Unit 5

???

5.1 Lecture 18: Olefin Polymerization

- Another huge industrial-scale reaction

- The Great Pacific Garbage Patch is largely composed of plastics made by this process.

  - Plastics get a bad rep, but they are a remarkable material.

    - We can melt them, form them, and they have durability properties.

  - However, because of their environmental impact, a big thing in chemistry is the pursuit of materials with similar properties that are biodegradable.

  - Inorganic chemistry plays a large role in their synthesis.

  - In 2008, the US alone made 58.3 million metric tons of polyethylene and 17 million metric tons of polypropylene.
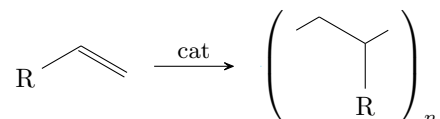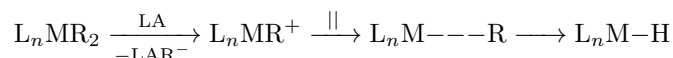
- General form:

Figure 5.1: The general form of olefin polymerization.

  - If R = H, we have polyethylene.
  - If R = Me, we have polypropylene.

- This is a thermodynamically favorable, exothermic reaction since π bonds are weaker than σ bonds.

- The catalyst is typically Ti, Zr, Hf, Cr (early Group 4 transition metals). Sometimes we use Fe, Co, Ni, and Pd (these are a bit more specific).

- Most of the materials that mediate this catalysis are called Ziegler-Natta catalysts.

  - These are heterogeneous, even though they operate via the same kind of catalytic cycle that homogeneous systems use.
  - Nobel prize (1963).

- Polymer terms:

- **Number averaged molecular weight**: The quantity $\frac{\sum N_x M_x}{\sum N_x}$, where N_x is the number of chains with x monomers and M_x is the molecular weight of a chain with x monomers. *Also known as $\boldsymbol{M_N}$.*

- **Weight averaged molecular weight**: The quantity $\frac{\sum N_x M_x^2}{\sum N_x M_x}$. *Also known as* $\boldsymbol{M_w}$.

- **Molecular weight distribution**: The quantity $\frac{M_w}{M_N}$. *Also known as* **polydispersity index**, **PDI**.

    - 1 is perfect. This means that you only have one type of chain.
    - 1.1 is good.
    - Above 1.5 is getting ill-defined.

- Stereochemistry:

    - Normally, the methyl groups in polypropylene all insert on the same side, but if one misinserts, then it faces the other direction.
    - If the catalyst corrects itself and continues on inserting in the original direction, this is **site control**.

- **Site control**: The catalyst controls the insertion.

    - More specifically, the direction the methyl groups point is controlled by the catalyst.

- **Chain end control**: One misinsertion causes the ensuing insertions to face the same way as the last inserted methyl group.

    - More specifically, the direction the methyl groups point is controlled by the last inserted methyl group.

- Mechanism:

$$\mathrm{L}_n\mathrm{MR}_2 \xrightarrow[-\mathrm{LAR}^-]{\mathrm{LA}} \mathrm{L}_n\mathrm{MR}^+ \xrightarrow{\;||\;} \mathrm{L}_n\mathrm{M}{-}{-}{-}\mathrm{R} \longrightarrow \mathrm{L}_n\mathrm{M}{-}\mathrm{H}$$

    - The three steps are activation, growth, and termination.
    - LA stands for Lewis acid. The lewis acid activates the catalyst by abstracting an anionic Lewis acid species.
    - Olefin insertion grows the polymer.
    - β-H elimination is the simplest way to terminate the chain, even though there are several possibilities.

- Activation:

    - $\mathrm{L}_n\mathrm{MCl}_2 \xrightarrow{\mathrm{AlR}_3/\mathrm{MAO}} \mathrm{L}_n\mathrm{MMe}_2 \xrightarrow[-\mathrm{AlR}_4{}^-]{\mathrm{AlR}_3/\mathrm{MAO}} \mathrm{L}_n\mathrm{Me}^+$.

    - $\mathrm{L}_n\mathrm{MCl}_2 \xrightarrow{\mathrm{AlR}_3/\mathrm{MAO}} \mathrm{L}_n\mathrm{MMe}_2 \xrightarrow[-\mathrm{MeBAr}^{\mathrm{F}}_4{}^-]{\mathrm{BAr}^{\mathrm{F}}_3} \mathrm{L}_n\mathrm{Me}^+$.

    - $\mathrm{L}_n\mathrm{MCl}_2 \xrightarrow{\mathrm{AlR}_3/\mathrm{MAO}} \mathrm{L}_n\mathrm{MMe}_2 \xrightarrow[-\mathrm{CH}_4]{\mathrm{HBAr}^{\mathrm{F}}_4} \mathrm{L}_n\mathrm{Me}^+$.

    - MAO is methylated aluminum oxide.
        - An ill defined, amorphous gunk with some oxygens created by adding a pinch of water to AlMe_3.
        - A cheap reagent that people chuck into their catalyst mixture.
        - Functions:
            1. Alkylating agent.
            2. Activator (pulls off methyls to generate cationic species).
            3. Scavenger for water (primarily) and oxygen.
    - The fluorinated aryl borates are really good because they're very weakly coordinating, and we really want an open coordination site.

- Chain growth:

    - MR($\|$) $\longrightarrow$ M$---$R $\xrightarrow{\;\|\;}$ M($\|$)($---$R) $\longrightarrow$ M$---$R $\longrightarrow$ $\longrightarrow$ $\longrightarrow$.
    - This is called the Cossee Arlman mechanism.
    - Sterics determine the rates: Ethylene > propylene > substituted olefins > disubstituted olefins $\approx$ geminal disubstituted olefins >>> trisubstituted or tetrasubstituted olefins.

