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:
$$ML_6 + L' \rightleftharpoons ML_5L' + L$$

- 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:
     $$\frac{d[ML_5L']}{dt} = k_{obs}[ML_6][L']$$

  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:
     $$\frac{d[ML_5L']}{dt} = \frac{k_2 k_1 [ML_6][L]}{k_{-1}[L] + k_2[L']}$$
     - Experimentally, we swamp the reaction with L' so that [L'] >>> than all other reagents. This makes it so that the rate is just $k_{obs}[ML_6]$, 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 Fe^{2+}(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].

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

■ Therefore, we synthesize it as follows.

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

■ 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:
$$M^{n+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{(n+1)+}$$
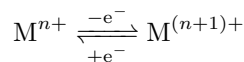
– The forward reaction is known as **oxidation** (metal oxidation state increases), while the reverse is known as **reduction** (metal oxidation state decreases).
– This is different than the oxidation/reduction reactions of organic chemistry, which involve removing or adding, respectively, a hydrogen.

• 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 $\rightarrow$ encounter complex $\rightarrow$ electron transfer state (an excited state) $\rightarrow$ 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:
   - $\Delta G = E_{1/2_A} - E_{1/2_B}$ where $E_{1/2_X}$ 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 ($\Delta(Ru-N) \approx 0.04$ 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

$$Co(NH_3)_5Cl^{2+} + Cr(H_2O)_5{}^{2+} \longrightarrow Co(NH_3)_5{}^{2+} + Cr(H_2O)_5Cl^{2+}$$
$$\xrightarrow{H_2O} Co(H_2O)_6{}^{2+} + Cr(H_2O)_5Cl^{2+}$$

  - The intermediates are $[(H_3N)_5Co^{III}-Cl-Cr^{II}(OH_2)_5]^{4+} \longrightarrow [(H_3N)_5Co^{II}-Cl-Cr^{III}(OH_2)_5]^{4+}$.
  - 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 ($Br^- > Cl^- > F^- > H_2O > NH_3$).

- Inner-sphere electron transfer: Mixed valency.

- Consider the Creutz-Taube ion.

$$\left[(NH_3)_5Ru \text{---} N \bigcirc N \text{---} Ru(NH_3)_5 \right]^{5+}$$
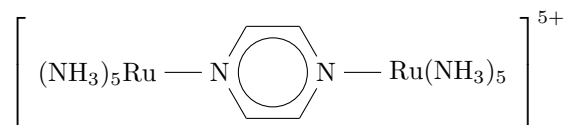
Figure 2.2: The Creutz-Taube ion.

  – 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**:
    $$k_{ET} = \nu_N k_e e^{-\Delta G^{\ddagger}/RT}$$
    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 $\lambda \to -\Delta G$, $\Delta G^{\ddagger} \to 0$. 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:
$$L_nM^Q + A{-}B \xrightleftharpoons[\text{red. elim.}]{\text{ox. adn.}} L_nM^{Q+2}AB$$
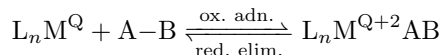
- Changes at the metal center during these two reactions (generically).

    - 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.
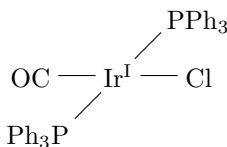
- Classic studies: On Vaska's complex.

$$\begin{array}{c}
\qquad\qquad\qquad\quad PPh_3 \\
\qquad\qquad\qquad\nearrow \\
OC{-}\!\!\!-Ir^I\!\!-\!\!{-}Cl \\
\qquad\swarrow \\
Ph_3P
\end{array}$$

Figure 2.3: Vaska's complex.

    - Characteristics of the reactant: d^8, $16\,e^-$, canary yellow color.
    - Characteristics of the product (after reacting with MeI, H_2, or O_2): d^6, $18\,e^-$.
    - 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.

