

CHEM 20200 (Inorganic Chemistry II) Notes

Steven Labalme

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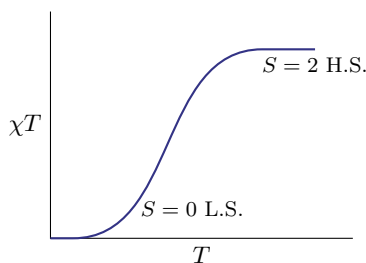
Unit 1

Electronic Phenomena

1.1 Lecture 1: Introduction/Key Trends

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

- **Lanthanide contraction:** In the transition metals, there is a small/no increase in size between the second and third rows.
 - This is because the shell added in between contains the f orbitals, which are small, do not extend past the noble gas core, and do not provide good shielding.
 - Z goes up a lot with little shielding, so the $5d$ orbitals are contracted; thus, $4d/5d$ orbitals are similar in size.
- **Oxidation state:** The number of electrons a metal center is below its valence.
 - Typically, the maximum oxidation state is defined by the d -count for the 0-valent metal.
- Having discussed four trends, how are they related?
 - As oxidation state increases, “electronegativity” and ionization potential will increase, and the radius will decrease.
 - This is because removing an electron \Rightarrow reduces shielding \Rightarrow higher positive charge \Rightarrow all orbitals decrease in energy \Rightarrow all orbitals decrease in size (hence radius decreases, too).
 - Watch out for discontinuities such as Mn^{2+} .
- **Magnetic properties:** Unique to the transition metals and the f block.
 - Consider $\text{Fe}^{\text{II}}\text{L}_6^{2+}$ (d^6).
 - Possible states: Low spin ($S = 0$), intermediate spin ($S = 1$; rare), and high spin ($S = 2$).
 - We predict which state dominates by the:
 - **Pairing energy.**
 - **Ligand field stabilization energy.**
- **Pairing energy:** The energy cost of putting two electrons in the same orbital. *Also known as PE.*
 - Trends with orbital size/radius.
 - Decreases down a column.
- **Ligand field stabilization energy:** *Also known as LFSE.*
 - Can be thought of in terms of crystal field theory.
 - Extra thoughts on Figure VI.10 of Labalme (2021): Donating negative charge to a free metal ion in a spherically symmetric fashion uniformly raises the energy of the d orbitals by increasing repulsions and size.
 - Low-spin LFSE: $6 \cdot -4\text{Dq} + 3\text{PE} = -24\text{Dq} + 3\text{PE}$.
 - Intermediate-spin LFSE: $5 \cdot -4\text{Dq} + 1 \cdot 6\text{Dq} + 2\text{PE} = -14\text{Dq} + 2\text{PE}$.
 - High-spin LFSE: $4 \cdot -4\text{Dq} + 2 \cdot 6\text{Dq} + 1\text{PE} = -4\text{Dq} + 1\text{PE}$.
 - Thus, the energy difference between the low-spin and high-spin configurations is $20\text{Dq} + 2\text{PE}$. It follows that if $10\text{Dq} > 1\text{PE}$, then the complex will be low spin; and if $10\text{Dq} < 1\text{PE}$, then the complex will be high spin.
 - This also explains why the intermediate spin state is rare: if 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):



- 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)

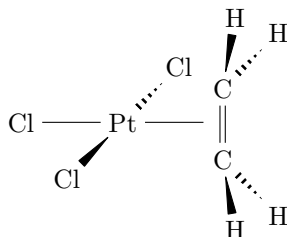
- 3/30:
- Electron affinity, not electronegativity, for the periodic trend?
 - At higher levels, people don't really distinguish between the two.
 - To what extent do we need to have the spectrochemical series memorized?
 - You don't need to memorize them, but it's good to know some of them off the top (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).

¹Hard 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, $18e^-$ Rule

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

– 4 coordinate:

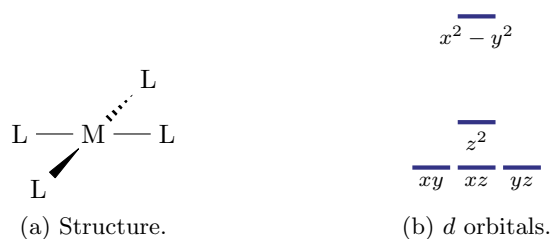


Figure 1.3: Square planar information.

