CHEM 20200 (Inorganic Chemistry II) Notes

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April 22, 2021

Units

List of Figures

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 contration**: 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 Mn^{2+}.
- Magnetic properties: Unique to the transition metals and the f block.
  - Consider $Fe^{II}L_6{}^{2+}$ (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 Δ_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 Fe^{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 χT of Fe^{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.

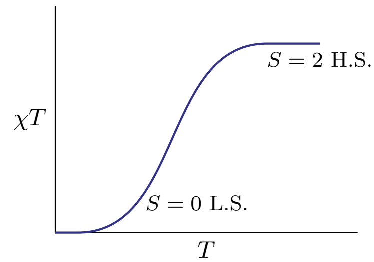


Figure 1.1: Magnetic moment vs. temperature for the Fe^{II} ion.

- Dq and PE values depend on:
  - Ligand field strength.
    - ΔO_h increases as σ donation increases.
    - ΔO_h increases as π acceptance increases.
    - ΔO_h decreases as π 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 ΔO_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, ΔO_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 σ-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):

$$\mathrm{Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pd^{4+}}$$

- Hard/soft acid-base theory:
  - Common Lewis acids:
    - Proton: H^+.
    - Molecules with no octet: $AlCl_3$, BR_3 (boranes), BeH_2.
    - Metal cations: Na^+, Ti^{4+}.
    - π acids: CO_2, CO, PR_3.
  - Common Lewis bases:
    - Carbanions: CR_3.

        - Hydrides: KH, NaH, $LiAlH_4$.
        - Amines, amides, and phosphines: NH_3, PR_4, NH_2^-.
        - OH_2, SR_2, OH^-.
        - Halides: F^-, Cl^-, Br^-.
        - Carbonyl: CO (means CO is amphoteric).
        - Olefins: C_2H_4.
    - Distinguishes hard vs. soft[1].

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 π systems.
- 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 CO in their bonding, such as NO and N_2, are frequently included" (Spessard & Miessler, 2010, p. 4).
- In the anionic component of Zeise's salt, the π electrons of ethene bond to a $PtCl_3^-$ 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).

[1] Hard vs. soft is the basis for the solubility rules!

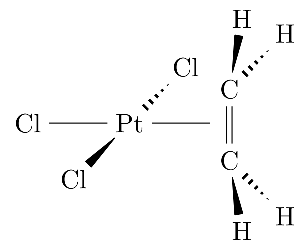


Figure 1.2: π bonding in Zeise's salt.

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, 18 e^- 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 1 e^- coupled.
     - Why?
  7. More difficult to reduce as you go down a triad (column).
- Common structures:

- 4 coordinate:

(a) Structure. (b) d orbitals.

Figure 1.3: Square planar information.

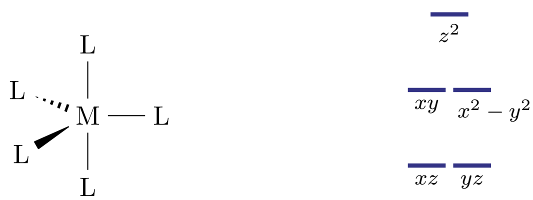
  - Square planar (note that the z^2 orbital can swap with the three degenerate orbitals beneath it fairly easily; what's important is that $x^2 - y^2$ is higher).

(a) Structure. (b) d orbitals.

Figure 1.4: Tetrahedral information.

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

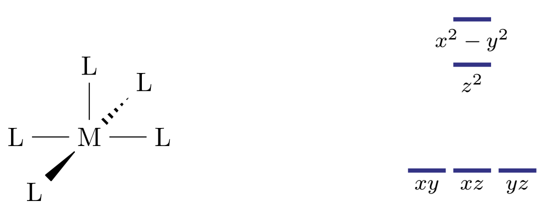
- 5 coordinate:



(a) Structure. (b) d orbitals.

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**).



(a) Structure. (b) d orbitals.

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.

(a) Structure. (b) d orbitals.

Figure 1.7: Octahedral information.

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

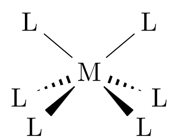


Figure 1.8: Trigonal biprysmatic information (structure).

- Trigonal biprysmatic (each pyramid is eclipsed, rather than staggered as in octahedral; Pfennig 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 σ donation, and Z if it participates in π acceptance).
  – Similar to how Cl^- can be both a σ and π 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 CH_4 for example, we want to fill the σ and π MOs with all 8 electrons that they can hold, but leave σ^* and π^* unfilled (see Figure III.17 in Labalme (2021)).
  – However, in ML_6 for example (considering only d orbital/ligand σ orbital interactions), we have nine σ/nonbonding orbitals that are ok to fill up and two σ^* 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 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 σ/NB ligand orbitals plus 4 nonbonding metal d orbitals gives 8 σ/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 benezene]). 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 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 $M-PR_3$ 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 $M-C\equiv O$ bond, but we can robustly treat this with the covalent method.
  - $M - C \equiv \overset{\oplus}{O}:$ has a +1 formal charge and 1 covalent bond, suggesting that CO is a 2-electron donor.
  - $M = C = \ddot{O}:$ has no formal charge and 2 covalent bonds, suggesting that CO is a 2-electron donor.
  - $M \equiv C - \overset{\ominus}{\ddot{O}}:$ has a −1 formal charge and 3 covalent bonds, suggesting that CO is a 2-electron donor.
  - $M \leftarrow :\overset{\ominus}{C} \equiv \overset{\oplus}{O}:$ 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 $M - \overset{\oplus}{N} \equiv \overset{\oplus}{O}:$ as a possible resonance structure).
  - If NO bonds bent, it's a 1-electron donor (take $M - \ddot{N} = \ddot{O}:$ 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 6π-electron aromatic system.
    - There are two of these anions, with a total charge of 2− between them, so iron must be in the Fe^{2+} oxidation state to compensate.
    - This makes iron d^6, which plays well with 18 electron systems.
  - Hexamethyl tungsten $W(CH_3)_6$ (covalent method):
    - Each 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.
  - $W(CH_3)_6$ (ionic method):
    - For each ligand, we split to W^+ and $CH_3{}^-$.
    - This makes the metal center oxidation state W^{VI}, with a resultant d^0 configuration.

- $W(CO)_6$ (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.
- $W(CO)_6$ (ionic method):
  - We split $W-CO$ into $W^0 + CO$.
- ${Pt(Cl)_4}^{2-}$ (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.
- ${Pt(Cl)_4}^{2-}$ (ionic method):
  - $Pt-Cl \longrightarrow Pt^+ + Cl^-$.
  - Thus, we have Pt^{4+}. But the charge is $2-$, so we actually have Pt^{2+}, which is d^8, which plays well with the 16-electron system.
- An enzymatic cofactor (covalent method):

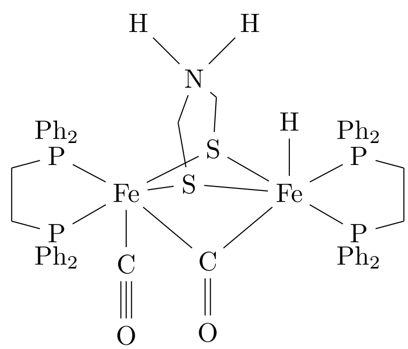


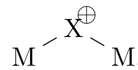
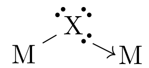
Figure 1.9: An enzymatic cofactor.

  - 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

$$\#\text{ of M}-\text{M bonds} = (18\,\text{e}^-\text{'s} \cdot \#\text{ of metals} - \#\text{ of e}^-\text{'s from L's and M}^0\text{'s})/2$$

  - 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: .
  - Alternatively, we can recognize what the nature of the interaction is: .
    - 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:

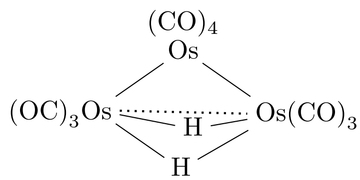


Figure 1.10: Electron counting for $Os_3(CO)_{10}(\mu_2\text{-}H)_2$.

  - 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 $Cr(CO)_6$ has 18 electrons and is stable that the isoelectronic compounds $V(CO)_6{}^-$ and $Mn(CO)_6{}^+$ 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 $Ni(CO)_4$, $Co(NO)(CO)_3$, and $Fe(NO)_2(CO)_2$.
  - Also $Mn(CO)_5$, $[CpMn(CO)_2]^-$, and $CpFe(CO)_2$ (these are isoelectronic, but not isolobal).
- We can also consider isolobal analogies between transition-metal-complex electron counts and organic fragments.
  - For example,

$$\begin{gathered}
18\,e^- \underset{0}{\longleftrightarrow} CH_4\\
17\,e^- \underset{0}{\longleftrightarrow} \cdot CH_3\\
16\,e^- \underset{0}{\longleftrightarrow} :CH_2\\
15\,e^- \underset{0}{\longleftrightarrow} \dot{\underset{\cdot}{\cdot C}}H\\
14\,e^- \underset{0}{\longleftrightarrow} \cdot\dot{\underset{\cdot}{C}}\cdot
\end{gathered}$$

  - We can also make analogies between other atoms/metal fragments: $\cdot\dot{\text{P}}\cdot \underset{\circ}{\longleftrightarrow} \,\vdots\text{CH} \underset{\circ}{\longleftrightarrow} (\text{CO})_3\text{Co}$.
  - Multiply bonded fragments can also work: M=O $\underset{\circ}{\longleftrightarrow}$ M=N−R $\underset{\circ}{\longleftrightarrow}$ $R_2C{=}O$ for double bonds, and for triple bonds: M≡O $\underset{\circ}{\longleftrightarrow}$ M≡N−R $\underset{\circ}{\longleftrightarrow}$ $[\text{R−C≡N−H}]^+$.
- **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 Fp^- (is this the right spelling? Does it have a charge by itself?) fragments (a Fp^- fragment is $\text{CpFe(CO)}_2{}^-$).

