $\text{Mo-N}\equiv\text{N} \xrightarrow{\text{H}^+, \text{e}^-} \text{M-N=N-H} \xrightarrow{\text{H}^+, \text{e}^-} \text{M}\equiv\text{N-NH}_2 \xrightarrow{\text{H}^+, \text{e}^-} \text{M}\equiv\text{N} \xrightarrow{\text{H}^+, \text{e}^-} \text{M}\equiv\text{NH} \xrightarrow{\text{H}^+, \text{e}^-} \text{M-NH}_2 \xrightarrow[-\text{NH}_3]{\text{H}^+, \text{e}^-, \text{N}_2} \text{Mo-N}\equiv\text{N}$ .
  - Note that molybdenum starts in the 3+ oxidation state at  $\text{M-N}\equiv\text{N}$  and goes up to 6+ at  $\text{Mo}\equiv\text{N}$  before cycling back down.
- Shilov had a number of systems, but they were poorly defined.

<sup>2</sup>Note that Chatt and Distal are interchangeable synonyms.

- Other selected examples.
  - Zirconium can do this catalysis in some cases.
  - Laplaza and Cummins (1995) find that molybdenum trisannelides and dinitrogen can go through a kinked transition state to yield two equivalents of  $L_3Mo\equiv N$ .
- Iron:
  - Present in all enzymatic cofactors that mediate nitrogen fixation.
    - Until 10-15 years ago, they thought it wasn't directly involved though.
  - $(PR_3)_4Fe(N_2) \xrightarrow{XS H^+}$  only trace amounts of  $NH_3$ .
  - Yuki et al. (2012) finds that simple iron salts and even substituted ferrocenes react with a strong reductant, sodium, and TMSCl to make  $N(TMS)_3$  (which is catalytic and can be transformed into ammonia). The yield is about 25 equivalents per iron.
    - This shows that iron can do this chemistry.
  - Dr. Anderson's thesis work with Jonas Peters finds that  $Fe(N_2)(B(PR_2Ph)_3) \xrightarrow[XS HBAr^F_4]{XS KC_8} NH_3^{[3]}$  (Anderson et al., 2013).
    - Seven equivalents per iron. More recent tinkering has brought it up to nearly 100 equivalents per iron.
    - Mechanism:  $L_3FeN_2^- \xrightarrow{2H^+} L_3Fe\equiv N-NH_2^+ \longrightarrow \longrightarrow \longrightarrow NH_3$ .
    - Suggests a Chatt/Distal mechanism.
  - Differing mechanistic proposal: Alternating mechanism.



- This doesn't require as many oxidation states as the Chatt mechanism (which favors iron, which doesn't easily form oxidation states other than 2+ and 3+).
- We also don't see a nitride or imide intermediate, but we do see a diazene, hydrazido 1-, and hydrazine adducts.
- Enzyme data supports this mechanism.

## 4.2 Office Hours (Anderson)

- How much strain is needed for ROMP to proceed?
  - Norbornene is a common one.
  - 4 membered rings.
  - 7- and 8-membered rings are usually not sufficiently strained.

---

<sup>3</sup>Note that the reactant is the same compound discussed in problem 3 of Homework 1.



- Cyclopropene does exist, and it does do ROMP, but it polymerizes so quickly that you can't do much with it.
  - If it's cold and you throw in a metathesis catalyst, it will probably work.
  - Recall that it also participates in Diels-Alder reactions.
- ROMP does *not* release ethylene.
  - Ring strain is the driving force.
  - Part (d) is a typo; ethylene gas is the common byproduct of *most* of these reactions. We should still show ROMP as is.
- How do metal  $d$  orbitals enable  $2 + 2$  cycloaddition?
  - Butadiene plus ethylene requires ethylene to have filled  $\pi^*$  orbitals (these have the appropriate symmetry).
    - Diels-Alder  $4 + 2$  cycloaddition is allowed.
  - The symmetry of the metal orbitals (esp.  $d_{z^2}$  and  $d_{xy}$ ) enables  $2 + 2$  cycloaddition.
- $\eta$  and  $\kappa$  bonding?
  - IUPAC likes  $\kappa$  more now, but  $\eta$  is historical.
  - $\eta$  indicates a contiguous  $\pi$  system while  $\kappa$  simply indicates denticity.
  - Figure 2.23a is  $\kappa^2$  as well.
  - Bidentate ligands bond in a  $\kappa^2$  fashion.
  - Numbers on these as well as  $\mu$  should exclusively be superscripts.
  - A metal bound face-on to a carboxylate would be  $\eta^3$ , but this is very atypical/nontextistent bonding. Side-on bonding (i.e., to both oxygens) would be  $\kappa^2$ .

### 4.3 Discussion Section

5/4:

- Midterm 2 is 5/25/2021.
- Final paper due 5/26/2021; Sophie has asked Dr. Anderson for more information.
  - Due at noon.
  - Sophie will post an example paper.
  - As the last assignment for this course, you will write a critical review of 1 of 6 available papers.
  - Some of these papers include material outside the scope of organometallic chemistry. Try to focus on topics relevant to this course. The reviews should be no longer than 700 words not including citations or figure captions, although additional citations are not required if you only use information presented in the paper or the class. The critique should be written with Times New Roman 12 point font and 0.5 inch margins.
  - General outline for the critiques:
    - Paragraph 1: Introduction.
    - Paragraph 2: Experimental summary.
    - Paragraph 3: Discussion.
    - Paragraph 4: critique.
    - Figures.
  - Sophie is willing to look over assignments (email them to her), but we have to get them to her by the 19th for her to take a look.
  - They should be professional but not excessively formal.

- A more detailed outline will be published later.
- A critique isn't necessarily a flaw, but more a suggestion of another experiment they could run or some other conclusion they could have drawn.
- Final is 6/3/2021.
- Midterm 1:
  - Biggest issues:
    - Running out of time.
    - Omitting parts of answers (generally not reading instructions in general). If it says draw orbitals, explain, or predict, you need to do that.
  - She'll talk to John about making it/the next one shorter.
  - Syntheses are only one point?
  - If we would like to know more feedback about our exams, we can reach out with specific questions about questions.
  - 1a: Reduce with Na or Hg metal and then throw in MeI.  $\frac{1}{2} \text{Mn}_2(\text{CO})_{10} \xrightarrow[-2 \text{NaCl}]{\text{Na/Hg}} \text{Na}[\text{Mn}(\text{CO})_5] \xrightarrow[-\text{NaI}]{\text{MeI}} \cdot$
  - 3a: Like-signed lobes donate (*correct notes?*). You can also show either  $d_{x^2-y^2}$  or  $d_{z^2}$  for  $\sigma$  donation.
  - 3b: We need charges on the metal in  $\text{M}-\text{C}\equiv\text{O}^+$  resonance structures (-, 0, +).
  - 3c: Also identify the dominant resonance structure.
  - 4c: Cp can ring-slip to stabilize the electron count.
  - 4d: Cone angle starts at metal center and includes specifically the full van der Waals radii of the phosphine R groups at the base of the cone. Most commonly forgotten: metal center, van der Waals radii.
  - 4f:  $\text{H}_2\text{CrO}_4$  is  $\text{Cr}^{6+}$ ,  $d^0$ , while  $\text{Cr}(\text{CO})_4^{4-}$  is  $\text{Cr}^{4-}$ ,  $d^{10}$ . The difference is different than you expect because they are actually very similar.
  - 5: First, backcalculate out spin-state to determine  $S = 1$  and  $S = 0$ . Second, luckily, they're 4-coordinate, so the simplest solution is to look for two geometries that give the two spin states. You interconvert the things in solution, giving a mixed magnetic moment.  $\mu = 2\sqrt{S(S+1)}$ .
  - 6:  $\text{Cp}^-$  is a  $\pi$  donor. Cyclobutadiene is both (the orbital drawing shows that you have a HOMO  $\pi$  donor and a LUMO  $\pi$  acceptor).
  - 7: No extra sites for a better bridge and only bad bridges present (if you draw them you can tell). Whenever you need to compare two ligands, think:
    1. Chelate? Neither ligand.
    2. Hard/soft affinity? Both hard.
    3. Strong field? Isocyanide much stronger, more likely all low spin.
    4. Trans effect? All the same ligand.

## 4.4 Lecture 16: Hydrogenation

- 5/5:
- Nobel prize (2001) to Knowles and Noyori, but could have gone to Jack Halpern.
    - A hugely important reaction.
  - General form:
 
$$\text{Y}=\text{X} + \text{H}_2 \xrightarrow{\text{cat}} \text{H}-\text{Y}-\text{X}-\text{H}$$
  - Both reagents are activated by the catalyst.

- The chemo, regio, and stereo selectivity has been determined for many of the mechanisms.
- History:
  - Melvin Calvin reports the first hydrogenation reaction in 1938.
    - Iguchi also studied rhodium-amine complexes around the same time.
  - Wilkinson discovers Wilkinson's catalyst ( $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ ) in the 1960s and does other foundational research in this area.
    - Halpern figures out the mechanism by which Wilkinson's catalyst works.
  - Knowles and Noyori: Developed asymmetric hydrogenations.
- Wilkinson's catalyst:
  - Two methods of synthesizing it are given.
- Mechanism (for generic catalyzed hydrogenation):

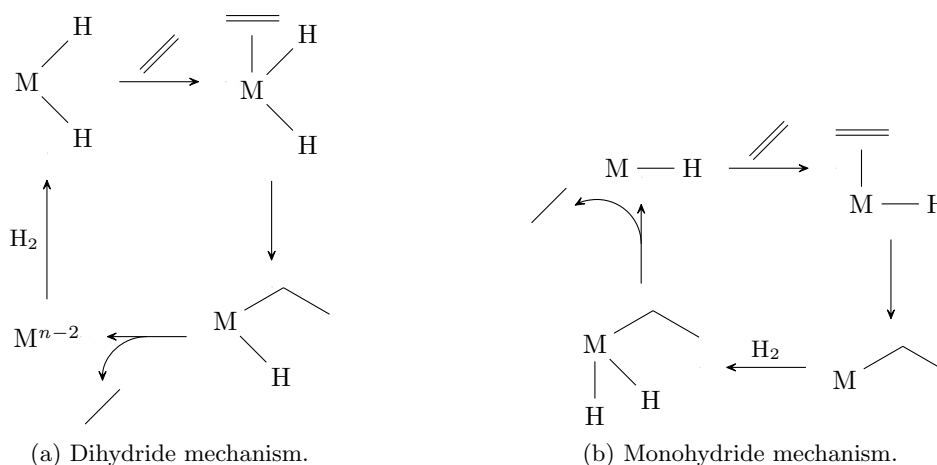
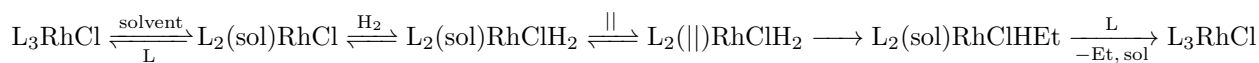


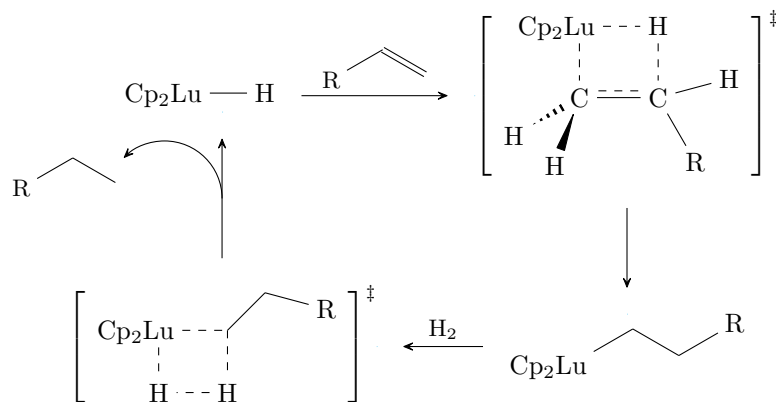
Figure 4.1: Hydrogenation mechanisms.

- Reactivity trends (for Wilkinson's catalyst):
  - Rates of hydrogenation for olefins: Cyclic > terminal > doubly substituted > *cis* > *trans* > triply substituted.
  - This trend can be utilized for **chemo selectivity**.
  - No reactivity with esters or arenes.
- **Chemo selectivity:** The selective hydrogenation of olefins that more readily hydrogenate in a poly-olefin compound.
  - In other words, chemo selectivity relies on the principle that in a compound with multiple types of double bonds, the ones with higher rates will be selectively hydrogenated first.
- Mechanism (for hydrogenation catalyzed by Wilkinson's catalyst):



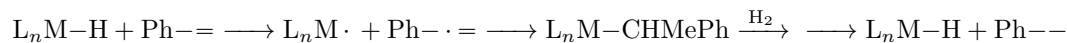
- Worked out by Jack Halpern
- No scrambling of  $\text{H}_2/\text{D}_2$  (you only observe products with two H's added, and products with two D's added; there are no products with an H *and* a D added).

- No scrambling with solvent.
- The above two observations suggest a dihydride mechanism.
- Note that the solvent is either an alcohol or acetonitrile (MeCN).
- Note that the step with no new reactants is the turnover limiting step (it is drawn with a monodirectional arrow because it is virtually irreversible).
- Catalyst optimization:
  - Cationic Rh complexes react much faster (e.g.,  $[\text{RhL}_2\text{H}_2(\text{sol})_2]^+$ ).
    - In effect, removing the chloride generates a noncoordinating counteranion, which is much more reactive.
  - If you use iridium instead, it's Crabtree's catalyst:  $[\text{Ir}(\text{COD})(\text{PCCl}_3)(\text{py})]^+[\text{PF}_6]^-$ .
- Compares rates of derivatives of Crabtree's and Wilkinson's catalyst at various temperatures in non-coordinating solvents.
  - We use noncoordinating solvents such as arenes because solvent-binding is a step in some mechanisms, and thus affects the rate.
  - Some variations have significantly less reactivity for cyclic olefins than Wilkinson's catalyst.
  - Conclusion: By making slight changes to the ligands and metal center, you can finely tune the activity of these catalysts to do the type of hydrogenation you want (regioselectivity).
- Directed hydrogenation.
  - We can use solvent binding to dictate the selectivity of a certain hydrogenation.
  - If we have a cyclic substrate with a coordinating ligand above one face, the catalyst can coordinate to that ligand and perform the hydrogenation from that face, heavily favoring a certain stereochemistry in the product.
  - Note that other ligands can affect the extent of substrate coordination.
- Other mechanistic details<sup>[4]</sup>.
  1. The species you observe (the resting state of the catalyst) may not be on the active catalytic pathway.
  2. To deduce the mechanism, the rates of the individual steps should be determined (recall kinetic competence).
- Noyori's bifunctional catalysis (heavily related to Figure 4.3).
- $\sigma$ -bond metathesis:

Figure 4.2: Hydrogenation by  $\sigma$ -bond metathesis.

<sup>4</sup>An important process is listed, possibly to be returned to later.

- This mechanism proceeds through two consecutive  $\sigma$ -bond metatheses.
- Note the use of an early transition metal (lutetium), 4-membered transition states, and the open coordination site (refer to Lecture 7 for the more on the characteristics of  $\sigma$ -bond metathesis).
- When catalyzed, the mechanism can be more complicated.
  - There can be nearly innumerable many offshoots.
  - There may only be one on-cycle chain among all of the intermediates. The question is just how to favor this one.
- Radical hydrogenation.