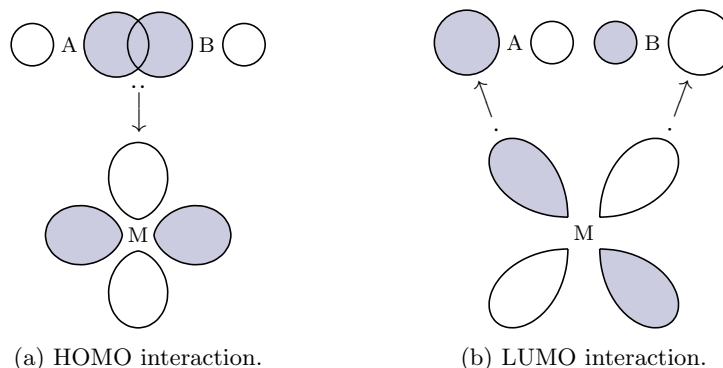Figure 2.4: The concerted mechanism for oxidative addition.

(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. S_N2.
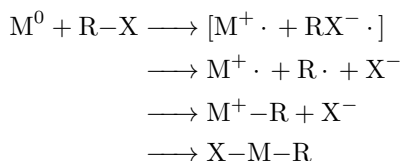$$M\!:\, + R-X \longrightarrow M^+-R + \ddot{\underset{..}{X}}{}^- \longrightarrow X-M-R$$

   – *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.

$$M + In \longrightarrow MIn \cdot$$
$$\xrightarrow{R-X} InM-X + R \cdot$$
$$\xrightarrow{M} R-M \cdot$$
$$\xrightarrow{R-X} R-M-X + R \cdot$$

   – 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.

$$M^0 + R\text{--}X \longrightarrow [M^+ \cdot + RX^- \cdot]$$
$$\longrightarrow M^+ \cdot + R \cdot + X^-$$
$$\longrightarrow M^+\text{--}R + X^-$$
$$\longrightarrow X\text{--}M\text{--}R$$

- 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 $I^- > Br^- >> Cl^-$, 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:

$$2 L_nM^0 + R\text{--}X \longrightarrow L_nM^I\text{--}R + L_nM^I\text{--}X$$
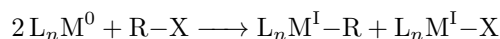
- Jack Halpern again writes Halpern and Maher (1965).

- 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: $2 L_nM + 2 RX \longrightarrow 2 L_nM\text{--}X + R\text{--}R$.

- For example, $Cp_2^*Yb(OEt_2) + CH_2Cl_2 \longrightarrow 2 Cp_2^*Yb\text{--}Cl + ClCH_2\text{--}CH_2Cl$.
- This can also occur through a radical mechanism. We form an $R \cdot$ radical that can recombine to form $R\text{--}R$ or make $M\text{--}R$.

- Stereochemistry of S_N2 type reactivity.

- George Whitesides writes Bock et al. (1974).

(a) The reactant.   (b) The reaction.
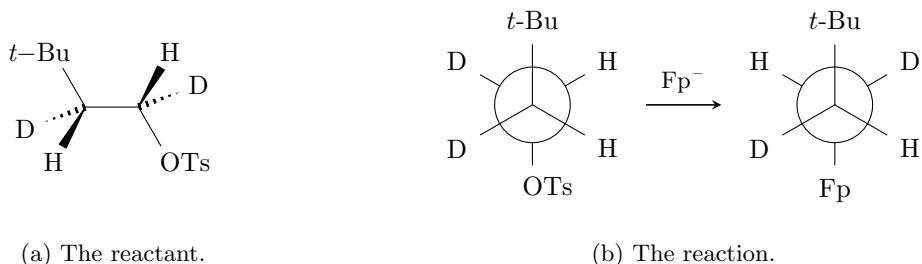
Figure 2.6: S_N2 stereochemistry.