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



Figure 1.4: Tetrahedral information.

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

– 5 coordinate:

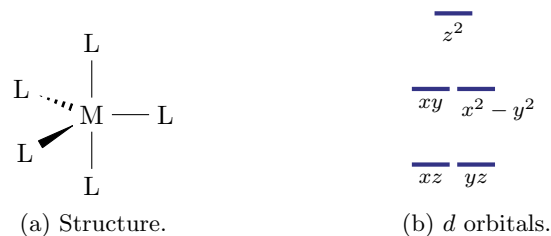


Figure 1.5: Trigonal bipyramidal information.

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

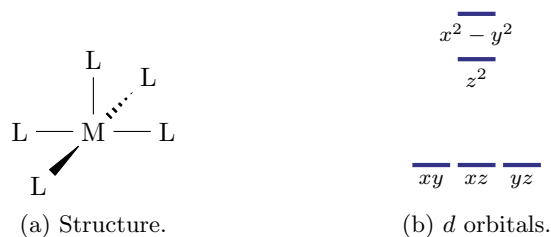


Figure 1.6: Square pyramidal information.

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

- 6 coordinate.

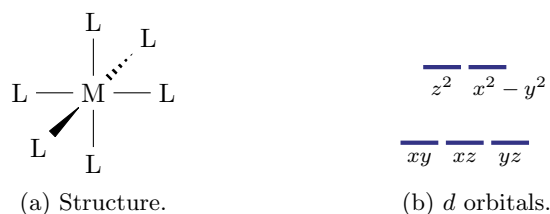


Figure 1.7: Octahedral information.

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

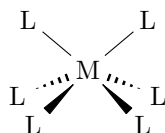


Figure 1.8: Trigonal bipyramidal information (structure).

- Trigonal bipyramidal (each pyramid is eclipsed, rather than staggered as in octahedral; Pfenig and Seppelt (1996) explores this geometry in greater depth).
- **Fluctional ligands:** A set of ligands that readily exchange positions around the molecular center via a **Berry pseudorotation**.
- Ligand types (see Labalme (2021, p. 93)).
- **X-type** (ligand): Typically anionic, covalent donors.
- **L-type** (ligand): Typically neutral. *Also known as dative donor*.
- **Z-type** (ligand): Typically neutral, but can be cationic (no electrons to donate; these are acceptors).
- Note that a carbonyl group can be both an L- and a Z-type ligand (L if it participates in 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 benzene]). Don't forget lone pairs.
2. The charge on the metal after step 1 is its oxidation state.	2. Assign formal charges (in a dative bond, these belong to the ligand).
3. From 2, assign a d -electron count.	3. The number of electrons that a given ligand donates is equal to its formal charge plus twice the number of dative bonds plus the number of covalent bonds.
4. The electron count equals the d^n count plus the ligand donors (typically 2 electrons per ligand).	4. The electron count is that d^n count for M^0 plus the sum of the ligand electron donations minus the charge on the complex.

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

- A phosphine PR_3 .
 - The phosphine has a lone pair to donate to the metal center, forming a **dative bond**.
 - Alternatively, the formal charge on phosphorous in a $\text{M}-\text{PR}_3$ situation is +1 and there is 1 covalent bond.
 - Either way, the phosphine is a 2-electron donor; this is further confirmed by the fact that phosphines are L-type ligands.
- CO.
 - We have multiple possible resonance structures for a $\text{M}-\text{C}\equiv\text{O}$ bond, but we can robustly treat this with the covalent method.
 - $\text{M}-\text{C}\equiv\text{O}^{\oplus}$ has a +1 formal charge and 1 covalent bond, suggesting that CO is a 2-electron donor.
 - $\text{M}=\text{C}=\text{O}^{\cdot\cdot}$ has no formal charge and 2 covalent bonds, suggesting that CO is a 2-electron donor.
 - $\text{M}\equiv\text{C}-\text{O}^{\ominus}$ has a -1 formal charge and 3 covalent bonds, suggesting that CO is a 2-electron donor.
 - $\text{M}\leftarrow\text{C}\equiv\text{O}^{\oplus}$ has a net 0 formal charge and 1 dative bond, suggesting that CO is a 2-electron donor.
- NO.
 - If NO bonds linearly, it's a 3-electron donor (take $\text{M}-\text{N}\equiv\text{O}^{\oplus}$ as a possible resonance structure).
 - If NO bonds bent, it's a 1-electron donor (take $\text{M}-\ddot{\text{N}}=\ddot{\text{O}}$ 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 $\text{W}(\text{CH}_3)_6$ (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.
 - $\text{W}(\text{CH}_3)_6$ (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.