- This can happen with porphyrins and  $HMn(CO)_5$ .
- Noyori's catalyst:

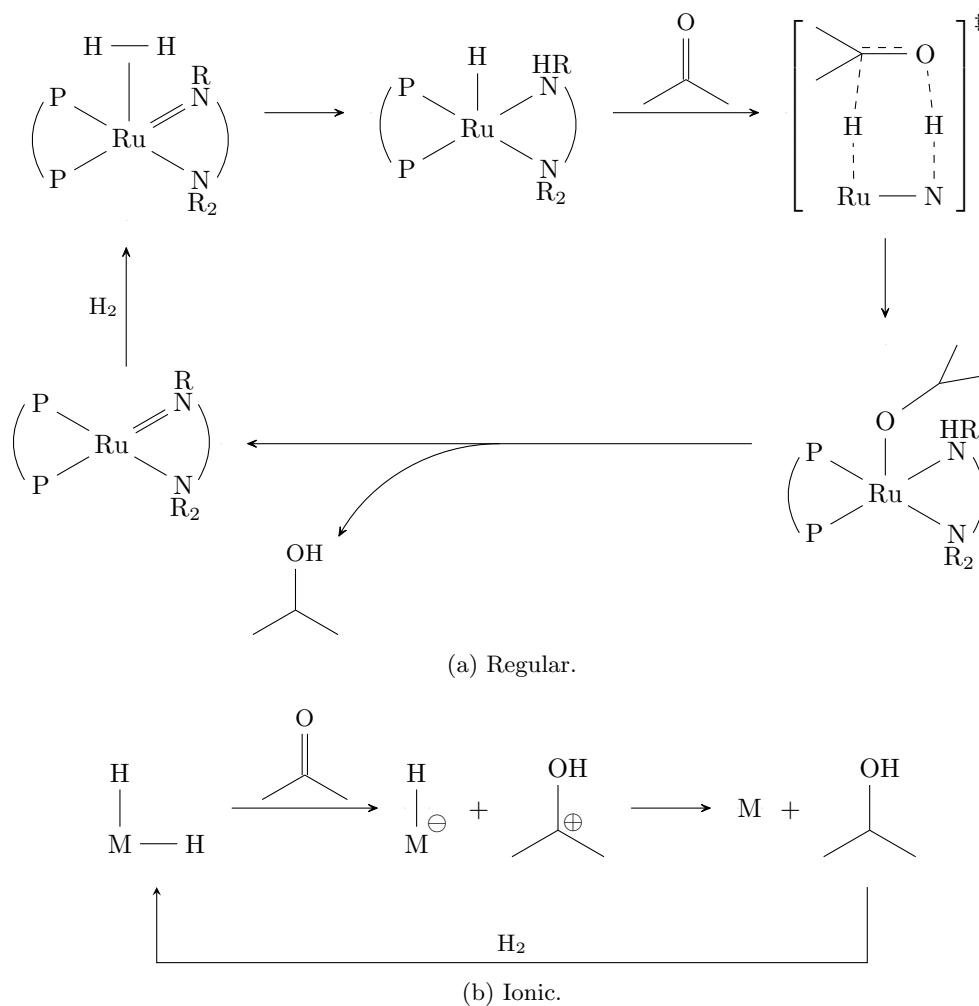


Figure 4.3: Noyori's catalyst mechanism.

- Partially reacts via a bifunctional mechanism, but primarily engages in a different mechanistic paradigm called an outer sphere hydrogenation (see Figure 4.3a).

- In the extreme, we can achieve an ionic pathway (see Figure 4.3b).
  - An example of a substance that does this is  $\text{CpW}(\text{CO})_2(\text{PPh}_3)(\text{OCEt}_2)^+$ .
- Asymmetric catalysis:
  - At this point in time, hydrogenation is a highly optimized reaction.
    - We can generate catalysts with millions of turnover numbers, very high ee's, etc.
    - Indeed, hydrogenation is one of the most reliable late-stage steps in drug development or natural product synthesis to define chiral centers.
  - Chiral phosphines really shine here.
  - Binap, biphenyl scaffolds with sufficiently large R groups, tri-chicken foot phos, ferrocene derivatives (e.g., chiral dppf derivatives), alkyl backbones (e.g., DIOP), etc.
  - One enantiomer is often bound over the other.
- Transfer hydrogenations:

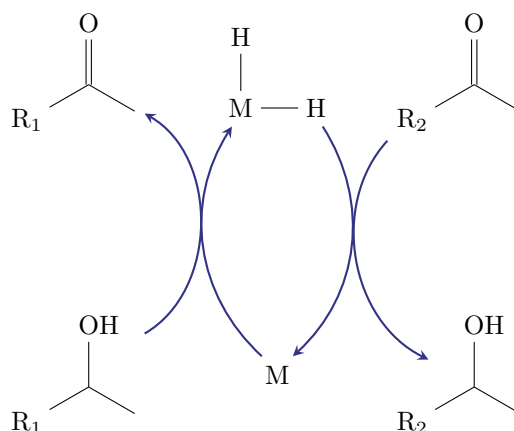


Figure 4.4: Transfer hydrogenation mechanism.

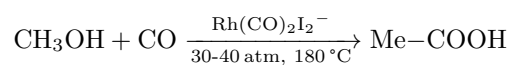
- Use these if you don't want to use hydrogen gas, e.g., because it's flammable.
- Basically, we use a transition metal catalyst to transfer two hydrogens (e.g., from an alcohol to a ketone) by means of gaining them to become a dihydride and losing them to return to being just a metal center.
- As in any hydrogenation reaction, these are all reversible reactions. As such, since we can't use excess hydrogen to push the reaction, we must rely on the electron richness of the alcohol (electron rich alcohols dehydrogenate more easily).
- The equilibrium can be pushed with Le Châtelier's principle, but we mainly have to consider thermodynamics here (the thermodynamics must be favorable).
  - For example, if  $\text{R}_2 = \text{Ar}$ , then we will transform the aryl ketone into an alcohol, but not in reverse (because the aryl is electron deficient and thus its alcohol does not dehydrogenate easily).
- Halpern's contributions to asymmetric catalysis:
  - Reviews some papers.
  - Increasing hydrogen pressure decreases stereoselectivity, which is often kinetically driven.

## 4.5 Lecture 17: Hydroformylation and Carbonylation

5/7:

- We will now talk about inserting carbonyls.
- Grandfather reaction: Monsanto Acetic Acid Synthesis.
  - Used for many years, but replaced within the last few years.
  - Huge scale: Produces approximately 17 billion pounds of acetic acid per year.
  - About 80% of all acetic acid we use is generated by this process.
  - Several iterations historically:
    - BASF (1965) uses cobalt and iodide.
    - Monsanto (1970) uses rhodium and iodide.
    - BP “Cativa” (1996) uses iridium and iodide.
- A big theme in catalysis right now is using first row metals instead of second- and third-row metals because they’re cheaper and more abundant.
  - However, it makes sense to use iridium here: 5 million dollars of iridium can run in a reactor for decades.

- General form:



- Mechanism:

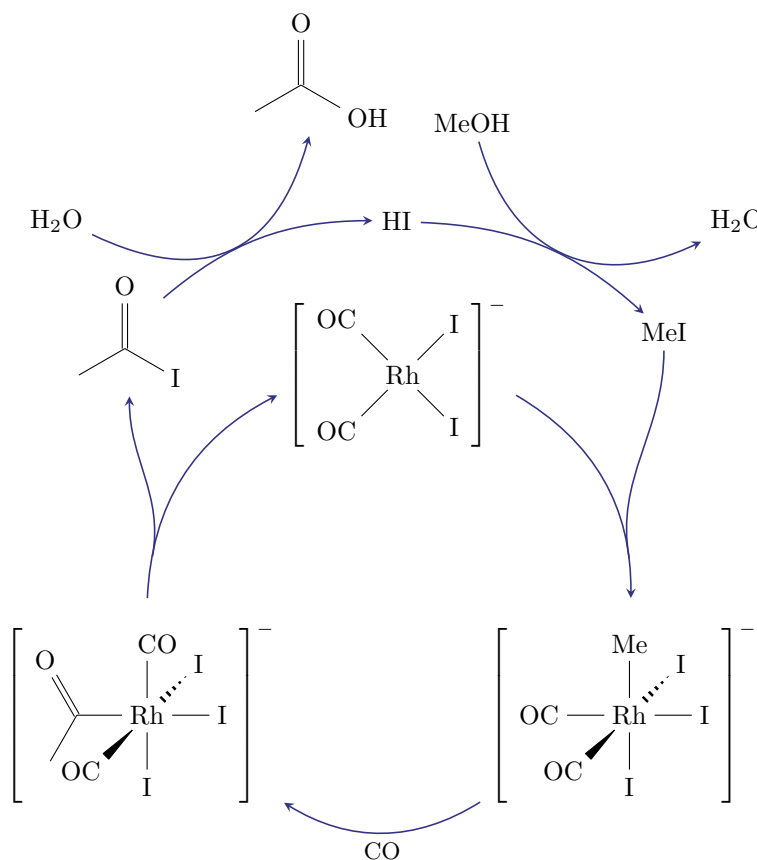


Figure 4.5: Carbonylation mechanism.

- There are cocatalytic reactions that enable this reactivity.
- Trace amounts of HI and H<sub>2</sub>O facilitate the overall reaction.
  - Inputs are MeOH and CO; output is acetic acid.
  - Everything else is catalytic, or generated in situ.
- Rate law:  $\text{Rate} = k[\text{Rh}][\text{MeI}]$ .
- Side reactions:
  - If the first intermediate is not immediately trapped by CO, it can insert to form a 5-coordinate intermediate that dimerizes in an inactive off-cycle.
  - This side reaction is not *necessarily* deleterious, but it can be.
- This complex has been heavily studied, giving us great insight into each step.
- Oxidative addition.
  - S<sub>N</sub>2-type reaction.
  - An attack of the initial catalyst by acetyl iodide can lead to the second intermediate, directly.
  - The 5-coordinate intermediate in the S<sub>N</sub>2 process can be attacked by methanol or acetic acid, giving you a methyl ester and acetic anhydride, respectively.
  - Undesirable side reactions:
    - The catalyst can react with HI, forming a RhI<sub>3</sub> precipitate and an RhI<sub>4</sub>(CO)<sub>2</sub><sup>−</sup> inactive ion; both steps serve to effectively remove rhodium from the catalytic cycle (this is a big problem). However, this can be fixed by adding H<sub>2</sub>O (about 10%). This increases the solubility of RhI<sub>3</sub> and turns on the water-gas shift reaction  $\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$ ; the H<sub>2</sub> product of the latter reaction serves as a reductant that transforms  $\text{Rh}^{\text{III}} \longrightarrow \text{Rh}^{\text{I}}$ .
    - Another undesirable side reaction is drawn out and its solution discussed. However...
    - Problem: H<sub>2</sub>O is hard to separate from acetic acid (they have similar boiling points and they're miscible). Thus, you would have to distill, but that's expensive and time-consuming. Additionally, acetic acid is corrosive. Therefore, this is not a great solution.
    - However, you can add the promotor LiI or LiOAc. It's not clear exactly what the promotor does, but one possible explanation is that you can get to a triiodide dianion that is nucleophilic to the point that it can speed up oxidative addition enough to promote the productive pathway.
    - Another possibility is that iodide binding at other steps can forward the productive pathway.
- You can intercept acetyl intermediates to foster another catalytic process:
- Kovach-Eastman Acetic Anhydride Process.
  - Invented in 1983.
  - Produces 800 million pounds of acetic anhydride annually.
- Mechanism:
  - The only difference between this and the Monsanto acetic acid process (Figure 4.5) is that in the nonorganometallic cycle, we add acetic acid and get acetic anhydride, and then add methyl ester and get acetic acid.
  - Inputs are CO and Me–COOMe.
- Cativa process:
  - Invented by BP.
  - 5 times more active than rhodium-catalysed.



- Uses iridium with a ruthenium promotor.
- Iridium is in the same group as iridium but is faster for oxidative addition.
- The rate law is complicated, depending on  $[\text{CO}]$ ,  $[\text{H}_2\text{O}]$ ,  $[\text{MeOAc}]$ ,  $[\text{MeI}]$  (which you don't actually want in there),  $[\text{Ru}]$ , and  $[\text{Ir}]$ .
  - This process is complex and nonlinear.
- The main species in solution is  $\text{Ir}(\text{CH}_3)(\text{CO})_2\text{I}_3^-$ .
- The turnover limiting step here is insertion since oxidative addition is so much faster (approximately 150 times faster). However, insertion is  $1 \times 10^5$  times slower for iridium.
  - Simplistic explanation: There are even stronger bonds for iridium than for rhodium. This favors bond formation (i.e., in oxidative addition), but not bond breaking (i.e., in insertion).
- However, we can fix the slower insertion rate with promoters, namely  $[\text{Ru}(\text{CO})_3\text{I}_2]_2$ .

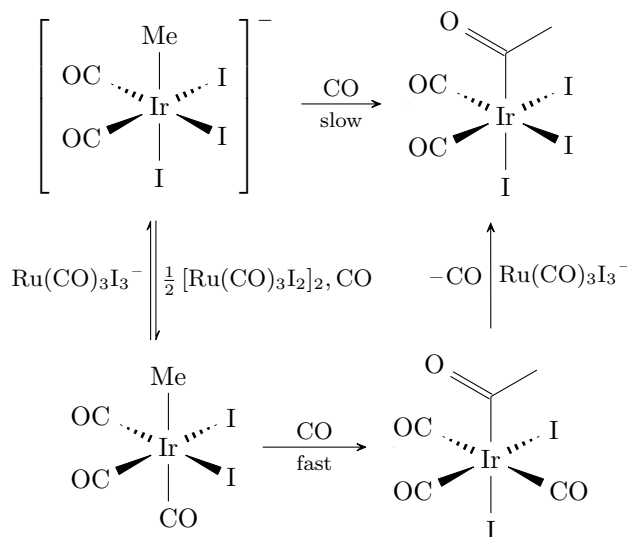


Figure 4.6: Promoting the Cativa process.

- $\frac{k_{\text{fast}}}{k_{\text{slow}}} \approx 700$ , so an almost 3 orders of magnitude gain.
- The overall mechanism for the Cativa process is drawn out.
- Hydroformylation.
- General form.

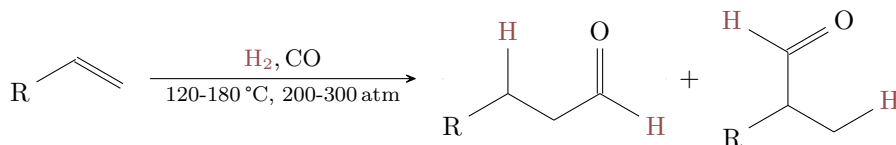


Figure 4.7: The general form of hydroformylation.

- The ratio of the first to the second product is 3-4 : 1.
- Typical catalysts:
  - $\text{HCo}(\text{CO})_4$  (synthesized from  $\text{Co}_2(\text{CO})_8$  as a precatalyst and  $\text{H}_2$ ).
  - $\text{HCo}(\text{CO})_3(\text{PR}_3)$ .

- $\text{HRh}(\text{CO})_2(\text{PR}_3)_2$ .
- On the gas used in this process ( $\text{CO}$  and  $\text{H}_2$  in a 1 : 1 ratio):
  - Called synthesis (or syn) gas.
  - Released when coal is heated.
  - Composed of  $\text{CO}$  and  $\text{H}_2$  in a 1 : 1 ratio.
- The rate at which the  $\text{HCo}(\text{CO})_4$  catalyst acts is given by  $\text{Rate} = k[\text{H}_2][\text{CO}]^{-1}$ .
  - Thus, we can tweak the rate by adjusting the relative concentrations of the gas.
  - Adding  $\text{H}_2$  will increase the rate of reaction, and adding  $\text{CO}$  will decrease the rate of reaction.
- Mechanism:

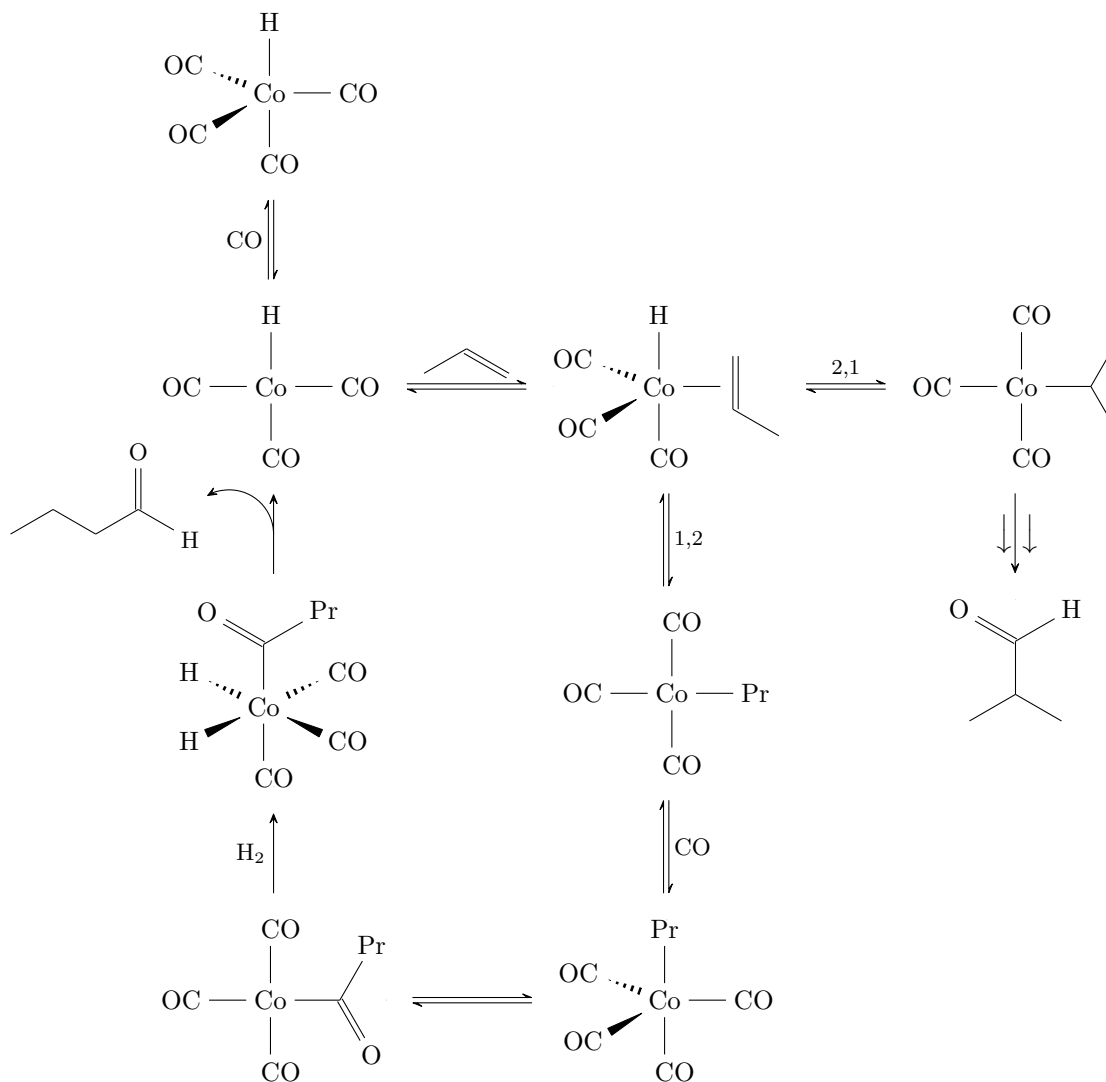


Figure 4.8: Hydroformylation mechanism.