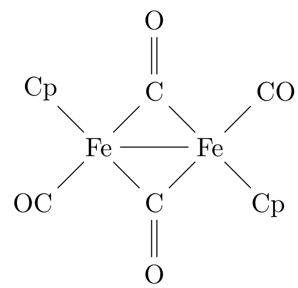


Figure 1.11: Two dimerized Fp^- fragments.

  - The oxidation state of each iron is Fe^{I} (since Cp is the only electronegative ligand).
  - The valence of each iron is Fe^{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 (Fe^{II}), not d^7 (Fe^{I}).
  - Does the iron have tetrahedral or square planar geometry and why?
- Now consider the compound $[\text{CpFe(CO)}_2\text{AlMe}_3]^-$.
  - The oxidation state of the iron is Fe^{II}.
  - The valence of the iron is Fe^{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 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.
  - κ can also be denoted by χ_V.
  - More on χ_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 χ_{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 μ 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)), β 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.

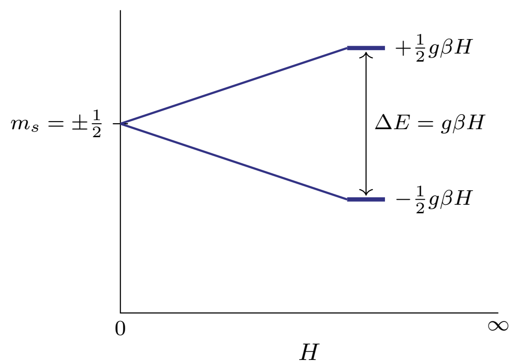


Figure 1.12: A Zeeman splitting diagram for a single electron.

    - 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 ΔE 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

$$M = \frac{Ng^2\beta^2}{4k_BT}H$$

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

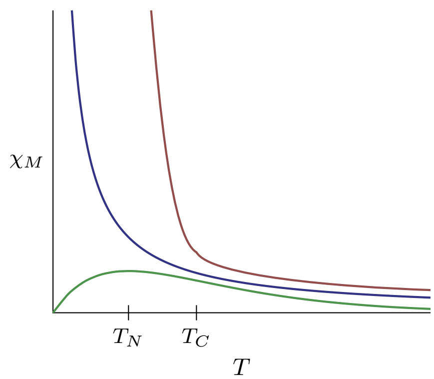
- But since $\chi_M = \frac{M}{H}$, this implies that

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

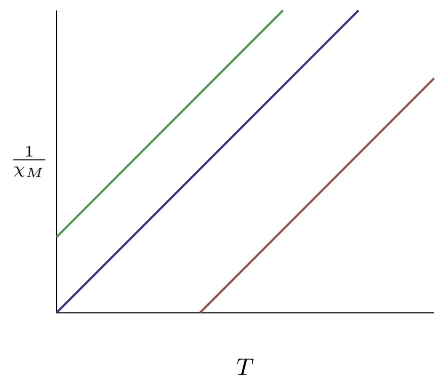
where $C = \frac{Ng^2\beta^2}{4k_B}$ is the Curie constant. How does this relate to Curie's law from last quarter?

- 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.



(a) Direct proportionality.



(b) Inverse proportionality.

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

- Measuring and observing magnetism:
  - Goes through the μ_S derivation on Labalme (2021, p. 119).
  - Arrives at the following important equations (defining our observables χT and μ_{eff}):

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

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

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

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

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

      where HE_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

$$m_i = \frac{\mathrm{d}}{\mathrm{d}H}\left(E_i^0 + E_i^0 H + E_i^2 H^2 + \cdots\right) = -E_i^1 + 2E_i^2 H$$

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

$$\chi_i = \left(-\frac{\mathrm{d}E_i}{\mathrm{d}H}\right)\frac{1}{H}$$

  - The final result above tells us that 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 χ.
  - 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

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

- Note that if $E_i^1 << k_BT$, 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

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

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

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

- This implies that

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

- **Van Vleck equation**: The above equation[2].
  - 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 λ.
    - For Ti^{3+} for example, $\lambda = 154\,\text{cm}^{-1}$.
    - For 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 closed 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 μ_{eff} / χT to be lower than the spin-only value, i.e., $g < 2$.
    - Typically μ_{eff} / χT is close to the spin-only value.

[2]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 μ_{eff} / χT to be larger than the spin-only value, i.e., $g > 2$.
    - μ_{eff} / χT can be much larger.
  - For a half-filled set of orbitals, we expect little to no S.O.C. Thus, μ_{eff} / χT 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 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 λ'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 generate; 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 π bond?
  - As in PSet 1 Questions 1.2 and 1.6.
  - Example: Ni^-ethene.
    - The π 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: $Ni(COD)_2$.
    - Electron count: 18 (8 from the ligands [2 from each of 4 π bonds] and 10 from the d^{10} nickel atom).
- Electron counting for a metal center bonded to a σ 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 $1\,e^-$ 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., NO^+, ${SO_4}^{2-}$, η^3-${C_3H_5}^+$, 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 lanthanium 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 π donation from a ligand to get a compound to 18 electrons.
- **Hapticity**: The number of carbons in the π system. *Also known as* $\boldsymbol{\eta}$.

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:
$$ML_6 + L' \rightleftharpoons ML_5L' + L$$
- 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 π 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]).
        - $18\,e^-$: it will not want to coordinate an additional L'.
        - $20\,e^-$: it will want to dissociate.
        - $16\,e^-$: it *can* associate.
            - However, it may not want to given that $16\,e^-$ 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:
        $$\frac{\mathrm{d}[\mathrm{ML_5L'}]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{ML_6}][\mathrm{L'}]$$
    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:
        $$\frac{\mathrm{d}[\mathrm{ML_5L'}]}{\mathrm{d}t} = \frac{k_2k_1[\mathrm{ML_6}][\mathrm{L}]}{k_{-1}[\mathrm{L}]+k_2[\mathrm{L'}]}$$
        - Experimentally, we swamp the reaction with $\mathrm{L'}$ so that $[\mathrm{L'}] >>>$ than all other reagents. This makes it so that the rate is just $k_{\mathrm{obs}}[\mathrm{ML_6}]$, 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 $\mathrm{L'}$ 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).
        - $10^8\,\mathrm{s}^{-1}$; close to the diffusion limit.

    II) Fast.
        - Higher valent ions; often M^{3+} such as Al^{3+}.
            - Higher charge ⇒ higher ligand affinity ⇒ slightly slower but still pretty fast.
        - 10^3-$10^8\,\mathrm{s}^{-1}$.

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

    IV) Inert.
        - Co^{3+}, Cr^{3+}, Pt^{2+}, and Fe^{2+}(L.S.).
        - 10^{-8}-$10^{-4}\,\mathrm{s}^{-1}$.
- The overlap between the rates reflects the fact that there is no hard and fast cut off between categories.
- The identity of $\mathrm{L'}$ also influences rates.
    - Reaction rates increase with the ligand field strength of $\mathrm{L'}$[1].

[1] 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): $\mathrm{Co^{III}} < \mathrm{Cr^{III}} < \mathrm{Mn^{III}} < \mathrm{Fe^{III}} < \mathrm{Ti^{III}} < \mathrm{V^{III}}$.
  - 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, σ 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 $\mathrm{Cu(MeNH_2)_4}^{2+}$ vs. $\mathrm{Cu(en)_2}^{2+}$ 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 $\mathrm{Fe^{3+}}$ for example, $K_f = 10^{25}\,\mathrm{mol^{-1}}$. What is $\mathrm{mol^{-1}}$ and why is it here?
       - Sidenophones and euterobactin are biology's own chelaters ($K_f = 10^{52}\,\mathrm{mol^{-1}}$).
       - These chelaters 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: *cis*-$\mathrm{Pt(NH_3)_2(Cl)_2} \longrightarrow$ *cis*-$\mathrm{Pt(NH_3)_2(H_2O)_2}$ 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: $[\mathrm{PtCl_4}]^{2-} \xrightarrow{2\,\mathrm{NH_3}}$ *trans*-$\mathrm{Pt(NH_3)_2Cl_2}$.

- Therefore, we synthesize it as follows.

$$\begin{aligned} K_2PtCl_4 &\xrightarrow{4\,KI} PtI_4{}^{2-} \\ &\xrightarrow{2\,NH_3} \textit{cis}\text{-}Pt(NH_3)_2(I)_2 \\ &\xrightarrow[2)\ XS\ KCl]{1)\ AgNO_3} \textit{cis}\text{-}Pt(NH_3)_2(Cl)_2 \end{aligned}$$

- 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.