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

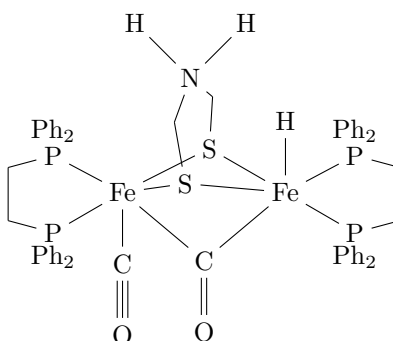
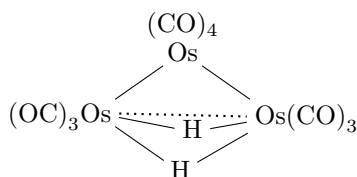


Figure 1.9: An enzymatic cofactor.

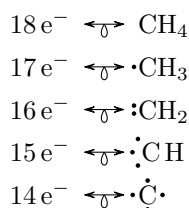
- Each phosphine and each carbonyl is a 2-electron donor.
 - The hydride is an X-type ligand with a covalent bond, and thus a 1-electron donor.
 - Now for the big bulky center bridging ligand: The sulfurs each carry a +1 formal charge and form two covalent bonds to the metal centers, so they each contribute 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

$$\# \text{ of M-M bonds} = (18 e^- \cdot \# \text{ of metals} - \# \text{ of } e^- \text{'s from L's and M}^0 \text{'s}) / 2$$
 - Essentially, one M–M covalent bond contributes one electron to each M, or two electrons to the complex as a whole.

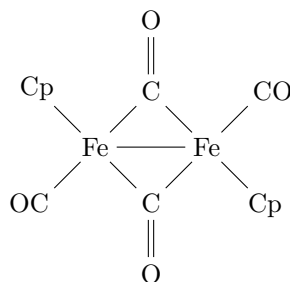
- As we can see, this number would be 0 for the enzymatic cofactor in Figure 1.9, which is why we'd expect no metal-metal bonding between the two iron centers.
- Bridging hydrides and halides:
 - We can treat this by putting a +1 formal charge on the bridging atom: $M-\overset{\oplus}{X}-M$.
 - Alternatively,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

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

- 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,



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

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 $[\text{CpFe}(\text{CO})_2\text{AlMe}_3]^-$.
 - 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.

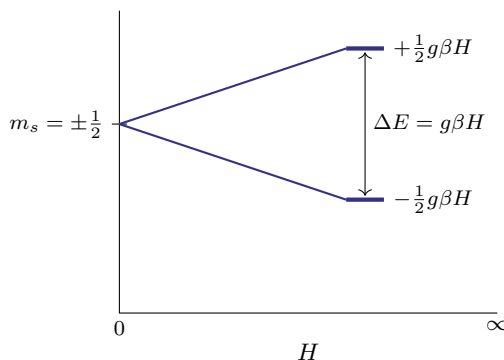


Figure 1.12: A Zeeman splitting diagram for a single electron.

- 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

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

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

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

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

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

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

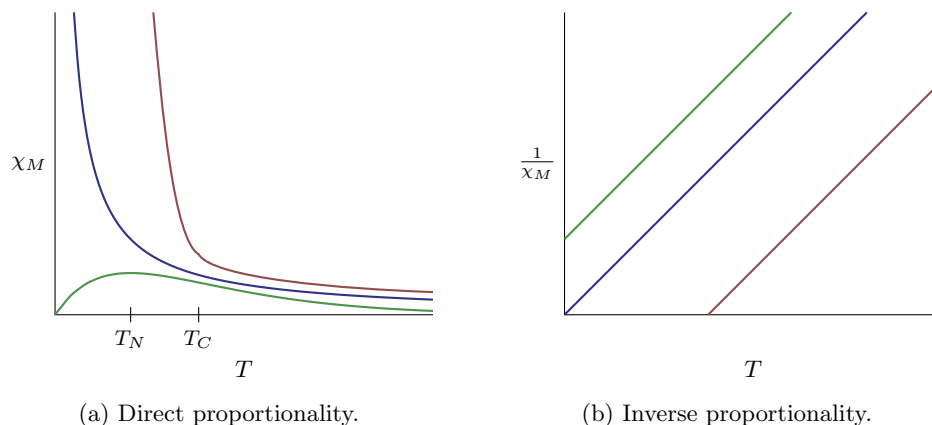


Figure 1.13: Temperature vs. magnetic susceptibility in different magnets.