- The active catalyst is a square planar,  $d^8$ ,  $16e^-$  complex.
- The first intermediate is the key intermediate to determine selectivity because it can insert in a 2,1 or a 1,2 fashion.

- The third intermediate along the 1,2 branch can be trapped by CO.
  - The off-cycle intermediate can be isolated. Thus, it's a kind of resting state.
- A similar process (as indicated by the triple arrow) can be used to get from the 2,1 branch to the final branched product.
- Control of branching:
  - It's complicated and not entirely clear.
  - However, we are aware of **chain walking**.
- **Chain walking:** The transition from the 1,2-inserted intermediate and the 2,1-inserted intermediate and vice versa.
  - An equilibrium process.
- How to control selectivity.
  - Switching  $\text{HCo}(\text{CO})_3(\text{PR}_3)$  increases the rate and selectivity.
  - With a special phosphine, the selectivity of linear to branched is 8 : 1.
  - This also enables the hydrogenation of aldehydes to alcohols.
    - An important industrial application of this is transforming (in one step) internal olefins into terminal aldehydes and terminal alcohols.
- First-row metals hydroformylate, but heavier ones do it better.
- Rh-catalyzed hydroformylation:
  - Uses  $\text{Rh}(\text{CO})_2(\text{PR}_3)_2$ .
  - Linear-to-branched ratio of 11 : 1.
  - Milder conditions (5-10 atm CO /  $\text{H}_2$  and 90 °C).
  - The mechanism is similar to that of Co.
  - We make the catalyst water soluble with bulky, heavy phosphines (such as tris(phenyl sulfato)phos) to aid in separation.
  - We are allowed to have two phosphines on rhodium because rhodium has a larger atomic radius. The larger atomic radius of rhodium also enables the use of chelating phosphines, such as...
    - dppe, dppp, dppb, bis(diphenylphosphino)ferrocene (dppf), DPE Phos, Xant phos, and BISBI (the best).
  - Selectivity of chelating phosphines depends on bite angle.
    - $\text{PPh}_3 \rightarrow 9 : 1$  ratio.
    - dppe  $\rightarrow 4 : 1$  ratio.
    - BISBI  $\rightarrow 30 : 1$  ratio.
  - Hypothesis: Larger bite angles will favor  $\text{PR}_3$  in the equatorial plane.
    - Favoring 5-coordinate intermediates over 4-coordinate intermediates.

## Unit 5

# More Catalytic Processes 2

### 5.1 Lecture 18: Olefin Polymerization

5/10:

- Another huge industrial-scale reaction
- The Great Pacific Garbage Patch is largely composed of plastics made by this process.
  - Plastics get a bad rep, but they are a remarkable material.
    - We can melt them, form them, and they have durability properties.
  - However, because of their environmental impact, a big thing in chemistry is the pursuit of materials with similar properties that are biodegradable.
  - Inorganic chemistry plays a large role in their synthesis.
  - In 2008, the US alone made 58.3 million metric tons of polyethylene and 17 million metric tons of polypropylene.
- General form:

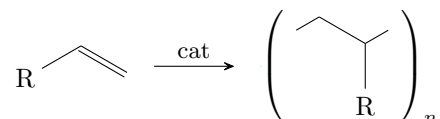
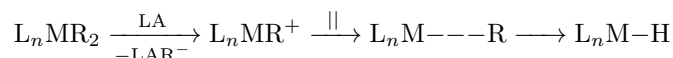


Figure 5.1: The general form of olefin polymerization.

- If  $R = H$ , we have polyethylene.
- If  $R = Me$ , we have polypropylene.
- This is a thermodynamically favorable, exothermic reaction since  $\pi$  bonds are weaker than  $\sigma$  bonds.
- The catalyst is typically Ti, Zr, Hf, Cr (early Group 4 transition metals). Sometimes we use Fe, Co, Ni, and Pd (these are a bit more specific).
- Most of the materials that mediate this catalysis are called Ziegler-Natta catalysts.
  - These are heterogeneous, even though they operate via the same kind of catalytic cycle that homogeneous systems use.
  - Nobel prize (1963).
- Polymer terms:
- **Number averaged molecular weight:** The quantity  $\frac{\sum N_x M_x}{\sum N_x}$ , where  $N_x$  is the number of chains with  $x$  monomers and  $M_x$  is the molecular weight of a chain with  $x$  monomers. *Also known as  $M_N$ .*

- **Weight averaged molecular weight:** The quantity  $\frac{\sum N_x M_x^2}{\sum N_x M_x}$ . Also known as  $M_w$ .
- **Molecular weight distribution:** The quantity  $\frac{M_w}{M_n}$ . Also known as **polydispersity index, PDI**.
  - 1 is perfect. This means that you only have one type of chain.
  - 1.1 is good.
  - Above 1.5 is getting ill-defined.
- **Stereochemistry:**
  - Normally, the methyl groups in polypropylene all insert on the same side, but if one misinserts, then it faces the other direction.
  - If the catalyst corrects itself and continues on inserting in the original direction, this is **site control**.
- **Site control:** The catalyst controls the insertion.
  - More specifically, the direction the methyl groups point is controlled by the catalyst.
- **Chain end control:** One misinsertion causes the ensuing insertions to face the same way as the last inserted methyl group.
  - More specifically, the direction the methyl groups point is controlled by the last inserted methyl group.
- **Mechanism:**



- The three steps are activation, growth, and termination.
- LA stands for Lewis acid. The lewis acid activates the catalyst by abstracting an anionic Lewis acid species.
- Olefin insertion grows the polymer.
- $\beta$ -H elimination is the simplest way to terminate the chain, even though there are several possibilities.
- **Activation:**
  - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-AlR_4^-]{AlR_3/MAO} L_nMe^+$ .
  - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-MeBAr^F_4]{BAr^F_3} L_nMe^+$ .
  - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-CH_4]{HBAr^F_4} L_nMe^+$ .
  - MAO is methylated aluminum oxide.
    - An ill defined, amorphous gunk with some oxygens created by adding a pinch of water to  $AlMe_3$ .
    - A cheap reagent that people chuck into their catalyst mixture.
    - Functions:
      1. Alkylating agent.
      2. Activator (pulls off methyls to generate cationic species).
      3. Scavenger for water (primarily) and oxygen.
  - The fluorinated aryl borates are really good because they're very weakly coordinating, and we really want an open coordination site.

- Chain growth:

- $\text{MR}(\text{||}) \longrightarrow \text{M}---\text{R} \xrightarrow{\text{||}} \text{M}(\text{||})(---\text{R}) \longrightarrow \text{M}---\text{R} \longrightarrow \longrightarrow \longrightarrow .$
- This is called the Cossee Arlman mechanism.

- Sterics determine the rates: Ethylene > propylene > substituted olefins > disubstituted olefins  $\approx$  geminal disubstituted olefins >>> trisubstituted or tetrasubstituted olefins.

- Termination:

- How you get variability in chain lengths.
- Control it by adding a chain-transfer reagent (a specific terminating reagent). Examples include...
  - $\text{H}_2$ :  $\text{L}_n\text{M}-\text{pl} \xrightarrow{\text{H}_2} \text{L}_n\text{M}-\text{H} + \text{H}-\text{pl}$ , where pl is a polymer<sup>[1]</sup>.
  - $\beta$ -H elimination:  $\text{L}_n\text{M}---\text{pl} \longrightarrow \text{L}_n\text{M}(\text{H})(\text{||pl}) \longrightarrow \text{L}_n\text{M}-\text{H} + =-\text{pl}$ .
  - $\beta$ -H abstraction:  $\text{M}(\text{||})(---\text{pl}) \longrightarrow \text{M}(\text{Et})(\text{||pl}) \longrightarrow \text{MEt} + =-\text{pl}$ .

- The relative rates of growth vs. determination dictate the type of material we get.

- $K_p$  is the rate of growth/propagation;  $K_t$  is the rate of termination.
- $K_p$  vs.  $K_t$  dictates the product.
- $K_p \gg \gg K_t$  yields high molecular weight polymers.
- $K_p \approx K_t$  (within the same order of magnitude) yields oligomers.
  - The geometric weight distribution of oligomers is called a **Schultz-Flory distribution**.
- $K_t \gg K_p$  yields dimers exclusively.
  - This can be valuable if you just want to transform ethylene into butadiene (a higher value product), for instance.

- Types of polyethylene.

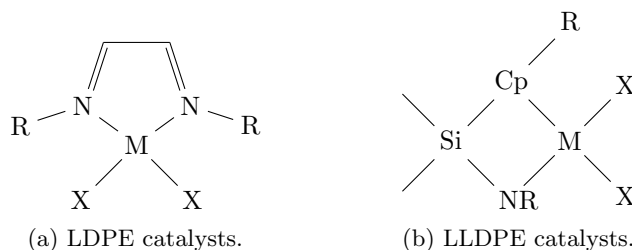


Figure 5.2: Polyethylene-type catalysts.

- A perfect zig-zag chain is HDPE (high density polyethylene).

- High melting point.
- Crystalline.
- Example uses: Helmets for army soldiers, bulletproof plastics.
- Usually formed with Ziegler-Natta catalysis:
  - $\text{TiCl}_x + \text{AlR}_x \longrightarrow$  a heterogeneous catalyst that's super active ( $> 1 \times 10^9$  kg of polymer per gram of catalyst).
  - Note that  $x = 3$  or 4.
  - Alternate catalysts:  $\text{Cr}^{\text{III}} + \text{silica} \xrightarrow{\text{O}_2, \Delta} \text{CrO}_4 \xrightarrow{\text{||}} \text{reduced Cr center (the active catalyst)}.$

<sup>1</sup>Be aware that Anderson uses a capital P in a circle.

- A mess with a ton of branching is LDPE (low density polyethylene).
  - Lower melting point.
  - Often made by radical processes.
  - Also made by late transition metal catalysts, where there's less control over chain growth:
    - Square planar,  $d^8$ ,  $16 e^-$  species.
    - Example metal centers: Ni, Pd.
    - High rates of  $\beta$ -H elimination leads to chain walking and branching.
- Longer chain with a few branches is linear low-density polyethylene (LLDPE).
  - Transition metal catalyzed.
  - Formed from a mixture of ethylene and substituted olefins or a controlled rate of branching from catalysts.
  - Catalysts:
    - Constrained geometry catalysts.
    - Example metal centers: Ti, Zr, Hf.
- Polyethylene gives a single chain, but polypropylene can be chiral depending on the orientation of the methyl groups. The orientation defines **tacticity**.
- **Isotactic** (polypropylene): All methyl groups are pointed in the same direction.
  - The most crystalline, highest melting point material.
- **Atactic** (polypropylene): Every methyl group is random.
  - The least crystalline, lowest melting point material.
- **Syndiotactic** (polypropylene): Every methyl group alternates.
  - Pretty highly ordered.
- **Hemiisotactic** (polypropylene): Every other methyl group points the same direction; the remaining ones are random.
- **Stereoblock** (polypropylene): Alternating blocks of isotactic polypropylene.
- Controlling stereochemistry:
  - Relies on the fact that propylene is pro-chiral.
  - Si (pro-S) and Re (pro-R) faces.
  - Catalyst symmetry controls tacticity.
- Catalyst types:

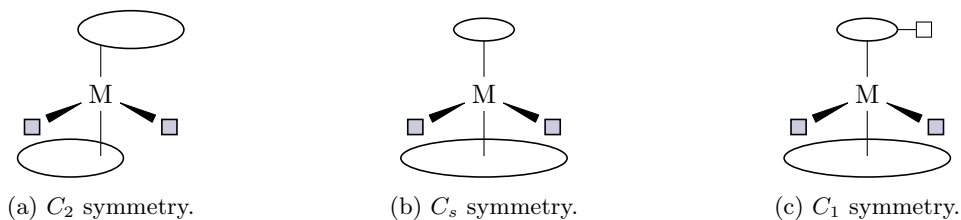


Figure 5.3: Polypropylene-type catalysts.

- Most well worked out for metallocenes.
- In Figure 5.3, boxes are open coordination sites; circles are space-filling ligands.
- Differences help dictate tacticity.
- $C_2$ : Both binding sites are the same.
  - Steric clashing forces the olefin to point in inverted ways; but because the polymer switches sides, this leads to consistency in the direction the methyl is added.
  - Generates isotactic polypropylene.
  - Si-face selective.
  - Example: A diindene metallocene.
- $C_s$ : Binding sites are enantiomers.
  - Generates syndiotactic polypropylene.
  - Two enantiotopic sites will alternate.
  - Example: A metallocene with Cp on top and fluorene on bottom.
- $C_1$ : Binding sites are diastereomers.
  - Generates hemiisotactic polypropylene.
  - Example: A metallocene with Cp-R on top and fluorene on bottom.
- To make this work, the Cp rings are often tethered to prevent rotation.
  - However, rotation can be harnessed to make stereoblock copolymers.
- Note that stereoblock copolymers can also be synthesized with two isotactic catalysts, relying on chain transfer.
- Late-metals: Chain walking.
  - A chain can grow or it can chain walk (do  $\beta$ -H elimination followed by a 2,1-insertion).
  - If it chain walks, we'll create a branch.
- We see this with late metals.
  - Early metals are terrible backbonders, so they will prefer to be on the alkyl side of the equilibrium.
  - Late metals can backbond, and will more readily form an olefin adduct (a necessary intermediate to chain walking).
- Thus, we use late metals...
  - Because sometimes we want branching, specifically finely tuned branching to a certain degree.
    - Recall that random branching can be achieved via a radical mechanism.
  - SHOP process:
    - We react ethylene with a nickel PO-type catalyst (a nickel catalyst with a bidentate ligand that chelates through a phosphorous and an oxygen), an enolate, or related phosphorous/oxygen based donors.
    - This creates olefin-terminating oligomers. This doesn't use chain walking, but rather the chain transfer process, which is much faster with late metals.
    - Products:  $C_4$ - $C_8$  (41%),  $C_{10}$ - $C_{18}$  (40.5%), and  $C_{20+}$  (18.5%).
    - The short ones and the long ones can be combined with  $Mo_2O_3/Al_2O_3$  to do olefin metathesis, yielding internal and terminal olefins.
    - Then, throwing in the medium-length ones and treating with  $HCo(CO)_4$  (our hydroformylation catalyst) and syn gas yields terminal aldehydes, which with enough hydrogen can give us terminal alcohols, which are commodity chemicals.



- Oligomerization mechanism:

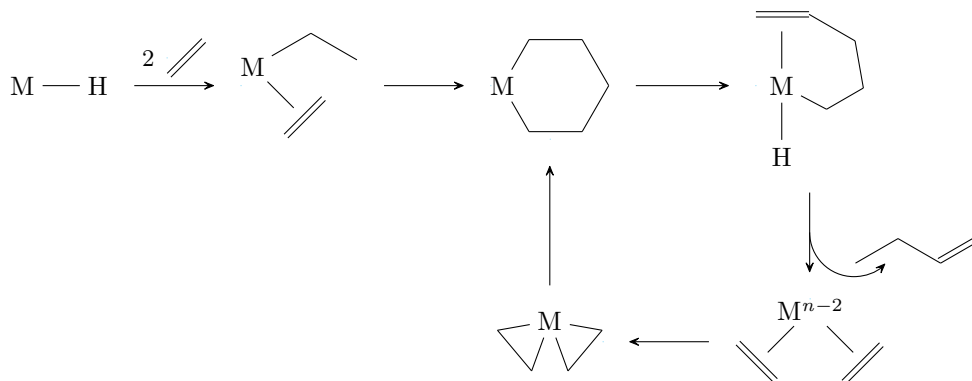


Figure 5.4: Oligomerization mechanism.