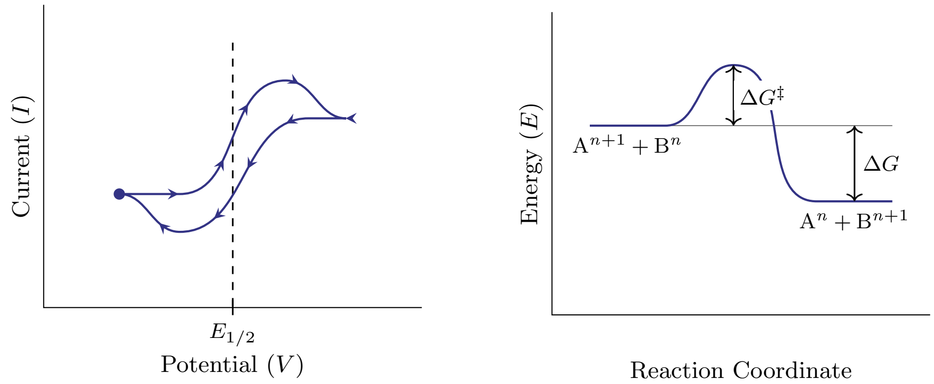
2.2 Lecture 5: Electron Transfer Reactions

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

$$M^{n+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{(n+1)+}$$

  – 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 $Fe(CN)_6{}^{4-} + Mo(CN)_8{}^{3-} \longrightarrow Fe(CN)_6{}^{3-} + Mo(CN)_8{}^{4-}$ (electron transfer from iron to molybdenum).
  – The energies at play: $A^{(n+1)} + B^n \longrightarrow [A^{(n+1)} + B^n] \longrightarrow [A^n + B^{(n+1)}]^* \longrightarrow A^n + B^{(n+1)}$.
  – Reactants → encounter complex → electron transfer state (an excited state) → products.

- Energies:



(a) Thermodynamics. (b) Kinetics.

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 ΔG? What is going on here? Why are the equilibria misaligned?
2. Kinetics:
   - $\Delta G = E_{1/2_{\text{A}}} - E_{1/2_{\text{B}}}$ where $E_{1/2_{\text{X}}}$ is the thermodynamic potential of substance X.
     - ΔG 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 countercations 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:
  - $Co(NH_3)^{2+}$ / $Co(NH_3)_6{}^{3+}$ 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:
  - $Ru(NH_3)_6{}^{2+}$ / $Ru(NH_3)_6{}^{3+}$.
  - k_{exch} is eight orders of magnitude faster than the previous example.
  - This is because ruthenium is low-spin throughout ($\Delta(\text{Ru}-\text{N}) \approx 0.04$ Å 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

$$\begin{aligned} \mathrm{Co(NH_3)_5Cl^{2+} + Cr(H_2O)_5{}^{2+}} &\longrightarrow \mathrm{Co(NH_3)_5{}^{2+} + Cr(H_2O)_5Cl^{2+}} \\ &\xrightarrow{\mathrm{H_2O}} \mathrm{Co(H_2O)_6{}^{2+} + Cr(H_2O)_5Cl^{2+}} \end{aligned}$$

  - The intermediates are $[\mathrm{(H_3N)_5Co^{III}{-}Cl{-}Cr^{II}(OH_2)_5}]^{4+} \longrightarrow [\mathrm{(H_3N)_5Co^{II}{-}Cl{-}Cr^{III}(OH_2)_5}]^{4+}$.
  - The rate is reasonably fast ($6 \times 10^5\,\mathrm{mol^{-1}\,s^{-1}}$).
  - How does this vary as a function of X^-?
    - As ligand size (more diffuse; better at bridging) and charge (more electrostatic influences) increase, so does rate ($Br^- > Cl^- > F^- > H_2O > NH_3$).

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

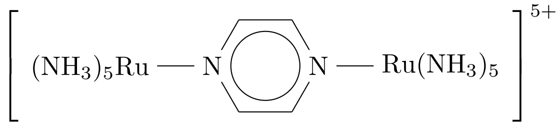


Figure 2.2: The Creutz-Taube ion.

  - The bridging ligand is a pyrazole.
  - The electron transfer is very fast; thus, the oxidation state is approximately ${Ru_2}^{2.5}$.
- 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 Ru^{II} and Ru^{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**:

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

    where ν_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 $\lambda \to -\Delta G$, $\Delta G^\ddagger \to 0$. Furthermore, as λ 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:

$$\mathrm{L}_n\mathrm{M}^{\mathrm{Q}} + \mathrm{A{-}B} \underset{\text{red. elim.}}{\overset{\text{ox. adn.}}{\rightleftharpoons}} \mathrm{L}_n\mathrm{M}^{\mathrm{Q}+2}\mathrm{AB}$$

- 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.

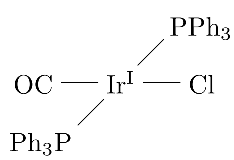


Figure 2.3: Vaska's complex.

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

1. Concerted.

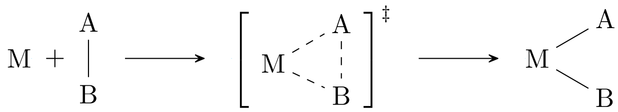
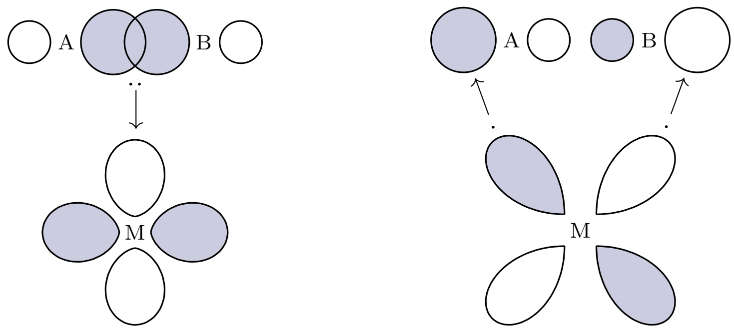


Figure 2.4: The concerted mechanism for oxidative addition.



(a) HOMO interaction. (b) LUMO interaction.

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 σ-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 σ^* antibonding orbital. It is these electrons that depopulate the σ bond and allow the A–B bond to split.

2. $\text{S}_\text{N}2$.

$$\text{M}\!: + \text{R}{-}\text{X} \longrightarrow \text{M}^+{-}\text{R} + \ddot{\text{X}}^- \longrightarrow \text{X}{-}\text{M}{-}\text{R}$$

   - *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.

$$\begin{aligned} \text{M} + \text{In} &\longrightarrow \text{MIn}\,\cdot \\ &\xrightarrow{\text{R}-\text{X}} \text{InM}{-}\text{X} + \text{R}\,\cdot \\ &\xrightarrow{\text{M}} \text{R}{-}\text{M}\,\cdot \\ &\xrightarrow{\text{R}-\text{X}} \text{R}{-}\text{M}{-}\text{X} + \text{R}\,\cdot \end{aligned}$$

   - We begin with a metal and an initiator (denoted In).
     - These react to form the adduct MIn $\cdot$, 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.

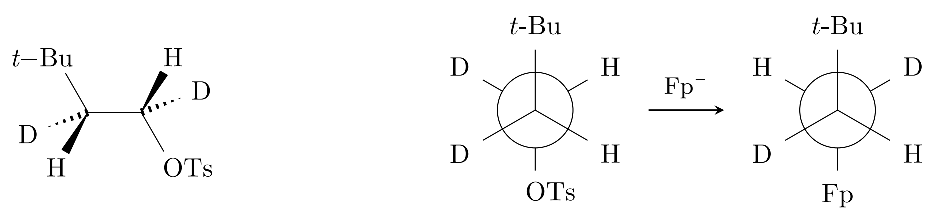
$$\begin{aligned}\mathrm{M^0 + R{-}X} &\longrightarrow \mathrm{[M^+\cdot + RX^-\cdot]}\\ &\longrightarrow \mathrm{M^+\cdot + R\cdot + X^-}\\ &\longrightarrow \mathrm{M^+{-}R + X^-}\\ &\longrightarrow \mathrm{X{-}M{-}R}\end{aligned}$$

   - Related to $\mathrm{S_N2}$ 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 $\mathrm{L_2IrClCo} \xrightarrow{\mathrm{MeX}} \mathrm{L_2IrClCoMeX}$, specifically the reaction rates as a function of X.
  - Determines that $\mathrm{I^-} > \mathrm{Br^-} >> \mathrm{Cl^-}$, and that Rate $= k[\mathrm{CH_3X}][\mathrm{Ir}]$.
  - $\Delta S^\ddagger = -43\,$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:

$$2\,\mathrm{L}_n\mathrm{M^0 + R{-}X} \longrightarrow \mathrm{L}_n\mathrm{M^I{-}R} + \mathrm{L}_n\mathrm{M^I{-}X}$$

- Jack Halpern again writes Halpern and Maher (1965).
  - Studies the reaction $2\,\mathrm{Co^{II}(CN)_5}^{3-} + \mathrm{MeI} \longrightarrow \mathrm{Co^{III}(CN)_5Me^{3-}} + \mathrm{Co^{III}(CN)_5I^{3-}}$.
  - 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: $2\,\mathrm{L}_n\mathrm{M} + 2\,\mathrm{RX} \longrightarrow 2\,\mathrm{L}_n\mathrm{M{-}X} + \mathrm{R{-}R}$.
  - For example, $\mathrm{Cp_2^*Yb(OEt_2) + CH_2Cl_2 \longrightarrow 2\,Cp_2^*Yb{-}Cl + ClCH_2{-}CH_2Cl}$.
  - This can also occur through a radical mechanism. We form an $\mathrm{R}\cdot$ radical that can recombine to form R–R or make M–R.
- Stereochemistry of $\mathrm{S_N2}$ type reactivity.
- George Whitesides writes Bock et al. (1974).



(a) The reactant. (b) The reaction.