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

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

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

where 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}):

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

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

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

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

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

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

- In the above equation, 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

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

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

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

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

- We can break this down even further.

- We find that

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

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

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

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

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

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

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

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

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

- This implies that

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

- **Van Vleck equation:** The above equation^[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 close to the spin-only value. (Quantum mechanical explanation: The electronic symmetry of a totally symmetric state precludes any mixing of the orbital angular momentum with the spin angular momentum.)
- A first approximation of S.O.C.:
 - For a less than half-filled set of orbitals, expect $\mu_{\text{eff}} / \chi T$ to be lower than the spin-only value, i.e., $g < 2$.
 - Typically $\mu_{\text{eff}} / \chi T$ is close to the spin-only value.

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

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

1.7 Office Hours (Anderson)

- 4/5:
- Electron counting for a metal center bonded to a π bond?
 - As in PSet 1 Questions 1.2 and 1.6.
 - Example: Ni^0 -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: $\text{Ni}(\text{COD})_2$.
 - 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 $1e^-$ coupled?
 - Referring to reactivity? B/c higher oxidation states are more stable for early row transition metals.
 - Figure VI.13 of Labalme (2021) says that *two* metal orbitals form bonding/antibonding orbitals with the ligand orbitals, so why does Dr. Anderson assert that only *one* does? Is it because of what he said about d_{z^2} being practically interchangeable with the $d_{xy,xz,yz}$ ligands in square planar complexes?
 - Yes it is.
 - Now this question could just be a relic of my previous understanding of bonding, and the answer may just be “MO theory,” but I’m still gonna ask: Where do the electrons in all of the bonds come from? It seems like if the osmiums are giving electrons to Os–Os and Os–H bonds, and we still count osmium as d^8 , we are counting some electrons twice.
 - It’s fine to count them twice. The electron count is a computational tool, not a count of electrons.
 - Does the electron count have physical meaning?
 - Guides you toward what compounds are more reactive. And other chemical properties.
 - What does isolobal mean?
 - The fic fragment: Right spelling/charge?
 - Does the iron in Figure 1.11 have tetrahedral or square planar geometry and why?
 - Copies Table VI.2 from Labalme (2021). Some differences?
 - Why these specific spins to higher and lower energy (Figure 1.12)? Or is it arbitrary?
 - What is a Boltzmann population?
 - Differences in Curie’s Law from last quarter?
 - How do you define d count? Green (1995) defines it as $d^n - x$ where d^n is the ground state configuration and x is the number of X-functions.
 - The d^n count should reflect the oxidation state.
 - Charges on compounds affect the oxidation state of the metal.
 - Where do the extra electrons come from in the CO resonance structures (the ones that are bonded to the metal)?
 - All M–C bonds are 2-electron? The IR stretching frequency just changes in some resonance structures so we call this a multiple M–C bond even though it isn’t.
 - How do we handle ligands with preexisting charges (i.e., NO^+ , SO_4^{2-} , $\eta^3\text{-C}_3\text{H}_5^+$, etc.)

1.9 Discussion Section

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

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

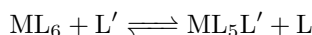
Unit 2

???

2.1 Lecture 4: Substitution Reactions

4/5:

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



- We investigate the position of the equilibrium with the three main characteristics that determine reactivity.

1. Sterics.

- Related to the metal coordination number.
 - C.N. > 6 is typically disfavored.
 - C.N. < 6 is possible.
- The size of L' is also important: If L' = PPh₃ 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, Fe⁰ will bind CO strongly since Fe⁰ 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:

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

2. Dissociative mechanism.

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

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

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

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

3. Interchange mechanisms.

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

- Kinetics and rates of these mechanisms.

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

- I) Very fast.

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

- II) Fast.

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

- III) Slower.

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

- IV) Inert.

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

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

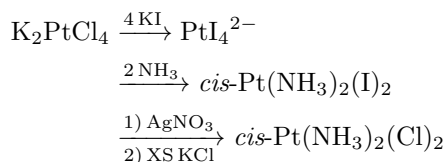
- The identity of L' also influences rates.