- A metathesis-like process.
- Example with nickel.
- Polar monomer incorporation.
  - One of the standing grand challenges in olefin polymerization.
  - Incorporating vinyl chlorides, vinyl ethers, vinyl esters, vinyl nitriles, etc.
  - We can do this with radical polymerizations, but there's no stereocontrol here.
  - PVC (pipe) is polyvinylchloride (robust, a great material, but opaque).
    - It's melting point would be even higher if we could make it isotactic (and it would be clear, which could potentially have applications).
  - The challenge with early metals is that if you  $\beta$ -Cl eliminate, the M-Cl bond will be too strong to break and reinsert the chloride. This kills the catalysis.
    - Additionally, the groups on the polymer adjacent to the metal center can donate to it, making the polymer a kind of chelating ligand and preventing olefin insertion. This also kills the catalysis.
  - Late metals are less halo/oxo-philic, which makes them better at incorporating these monomers.

## 5.2 Office Hours (Anderson)

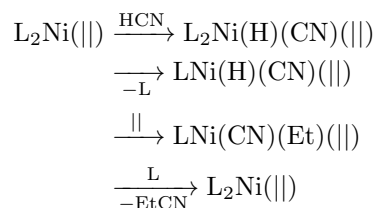
- Chain walking is when the metal bonds to a  $\sigma$  bond, moves to an adjacent carbon, moves to a double bond next, and on and on.
  - The terminal olefins are sterically favored, even though the internal ones are typically thermodynamically favored.
  - Early metals typically make linear polyolefins, while late metals prefer branched ones.
- What is the difference between a Chatt, distal, and alternating mechanism?
  - Chatt and distal mechanisms are the same thing (known as Chatt due to Eurocentrism).

## 5.3 Discussion Section

- 5/11:
- HW5 is due 5/21/2021.
  - Discussion recordings will be posted in the Panopto folder from now on, but there may be a delay.
  - Point out dipole on CO in Homework 4.1a.
  - Iron starts from Fe<sup>I</sup>.
  - Draws out and discusses the FeMoCO enzyme (which is actually an enzyme, not just iron, molybdenum, and a carbonyl ligand).
    - FeMoCO possibly binds to CO in bidentate fashion through two irons.
      - This could support a Chatt mechanism since it would be easier to delocalize the higher oxidation state across two irons.
    - The iron in the center of FeMoCO that forms six partial bonds and doesn't really make any sense is sometimes called a **Texas iron**.
  - Considers the 4-membered transition state and arrow-pushing for ROMP.
  - It's good to know what the end groups are for the purposes of NMR.
  - Goes over Figure 4.8 and Homework 4.4 in a bit more detail.
  - Goes over Homework 3.

## 5.4 Lecture 19: Oxidative Olefin Functionalization

- 5/12:
- More fine molecule synthesis than industrial, although there are industrial applications.
  - General form:
 
$$\text{R}-\equiv \xrightarrow[\text{cat}]{\text{HX}} \text{R}-\text{X} + \text{R}-\text{CX}=\text{}$$
    - Can also start from a double bond and make singly bonded products.
  - Hydrocyanation:
 
$$\text{R}-\text{CH}=\text{CH}_2 + \text{HCN} \xrightarrow{\text{cat}} \text{R}-\text{CH}_2-\text{CH}_2-\text{CN}$$
    - HCN is really toxic, so surrogates are used in some cases.
    - Used in the synthesis of adiponitrile, which becomes nylon.
  - Controlling selectivity w/ catalysts:
    - Ni(P(o-Tol)<sub>3</sub>)<sub>4</sub><sup>[2]</sup>: Selects for the terminal product, especially with sterically encumbered (i.e., geminal) olefins.
    - Styrene: Selects for the branched product.
  - Mechanism:




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<sup>2</sup>o-Tol is an ortho-tolyl group.

- The precatalyst is  $L_3Ni$ , and is activated when ethylene kicks out a ligand.
- The reductive elimination step is hard and requires a Lewis acid and a ligand to kick out ethyl cyanide.
- Can also have chain walking.
- Hydrosilylation:
 
$$R- = + HSiR_3 \xrightarrow{cat} R- - SiR_3$$
  - Note that our starting material can also be  $R = X$  (where X can be oxygen, for instance), giving us  $R-CH(SiR_3)-XH$  as a product.
  - Industrially important for making non-stick coatings.
- Common catalysts:  $Pd^0$  and Karstedt's catalyst (a bridging mess of siloxanes bound to olefins and chelating).

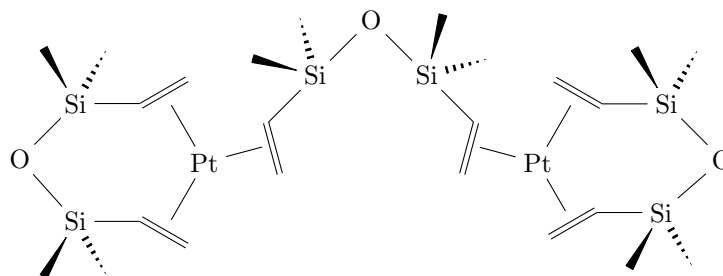
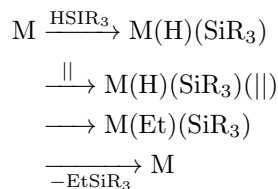
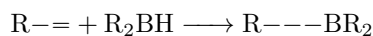


Figure 5.5: Karstedt's catalyst.

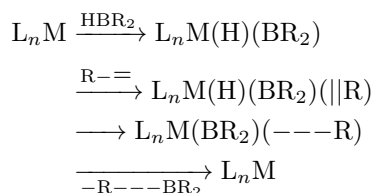
- $H_2PtCl_6$  also works (known as Speier's catalyst).
- We can also observe chain walking to bond a silyl away from where the olefin originally was.
- Mechanism:



- The above mechanism is called the Chalk-Herrod mechanism.
- However, we can also add the silyl group to the olefin first and the hydrogen second; this is the modified Chalk-Herrod mechanism.
- $\sigma$ -bond metathesis is also possible.
- Hydroboration:

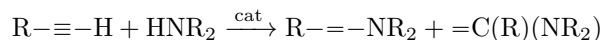


- We need a catalyst because otherwise we're stuck at the mercy of the electronics of this reaction.
- A catalyst is necessary for less electron-rich boranes.
- Mechanism:



- We could also get from the second intermediate to  $L_nM(H)(-C(H)(BR_2)(R))$ , from which we can reductively eliminate to get  $Me-C(H)(BR_2)(R)$  or  $\beta$ -H eliminate to get  $=C(BR_2)(R)$ .
- Alternate mechanism:  $L_nRh(||R)(BR_2) \xrightarrow{-R---BR_2} L_nRh(||R)(BR_2) \xrightarrow{R_2BH} L_nRh(H)(BR_2)(CRH---BR_2) \xrightarrow{-R---BR_2} L_nRh(H)(BR_2)(---R) \xrightarrow{-R---BR_2} L_nMH$ .
- With early metals:  $L_nMH \xrightarrow{||R} L_nM(H)(||R) \longrightarrow L_nM---R \xrightarrow{HBR_2} L_nM(H)(BR_2)(---R) \xrightarrow{-R---BR_2} L_nMH$ .
  - Done to avoid oxidative addition type processes.

- Hydroamination:



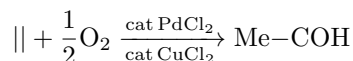
- Can also be done from a doubly bonded reactant (remove the double bond from each product).

- Mechanisms:

1. Nucleophilic attack:  $L_nM \longrightarrow L_nM-|| \xrightarrow{RNH_2} M---NH_2R \xrightarrow{-EtNRH} L_nM$ .
2. Insertion:  $L_nM-NHR \xrightarrow{||} L_nM(||)(NHR) \longrightarrow L_nM---NRH \xrightarrow[-EtNRH]{RNH_2} L_nM-NRH$ .
3. 2 + 2:  $L_nM=NR \xrightarrow{||} \begin{array}{c} L_nM \text{ --- } NR \\ | \quad \quad | \\ \hline \end{array} \xrightarrow{H_2NR} L_nM(NRH)(NREt) \xrightarrow{-EtNRH} L_nM=NR$ .
  - Goes through a 4-membered 2 + 2 transition state in the first step, as in Figure 3.17.

- Oxidative olefin functionalization.

- Wacker oxidation:



- Millions of tons per year; acetaldehyde feeds into a lot of processes.

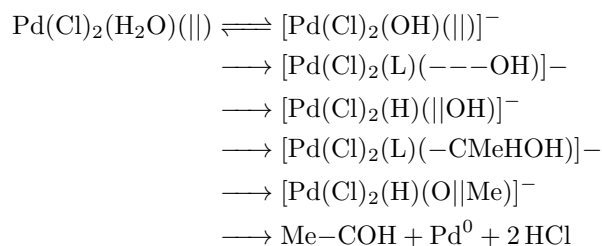
- Stoichiometry:

- It was discovered in the 1950s and 1960s that  $|| + H_2O + PdCl_2 \longrightarrow Me-COH + Pd^0 + 2 HCl$ .
- On the role of copper:
  - It was known that  $Pd^0 + 2 CuCl_2 \longrightarrow PdCl_2 + 2 CuCl$ . Thus, we can use  $CuCl_2$  to regenerate our palladium catalyst.
  - Additionally,  $2 CuCl + \frac{1}{2}O_2 + 2 HCl \longrightarrow 2 CuCl_2 + H_2O$ .
- Summing these three reactions, we have  $|| + \frac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} Me-COH$ .

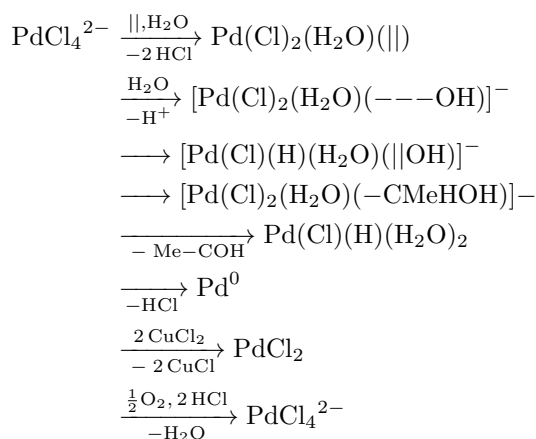
- Mechanism:

- Rate =  $\frac{[PdCl_4^{2-}][C_2H_4]}{[Cl^-]^2[H^+]}$ .
- $[PdCl_4]^{2-} + || + H_2O \longrightarrow Pd(Cl)_2(OH)(||)$ .
- C–O bond formation: Three main possibilities.

1. Insertion:



2. External attack at a ligand: React the starting compound with  $\text{OH}^-$  to produce  $[\text{Pd}(\text{Cl})_2(\text{H}_2\text{O})(---\text{OH})]^-$ , which then feeds into the third intermediate.
  3. Water nucleophilic attack: React the starting compound with  $\text{H}_2\text{O}$  and remove a proton to produce  $[\text{Pd}(\text{Cl})_2(\text{H}_2\text{O})(---\text{OH})]^-$ , which then feeds into the third intermediate.
- The  $\beta$ -H elimination step can also occur by a  $\text{Cl}^-$ -assisted process where the chloride abstracts the  $\text{H}^+$  from the alcohol.
  - All four hydrogens in acetaldehyde come from ethylene.
- Stereochemical experiments:
    - Draws a mechanism yielding stereochemistry consistent with mechanisms 2 and 3, but not 1. This means it's probably actually external attack at a ligand.
    - If  $[\text{Cl}^-]$  is high, we activate the following pathway:  $[\text{Pd}(\text{Cl})_2(\text{L})(---\text{OH})]^- \longrightarrow [\text{Pd}(\text{Cl})_3(---\text{OH})]^{2-} \longrightarrow \text{Cl}---\text{OH}$ .
    - $\text{Rate} = \frac{[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-][\text{H}^+]}$ .
    - Therefore, we'll make the chlorinated pathway more than the productive pathway if we add a bunch of chloride.
  - Overall mechanism:



- Other applications:
  - Higher olefins:  $\text{R}- = + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Pd}^{\text{II}}, \text{CuCl}_2, \text{H}_2} \text{R}-\text{COH}$ .
  - The nucleophile need not be  $\text{H}_2\text{O}$ :
    - $|| + \text{ROH} \longrightarrow ||\text{OR}$ .
    - $|| + [\text{COOR}]^- \longrightarrow \text{C}(\text{O})(\text{R})(\text{O}||)$ .
  - Draws out another few useful processes.
  - Useful chemistry with dienes.
    - Cyclohexadiene can become cyclohexene with para-acetates.
    - Useful applications of the above reaction in total synthesis: Setting stereochemistry with a catalytic attack, as used in the synthesis of paenilactane B.
  - This chemistry also works with nitrogen-based nucleophiles.

## 5.5 Office Hours (Anderson)

- 5/17:
- Which molecules are anionic in the carbonylation mechanism and why?
    - They're all anions.
  - What is  $M_x$  in the definition of number averaged molecular weight?
    - $N_x$  is number of chains with  $x$  number of monomers.  $M_x$  is the molecular weight of a chain with  $x$  monomers.
    - From the perspective of the video, you could think of  $N_x$  as the number of chains with molecular weight  $M_x$ .
  - Can you explain the oligomerization mechanism?
    - Oligomerization is baby polymerization (potentially more useful).
    - In principle, it could go through a regular insertion mechanism.
    - If you have competitive elimination of polymers, your polymers will be shorter on average.
    - Butene is a higher value product than oligomers.
    - Use half-type mechanisms to balance the stoichiometry. Necessitates bimolecular chemistry in real life.
  - Olefin polymerization catalysts are classically Group 4,  $d^0$  metals.
  - Homework 5.3:
    - Use chain walking or chain transfer.
    - You'll have a statistical mixture of branches if you're chain walking, so it's not this.
  - Is the catalyst resting state always the one before the step with the highest energy of activation?
    - The precatalyst can't technically be the resting state because it's an off-cycle intermediate.
    - Homework: It's the major species in solution; the other enantiomer being bound.
      - Each pathway could have a different resting state.
      - Recognize what state of the catalyst is sitting in the mixture; draw the two cycles and decide.
  - **Principle of microscopic reversibility:** To be mechanistically allowed, a reaction must be irreversible to *some* extent.
  - Homework 5.6:
    - Use either Chalk-Herrod or modified Chalk-Herrod.
  - Midterm 6:
    - $\text{NR}_2^-$  is a  $\sigma$  donor and a  $\pi$  donor because it has filled  $\pi$  orbitals on the nitrogen.
    - Phosphines are  $\pi$  acids.
    - Cp is all three.
    - Methyl is a pure  $\sigma$  donor.
    - Cyclobutadiene is both.
    - $\text{O}_2^-$  is a  $\pi$  donor.
    - Draw out like a Lewis structure – two lone pairs on  $\text{NR}_2^-$  means filled  $\sigma$  and  $\pi$  orbitals;  $\text{CH}_3$  has only filled  $\sigma$  orbitals.
    - Orbital diagrams.
    - If he wants an MO diagram, he'll say "MO diagram."

## 5.6 Discussion Section

5/18:

- Homework 5 today.
- Next Tuesday's discussion section might get moved to this coming Saturday at 1:00 PM CT.
- Sophie will publish a list of midterm 2 topics.
- Homework 5.2:
  - Early metal resting state: Metal alkyl.
    - Insertion of olefin is very fast so a bound olefin is almost never observed for these systems.
    - Favors linear polyethylene.
  - Late metals: Metal-olefin adduct.
    - Olefins are more likely to dissociate.
    - Insertion of an olefin is not as fast; this helps lead to more chain transfer.
    - Late metal catalysts are more susceptible to  $\beta$ -H elimination so chain walking is also more common than with early metals.
    - Favors branched polyethylene via the chain transfer and chain walking mechanisms.
  - Chain transfer mechanism:
    - Termination mechanisms.
    - $\beta$ -H elimination to form a metal-olefin adduct, and then the olefin dissociates from the metal.
    - If you react with ethylene time and time again to create a polymer, there's no reason you can't suddenly interact with another polymer in solution.
  - Chain walking was discussed last week.
- Homework 5.3:
  - Some catalysts polymerize ethylene to HDPE that contain a few long branches (ca. 1-2 per chain). Explain how long the branches might form. What distribution of branch lengths do you expect for your mechanism?
  - Which of the two branch forming pathways does the product here most resemble?
    - Chain transfer.
  - What kind of catalysts lead to this selectivity?
    - Open sterics, but maybe still some early metals to make sure you don't get shorter chains, maybe CGCs — can bind sterically crowded  $\alpha$ -olefins competitively with ethylene.
    - Likely need high temp to keep polymer in solution.
- Homework 5.5:
  - Wacker-type reactions: Generally alkene to ketone, but there are variants with other heteroatoms and other levels of reduction (e.g., allylIN and allylO, C=N and C=O).
- Alternate Wacker oxidation mechanism (for an alcohol; see Figure 5.6):
  - Look back at the traditional mechanism but be aware of such derivatives. Know the similarities. The starting material should drive you toward the product.
  - Does it matter when the ligands are being lost and coordinated.
    - Not really.
    - Anderson's way is probably a bit more realistic.