Figure 2.6: $\mathrm{S_N2}$ stereochemistry.

- Observes inversion (by looking at J_{H-H} coupling by NMR) of H and D at a single stereocenter.
- React the compound in Figure 2.6a with a Fp^- fragment.
- Observe inversion, as in Figure 2.6b, so it's S_N2.

- Another synthesis:

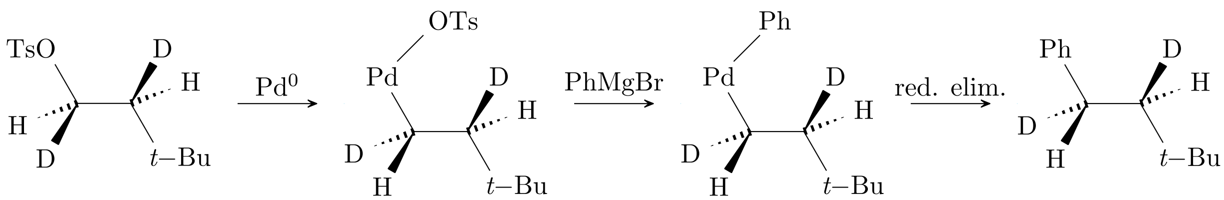


Figure 2.7: An additional way of probing S_N2 addition/elimination.

- 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 M−Cl.
  - Since iodides are easier to reduce than bromides, bromomethylcyclopropane will react in a straightforward manner with Fp^-, but iodomethylcyclopropane and 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, I^- is a better leaving group than Cl^-.
     - However, there are exceptions, too: 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:

$$\mathrm{L{-}M^Q{-}X} \underset{\text{deinsertion}}{\overset{\text{insertion}}{\rightleftharpoons}} \mathrm{M^Q{-}L{-}X}$$

  - 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: Me−M−CO $\rightleftharpoons$ M−C(=O)−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: $\mathrm{Cp_2Zr(-||)Me} \rightleftharpoons \mathrm{Cp_2ZrPr}$.
    - 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):

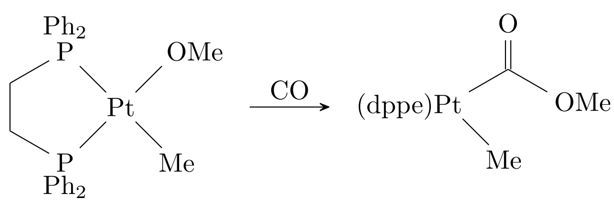


Figure 2.8: Insertion into an M−O bond.

- 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 σ bond of the migrating ligand attacks the site to which it bonds or the L group moves into the σ 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 $\mathrm{Mn(CO)_5Me}$?
- β-H elimination: $\mathrm{L_2NiEt} \rightleftharpoons \mathrm{L_2Ni(-||)H}$.

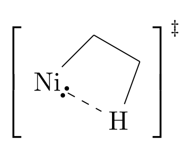


Figure 2.9: The transition state in a β-H elimination.

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

- α-elimination[2].

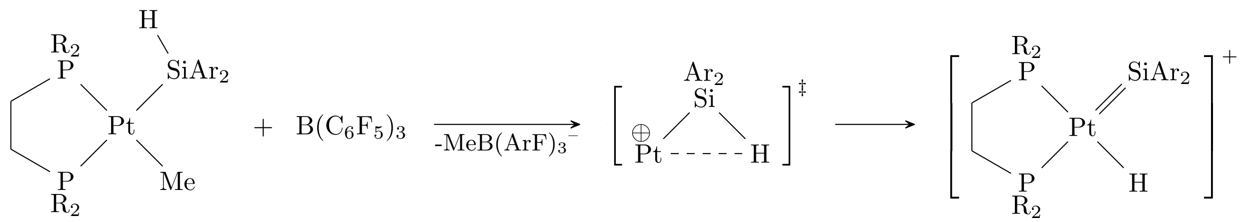


Figure 2.10: An example of α-elimination.

- External attack at a ligand.

$$L_nM^Q{=}X + Nu^- \rightleftharpoons [L_nM^{Q-2}{-}X{-}Nu]^-$$

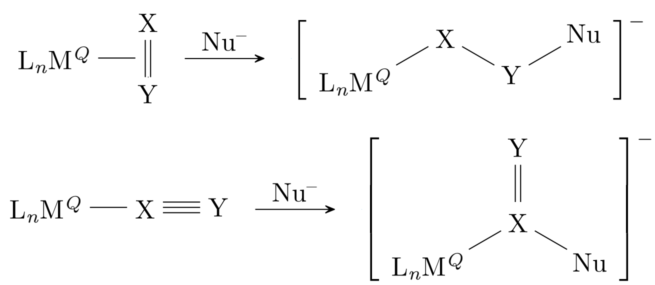


Figure 2.11: Types of external attack at a ligand.

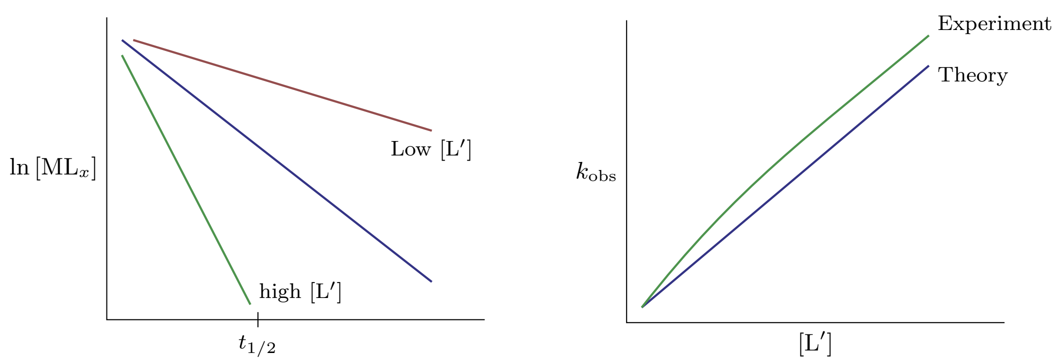
  - Somewhat more related to organic chemistry.
  - Lists some examples.

- 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 $16\,e^-$ 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.

[2] Note that Ar stands for an aryl group.

- σ-bond metathesis: $\mathrm{L}_n\mathrm{M}^{\mathrm{Q}}{-}\mathrm{X} + \mathrm{Y}{-}\mathrm{Z} \rightleftharpoons \mathrm{L}_n\mathrm{M}^{\mathrm{Q}}{-}\mathrm{Y} + \mathrm{X}{-}\mathrm{Z}$.
  - Usually observed for d^0 systems.
- Example: $\mathrm{Zr^{IV}(N(SiR_3)H)_3Me} \longrightarrow \mathrm{Zr(N(SiR_3)H)_2({=}N{-}SiR_3) + CH_4}$.
  - 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 σ-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" σ-bond metathesis and oxidative addition/reductive elimination.
  4. This still requires an open coordination site and $\leq 16\,\mathrm{e}^-$.
     - Because the first step is coordination, usually to form some kind of σ-adduct.
- Kinetics of associative substitution.

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{ML}_x]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{ML}_{x-1}\mathrm{L}']}{\mathrm{d}t} = k[\mathrm{ML}_x][\mathrm{L}']$$



(a) Reaction coordinate and [ML$_x$]. (b) Rate and [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 rate $= k_{\mathrm{obs}}[\mathrm{ML}_x]$ where $k_{\mathrm{obs}} = k[\mathrm{L}']$.
  - 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.
    - $\mathrm{L}_x\mathrm{M} + \mathrm{solv} \xrightleftharpoons{k_s} \mathrm{L}_{x-1}\mathrm{ML(solv)} \xrightarrow[\text{fast}]{\mathrm{L}'} \mathrm{L}_{x-1}\mathrm{ML}' + \mathrm{solv} + \mathrm{L}$.
    - 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.

i) $\mathrm{ML}_x \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{ML}_{x-1}] + \mathrm{L}$.

ii) $[\mathrm{ML}_{x-1}] + \mathrm{L}' \xrightarrow{k_2} \mathrm{ML}_{x-1}\mathrm{L}'$ (assume irreversible).

- There are now two cases:
  a) Fast pre-equilibrium, i.e., $k_1, k_{-1} >> k_2$. This gives us

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

  b) Steady state approximation: $\mathrm{d}[\mathrm{ML}_{x-1}]/\mathrm{d}t = 0 = k_1[\mathrm{ML}_x] - k_{-1}[\mathrm{ML}_{x-1}] - k_2[\mathrm{ML}_{x-1}][\mathrm{L}']$. If we solve the above for $[\mathrm{ML}_{x-1}]$, then we get

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

  If we now assume that $k_2[\mathrm{L}']$ is large, then we get rate $= k_1[\mathrm{ML}_x]$.
    - 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 $[\mathrm{ML}_{x-1}] = 0$.
- To do this experimentally, we add a large concentration of $[\mathrm{L}']$, or $[\mathrm{L}]$ in some cases.
  - This gives us rate $= k_{\text{obs}}[\mathrm{ML}_x]$ where k_{obs} denotes the mess from the above equation.

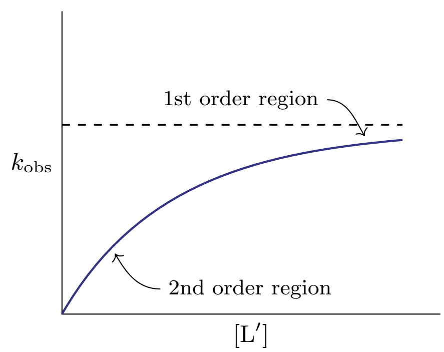


Figure 2.13: The effect of $[\mathrm{L}']$ on rate.