– 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:

$$\text{L}-\text{M}^Q-\text{X} \xrightleftharpoons[\text{deinsertion}]{\text{insertion}} \text{M}^Q-\text{L}-\text{X}$$

  - 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: $\text{Me}-\text{M}-\text{CO} \rightleftharpoons \text{M}-\text{C}(=\text{O})-\text{Me}$.

    ■ So named because the metal and the migrating group end up at the same position on the carbonyl ligand (the 1 position).

  - 1,2-migration: $\text{Cp}_2\text{Zr}(-||)\text{Me} \rightleftharpoons \text{Cp}_2\text{ZrPr}$.

    ■ So named because the metal ends up on the 1 position of the ethylene olefin and the migrating group ends up on the 2 position of the ethylene olefin (remember that we number substituents from the metal center outwards).

- More groups than methyl can migrate; it's just that methyl commonly migrates.

- Insertions into $\text{M}-\text{C}$ bonds are common.

  - Insertions into $\text{M}-\text{H}$ bonds are common for olefins, but uncommon for CO because metal carbonyl species are unstable.

 - You can also insert into $\text{M}-\text{O}$ bonds (note that dppe stands for diphenylphosphinoethane):

Figure 2.8: Insertion into an $\text{M}-\text{O}$ 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 $\text{M}-\text{X}$ 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 $\text{Mn(CO)}_5\text{Me}$?

- β-H elimination: $\text{L}_2\text{NiEt} \rightleftharpoons \text{L}_2\text{Ni}(-||)\text{H}$.
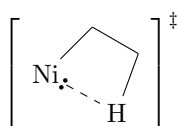
Figure 2.9: The transition state in a β-H elimination.

– The transition state (see Figure 2.9) shows an **agostic interaction**.
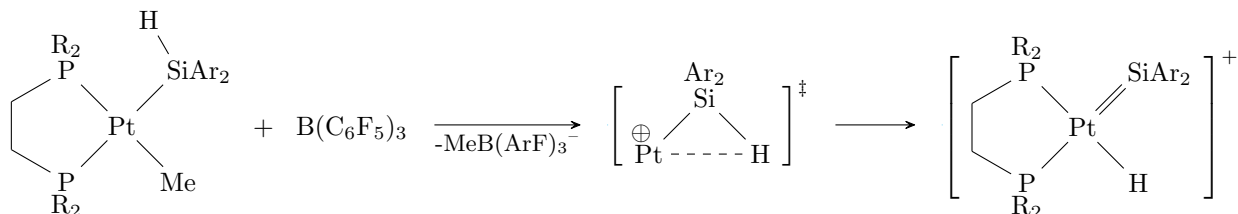
• α-elimination[2].

Figure 2.10: An example of α-elimination.

• External attack at a ligand.

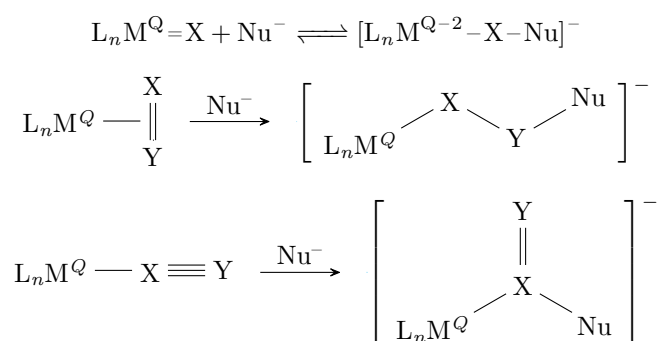$$L_nM^Q{=}X + Nu^- \rightleftharpoons [L_nM^{Q-2}{-}X{-}Nu]^-$$

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.

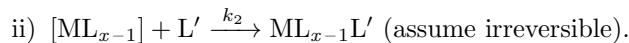[2]Note that Ar stands for an aryl group.

- σ-bond metathesis: $L_nM^Q-X + Y-Z \rightleftharpoons L_nM^Q-Y + X-Z$.

    - Usually observed for d^0 systems.