- Reaction rates increase with the ligand field strength of L'^[1].

¹Goes over Table IX.1 from Labalme (2021).

- Characteristics of the metal that control the observed rates.
 - Ranking L.S. metal centers (slowest to fastest): $\text{Co}^{\text{III}} < \text{Cr}^{\text{III}} < \text{Mn}^{\text{III}} < \text{Fe}^{\text{III}} < \text{Ti}^{\text{III}} < \text{V}^{\text{III}}$.
 - Considering the d counts, we have $d^6 < d^3 < d^4 < d^5 < d^1 < d^2$.
 - Now think of this in terms of the d -orbitals splitting diagram (Figure 1.7b).
 - As the antibonding orbitals get filled, 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 $\text{Cu}(\text{MeNH}_2)_4^{2+}$ vs. $\text{Cu}(\text{en})_2^{2+}$ to emphasize the importance of entropy (see the related discussion in the notes on Chapter 10 in Labalme (2021)).
 - EDTA is a hexadentate ligand that is commonly used in biology to pull all metal centers out of solution.
 - For Fe^{3+} for example, $K_f = 10^{25} \text{ mol}^{-1}$. What is mol^{-1} and why is it here?
 - Siderophores and eubacterin are biology's own chelators ($K_f = 10^{52} \text{ mol}^{-1}$).
 - These chelators involved because if bacteria are going to invade a host, they need to scavenge iron, but iron is pretty tightly regulated. Thus, there has been an arms race of molecules that can scavenge iron or prevent iron from being scavenged.
 - Chelation therapy: If exposed to a heavy metal, you will be given chelating agents that will bind to metal ions and cause them to be excreted from the body.
 4. Trans effect.
 - Reviews some info from Labalme (2021).
 - Helps predict the **regiochemistry** of where a given ligand will substitute.
 - Cis-platin reaction mechanism: $\text{cis-Pt}(\text{NH}_3)_2(\text{Cl})_2 \longrightarrow \text{cis-Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2$ in the body, which binds to DNA on the *cis*-water side, causing a kink, stopping transcription, and initiating apoptosis.
 - Cis-platin is quite toxic (people are trying to develop formulations that are less so), but highly effective at stopping cancer.
 - Can't have *trans* because it doesn't have the *cis*-water side. Thus, this synthesis mechanism doesn't work: $[\text{PtCl}_4]^{2-} \xrightarrow{2\text{NH}_3} \text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$.

- Therefore, we synthesize it as follows.

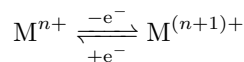


- Note that we start from tetrachloroplatinate because it is the most common form of platinum.
- Also note that XS stands for “excess.”
- Trans-effect order listed.
- The trans-effect is kinetic; concerned with rates of exchange.
 - Stronger *trans*-directors **labelize** the ligands opposite them.
-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

2.2 Lecture 5: Electron Transfer Reactions

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

- General form:



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

- Energies:

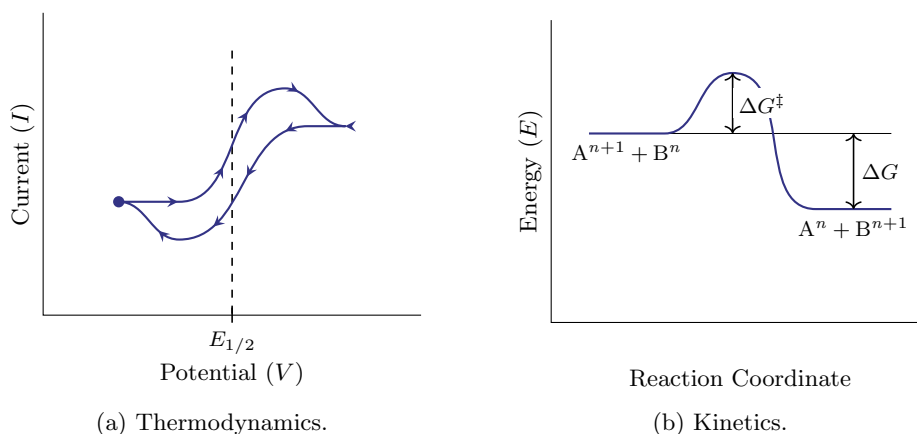


Figure 2.1: Electron transfer reaction energies.