- If we plot k_{obs} vs. $[\mathrm{L}']$, we get Figure 2.13.
  - In the second order region, $\mathrm{ML}_x \overset{\text{fast}}{\rightleftharpoons} \mathrm{ML}_{x-1}$ many times before product formation.
  - In the first order region, every time ML_{x-1} forms, it goes on to become a product.
- In other words, k_{obs} should approach k_1 when $k_2[\mathrm{L}'] >> k_{-1}[\mathrm{L}]$.
- Importantly, as 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. $\frac{[\mathrm{L}]}{[\mathrm{L}']}$ 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 $k = A\mathrm{e}^{-E_A/RT}$, 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.

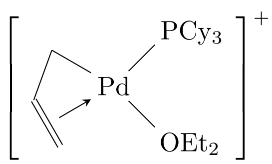
  - This allows us to create a linear $\ln k$ vs. $\frac{1}{T}$ plot from which we can pull out important information.
- In the 1930s, Eyring comes up with the Eyring equation

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

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 ΔG 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 ${SO_4}^{2-}$ 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 Pd^{2+}.
    - The synthetic route by which we get to this compound has no bearing on it's properties (electron count, oxidation state, etc.).
    - In one reaction mechanism, it's ${C_3H_5}^+$ before, and then it's ${C_3H_5}^-$ after splitting.
  - 8:
    - 8b: Solve with electron counts? MoL_2X_4 is $14\,e^-$, whereas MoL_4X_2 is $16\,e^-$.
    - 8d: Donates the same number of electrons in each case! They're just different resonance structures!!
    - 8e: Cp is an L_2X-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 $16\,e^-$.

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

$$Mg^0 + R-X \longrightarrow XMgR(solv)_2 \rightleftharpoons MgR_2 + MgX_2 \xrightarrow{\text{dioxane}} X_2Mg-diox-MgX_2$$

  - 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, thalium, aluminum, etc. alkyls.
- Transition metal alkyls:
  - β-H elimination is a problem (this is why TM alkyls were only discovered later).
    - An elecronically 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.
    - ${I_x Pt-Me_{4-x}}^{2-}$ and ${IPt-Me_3}^{2-}$ were partially characterized.
  - First quasi-stable example: $FeCp(CO)_2Et$ has $18\,e^-$. 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 β-hydrogens or unreactive β-hydrogens.
    - They made compounds such as $W(CH_3)_6$, $M-CH_2-Ph$, $M-CH_2-t\text{-Bu}$, and $M-CH_2-TMS$[3].
    - 1-adamantyl, norbornyl have β-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 β-hydrogen is once again in the wrong position).
- Types of synthesis of transition metal alkyls.
  1. Nucleophilic attack on M:
  $$y\,R^- + MX_y \longrightarrow MR_y + y\,X^-$$
     - 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).

[3]TMS is trimethylsilyl, a ligand of the structure $SiMe_3$.

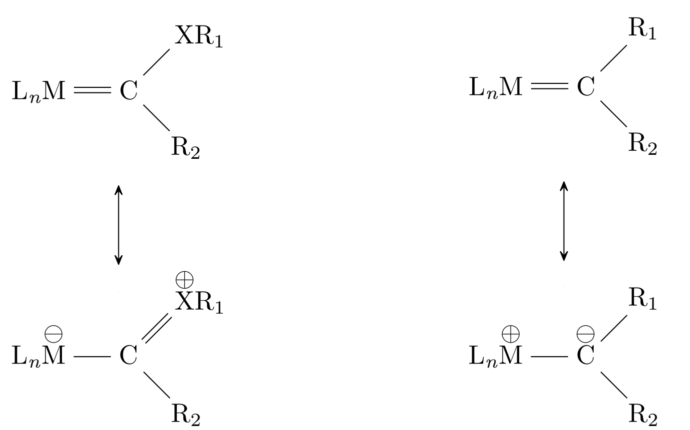
    - There is also the possibility of productive radical mechanisms, but there is lots of side reactivity in radical mechanisms, too. We can limit side reactions with a less reducing nucleophile.
2. Electrophilic attack on M.
    - For example, $Mn(CO)_5{}^- + MeI \longrightarrow MnMe(CO)_5 + I^-$.
    - Also, $Fp^- + Ph_2I^+ \longrightarrow CpFe(CO)_2Ph + IPh$. Note that Ph_2I^+ is an **arylating reagent**.
3. Oxidative addition.
    - Vaska's complex and MeI.
    - Also C–H activation: $M + H{-}CR_3 \longrightarrow H{-}M{-}CR_3$.
        - 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.

$$X{-}M{-}|| \longrightarrow M{-}CH_2{-}CH_2{-}X$$

    - X can be an alkyl or a hydride.
    - $(Et_3P)_2Pt^{II}ClH \xrightarrow{||} (Et_3P)_2PtClEt$.
    - $(Et_3P)_2Pt^{II}ClH \xrightarrow{|||} (Et_3P)_2PtClVinyl$.
        - 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, $Cp(CO)_3MoH \xrightarrow{N_2CH_2} Cp(CO)_3Mo{-}CH_3$ (note that the compound above the arrow is diazomethane, a common CR_2 transfer reagent).
    - All of these require an open coordination site.
5. External nucleophilic attack on an olefin.

$$M{-}|| + {:}Nu \longrightarrow M{-}CH_2{-}CH_2{-}Nu$$

- **Aryl**: Similar to an alkyl group, but no β-H's to eliminate.
- M–C multiple bonds.
- Three types of compounds: Carbenes/alkylidenes ($M{=}CR_2$), carbynes/alkylidynes, and carbides.
    - We will focus on carbenes today.
- Two limiting regimes (for carbenes):



(a) Fischer carbenes. (b) Schrock alkylidenes.

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.
   - π-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.
   - π-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, $W(CO)_6 + MeLi \xrightarrow[-CO]{2\,KC_8} K_2[W(CO)_5] \xrightarrow[R-X]{Cl-C(=O)-OR} (CO)_5W{=}C(OMe)(Me)$.
    - 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, $W(CO)_6 + MeLi \xrightarrow[-CO]{2\,KC_8} K_2[W(CO)_5] \xrightarrow{R_1-C(=O)-NR_2} (CO)_5W{-}C(O{-})(R_1)(NR_2) \xrightarrow{TMSCl} (CO)_5W{=}C(NR_2)(R_1)$.
  - More syntheses listed.
- Classic alkylidenes:
  - $TaCl_5 + \frac{3}{2}Np_2Zn \longrightarrow (Np)_3TaCl_2 \xrightarrow{2\,NpLi} Np_3Ta{=}C(t\text{-Bu})(H)$[4].
  - $TaCl_5 + Np_2Zn \longrightarrow Np_2TaCl_3 \xrightarrow{2\,L} Ta({=}C(t\text{-Bu})(H))Cl_3L_2$.
  - 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.

[4]Note that we are using Np to denote a neopentyl group.

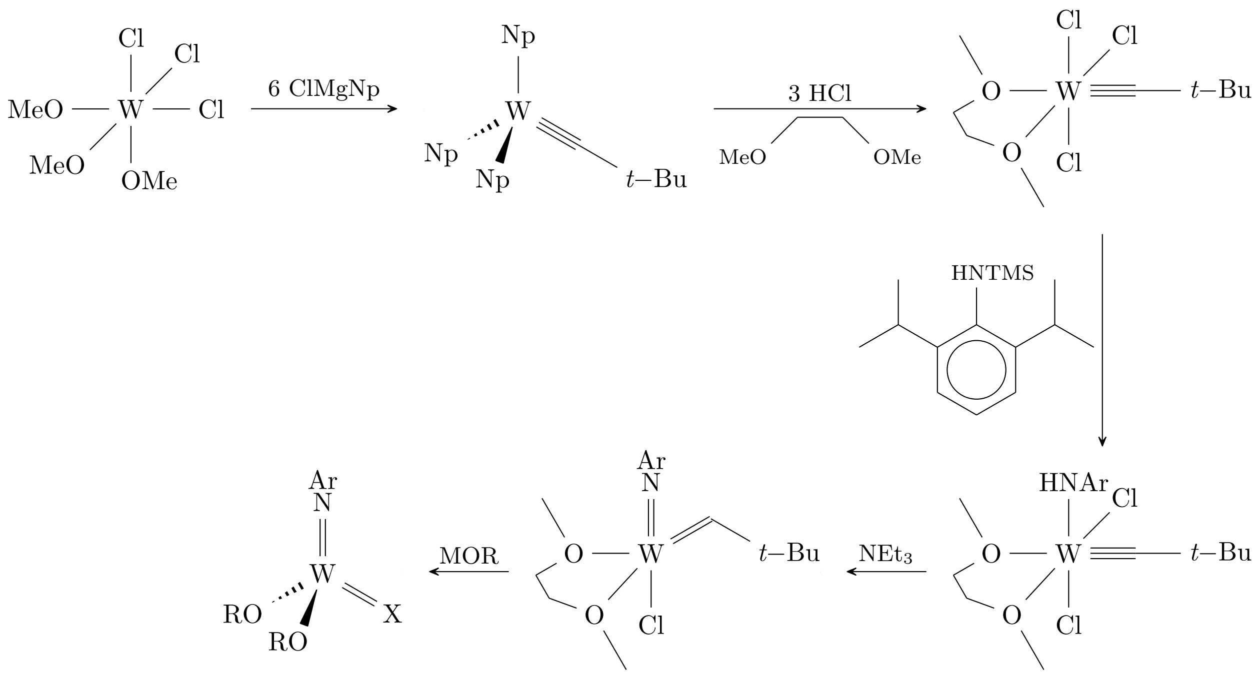


Figure 2.15: Tungsten olefin metathesis.