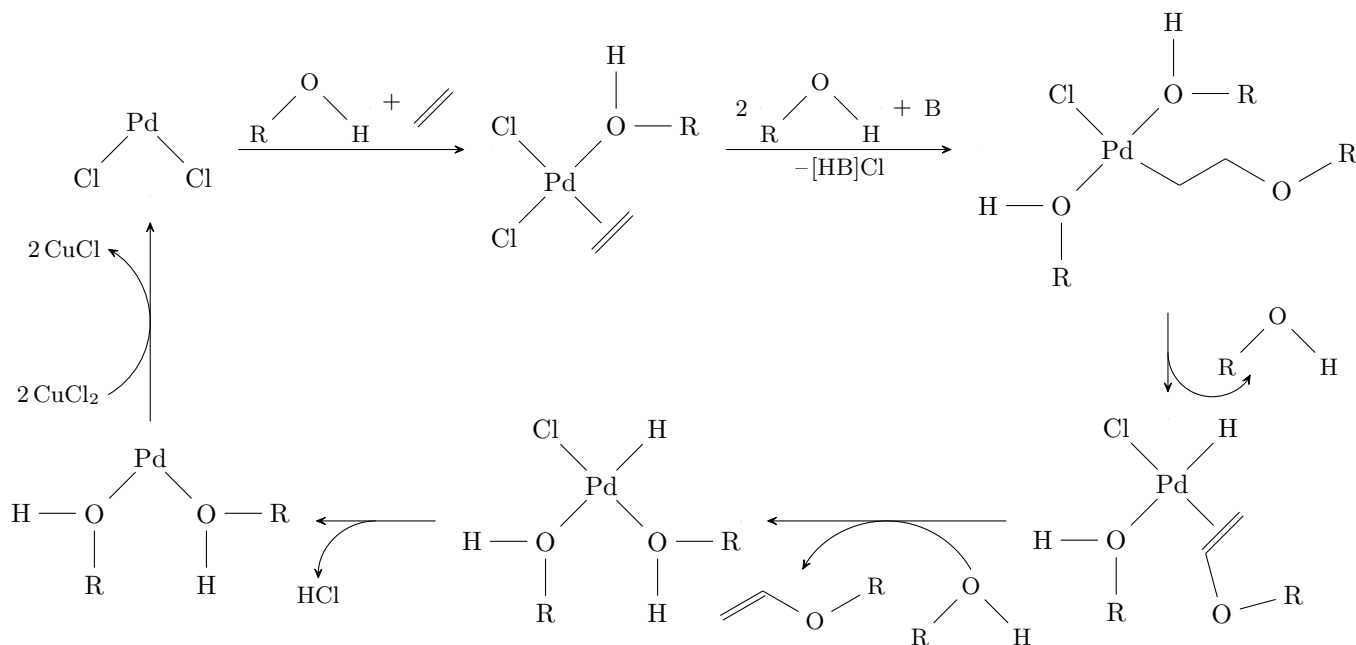


Figure 5.6: Wacker oxidation mechanism (for an alcohol).

- Brookhart type nickel- and palladium-based polymerization catalysts are introduced in Section 11.3.3 of the text. These catalysts differ from metallocene catalysts in that (1) the resting state is the (diimine)MR(ethylene)+ adduct 1, (2) chain walking is much faster than chain growth, (3) ethylene insertion into secondary alkyl metal species is fast, and (4) a hyper branched polyethylene is produced (ca. 100 branches at 1000 °C).
- A mechanism for polymerization showing how branches are formed (see Figure 5.7).
  - We start from a precatalyst and go through a couple of activation steps.
  - Then we show three possible pathways.
    - The top one creates no branches but leaves the possibility open for a chain transfer.
    - The middle one creates a methyl branch.
    - The bottom one creates an ethyl branch.
  - Note that if R contains more carbons, we can see even more chain walking, leading to longer branches and our ultimate hyperbranched product.
- What property or properties give rise to the differences in polymerization behavior between (diimine)PdR<sup>+</sup> and Cp<sub>2</sub>ZrR catalysts?
  - It's Zr(IV) as a cation.
  - Palladium(II) is  $d^8$  and soft, while zirconium(IV) is  $d^0$  and hard. While both are poor backbonders, the soft character of the former leads to stronger metal olefin coordination. This enables  $\beta$ -H elimination of (diimine)PdCH<sub>2</sub>CH<sub>2</sub>R<sup>+</sup> to form (diimine)PdHCH=CHR<sup>+</sup> to compete with trapping by ethylene to form the resting state, and thus enables chain walking to compete with growth.
  - Palladium is a much better backbonder because it *has*  $d$  electrons.



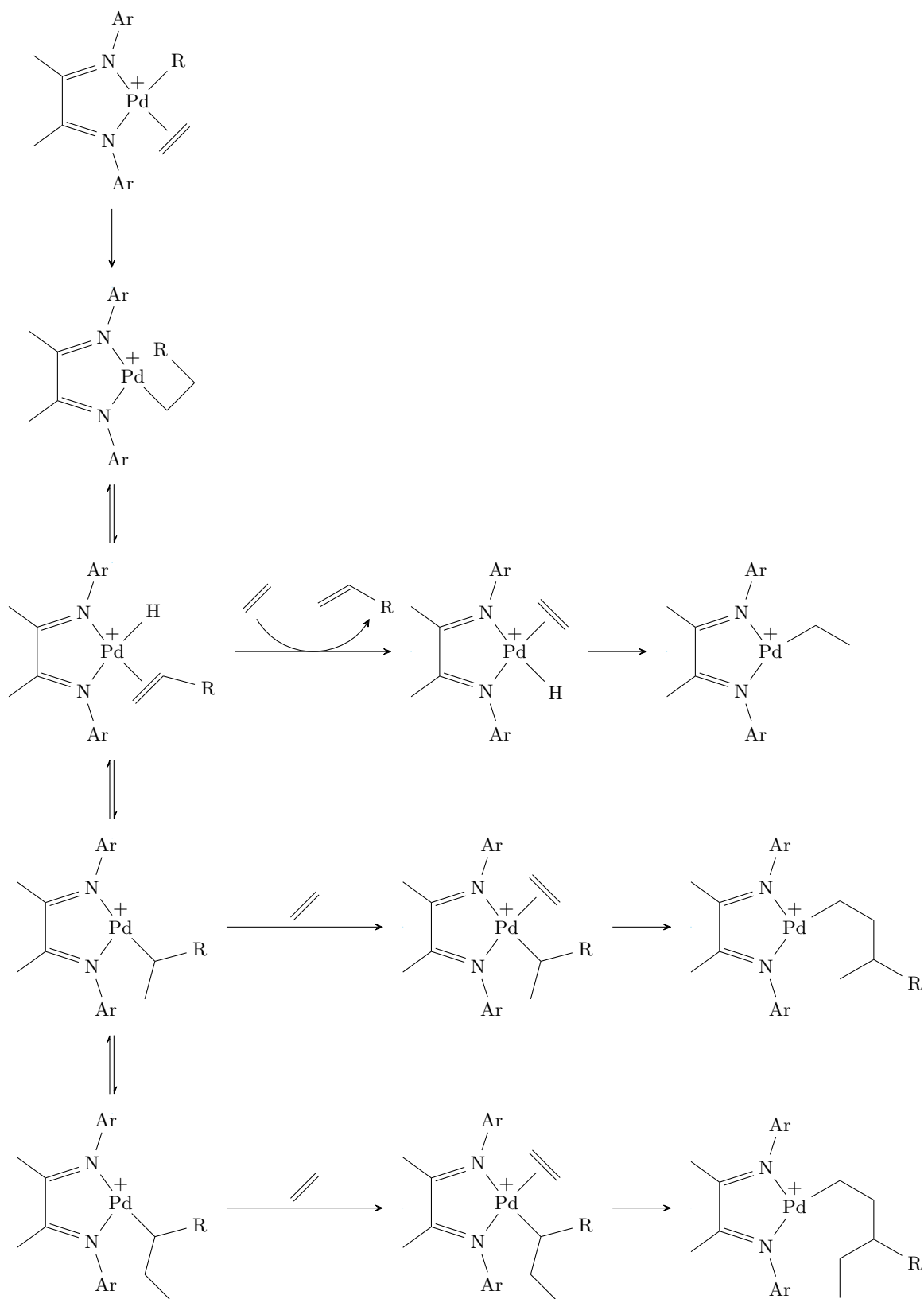


Figure 5.7: Polymerization with Brookhart catalysts.

- The isopropyl substituents on the aryl rings of the diimine ligand in catalyst 1 are critical for the generation of high molecular weight polymer. These aryl rings are oriented perpendicular to the palladium square plane as indicated. Catalysts with small groups in these positions, such as 2, produce only low molecular weight oligomeric products. Rationalize the difference. Hint: Consider the mechanism of ligand substitution.
  - Large substituents inhibit chain transfer! They stop ethylene from knocking out the polymer.
  - Charge transfer requires  $\beta$ -H elimination and substitution of  $\text{H}_2\text{C}=\text{CH}_2\text{pl}$  by  $\text{H}_2\text{C}=\text{CH}_2$  to begin substitution at square planar complexes normally proceeds by an associative mechanism in which the incoming ligand binds at an axial site. Large substituents at the ortho positions of the N-Ar rings of the Brookhart catalysts disfavor this process, leading to high molecular weight. The ortho-methyl substituents in 2 are too small to inhibit ligand substitution and hence chain transfer, and so a low molecular weight product is formed.
- Normal polypropylene, which contains only  $(-\text{CH}_2\text{CHMe}-)$  units, contains 333 Me branches per 1000 carbons. However,  $(\alpha\text{-diimine})\text{PdR}^+$  catalysts polymerize polypropylene to a chain straightened polypropylene that contains only about 200 branches per 1000 carbons, indicating the presence of many  $\text{CH}_2\text{CH}_2\text{CH}_2$  units. Explain these results. (Hint: Consider insertion regiochemistry.)
  - A 2,1-insertion followed by chain walking leads to a net 1,3 insertion, i.e., incorporation of a linear  $\text{C}_3$  unit in the polymer. About a third of the time the catalyst undergoes 2,1-insertion, resulting in a chain-straightened polypropylene.
- $\text{CF}_3$  is a strong electron withdrawing group, and will affect the electrons of the phenyl group. C-F bonds are also stronger than C-H bonds. Fluorine makes organic compounds more lipophilic, and more hydrophobic.

## 5.7 Homework 5 One-On-One (Anderson)

- Homework 5.3:
  - What do you mean, “what distribution of branch lengths do you expect for your mechanism?”
    - Explain why your mechanism consistent with the expected distribution of branch lengths.
- Homework 5.4:
  - How exactly does the transfer take place? What attacks what? Where do the groups bend and why?
    - Use your hand as a propylene. When the methyl points away from the polymer, that’s not good. We want the methyl pointing towards the polymer. The face that is bound to the metal center is attacked by the alkyl group in metallocene catalysts. External nucleophiles in other reactions attack from the outside. This is very much related to  $\sigma$ -bond metathesis.
- Homework 5.5:
  - Activation step?
    - What I have is correct.
  - Charge on Pd?
    - Neutral.
  - Does MeCN bond datively?
    - Yes.
  - Ridiculous arrow pushing step?
    - It’s ok to have so much stuff happen because it’s a concerted reaction. It doesn’t have to be concerted, but it can be. Tertiary collisions are bad, but intramolecular is fine.

- 2-coordinate species?
  - Keep it tetrasolvated.
- Shannon Stahl is applying the Wacker oxidation to many things. Aerobic oxidations with palladium.
- Homework 5.6-3:
  - Alkynes?
    - Instead of reductive eliminations, use  $\beta$ -H elimination to get a dihydride metal species.
- Misc. test thoughts.
  - He likes bonus reactions. What bonds are being formed? Our Pd cycles from 0 to II. Think of it like a mathematical proof. You've got a toolbox of things that you can do and just see if it gets you closer. So (A) leave it to the end of the test and (B) just try to keep track of electrons, oxidative addition, reductive elimination, etc.
- Misc. thoughts on the class.
  - 201 is a class that builds up. 202 draws on a lot of background knowledge and chemical intuition that takes time to develop.
- Thoughts on PChem.
  - PChem is pretty self-contained. Talk with the instructors.

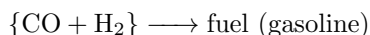
## Unit 6

# More Catalytic Processes 3

### 6.1 Lecture 20: Fischer-Tropsch

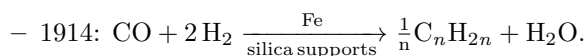
5/19:

- Industrial process mainly, but also has applications to renewable energy.
- Mechanism of the industrial catalysis in the first video; more on the molecular chemistry in the second video.
- General form:

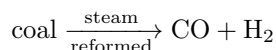


- Clearly, the reactants are Syn gas.
- Thermodynamics of  $\text{CO} + x \text{H}_2 \longrightarrow \text{stuff}$ .
  - As  $x$  increases,  $\Delta H$  and  $\Delta G$  decrease.
  - Conclusion: The more C–H bonds you make, the more thermodynamically favorable the process is.
    - A lot of this comes from the thermodynamic reducing power of hydrogen.

- History:

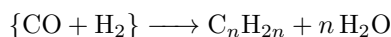


- The ratio of the reactants can be tuned.
- Iron is a solid-state catalyst here. Note that other metals can be used, but iron was the most common.
- The products are a mixture of medium to long chain alkanes, alkenes, and methane.
- The challenge and limitation of this process is that it yields a mixture (a Schultz-Flory distribution) of products.
- This means that there is no real selectivity, although  $\text{C}_7$  is most common.
- This is also why chemists became interested in homogeneous catalysis for this area, because in principle it could give you better selectivity here.
- Industrially:



- This is commonly done in South Africa because they have a lot of coal.
  - $\text{CH}_4$  can also be used as a reactant.
- The ratio of the product gasses can be tuned by the water-gas shift reaction (see Lecture 17), which is  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$  (in the forward direction).