- Example: $Zr^{IV}(N(SiR_3)H)_3Me \longrightarrow Zr(N(SiR_3)H)_2(=N-SiR_3) + CH_4$.

    - $C-H$ activation is a big thing in synthetic chemistry, and a lot of the pathways go through d^0, early, reactive transition metals.

- More on 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 $\leq 16\,e^-$.
        - Because the first step is coordination, usually to form some kind of σ-adduct.

- Kinetics of associative substitution.

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

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

- Kinetics of dissociative substitutions.

i) $ML_x \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ML_{x-1}] + L$.

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

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

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

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

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

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

Figure 2.13: The effect of $[L']$ on rate.

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

  - In the second order region, $ML_x \overset{\text{fast}}{\rightleftharpoons} ML_{x-1}$ 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 $k_2[L'] >> k_{-1}[L]$.
- 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. $\frac{[L]}{[L']}$ and run a linear regression, the slope will be $\frac{k_{-1}}{k_1 k_2}$ and the y-intercept will be $\frac{1}{k_1}$.

- Transition state theory basics:

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

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

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

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

– In the 1930s, Eyring comes up with the Eyring equation

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

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

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

2.5 Office Hours (Anderson)

• Explain cyclic voltammetry.

– SOP for CV in the modules explains cyclic voltammetry.

– You have a working and a reference electrode, as well as an auxiliary platinum wire. All of these are submerged in the same solution (of a polar solvent and your compound).

– You apply a voltage across the working and auxiliary electrodes.

– With nothing in your solution, you have pseudo-capacitance/polar something-or-other. It's basically just a loop with spikes on the end (D_{2h} symmetry) in your voltage vs. current graph.

– However, if we have a compound, we pass some current in the forward and reverse directions at the thermodynamic potential point (the free energy of the reduction/oxidation vs. some other reduction/oxidation process; we can convert to 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· + ·B ⟶ 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.
        - $I_xPt-Me_{4-x}{}^{2-}$ 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 $M-CH_2-TMS$.
        - 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:
$$y\,R^- + MX_y \longrightarrow MR_y + y\,X^-$$
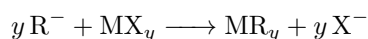
        - For example, $WCl_6 + 6\,MeLi \longrightarrow WMe_6 + 6\,LiCl$.
        - Electron transfer can also be an issue (alkyl lithium agents can be strongly reducing).

- 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.

$$X-M-|| \longrightarrow M-CH_2-CH_2-X$$
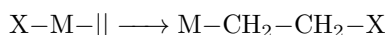
   - X can be an alkyl or a hydride.
   - $(Et_3P)_2Pt^{II}ClH \xrightarrow{||} (Et_3P)_2PtClEt$.
   - $(Et_3P)_2Pt^{II}ClH \xrightarrow{|||} (Et_3P)_2PtClVinyl$.
     - ■ Insertion almost always happens with a *trans* disposition to the metal so the H that was originally attached to the metal ends up on 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 typse 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.
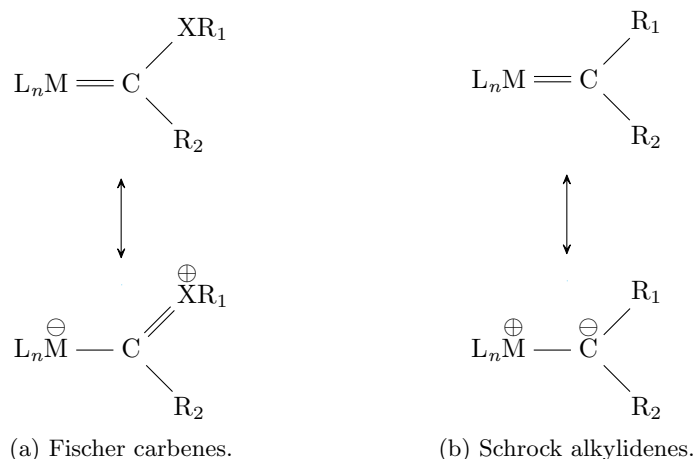
Figure 2.14: Carbene regime resonance structures.