1. Thermodynamic:

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

2. Kinetics:

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

- The role of ΔG^\ddagger in an electron transfer.

- Electrons move very quickly and are highly delocalized with respect to the nuclei, so what dictates kinetics in these processes is nuclear motion (recall reorganization energy).
- In a simplistic sense, the key is the $[A^n + B^{(n+1)}]^*$ encounter complex.
- Electron transfer changes bond length.
 - There is a kinetic barrier to the electron transfer because the thermodynamic energy is based on minimizing the energy in the reduced and oxidized forms.
- Bond lengths change upon redox, so the solvent and counteranions have to reorganize.
- This **reorganization energy** leads to a kinetic barrier (i.e., ΔG^\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 ΔG^\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 $\Delta G^\ddagger = \Delta G_t^\ddagger + \Delta G_v^\ddagger + \Delta G_0^\ddagger$.
 - ΔG_t^\ddagger is the translational energy, which is moving the two species together.
 - ΔG_v^\ddagger is vibrational, which is concerned with the bond lengths of the irons' matching structures.
 - ΔG_0^\ddagger is the solvent, dipole, counterion, etc. This can be large (so one of the greatest contributors is the environment in which the system lies).
- Example:
 - $\text{Co}(\text{NH}_3)_6^{2+} / \text{Co}(\text{NH}_3)_6^{3+}$ is H.S. d^7 / L.S. d^6 .
 - Self-exchange is slow because nuclear reorganization is large (0.2 Å difference in bond length, which is significant).
 - Note that this arises from the different electronic configurations.
 - The ion is getting smaller *and* going low-spin during reorganization.
- Another example:
 - $\text{Ru}(\text{NH}_3)_6^{2+} / \text{Ru}(\text{NH}_3)_6^{3+}$.
 - k_{exch} is eight orders of magnitude faster than the previous example.
 - This is because ruthenium is low-spin throughout ($\Delta(\text{Ru}-\text{N}) \approx 0.04 \text{ Å}$ 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

$$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} + \text{Cr}(\text{H}_2\text{O})_6^{2+} \longrightarrow \text{Co}(\text{NH}_3)_5^{2+} + \text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$$

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

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



Figure 2.2: The Creutz-Taube ion.

- The bridging ligand is a pyrazole.
- The electron transfer is very fast; thus, the oxidation state is approximately $\text{Ru}_2^{2.5}$.
- Such electron transfers are measured with Near-IR spectroscopy, which can see inter-valence charge transfer bands (IVCT), which include bonds.
 - This very low energy form of spectroscopy observes the energy that it takes to excite an electron between the two ruthenium centers.
- Robin-Day classification:
 - I) Completely localized.
 - Regardless of the spectroscopic technique used, a difference between 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:**

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

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 $\lambda \rightarrow -\Delta G$, $\Delta G^\ddagger \rightarrow 0$. Furthermore, as λ passes $-\Delta G$, ΔG^\ddagger increases.

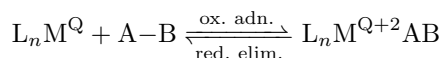
- This has important implications in biology, catalysis, etc. For example, if you want to slow down an undesirable side reaction and speed up your main reaction, provide more driving force. This accelerates your main reaction and moves your side reaction into the inverted region.

2.3 Lecture 6: Oxidative Addition and Reductive Elimination

4/9:

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

- General form:



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

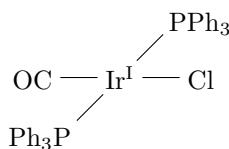


Figure 2.3: Vaska's complex.

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

1. Concerted.

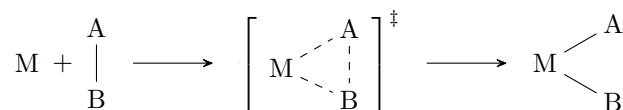


Figure 2.4: The concerted mechanism for oxidative addition.