- CO<sub>2</sub> can then be removed.
- One potentially interesting exciting direction that's not been industrially accomplished due to cost is the reverse water-gas shift reaction, which is just the reverse direction.
- The reverse water-gas shift reaction is interesting because if you could convert CO<sub>2</sub> into CO + H<sub>2</sub>O and remove the water, you could feed the CO back into the original process to make gasoline.
- Challenges:
  - Selectivity in the Fischer-Tropsch process.
  - Source of H<sub>2</sub> (right now we get it from fossil fuels). There is research into how to reduce CO<sub>2</sub> into fuels, but if we can get H<sub>2</sub> from somewhere other than fossil fuels, it's a solved problem.
- Conditions (for the following reaction):



- High temperatures (150-300 °C).
  - Favor faster rates and better conversion yield percentages, but more methane (the least valuable product).
- High pressure (1-30 atm).
  - Favors longer chain alkanes and better conversion since methane is a gas (lower likelihood of eliminating it).
- Optimal CO / H<sub>2</sub> concentration.
  - Cobalt catalysts use 1 : 2.
  - Iron catalysts should have relatively more CO.
- Product (Schultz-Flory) distribution:

$$\frac{W_n}{n} = (1 - \alpha)^2 \alpha^{n-1}$$

- $\frac{W_n}{n}$  is the average molecular weight?
- $W_n$  is the weight fraction of hydrocarbons containing  $n$  carbon atoms and  $\alpha$  is the chain growth probability (controlled by the catalyst and the conditions).
- If  $\alpha < 0.5$ , then methane dominates.
- However, as  $\alpha \rightarrow 1$ , the methane fraction decreases relative to the sum of heavy products.
- Sasol (a South African company) mediates this process.
- We can use the products for a variety of different things (heptane for fuel, heavier ones for wax [you can buy Sasol wax], etc.).
- If we were going to do this globally for fuel, we'd have a lot of wax as a byproduct, which we neither have a place to store nor can afford to do since it's so wasteful. Thus, there is great interest in selectivity for C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, or even butene, from which we could do olefin metathesis to make hexanes.
- Two necessary things to use this process for renewable energy:
  1. Find a good source of hydrogen so that we could run the reverse water-gas shift reaction.
    - The reaction might need to be optimized a bit as well, but in principle that can be done; hydrogen is the real problem.
  2. Improve the selectivity of the Fischer-Tropsch chemistry.
- As with the Haber-Bosch process, this is solid support chemistry.
- Mechanism (initial proposal):

- Solid-state iron binds hydrides and CO on its surface, leading the formation of a formyl species before adding another hydrogen to go to a bound alcohol species, losing H<sub>2</sub>O to go to a bound carbene (the carbene is important because it facilitates chain growth), and then proceeding to a bound methyl species. With enough methyl species, you could do other things.
- Gerhard Ertl proves this wrong.
- Mechanism (actual):
  - Solid-state iron binds hydrides and carbonyls on its surface. Next, we split CO to make bound carbides and bound oxides. With more H<sub>2</sub>, we can mix and scramble the carbides, oxides, and hydrides, kicking out H<sub>2</sub>O and making bound carbene species, which can then go on and form the product that we want as described in the initial proposal.
  - Proven with in situ studies performed on the surface of these materials.
- Another key contribution to the proof came from molecular chemistry, which showed that formyl species are generally unstable:

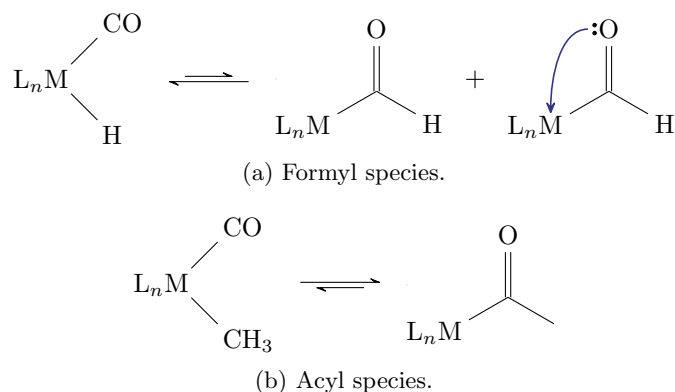
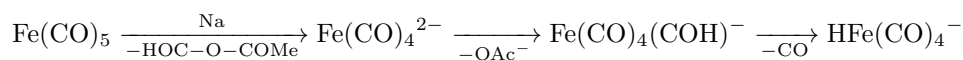
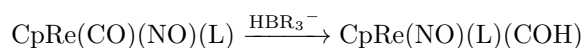


Figure 6.1: Stability of metal-carbonyl derivatives.

- In Figure 6.1a, the reactant is generally favored because it has two bonds instead of one, and metal-hydride bonds are highly thermodynamically favored over metal alkyl bonds.
- In Figure 6.1b, the product is generally favored.
- Think about the equilibrium in terms of the nucleophilicity of the X group. Hydrides are not nucleophilic, whereas alkyl species are.
- The synthesis of metal formyl species was pioneered by Jim Collman in 1973.

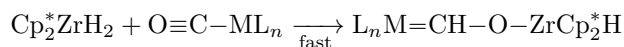


- The first step is ill defined, and the products of it are a messy mixture of carbon-containing products.
- The second intermediate (the formyl species) is unstable and will decompose over time to form the final product.
- Chuck Casey and John Gladys found stable formyl species (the product of the following reaction):



- The reactant is a chiral, 18 e<sup>-</sup>, d<sup>6</sup> species.

- John Bercaw did more with metal-formyl species:



- The first species is an extremely hydridic metal hydride that has very similar properties to LiAlH. It is a  $16e^-$ ,  $d^0$  species.
- This chemistry is driven by the strength of the zirconium bond ( $\approx 130$  kcal/mol).
- Note that although this is technically a formyl species, it's in practice more of a Fischer carbene structure.
  - The bonding is very different and the Lewis acid activation of that strong  $\text{Zr}^{\text{IV}}$  Lewis acid makes this more of a carbene structure.
  - This is useful in C–C coupling reactions.
- One example of  $\text{ML}_n$  is  $\text{Cp}_2\text{W}$ .
- Another one is  $\text{Cp}_2\text{Nb}(\text{H})(\text{CO}) + \text{Cp}_2^*\text{ZrH}_2 \longrightarrow \text{Cp}_2\text{Nb}(\text{H})(\text{CH}-\text{O}-\text{ZrCp}_2^*\text{H}) \xrightleftharpoons{\text{fast}} \text{Cp}_2\text{Nb}(\text{H})(\text{CH}_2-\text{O}-\text{ZrCp}_2^*) \xrightarrow{\text{H}_2} \text{Cp}_2\text{NbH}_3 + \text{Cp}_2^*\text{Zr}(\text{H})(\text{OCH}_3) \xrightarrow{\text{no rxn}} \cdot$ 
  - Nb is niobium.
  - A major problem is once we form that extremely strong metal-oxygen bond, it will not break, so it's very hard to get  $\text{H}_2\text{O}$  off of these species.

- How we think about the molecular systems that form C–C bonds.

- This is ultimately what happens on solid support surfaces in industrial catalysis.
- The challenge is that those industrial systems don't have selectivity; molecular systems could in principle provide this (this is an area of active research).

- To recap, we just talked about the potential of early metal hydrides to activate CO (Bercaw's niobium system took it all the way to a methanol equivalent).

- Bercaw (a titan of organometallic chemistry):

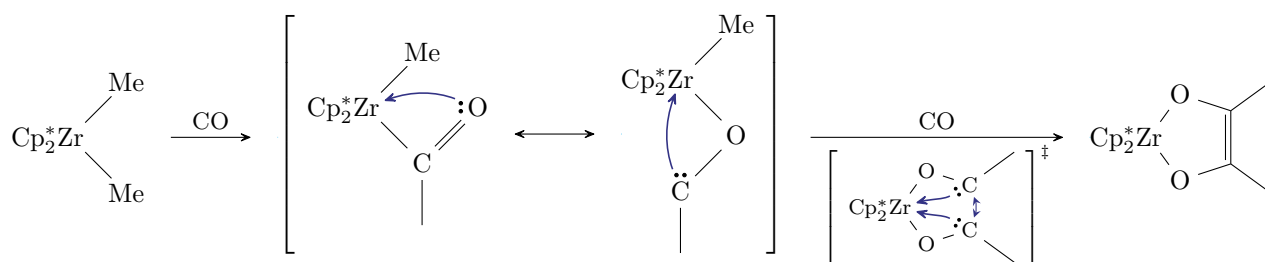


Figure 6.2: Bercaw's first C–C coupling.

- The first ever C–C coupling that was observed in a well-defined and pretty clean way from CO.
  - Using methyl groups makes it imperfect.
  - The mechanism isn't entirely clear.
- The second step proceeds from the second resonance structure.
- Additionally, Bercaw studied reactions with  $\text{Cp}_2^*\text{ZrH}_2\text{CO}$ , a compound with virtually no  $\pi$  back-bonding:
  - $\text{Cp}_2^*\text{ZrH}_2\text{CO} \xrightarrow{\text{H}_2} \text{Cp}_2^*\text{Zr}(\text{H})(\text{OCH}_3)$ , where  $-\text{OCH}_3$  is a methanol equivalent.
  - $\text{Cp}_2^*\text{ZrH}_2\text{CO} \xrightarrow{\text{CO}} \text{Cp}_2^*\text{Zr}(\text{H})-\text{O}-\text{O}-\text{Zr}(\text{H})(\text{Cp}_2^*)$ . Here, we actually see C–C coupling.

- $\text{Cp}_2^*\text{ZrH}_2\text{CO} \xrightarrow{\text{CO}, \text{H}_2} \text{Cp}_2^*\text{Zr}(\text{H})-\text{O}-\text{O}-\text{Zr}(\text{H})(\text{Cp}_2^*)$ . This is even closer to ethylene glycol, but the Zr-O bonds are still an issue.
  - $\text{Cp}_2^*\text{ZrH}_2 + \text{Cp}_2^*\text{Zr}(\text{CO})_2 \longrightarrow \text{Cp}_2^*\text{Zr}(\text{H})-\text{O}-\text{O}-\text{Zr}(\text{H})(\text{Cp}_2^*)$
- Similarly, Tobin Marks looked at  $\text{Cp}_2^*\text{Th}(\text{OR})(\text{H})$  (thorium hydride alkoxides), where  $\text{R} = \text{CH}(t\text{-Bu})_2$  is a pretty bulky super-isopropal ligand abbreviated *i*-Pr\*:

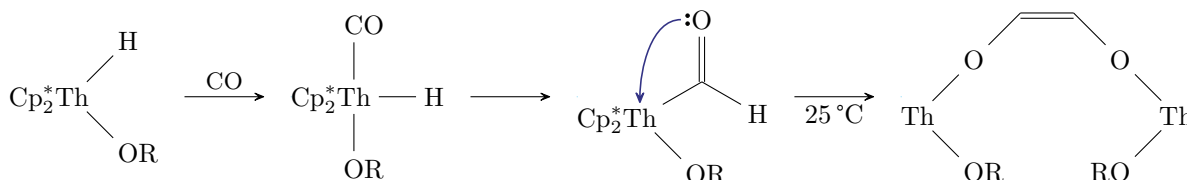


Figure 6.3: Marks' C-C coupling.

- The theme with early metals: If you can get to the Fischer carbene type structure, you can get coupling.
- Pete Wolczanski worked with tantalum silox complexes.
  - $\text{Ta}(\text{OSi}(t\text{-Bu})_3)_3 + 2 \text{CO} \longrightarrow 2 (\text{silox})_3\text{TaO} + (\text{silox})_3\text{Ta}=\text{C}=\text{C}=\text{Ta}(\text{silox})_3$ .
  - This is C-C coupling *and* complete deoxygenation.
- Challenge with all of this chemistry: early-metal oxygen bonds are an extreme thermodynamic sink.
  - Unfortunately, the transition from metal-carbon bonds to metal-oxygen bonds is also the driving force of this reactivity.
  - We can get around this issue by trapping the oxygen with other electrophiles.
- Kit Cummins:  $\text{MoL}_3 \xrightarrow{\text{CO}} \text{L}_3\text{MoCO} \xrightarrow{1 \text{ Na}} \text{Na}[\text{L}_3\text{MoCO}] \xrightarrow[\text{-NaCl}]{\text{Bu}^t-\text{COCl}} \text{L}_3\text{Mo}\equiv\text{C}-\text{O}-\text{COBu}^t \xrightarrow[\text{-CO}_2, \text{H}_2\text{C}=\text{CMe}_2]{\Delta} \text{L}_3\text{Mo}\equiv\text{C}-\text{H} \xrightarrow{\text{KBn}} [\text{L}_3\text{Mo}\equiv\text{C}]^-$ .
  - $\text{L} = \text{N}(t\text{-Bu})(\text{xylyl})$ .
  - The third step is more explained in organic chemistry, where an electrophile like the one added (pivaloyl chloride) should create an ester species and lose NaCl.
  - Note that KBn is benzyl potassium.
  - There are very few examples of terminal carbides, but note that this is similar to what happens on the surface of the solid state iron catalyst.
  - This isn't perfect because we're releasing  $\text{CO}_2$ , but it is a step where the oxygen isn't trapped on the metal center.
- Theodor Agapie (with his graduate student Joshua Buss):

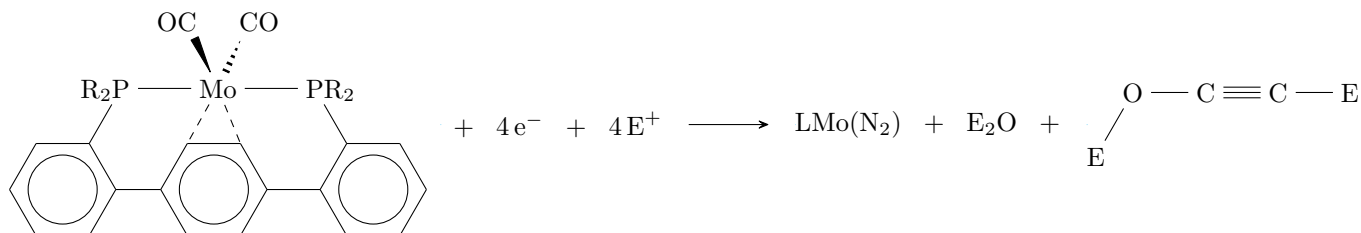


Figure 6.4: Agapie's C-C coupling.



- $\text{KC}_8$  yields the  $4e^-$ .
- The electrophile  $E^+$  is something like  $\text{TMSCl}$ , a silane, or another silyl electrophile.
- This also proceeds through carbides.
- Jonas Peters (on iron):  $\text{Fe}\equiv\text{C}-\text{O} + \text{TMSCl} \longrightarrow \text{Fe}\equiv\text{C}-\text{OTMS}$ .
  - We are trapping the oxygen with an oxygen-silicon bond, which thermodynamically are quite strong.
  - Problem: While a silyl electrophile is substantially better than trapping the metal center (which entirely precludes catalysis), the silyl electrophiles generate stoichiometric waste. We need to trap the oxygen with water, not a silyl ether.
  - Thus, what you ultimately want to do is use later metals (like iron), but use hydrogen instead.
- Dan Suess (graduate student of Jonas Peters):

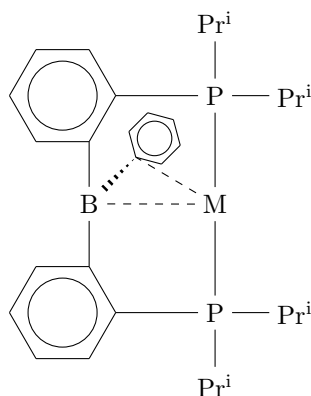


Figure 6.5: The DPB ligand.

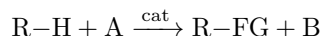
- Investigates various reactions of DPB-bound irons.
- $\text{DPBFe}-\text{N}\equiv\text{N}-\text{FeDPBB} \xrightarrow{4\text{CO}} \text{DPBFe}(\text{CO})_2 \xrightarrow{\text{XS CO}} \text{FeP}_2\text{B}(\text{CO})_3$ .
  - The product here is formally  $\text{Fe}^0$ , but actually slightly higher than that.
- $\text{DPBFe}-\text{N}\equiv\text{N}-\text{FeDPBB} \xrightarrow{4\text{CO}} \text{DPBFe}(\text{CO})_2 \xrightarrow{\text{H}_2} \text{FeP}_2(\kappa^2\text{-BH})\text{H}(\text{CO})_2$ .
- $\text{DPBFe}-\text{N}\equiv\text{N}-\text{FeDPBB} \xrightarrow{4\text{CO}} \text{DPBFe}(\text{CO})_2 \xrightarrow{1\text{K}^0} [\text{FeP}_2(\kappa^2\text{-PhB})(\text{CO})_2]^- \xrightarrow{\text{XS K}^0} [\text{FeP}_2\text{B}(\text{CO})_2]^{2-} \xrightarrow{2\text{TMSOTf}}$  a very weird product.
  - The third intermediate is highly activated and somewhat analogous to  $\text{Fe}(\text{CO})_5^{2-}$ .
  - The product has a  $-\text{C}-\text{OTMS}$  substituent, as well as a tridentate derivative of the DPB ligand that still bonds through the two phosphines, but instead of partially bonding through the boron and the ipso-carbon of the phenyl ring, the boron binds to an additional  $\text{C}-\text{OTMS}$  ligand through the carbon, which in turn binds back to the iron center.
  - This product has many resonance structures; one with particular merit is  $\text{Fe}(\equiv\text{C}-\text{OTMS})_2$  with one of the triple bonds bonding datively to the boron, although it implies an  $\text{Fe}^{\text{VI}}$  oxidation state that is likely an overestimation, even though the iron is certainly high-valent here.
  - Note that if the product is treated with hydrogen, we selectively create (Z)- $\text{TMSO}-\text{C}\equiv\text{C}-\text{OTMS}$ .
  - This is not catalytic, but it is one of the few examples where we don't generate an intractable metal-oxide, and we do generate a  $\text{C}-\text{C}$  coupled product.
- Conclusion: There's a lot of interesting organometallic chemistry surrounding  $\text{C}-\text{O}$  activation and getting that prepped for functionalization, specifically via  $\text{C}-\text{C}$  bond formation.

- This is not a solved problems.
  - While molecular chemistry offers the promise of selectivity, there are real challenges with activating it and getting H<sub>2</sub>O out instead of trapping the oxygen with silyl electrophiles.
  - Part of the issue is the stability of the molecular complexes (they're not as stable as a solid iron surface) and you need a lot of energy to split C≡O bonds. On the other hand, if you apply that energy thermally, it will hurt your selectivity.
- There's some extra molecular chemistry in the notes.