- Tebbe's reagents:

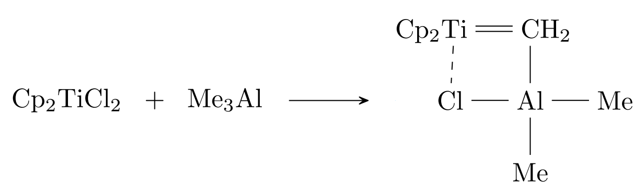


Figure 2.16: Tebbe's reagents.

  - 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 σ-donors (much stronger than phosphines), but very weak π-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 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 attatched to one of the cyclopropane carbons.
- **Carbide**: A terminal carbon atom; a C^{4-} ligand.

2.9 Lecture 9: Olefins, Carbonyls, and Phosphines

4/16:
- Top π-acceptors: CO, NO^+, and PF_3.
  - CO is also a decent σ donor.
- CO provides a great IR handle, enabling characterization.
  - ν_{CO} is a measure of the electron density on the metal center.
- We generally consider CO in the resonance structure $:\overset{\ominus}{C}\equiv\overset{\oplus}{O}:$.
  - Each atom in CO has four π^* 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 σ orbital originating from atomic p orbitals that runs along the bond axis.
  - Recall the CO resonance structures.
- Free CO has a stretching frequency of $\nu_{CO} = 2143\,\text{cm}^{-1}$.
  - 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 $Mn(CO)_5Me$, the Mn−Me bond is 2.18 Å and the Mn−CO bonds are 1.86 Å, 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: $NH_3 + NaCl + CO_2 \longrightarrow Na_2CO_3 + NH_4Cl$.
    - 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 $Ni(CO)_4$, a volitile 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:
    - $Co + CO \xrightarrow[\text{RT}]{\text{35 atm}} Co_2(CO)_8$[5].
    - $Fe + CO \xrightarrow[300\,^\circ\text{C}]{\text{300 atm}} Fe(CO)_5$.
  - Reduce with CO:
    - $Re_2O_7 \xrightarrow{CO} Re_2(CO)_{10} + CO_2$. CO_2 is given off by reductive elimination from an intermediate.
    - More syntheses listed.
- We predict stoichiometry (i.e., constitutional isomerism) with the $18\,e^-$ rule (except for square planar).
  - Group 9: $M_4(CO)_{12}$ is common.
  - Group 8: $M_3(CO)_{12}$ is common.
- IR signatures.
  - Ketones are usually 1750-1720 cm^{-1}.
  - R_3COH compounds are usually 1100 cm^{-1}.

[5] RT is short for room temperature.

  - ν_{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):
  - $\text{Fe(CO)}_5 \xrightarrow[-\text{CO}]{2\,\text{Na}\,/\,\text{THF}} \text{Na}_2\text{Fe(CO)}_4{}^{2-}$.
  - $\text{M(CO)}_n \xrightarrow[-\text{CO}]{2\,\text{Na}} \text{Na}_2\text{M(CO)}_{n-1}{}^{2-}$.
  - $\text{Re}_2\text{(CO)}_{10} \xrightarrow{\text{Na}} \text{Na}^+\text{Re(CO)}_5{}^-$.
  - $\text{Re}_2\text{(CO)}_{10} \xrightarrow[-2\,\text{CO}]{6\,\text{Na}\,/\,\text{HMPA}} \text{Na}_3\text{Re(CO)}_4{}^{3-}$.
  - $\text{Mo(CO)}_6 \xrightarrow{2\,\text{Na}} \text{Mo(CO)}_5{}^{2-}$.
  - $\text{Mo(CO)}_6 \xrightarrow{\Delta\,\text{TMEDA}} \text{(CO)}_4\text{Mo(EDA)} \xrightarrow{4\,\text{NaNH}_3} \text{Na}_4\text{Mo(CO)}_4{}^{4-}$.
    - This is d^{10} and thus $\nu_{\text{CO}} <<< 2000\,\text{cm}^{-1}$.
    - TMEDA is tetramethylethylenediammine.
- We can also go the other direction to find carbonyls with a very low degree of backbonding.

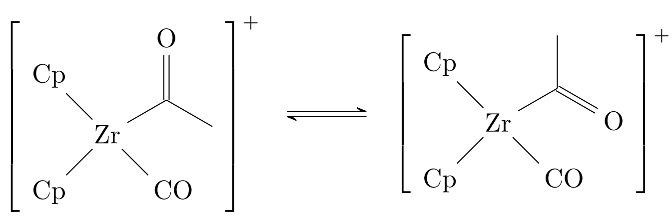


Figure 2.17: Low backbonding carbonyl complexes.

  - The reactant has $\nu_{\text{CO}} = 2123\,\text{cm}^{-1}$, which is slightly lower than that of free CO due to some σ 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: $2\,\text{IrF}_6 + 15\,\text{CO} + \text{HSbF}_5 \xrightarrow[60\,^\circ\text{C},\,12\,\text{h}]{\text{SbF}_5} 2\,[\text{Ir(CO)}_6]^{3+}$.
    - This gives us $\nu_{\text{CO}} = 2254\,\text{cm}^{-1}$.
    - We also have $\text{Au(CO)}_2{}^+$ at $2217\,\text{cm}^{-1}$.

  - Reducing extreme:
    - $Zr(CO)_6{}^{2-}$ is $1757\,cm^{-1}$.
    - $W(CO)_6$ is $1983\,cm^{-1}$.
- Neutral L-type olefins: M−||.
- Dewar-Chatt-Duncanson model: Very related to Figure 2.5.
  - Thus, the ethylene is both a σ donor and π acceptor.
    - This relates it to CO as a ligand. Of course, CO is $C_{\infty v}$ and CO has 2 π-accepting orbitals instead of just one, but there is a relation nonetheless.
- Use ionization potential to measure the magnitude of σ donation:
  - Ethylene: 10.5 eV.
  - CO: 14 eV.
- Thus, ethylene is a better σ donor but worse π acceptor.
- Comparing C=C bond length in Zeise's salt (see Figure 1.2), $(Ph_3P)_2Pt$−||, and C_2H_4.
  - Bond length is significantly elongated (close to a C−C single bond) for $(Ph_3P)_2Pt$−|| but similar for the other two.
  - We can also see that the C−H bonds are bent back by 15° in $(Ph_3P)_2Pt$−||, 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 X_2-type ligand, but by convention we almost always treat olefins as L-type ligands.
  - Both are $2\,e^-$ donors.
- Polyolefins.
- Example: Butadiene.

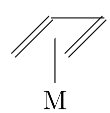


Figure 2.18: Butadiene.

  - We have four bonding modes: σ, π, π^*, and δ^*.
    - Each corresponds to a different orientation of the p_z orbitals at each carbon and has a different number of nodes.
  - π and π^* orbitals are the major contributors.
    - The metal d orbitals will project toward butadiene in a π-symmetry fashion, and the s orbitals (which would bond with the butadiene σ orbital) are more secondary for a transition metal.
    - σ contributions are reduced because of symmetry.
  - σ and π orbitals are σ donors; π^* engages in backbonding.
  - Lowering the energy of the π orbital and populating the π^* 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: Metallacyclopropane and direct π-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 σ donor, and donates into d_{xy} metal orbitals.
  - It's also a π 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 = 1075 kJ/mol[6].
    - 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:

$$\mathrm{Ta^{III}(OSi(\mathit{t}\text{-}Bu)_3)_3} \xrightarrow{2\,\mathrm{CO}} 2\,\mathrm{R_3SiO_3Ta^{V}{=}O} + \mathrm{(R_3SiO)_3Ta{=}C{=}C{=}Ta(OSiR_3)_3}$$

    - 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 coordintion number 2.
- Are alkyl groups more stable?
- Synthesis questions.
  - Try to stay under 18 e^-.
    - Don't include the electron counts as part of the synthesis but think about them for yourself.
    - $ZrCl_4$ has 8 e^-? 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).