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:

   – $TaCl_5 + \frac{3}{2}Np_2Zn \longrightarrow (Np)_3TaCl_2 \xrightarrow{2\,NpLi} Np_3Ta{=}C(t\text{-}Bu)(H)^{[3]}$.

   – $TaCl_5 + Np_2Zn \longrightarrow Np_2TaCl_3 \xrightarrow{2\,L} Ta({=}C(t\text{-}Bu)(H))Cl_3L_2$.

   – 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.

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[3]Note that we are using Np to denote a neopentyl group.
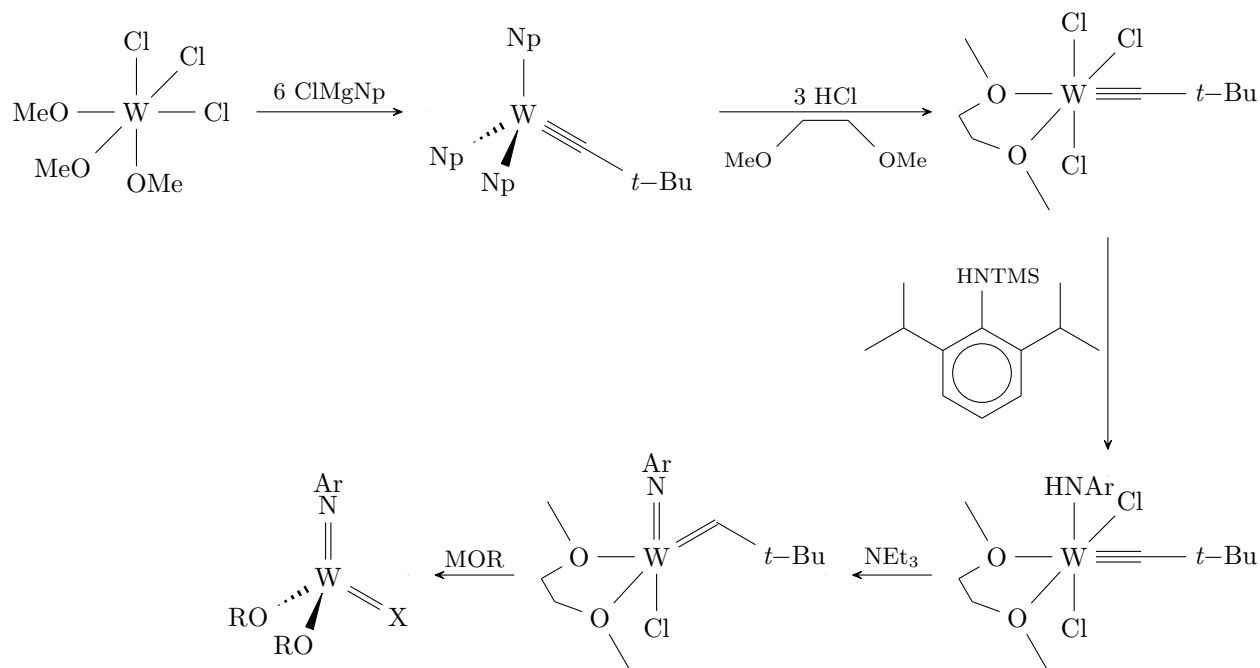
Figure 2.15: Tungsten olefin metathesis.
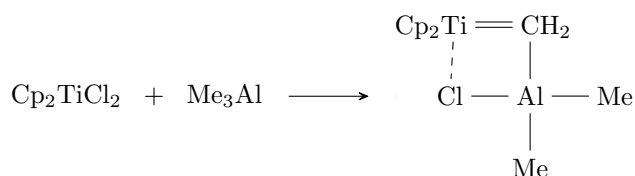
- Tebbe's reagents:

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 bigger 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 $\nu_{CO} = 2143\,\mathrm{cm}^{-1}$.