## 6.2 Lecture 21: C–H Activation

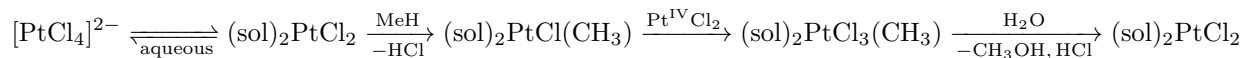
5/21:

- A really active area within the last ten years, and a really powerful synthetic technique for functionalizing molecules.
  - The major problem with selectivity is not yet solved though.
- General form:



- A is a functionalizing reagent, FG is a functional group, and B is a byproduct that usually accepts the proton.
- Examples from organic chemistry:
  - $\text{C}_4\text{H}_{10} \xrightarrow{\text{Br}_2} \text{C}_4\text{H}_9\text{Br}$ .
  - $\text{C}_4\text{H}_{10} \xrightarrow[\Delta]{\text{O}_2} \text{CO}_2 + \text{H}_2\text{O}$ .
- The real challenge from an organometallic perspective is selectivity:
  1. Internal C–H bonds are typically more reactive.
  2. The product is typically more reactive than the starting material.
    - We need to prevent over-oxidation.
- Another challenge is the thermodynamics of this process.
- For example:
  - $\text{C}_6\text{H}_6 + \text{CO} \longrightarrow \text{C}_6\text{H}_5(\text{COH})$  has  $\Delta H = 1.7 \text{ kcal/mol}$ .
  - $\text{R-H} + \text{H-X} \longrightarrow \text{R-X} + \text{H}_2$  has  $\Delta H = 22 \text{ kcal/mol}$  when  $\text{X} = \text{OH}$ .
  - $\text{R}-\text{--} \longrightarrow \text{R}=\text{+} + \text{H}_2$  has  $\Delta H = 30 \text{ kcal/mol}$ .
  - You will get some entropic favorability, but you need to put in a lot of driving force — and whenever you do this, selectivity and over-oxidation become problems.
- Classic studies (Shilov's catalyst):
  - $\text{K}_2\text{PtCl}_6 + \text{CH}_3\text{CO}_2\text{D} + \text{D}_2\text{O}$  can be mixed with alkanes to incorporate deuterium into said alkanes.
    - Note that  $\text{K}_2\text{PtCl}_6$  is an oxidant.
  - Data listed.
  - Conclusion: Higher degrees of substitution at less substituted carbons.
  - Basically, you can do this:  $\text{R-H} \xrightarrow[\text{DClO}_4, \text{CH}_3\text{CO}_2\text{D}, \text{D}_2\text{O}]{\text{K}_2\text{PtCl}_4 (12\%)} \text{R-D}$ .
  - Also:  $\text{C}_5\text{H}_{12} + \text{H}_2\text{PtCl}_6 \xrightarrow[\text{H}_2\text{O}]{\text{NaPtCl}_4} \text{C}_5\text{H}_{11}\text{Cl}$  on both the 1- and 2-carbons.

- Mechanism (monooxidation to form alcohols [very useful]):



- The fact that this process activates methane (MeH) is very good because we have a lot of it and the only thing it's good for is burning.
  - It's not economically viable to capture all the extra methane on oil fields and transport it (instead, they flare it off because that's better for the environment than just releasing it).
  - However, if they could functionalize it immediately and turn it into methanol liquid, which can be transported, that would be a huge boon to industry and the environment.
- In the last step, water attacks the methyl group on the platinum catalyst, releasing methanol and then reductively eliminating HCl.
- However, the challenge with this is the second step (with  $\text{Pt}^{\text{IV}}\text{Cl}$ )
  - For whatever reason, the only oxidant that kinetically works is  $\text{Pt}^{\text{VI}}$ . But we need a lower oxidation state oxidant to solve this problem. Yet we haven't despite decades of research.
- The closest we've come to a solution is work by Periana:  $\text{CH}_4 + \text{H}_2\text{SO}_4 \xrightarrow{\text{cat}} \text{CH}_3\text{SO}_3\text{H} + 2\text{H}_2\text{O} + \text{SO}_2$ .
  - $\text{CH}_3\text{SO}_3\text{H}$  is methyl sulfuric acid.
  - The catalyst is a dichloride platinum species with a bidentate chelating dipyrmidine species.
  - $\text{TOF} = 1 \times 10^{-2} \text{ s}^{-1}$ .
  - $\text{TON} \approx 7500$ .
  - The TOF and TON are not viable for a large scale industrial process with platinum, but are pretty good.
- Thus, in principle, we could do this industrially with the following.

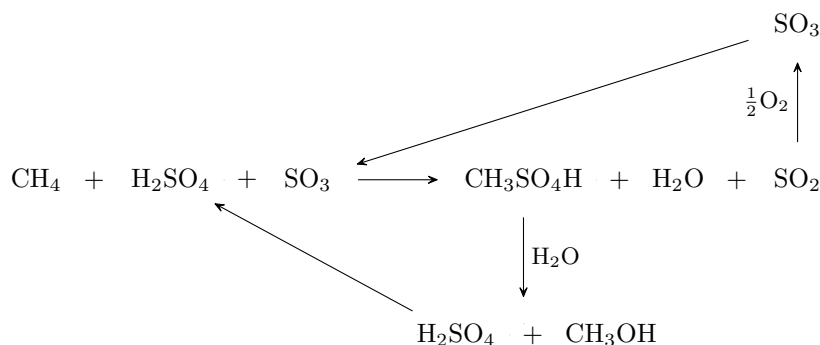
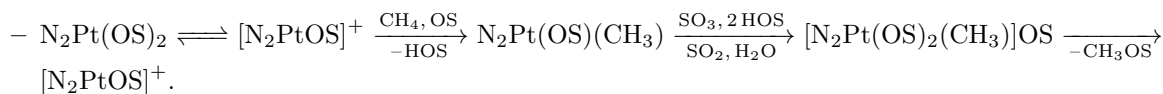


Figure 6.6: An industrial version of Shilov's monooxidation to form alcohols.

- This is pretty powerful, but there are problems:
- $\text{H}_2\text{SO}_4$  is corrosive, which means that this process is hard to scale up.
- Separation of  $\text{CH}_3\text{OH}$  from  $\text{H}_2\text{SO}_4$  is also hard (adds cost).
- The platinum catalyst is also expensive, so you would need a much higher turnover number to make it viable.
  - This is more of a solvable issue; the others, not so much.
- Mechanism:



■ Sulfate and related species are abbreviated to OS.

– This is the closest we've gotten to a catalytic process for converting methane into methanol so far.

– Mechanistic notes:

1.  $\sigma$  adducts.

■ A key step is binding methane, but methane is a terrible ligand.

■  $\text{M}(\text{H})(\text{CH}_3) \longrightarrow \text{M}(\text{H})(\text{CH}_3)$ .

■ There exist other platinum systems where we can study this process in some detail, such as:  $(\kappa^2\text{-Ph}_2\text{B}(\text{CH}_2\text{PR}_2)_2)\text{Pt}(\text{THF})(\text{CH}_3) \xrightarrow[\text{-CH}_4]{\text{C}_6\text{H}_6, 50^\circ\text{C}} \text{Pt}(\text{THF})(\text{C}_6\text{H}_5)$ .

· This presumably proceeds through benzene as a  $\sigma$  adduct.

2. Oxidation.

■ In the Shilov system, if you use labels, quenching  $^{195}\text{PtCl}_6^{2-}$ , you get no  $^{195}\text{PtMe}$  complexes.

■ Indeed, it appears that  $\text{PtCl}_6^{2-}$  is acting purely as a  $\text{Cl}_2$  source.

3. Reductive elimination.

■ An external nucleophilic attack, as generally supported by mechanistic studies.

■  $(\kappa^2\text{-PR}_2\text{CH}_2\text{CH}_2\text{PR}_2)\text{Pt}(\text{CH}_3)_3\text{OR} \rightleftharpoons [(\kappa^2\text{-PR}_2\text{CH}_2\text{CH}_2\text{PR}_2)\text{Pt}(\text{CH}_3)_3]\text{OR} \xrightarrow{\text{OR}'} (\kappa^2\text{-PR}_2\text{CH}_2\text{CH}_2\text{PR}_2)\text{Pt}(\text{CH}_3)_2 + \text{CH}_3\text{OR} + \text{CH}_3\text{OR}'$ .

■  $[\text{PtCl}_5(\text{CH}_3)]^{2-} \xrightarrow[\text{-Cl}^-]{\text{H}_2\text{O}} [\text{PtCl}_4\text{Me}]^- \text{Cl}^- \xrightarrow{\text{H}_2\text{O}} \text{PtCl}_4^{2-} + \text{MeOH} + \text{H}^+$ .

■  $[\text{PtCl}_5(\text{CH}_3)]^{2-} \xrightarrow[\text{-Cl}^-]{\text{Cl}} [\text{PtCl}_4\text{Me}]^- \text{Cl}^- \xrightarrow{\text{Cl}} \text{PtCl}_4^{2-} + \text{CH}_3\text{Cl}$ .

■ Labeling studies also support the inversion of stereochemistry.

• While methane activation may not yet be feasible industrially, it is in the pharmaceutical industry.

• Directed C–H activation.

• Examples:

– Early:  $(i\text{-Pr})(\text{H}_2\text{N})(\text{H})\text{C}-\text{COOH} \xrightarrow{\text{cat/ox}} \text{H}_2 + \text{the cyclized product}$ .

■ Catalyst is  $\text{K}_2\text{PtCl}_4$ .

■ Using  $\text{PtCl}_6^{2-}$  (10%) as an oxidant gives a 21% yield.

■ Using  $\text{CoCl}_2$  (10%) as an oxidant and a lower catalyst loading gives a 67% yield.

■ Using  $\text{CoCl}_2$  (5%) as an oxidant and a dramatically lower catalyst loading gives a 20% yield.

■ Because this is giving a higher yield than catalytically, something else is probably going on.

– Palladium has started to dominate over platinum.

– Sanford:  $(\text{Me})(\text{CH}_3\text{N})\text{C}-\text{CMe}_3 \xrightarrow{\text{Pd}(\text{OAc})_2} [(\text{Me})(\text{CH}_3\text{N})\text{C}-\text{CMe}_2\text{CH}_2\text{Pd}(\mu\text{-OAc})]_2 \xrightarrow{\text{PhI}(\text{OAc})_2} (\text{Me})(\text{CH}_3\text{N})\text{C}-\text{C}(\text{CH}_2\text{X})(\text{CH}_2\text{Y})(\text{MeOAc})$  where X and Y are functional groups.

■ This gives a picture of where palladium can directly activate a C–H bond.

– Further examples from Jin-Quan Yu and Guangbin Dong (UChicago).

– The key in all of these examples is a directing nitrogen, to which the palladium catalyst bonds, bringing it close to the hydrogen that we want to activate.

■ This is nicely demonstrated by Guangbin Dong's example, as seen in Figure 6.7.

■ By placing the palladium and hydrogen close together, we can facilitate the oxidative addition even if it is unfavorable or has a high barrier. The chelate effect really helps here.

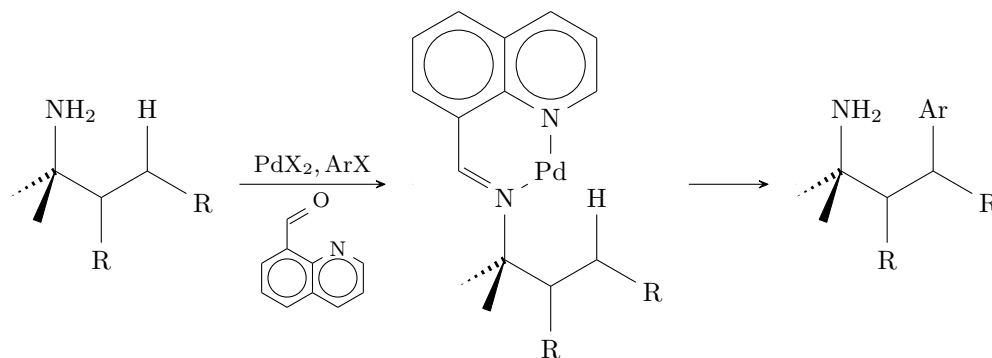


Figure 6.7: Dong's directed C-H activation.

- One of the key features of C-H activation is C-H's are terrible ligands, so tricks like this are essential to get a high effective concentration to drive the forward reaction.
- You can also intercept C-H activations to do carbonylations.
- Examples:
  - $\text{C}_6\text{H}_6 + \text{CO} \xrightarrow[\text{K}_2\text{S}_2\text{O}_8 / \text{TFA}]{\text{Pd}(\text{OAc})_2 (10\%)}$   $\text{C}_6\text{H}_5\text{CO}_2\text{H} (100\%)^{[1]}$ .
    - Persulfate is our oxidant here.
    - Run at room temperature for 20 hours.
  - $\text{C}_6\text{H}_{12} + \text{CO} \xrightarrow[\text{K}_2\text{S}_2\text{O}_8 / \text{TFA}]{\text{RT} (10\%)}$   $\text{C}_6\text{H}_{11}\text{CO}_2\text{H} (4\%)$ .
  - $\text{CH}_4 + \text{CO} \xrightarrow[\text{K}_2\text{S}_2\text{O}_8 / \text{TFA}]{\text{VO}(\text{acac})_2, 80^\circ\text{C}}$   $\text{HC}_2\text{H}_3\text{O}_2 (93\%)^{[2]}$ .
    - Run at  $80^\circ\text{C}$  for 20 hours.
    - TON = 18.
    - We can also do this without persulfate:
  - $\text{CH}_4 + \text{CO} + \frac{1}{2}\text{O}_2 \xrightarrow[\text{H}_2\text{O}]{\text{RhCl}_3}$   $\text{HC}_2\text{H}_3\text{O}_2$ .
    - Run at  $100^\circ\text{C}$ .
  - $2\text{CH}_4 + \text{H}_2\text{SO}_4 \xrightarrow{\text{Pd}^{\text{II}}} \text{CH}_3\text{CO}_2\text{H} + 4\text{SO}_2 + 6\text{H}_2\text{O}$ .
    - Work by Periana.
    - C-C coupling reactivity (related to Fischer-Tropsch).
    - Can pretty easily be pushed to make methane: Reverse water-gas shift to syn gas, Fischer-Tropsch to methane, couple methane to an acetic acid product, to make a chain, to make higher order C-C-coupled products, to feed into other industrial processes.
    - Mechanism shown (not a ton is known, but there are a lot of proposed possible interconversions).
- The key equilibrium that one needs to control for C-H activation:  $\text{M} + \text{H}-\text{CR}_3 \rightleftharpoons \text{M}(\text{H})\text{CR}_3 \rightleftharpoons \text{M}(\text{H})(\text{CR}_3)$ .
  - Typically, the first step is the hard step because C-H ligands are very poor ligands.
    - Even if the C-H activation is thermodynamically stable, you're stuck without the adduct.
  - How to control these equilibria:

<sup>1</sup>Note that TFA is trifluoro acetic acid.<sup>2</sup>VO(acac)<sub>2</sub> is vanadyl acetylacetonate.