[6] 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 −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 KC_8 (potassium graphite), Na^0 (sodium metal), or NaNapth (sodium napthalanide), 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: $CoCp_2$ (cobaltacene) and $CoCp^*$.
  - We reduce before adding COs because if we added two COs right now, we'd get a $20\,e^-$ species.
  - *In situ* means in the situation. Anything you do in the same mixture is something you've done *in situ*.
  - Oxidants:
    - $AgPF_6$: 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 it's 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 MeI and 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 survery of other π acceptors.
  - Many of these are analogous to CO.
- C≡S (carbon sulfide).
  - $2\,\mathrm{e}^-$ 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 π acceptor than CO even though the polarization is a bit off.
- $[\mathrm{C{\equiv}N}]^-$ (cyanide).
  - $1\,\mathrm{e}^-$ X-type.
  - Much better σ donor, but a much weaker π acceptor.
- C≡N−R (isocyanides).
  - Quite similar to CO (via the isolobal/isoelectronic analogy).
  - Slightly stronger σ donor, but a slightly weaker π acid.
- $\mathrm{PR_3}$ (phosphines).
  - Good σ donors (better than CO), and ok π acceptors.
  - π acceptance occurs through the σ^* orbitals.
    - More polarized the P−R bond ⇒ more π^* character on the phosphorous ⇒ better π acceptor $\mathrm{PR_3}$ will be.
    - Phosphines with strong electron-donating R groups will be better σ donors but worse π acceptors.
  - Know $\mathrm{P(OR)_3}$ ligands (phosphites).
    - Very good π acceptors.
  - $\mathrm{PF_3}$ is almost as good as CO in terms of its π-acceptance.
- $[\mathrm{N{\equiv}O}]^+$ (nitrosyls).
  - Isoelectronic/isolobal to CO, so it engages in the same types of interactions.
  - Probably the strongest π acceptor known.
  - Two main modes of binding (linear and bent).
  - Bioinorganic chemistry of $\mathrm{NO^+}$: 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**
$\mathrm{M}-\overset{\oplus}{\mathrm{N}}\equiv\overset{\oplus}{\mathrm{O}}\!:$	$\mathrm{M}\diagup\ddot{\mathrm{N}}\diagdown\!\!=\underset{\cdot\cdot}{\mathrm{O}}\!:$
LX-type.	X-type.
$3\,\mathrm{e}^-$ donor.	$1\,\mathrm{e}^-$ donor.
3 CO's provide similar stability to 2 NO's (in terms of electron counting).	
Oxidation state: Formally $\mathrm{NO^+}$ but this is not a good description (it would imply $\mathrm{M^-}$).	Oxidation state: Formally anionic, so $\mathrm{M^+}$.

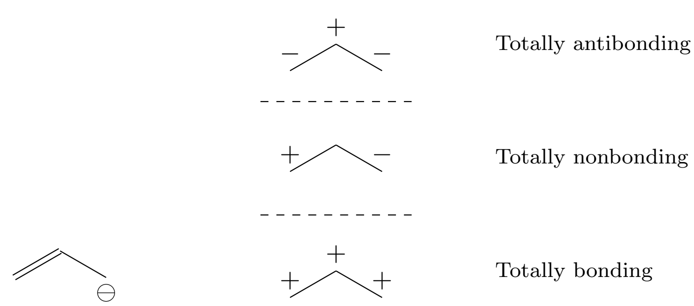
- Oxidation state debates led to the development of **Enemark-Feltham notation**.
- **Enemark-Feltham notation**: Considers the d count of the metal center and any extra electrons beyond NO^+ that the NO brings.
- Consider heme centers.
  - Hemes bind to porphyrins.
    - Porphyrins are the macrocyclic 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 FeNO is neutral, $\cdot NO$ bound as a radical: $\{FeNO\}^7$.
  - If heme $FeNO^-$ is anionic, NO^- bound as an anion: $\{FeNO\}^8$.
  - If heme $FeNO^+$ is cationic, NO^+ bound as a cation: $\{FeNO\}^6$.
- Nitrosyl geometry (linear vs. bent) is sensitive to the d count of the metal.
  - If the metal wants to get an extra $3\,e^-$, NO^+ will be linear. Otherwise, NO^+ will be bent.
  - An example of a limiting case: When bonding to benzene, NO^+ will be bent because there is no possible π bonding.
- Synthesis of nitrosyls:
  - Two main routes:

$$M^0 + NO^+X^- \longrightarrow [M{-}NO]^+X^-$$
$$M^0 + \cdot NO \longrightarrow M{-}NO$$

    - 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 X^- as a counteranion.
    - In the second case, we react a metal center with $NO\cdot$ gas, which is a radical and pretty nasty.
  - One less common route:

$$R{-}O{-}N{=}O \xrightarrow{H^+} ROH + NO^+$$

    - An analogous reaction with metals is $M{-}N({=}O){-}O \xrightarrow{PR_3} M{-}NO + R_3PO$.
- Note that in general, because NO and CO are both such strong π acceptors, they do not go *trans* to each other.
  - One notable exception: $V(CO)_5(NO)$.
- Allyls:

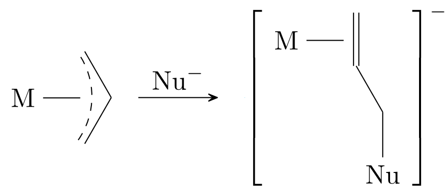


(a) The ligand. (b) The π system.

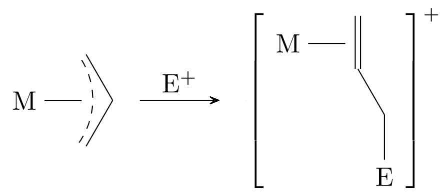
Figure 2.19: The allyl ligand.

  - $3\,e^-$ LX-type donor.
  - Barry Trost's palladium allyls: Changing side-on vinyl ethers into allyls (structures shown).

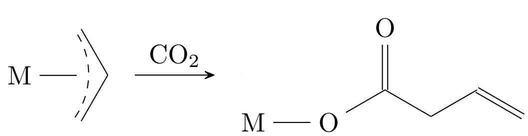
- Synthesis of allyls:
  - We can synthesize allyls (from olefins) that bind to their metal center from above and below the molecular plane.
  - We can synthesize allyls by oxidizing a butadiene with acid.
  - There also exist allyls in the form of isobutane with conjugated electron systems between each carbon. This bonds to metal centers from above.
  - More syntheses listed.
- Note: Sodium is a possible reductant ($Mn_2(CO)_{10} \xrightarrow{Na} 2\,Mn(CO)_5{}^-$).
- Allyl reactivity:



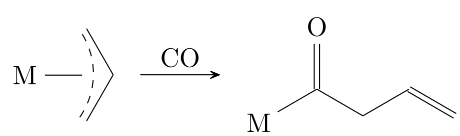
(a) Nucleophilic attack.



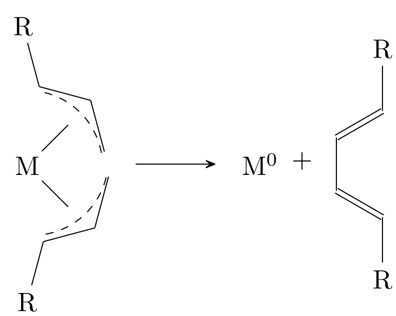
(b) Electrophilic attack.



(c) Insertion (1).



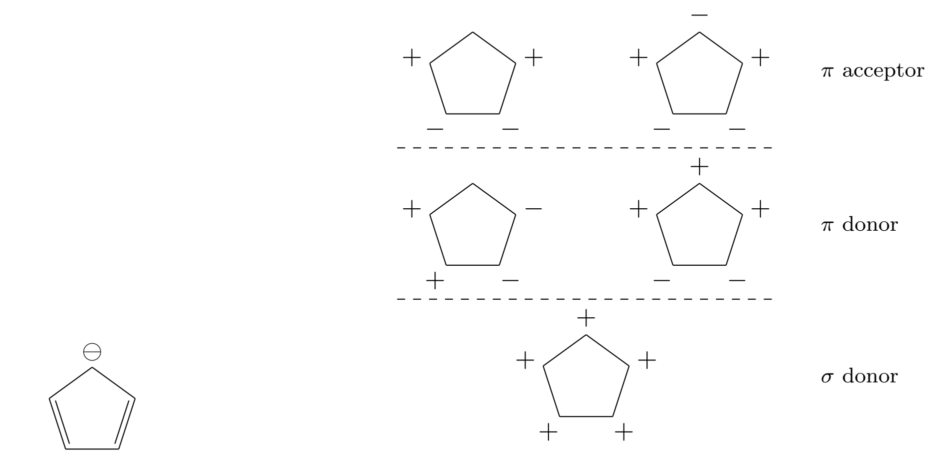
(d) Insertion (2).



(e) Coupling/reductive elimination.

Figure 2.20: Allyl reactivity.

- Other extended π systems.
- Cyclopentadienyl (Cp).



(a) The ligand. (b) The π system.

Figure 2.21: The cyclopentadienyl ligand.

  - Strong field ligand.
  - $5\,e^-$ 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 °C (thus, a clean melting point transition).
    - Stable up to 500 °C.
    - Water stable.
  - To characterize it as a sandwich compound, scientists used the fact that it has 1 ν_{C-H} stretch in the IR spectrum, 1 peak in ^{1}H (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 π 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, $Ru(\eta^6\text{-}C_6H_6)_2 \longrightarrow Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$. The driving force is a $20\,e^-$ to $18\,e^-$ transition.
- Triple bonds:
  - σ donation, (weak) π donation, and π acceptance (same idea, orbitally, as answer to Homework 2, problem 11a).
  - Upon binding, we see lengthening of the C≡C bond and the C−H bonds bending backwards away from the metal center.
- Phosphines (and derivatives):
  - PR_3: Bulky, soft, good donors, strong field ligands.
  - $P(OR)_3$: 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., PPh_3 is weak while PMe_3 is strong]).
- **Tolman electronic parameter**: The ν_{CO} value for $(CO)_3NiL$ where L is some ligand.
  - Allows us to guage the π-accepting character of different ligands: Stronger π acceptors will invoke a higher ν_{CO} value.
  - Weakly basic ligands do not do much σ or π donation and thus do a lot of π acceptance. It follows that these ligands will have a higher Tolman electronic parameter.
  - There is a good Wikipedia page for this.
  - Judges σ/π donation/acceptance properties all together (i.e., their ratio), not each individually.
    - For example, a ligand that is a strong σ donor and a strong π acceptor will have a middling Tolman electronic paramenter, whereas a ligand that is a weak σ donor and a strong π acceptor will have a high Tolman electronic parameter.
- π-accepting character of various ligands:

$$NMe_2 < NH_3 << py < PR_3 < P(OR)_3 << PF_3 < PCl_3 <<< CO$$

  - Ranked on a scale of 0-100 where the π-accepting character of CO is defined to equal 100.
- **Tolman cone angle**: The angle for the cone that encapsulates all of the R groups.