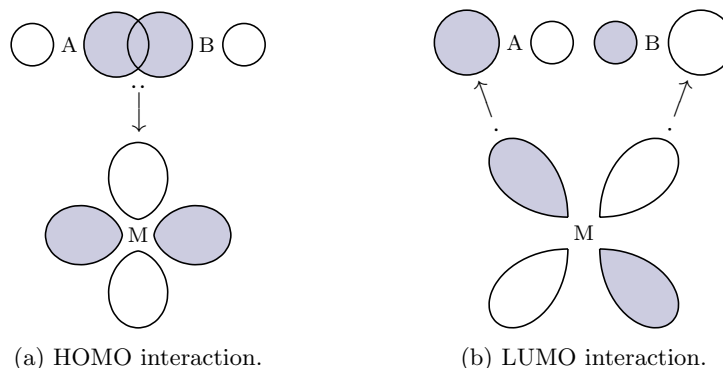
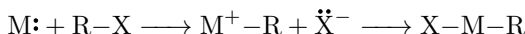


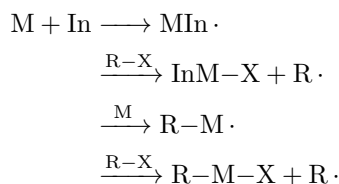
Figure 2.5: Orbital interactions in concerted oxidative addition.

- *cis* products.
 - If you see a *trans* product, this is not the mechanism.
- HOMO interaction: The A–B 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. S_N2 .

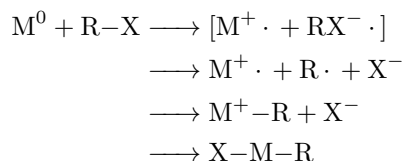
- *cis* or *trans*; no clear preference.
- One signature of this reactivity is a steric preference where primary > secondary > tertiary.
 - Some of the trends of organic reactions can appear in inorganic reactions!

3. Radical chain.



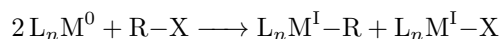
- We begin with a metal and an initiator (denoted In).
 - These react to form the adduct $\text{MIn} \cdot$, which is a radical.
 - This radical grabs an X from $\text{R}-\text{X}$ to form $\text{InM}-\text{X}$ (this product is worthless and the final step of initiation). A $\text{R} \cdot$ is also generated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

4. Electron transfer.

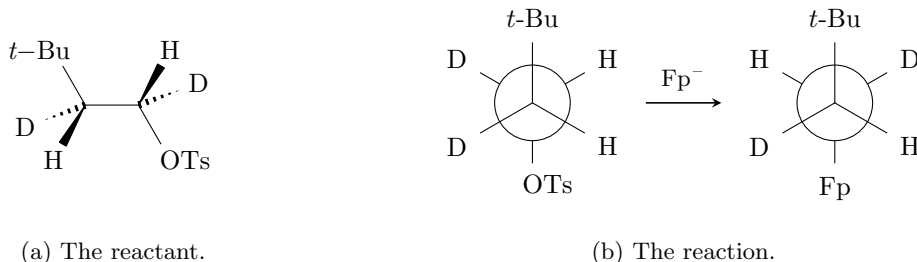


- Related to S_N2 again.
- This is not a radical chain process (no propagation); it's just an electron transfer followed by fragmentation and recombination.
- Jack Halpern of UChicago writes Chock and Halpern (1966).
 - Studies $L_2IrClCo \xrightarrow{MeX} L_2IrClCoMeX$, specifically the reaction rates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

• Bimolecular oxidative addition:



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

Figure 2.6: S_N2 stereochemistry.

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

• Another synthesis:

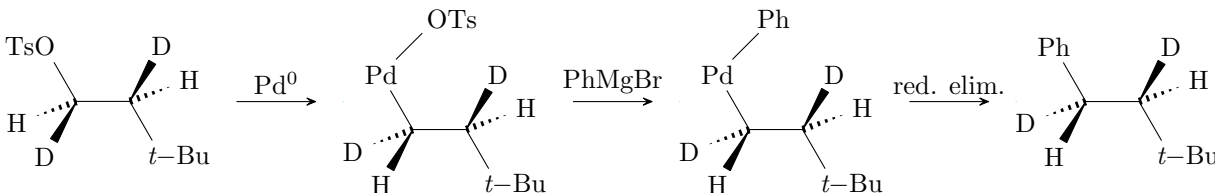


Figure 2.7: An additional way of probing $\text{S}_{\text{N}}2$ addition/elimination.

- This one shows us that palladium causes an inversion once again, but reductive elimination does not.
- Radical mechanisms.
- We probe these with **radical clocks**.
 - The unzipping of the methylcyclopropane radical ring happens so fast that it will necessarily be faster than any recombination with 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.

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