1. Ligands that are good  $\sigma$ -donors (i.e., electron-rich metal centers) favor the products.
  2.  $M^{n+2} d^6$  is common, e.g.,  $\text{Ir}^{\text{I/III}}$ ,  $\text{Pt}^{\text{II/IV}}$ ,  $\text{Pd}^{\text{II/IV}}$ .
  3. Most common for  $4d$  and  $5d$  metals because higher oxidation states are more stable as you go down a column and there are stronger bonds that will push the equilibrium toward the right.
  4. Small(ish) R's help.
  5. Less sterically hindered metals.
  6. Electronically unsaturated metals ( $\leq 16e^-$ ) help.
- Thermodynamics of activating C–H bonds.
    - Data listed.
    - Conclusion 1: Thermodynamically, it's more favorable to activate secondary and tertiary C–H's, but sterically, it's more favorable to activate primary ones.
    - Conclusion 2: Thermodynamically, it's more favorable to activate  $\text{H}_3\text{C}-\text{H} > \text{Ph}-\text{H} > \text{RC}\equiv\text{C}-\text{H}$ . It's easier to activate Ph–H bonds over  $\text{H}_3\text{C}-\text{H}$  bonds despite the inverse difference in bond strengths because metals can form  $\pi$  adducts with arenes. This bypasses the hard step, allowing the oxidative addition to HMPH to proceed relatively easily.
  - Thinking more about  $\sigma$  adducts and oxidative addition:
  - Bob Bergman:  $\text{Cp}^*\text{IrH}_2(\text{PMe}_3) \xrightarrow[-\text{H}_2]{h\nu} [\text{Cp}^*\text{Ir}(\text{PMe}_3)] \xrightarrow{\text{C}_6\text{H}_{12}} \text{Cp}^*\text{Ir}(\text{PMe}_3)(\kappa^2\text{-C}_6\text{H}_{12}) \xrightarrow[\text{chromatography}]{h\nu} \text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{Cy})(\text{H}) \xrightarrow[-\text{C}_6\text{H}_{12}]{\text{C}_5\text{H}_{12}} \text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})(\text{C}_5\text{H}_{11})^{[3]}$ .
    - There could also be  $\sigma$ -bond metathesis pathways, but it's likely a reductive elimination type process.
  - Isotope effects:
    - Kinetic isotope effects (KIEs) are common mechanistic probes.
    - Data listed.
    - In a primary KIE, you would expect protons to react faster than deuterium because they're lighter, they tunnel faster, etc.
      - Symbolically, you would expect  $\frac{k_{\text{H}}}{k_{\text{D}}} > 1$ .
    - However, tungsten and iridium have an inverse KIE (deuterium is faster than hydrogen).
    - Explaining KIEs (in terms of vibrational energy).
    - Normal KIEs:

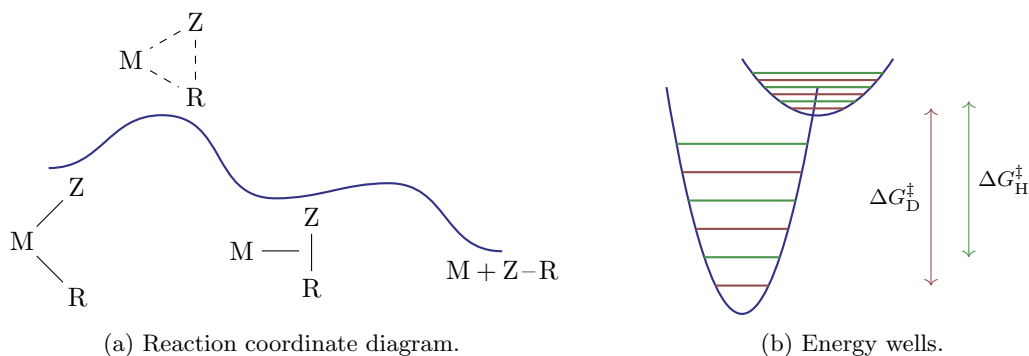


Figure 6.8: Normal KIE.

<sup>3</sup>Note that Cy is an abbreviation for cyclohexyl.

- In Figure 6.8a, Z is either a proton or deuterium.
  - Notice that this is a downhill reaction.
  - The key transition state is the first one.
  - Because we're eliminating a strong bond (a C–H bond), we have a transition state with a weaker bond.
  - Recall that  $E = h\nu$  and  $\nu \propto \sqrt{1/\mu}$ , where  $\mu$  is the effective mass of the oscillators and the transition state. Thus, energy decreases as effective mass increases.
  - Now think of vibrational wells for the reactant and the transition state (see Figure 6.8b). A proton and deuterium will have identical vibrational spacing, but the levels for deuterium will be lower because deuterium has lower energy. Note also that the spacing is closer together in the wider well because it is wider.
  - Thus, we have here that  $\Delta G_{\text{H}}^{\ddagger} < \Delta G_{\text{D}}^{\ddagger}$  due to zero-point energy effects.
  - Essentially, if the transition state has weaker bonds than the starting material, a normal KIE is expected.
- Inverse KIE:

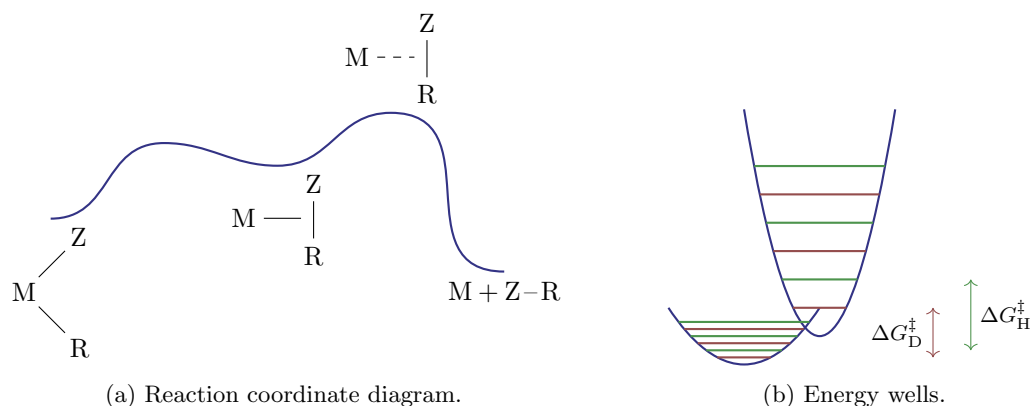


Figure 6.9: Inverse KIE.

- Notice that this is an uphill reaction.
  - The key transition state is the second one.
  - Here, we have a transition state with a stronger bond.
  - Thus, we have here that  $\Delta G_{\text{D}}^{\ddagger} < \Delta G_{\text{H}}^{\ddagger}$ .
  - Essentially, an inverse KIE originates from a transition state having stronger bonds than the starting material, i.e., “later” transition states.
- This can also arise from equilibrium isotope effects.
- Bernskoetter et al. (2009): Observed  $\sigma$  adducts with  $\text{CH}_4$ .
    - Took rhodium bound to a pincer ligand and a methyl group.
    - Treated it with an acid ( $[\text{HBAr}^{\text{F}}] \cdot 2\text{Et}_2\text{O}$  [an etherate]) and a funky solvent ( $\text{CD}_2\text{Cl}_2\text{F}$ ) at a very cold temperature ( $-110^\circ\text{C}$ ) to make a rhodium  $\kappa^2$  methane complex.
    - With NMR spectroscopy, they can tell that the methane is rapidly spinning around, so all hydrides are bonding now and then (equilibrating).
    - Comparing the C–H coupling constants for the adduct vs. free methane reveals a slight weakening of the C–H bond, but more importantly, the Rh–H coupling constant is quite a bit weaker than you would expect for a full hydride.
  - Primary take away: Directed C–H activation is a very powerful technique because you can put these C–H bonds in close proximity, but one of the biggest challenges is forming  $\sigma$  adducts; in doing this, we can observe the weird inverse KIEs of Figures 6.8 and 6.9.

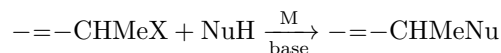
## 6.3 Midterm 2 Review

- 5/22:
- Midterm 2: 5/25 from 6:00-8:00 PM (proctored by Sophie).
  - No discussion on the 25th — this is replacing that. Office hours are still on.
  - If we follow her comments on the papers, we're almost guaranteed to get a good grade.
    - She's taking time — if she gets our drafts back late, she'll give us an extension.
  - Midterm 2 content (top things to focus on in order):
    1. N<sub>2</sub> reduction (the question on dinitrogen reduction from one of your homeworks; really know this).
      - The Schrock paper is really helpful for this!
      - Be able to understand  $\sigma$  donation and  $\pi$  acceptance.
      - Be able to draw orbitals.
      - Know Chatt and Hoffmann mechanisms.
      - First row vs. late row metal preferences.
      - We can show adding a proton and electron together (we don't need to do this separately).
      - Show oxidation states for every intermediate!
    2. Polymerization (chain walking and transfer, how to get the different tacticities).
      - Know the example from your homework.
      - Know the Wacker oxidation.
    3. Hydrogenation/dehydrogenation.
    4. Metathesis (last question on HW 3).
    5. Hydroformylation, hydrocyanation.
    6. Fundamentals of organometallic reactions: Coordination preferences, insertion/elimination preferences, dihydrogen vs. dihydride, just practice going through and drawing mechanisms.
    7. Strong foundation in ligand donor properties — seriously study homeworks and past tests.
      - Relate to “is this exam cumulative?” question.
      - Know CO, ligand binding properties, high spin/low spin, etc.
  - The best way to get better at time is to just practice drawing these mechanisms.
    - Go through it when you first get it, do the questions you know quickly, and then proceed to the harder ones.
  - See example questions posted!
  - Explain how a  $C_i$  catalyst gives a hemi-isotactic polypropylene after activation with MAO to give a Zr alkyl and draw the mechanism of chain growth.
    - Activation step:  $L_nMCl_2 \xrightarrow{MAO} L_nMMe^+$ .
      - MMAO is another catalyst that's even more spicy.
    - Squiggly methyl means methyl bound with either/unknown stereochemistry.
  - TEMPO is a well-known radical trap.



## 6.4 Lecture 22: Allylic Substitution

5/24: • General form:



- We feed in an allylic olefin.
- You don't always need a base.
- Seems like a simple  $S_N2$ , but there is also other regiochemistry (for instance, the double bond can migrate; see the two products in Figure 6.10).
- Additionally, the mechanism is quite different than that of  $S_N2$ , which grants alternative selectivity in terms of both enantiocontrol and regiocontrol.

• Mechanism:

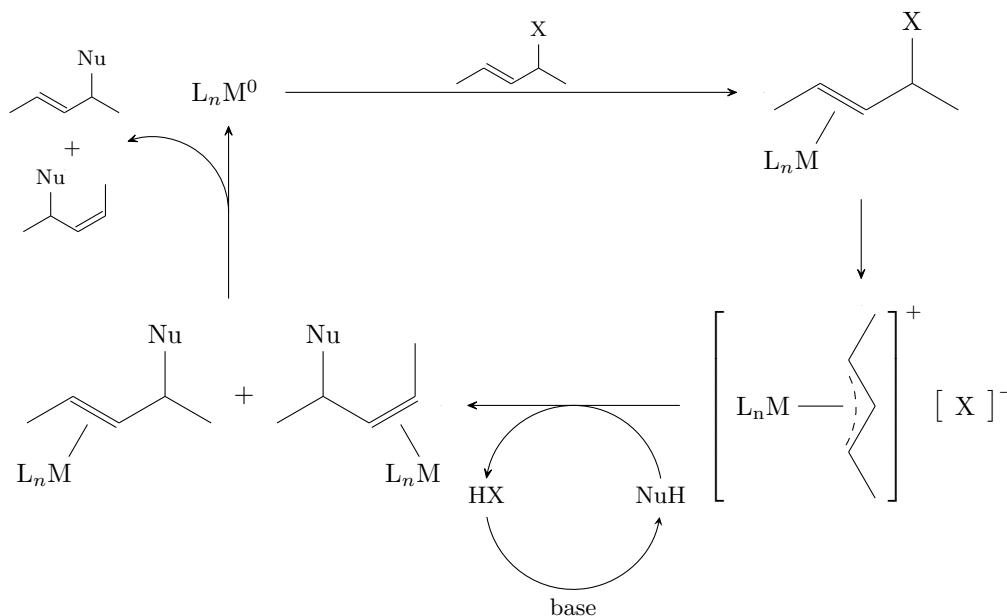
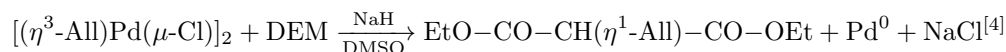


Figure 6.10: Allylic substitution mechanism.

- M is frequently palladium.
- X can be an ester, carbonate, phosphonate, hydroxyl, acetate, etc.
- Nu can be an aryl oxide, amine, malonate, etc.
- $L_nPd$  can be  $Pd(PPh_3)_4$  or  $Pd(acac)_2(PPh_3)$ .
- The second step is an oxidative addition to form an allylic species.
- Most cases are an external attack opposite of the metal.

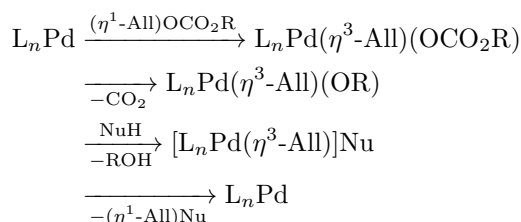
• Tsuji:



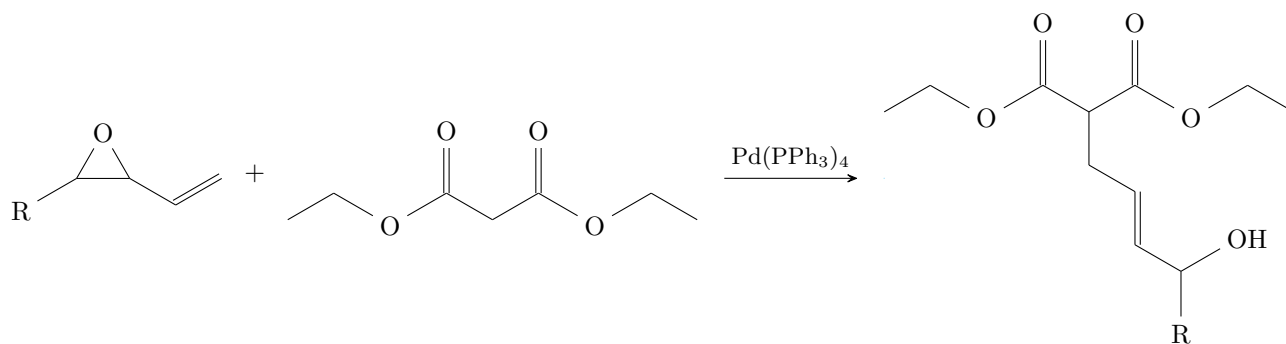
- One of the earliest stoichiometric examples.
- Taking a process that is not catalytic and making it catalytic.

<sup>4</sup>All is an allyl group. DEM is diethyl malonate (see the second reactant in Figure 6.11a).

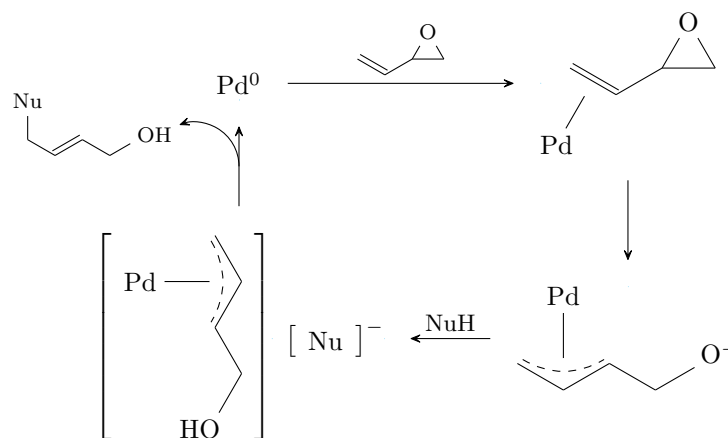
- Trost pioneers enantioselectivity for this process, which is highly sought after.
  - Achieves 24% ee at first with a chiral ligand at  $-40^{\circ}\text{C}$ .
  - Enantioselectivity is easy because you're erasing any enantioselectivity of the starting material when you planarize into an allyl group and then you can selectively install the enantiochemistry you want in the second step by controlling which face binds to the metal center.
- Nucleophile reactivity: Allyl carbonates > phosphates > acetates.
  - Between an allyl acetate and an allyl carbonate, we might expect the acetate species to be more reactive on the basis of sterics.
    - Note that sterics do have some effect: Using bulkier ligands favors allyl acetates.
  - However, the allyl carbonate is more reactive since they make it so that you don't need a base:



- The loss of  $\text{CO}_2$  and the subsequent formation of an alkoxide generates base in situ.
  - Normally, you would eliminate  $\text{HX}$ , but here you don't so you don't have to deal with it.
- Epoxides are similar in that they don't need a base.



(a) General form.



(b) Mechanism.

Figure 6.11: Epoxide allylic substitution.

- The reaction in Figure 6.11a has an 84% yield.
- Nucleophiles:
  - Very broad scope of possible ones.
    - Less common with hard, anionic nucleophiles (e.g., amines, amides, imides, aryl oxides).
    - Softer nucleophiles are preferred (malonates, enolates, malononitriles).
    - These preferences originate from the softness of the palladium center.
  - Thus, very useful.
- One last example (electrophile and nucleophile in the same substrate):

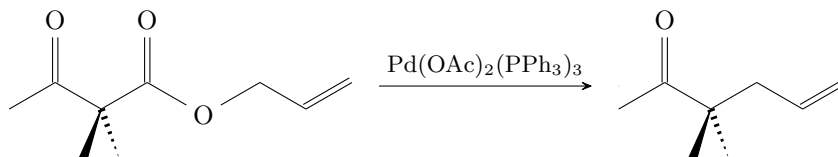


Figure 6.12: Decarbonylization using allylic substitution chemistry.

- A decarbonylative process that proceeds through allylic chemistry.
- Mechanism shown.

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