$$PMe_3 < P(Ph_3)_3 < P(t\text{-}Bu)_3$$

  - Describes the sterics of the phosphine.
  - Lists the cone angles of several common phosphines.
- AsR_3 (arsenes):
  - Isoelectronic/isolobal to phosphines.
  - Not as common, but typically better π acceptors.
- N-heterocyclic carbenes:

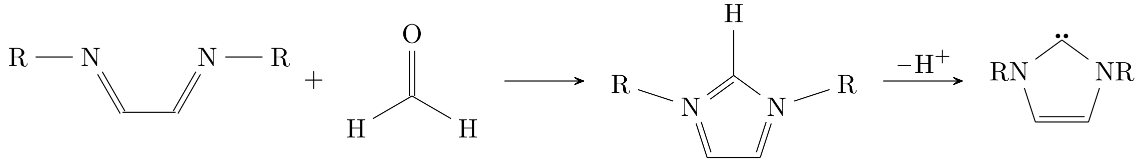
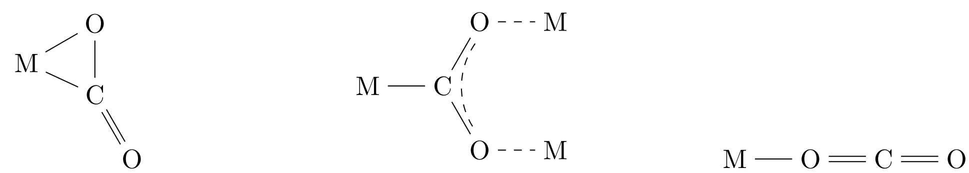


Figure 2.22: Synthesis of N-heterocyclic carbenes.

- A new class of ligands that are extremely strong donors.
- Many resonance structures.
- A very strong σ donor and a very weak π acceptor. Essentially pure σ donors.
  - σ donor properties: Orignate from the lone pair on the carbon.
  - π acceptor properties: These exist in principle since the carbon has an empty p orbital, but in practice, it's π 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 π acceptors.
  - π donor properties: Nonexistent.
- Stronger σ donors than phosphines.

- Other π-bound ligands.
- CO_2 / CS_2.



(a) η^2 bonding. (b) κ^1 bonding. (c) End-on bonding.

Figure 2.23: Bonding of CO_2 to metal centers.

  - There's a lot of interest in bonding CO_2 to transition metals in terms of catalytic reduction/functionalization of CO_2.
  - What is κ^1 bonding?
- Aldehydes / ketones.
  - Binding η^2 and end-on through the oxygen.

2.12 Hydrides and Silyls

4/21: - M$-$SiR$_3$ (silyl).
  - 1 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 $\text{Fp}^- \xrightarrow{\text{TMSCl}} \text{CpFe(CO)}_2\text{(SiMe}_3)$.
  - 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 β-H elimination is not a problem typically as Si=CR$_2$ bonds are not stable (unless you add a lot of steric bulk).
       - Thus, $SiMe_3$ does not undergo β-H elimination.

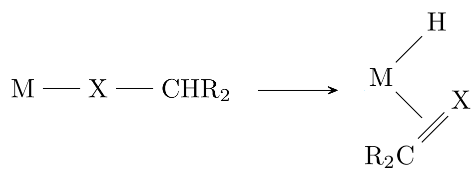
2. Oxidative addition: $L_nM^0 + HSiR_3 \rightleftharpoons L_nMH(SiR_3)$.
   - Almost always occurs through Si−H bonds.
   - C−H addition can be quite hard, but Si−H addition can be quite easy.
     - Thus, for example, $HSiR_2Cl$ will add through the Si−H bond, not the Si−Cl bond since the latter are thermodynamically strong.
   - Si−H bonds form and break in a mobile and dynamic equilibrium.
     - The larger orbital radius of silicon helps form the σ 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) σ 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: $\overset{\oplus}{M} — \overset{\ominus}{H}$
  - Early metal hydrides are very polar and anionic; late transition metal hydrides are more covalent.
  - Hydrides can react like H^+, $H\cdot$, and H^-.

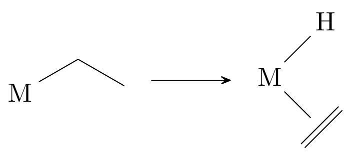
- Electronegativity trends can influence reactivity.
- Hydries acting as acids:
  - $HCo(CO)_4 \rightleftharpoons H^+ + Co(CO)_4{}^-$, p$K_a < 0$ (favorable).
  - $HCo(CN)_5{}^{3-} \rightleftharpoons H^+ + Co(CN)_5{}^{4-}$, p$K_a > 20$ (unfavorable).
  - Think about the electronegativity and how electron rich or poor a metal center to determine whether or not it will want to ionize.
- Hydrides acting as classic hydrides:
  - $Cp^*_2ZrH_2 \xrightarrow{HCl} H_2 + Cp^*_2ZrHCl$.
  - $Cp^*_2ZrH_2 \xrightarrow{2\,O{=}CH_2} Cp^*_2Zr(OCH_3)_2$.
- Hydrides acting somewhere in-between these two extremes (actin acidic and hydritic):
  - $Cp_2MoH_2 \xrightarrow{LDA} [Cp_2MoH^-\ Li]_4$.
  - Note that LDA is a strong base.
  - $Cp_2MoH_2 \xrightleftharpoons{H^+} Cp_2MoH_3{}^+$.
  - Note that H^+ is just a generic acid, and the product is an H_2 adduct.
- Radical:
  - $M{-}H \longrightarrow M\cdot + H\cdot$.
  - The classic example of this is $(CO)_5Mn{-}H$ which can homolyze pretty easily.

- Synthesis of hydrides (the first four are fundamental reactions, but the latter ones are also important):
  1. H_2 directly:
     - $CoS + [CO + H_2] \xrightarrow[Cu\,/\,200\,^\circ C]{200\,atm} HCo(CO)_4 + CuS$.
       - $[CO + H_2]$ 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.
     - $FeI_2 + PF_3 + H_2 \xrightarrow[Zn\,/\,250\,^\circ C]{100\,atm} H_2Fe(PF_3)_4 + ZnI_2$.
       - Zinc serves as a reductant here.
     - Other examples exist, but no more are shown.
  2. Protonation of metal anions:
     - $Ru(CO)_5 \xrightarrow[-CO]{Na} Na_2Ru(CO)_4 \xrightarrow{HA} H_2Ru(CO)_4$.
     - Similar chemistry exists with Os and Fe.
  3. Oxidative addition across a M−M bond.
     - $Cp(CO)_3Cr{-}Cr(CO)_3Cp \xrightarrow{H_2} 2\,CpCr(CO)_3H$.
     - $Os_3(CO)_{12} \xrightarrow[80\,atm]{H_2} H_2Os(CO)_4$.
  4. Oxidative addition to a single metal center.
     - $IrCl(CO)(PPh_3)_2 \xrightarrow{H_2} IrClH_2(CO)(PPh_3)_2$.
     - $HCo(N_2)(PPh_3)_3 \xrightarrow[H_2]{-N_2} H_3Co^{III}(PPh_3)_3$
  5. Hydrogenations of M−L bonds with H_2.
     - $M{-}R + H_2 \longrightarrow [MRH_2]^\ddagger \longrightarrow M{-}H + R{-}H$.
     - $M{-}OR + H_2 \longrightarrow M{-}H + HOR$.
       - Much harder to do since the M−O bond is typically more ionic, and thus stronger.
     - Example: $Cp^*_2Ta(CH_3)_4 \xrightarrow{H_2} Cp^*_2TaH_4 + 4\,CH_4$.
       - This reaction must proceed through σ-bond metathesis.

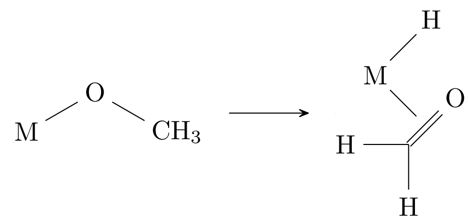
6. Electrophilic metal centers with hydride reagents.
   - $L_3IrCl_2 \xrightarrow[\text{THF}]{\text{LAlH}} IrH_3L_3 + H_3Al{-}THF$.
   - $Cp_2ZrCl_2 \xrightarrow{BH_4{}^-} Cp_2Zr(BH_4)_2 \xrightarrow{NR_3} [Cp_2ZrH_2]_2 + R_3N{-}BH_3$.
7. β-H elimination.



(a) General case.



(b) Simplest case.

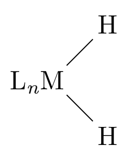


(c) Alternate case.

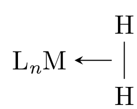
Figure 2.24: β-H elimination synthesis of metal hydrides.

   - 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 H_2 adduct.

Figure 2.25: Non-classical hydrides.

  - L_nMH_2 could be a dihydride or an 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}H hydrides are usually upfield (-1 to -15 ppm).
  - A T_1 relaxation also provides the H−H distance.
  - Lastly, H_1D 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.

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