  - This is also a range of the spectrum with little else going on, making these peaks easily identifiable.

  - CO has a large dipole (about $\mu = 4.80\,\mathrm{D}$). This also really helps it stick to transition metals.

- In $Mn(CO)_5Me$, the $Mn-Me$ bond is $2.18\,\text{Å}$ and the $Mn-CO$ bonds are $1.86\,\text{Å}$, 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 volitle 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:
    - $Co + CO \xrightarrow[\text{RT}]{35\text{ atm}} Co_2(CO)_8$[4].
    - $Fe + CO \xrightarrow[300\,°C]{300\text{ atm}} Fe(CO)_5$.

  - 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., constitutinal isomerism) with the $18\,\mathrm{e}^-$ 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}.

---

[4]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):

  - $Fe(CO)_5 \xrightarrow[-CO]{2\,Na\,/\,THF} Na_2Fe(CO)_4{}^{2-}$.

  - $M(CO)_n \xrightarrow[-CO]{2\,Na} Na_2M(CO)_{n-1}{}^{2-}$.

  - $Re_2(CO)_{10} \xrightarrow{Na} Na^+Re(CO)_5{}^-$.

  - $Re_2(CO)_{10} \xrightarrow[-2\,CO]{6\,Na\,/\,HMPA} Na_3Re(CO)_4{}^{3-}$.

  - $Mo(CO)_6 \xrightarrow{2\,Na} Mo(CO)_5{}^{2-}$.

  - $Mo(CO)_6 \xrightarrow{\Delta\,TMEDA} (CO)_4Mo(EPA) \xrightarrow{4\,NaNH_3} Na_4Mo(CO)_4{}^{4-}$.
    - This is d^0 and thus $\nu_{CO} <<< 2000\,cm^{-1}$.
    - TMEDA is tetramethylethylenediammine.

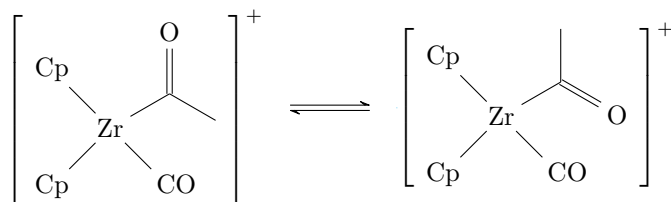- We can also go the other direction to find carbonyls with a very low degree of backbonding.

Figure 2.17: Low backbonding carbonyl complexes.

- The reactant has $\nu_{CO} = 2123\,cm^{-1}$, which is slightly lower than that of free CO due to some σ donation from the acetyl ligand.
  - The product has $\nu_{CO} = 2176\,cm^{-1}$, 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*-PtCl$_2$(CO)$_2$ exhibit CO stretching frequencies that are very similar to that of free CO.
- More extreme: $2\,IrF_6 + 15\,CO + HSbF_5 \xrightarrow[60\,°C,\,12\,h]{SbF_5} 2\,[Ir(CO)_6]^{3+}$.

  - This gives us $\nu_{CO} = 2254\,cm^{-1}$.
  - We also have $Au(CO)_2{}^+$ at $2217\,cm^{-1}$.

- 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 $= 1075\,\text{kJ/mol}^{[5]}$.
    - 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:

  $$\text{Ta}^{\text{III}}(\text{OSi}(t\text{-Bu})_3)_3 \xrightarrow{2\,\text{CO}} 2\,\text{R}_3\text{SiO}_3\text{Ta}^{\text{V}}{=}\text{O} + (\text{R}_3\text{SiO})_3\text{Ta}{=}\text{C}{=}\text{C}{=}\text{Ta}(\text{OSiR}_3)_3$$

    - 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.

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[5]Note that BDE is short for boond dissociation energy.