- Termination:

    - How you get variability in chain lengths.
    - Control it by adding a chain-transfer reagent (a specific terminating reagent). Examples include...

        - H_2: L_nM$-$pl $\xrightarrow{H_2}$ L_nM$-$H $+$ H$-$pl, where pl is a polymer[1].
        - β-H elimination: L_nM$---$pl $\longrightarrow$ L_nM(H)($\|$pl) $\longrightarrow$ L_nM$-$H $+ =-$pl.
        - β-H abstraction: M($\|$)($---$pl) $\longrightarrow$ M(Et)($\|$pl) $\longrightarrow$ MEt $+ =-$pl.

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

    - K_p is the rate of growth/propogation; K_t is the rate of termination.
    - K_p vs. K_t dictates the product.
    - $K_p >>> K_t$ yields high molecular weight polymers.
    - $K_p \approx K_t$ (within the same order of magnitude) yields oligomers.

        - The geometric weight distribution of oligomers is called a **Schultz-Flory distribution**.

    - $K_t >> K_p$ yields dimers exclusively.

        - This can be valuable if you just want to transform ethylene into butadiene (a higher value product), for instance.

- Types of polyethylene.

(a) LDPE catalysts.   (b) LLDPE catalysts.
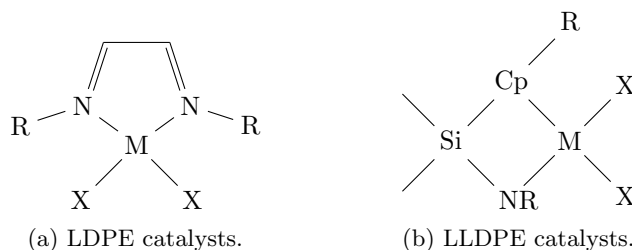
Figure 5.2: Polyethylene-type catalysts.

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

    - High melting point.
    - Crystalline.
    - Example uses: Helmets for army soldiers, bulletproof plastics.
    - Usually formed with Ziegler-Natta catalysis:

        - $TiCl_x$ + AlR_x $\longrightarrow$ a heterogeneous catalyst that's super active ($> 10^9$ kg of polymer per gram of catalyst).
        - Note that $x = 3$ or 4.
        - Alternate catalysts: Cr^{III} + silica $\xrightarrow{O_2, \Delta}$ CrO_4 $\xrightarrow{\;\|\;}$ reduced Cr center (the active catalyst).

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[1]Be aware that Anderson uses a capital P in a circle.

- A mess with a ton of branching is LDPE (low density polyethylene).

  - Lower melting point.
  - Often made by radical processes.
  - Also made by late transition metal catalysts, where there's less control over chain growth:
    - Square planar, d^8, $16\,\mathrm{e}^-$ species.
    - Example metal centers: Ni, Pd.
    - High rates of β-H elimination leads to chain walking and branching.

- Longer chain with a few branches is linear low-density polyethylene (LLDPE).

  - Transition metal catalyzed.
  - Formed from a mixture of ethylene and substituted olefins or a controlled rate of branching from catalysts.
  - Catalysts:
    - Constrained geometry catalysts.
    - Example metal centers: Ti, Zr, Hf.

- Polyethylene gives a single chain, but polypropylene can be chiral depending on the orientation of the methyl groups. The orientation defines **tacticity**.

- **Isotactic** (polypropylene): All methyl groups are pointed in the same direction.

  - The most crystaline, highest melting point material.

- **Atactic** (polypropylene): Every methyl group is random.

  - The least crystaline, lowest melting point material.

- **Syndiotactic** (polypropylene): Every methyl group alternates.

  - Pretty highly ordered.

- **Hemiisotactic** (polypropylene): Every other methyl group points the same direction; the remaining ones are random.

- **Stereoblock** (polypropylene): Alternating blocks of isotactic polypropylene.

- Controlling stereochemistry:

  - Relies on the fact that propylene is pro-chiral.
  - Si (pro-S) and Re (pro-R) faces.
  - Catalyst symmetry controls tacticity.

- Catalyst types:

(a) C_2 symmetry.   (b) C_s symmetry.   (c) C_1 symmetry.
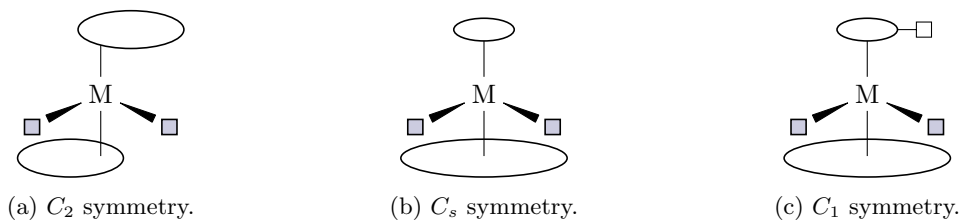
Figure 5.3: Polypropylene-type catalysts.

- Most well worked out for metallocenes.
- In Figure 5.3, boxes are open coordination sites; circles are space-filling ligands.
- Differences help dictate tacticity.
- C_2: Both binding sites are the same.
  - Steric clashing forces the olefin to point in inverted ways; but because the polymer switches sides, this leads to consistency in the direction the methyl is added.
  - Generates isotactic polypropylene.
  - Si-face selective.
  - Example: A diindene metallocene.
- C_s: Binding sites are enantiomers.
  - Generates syndiotactic polypropylene.
  - Two enantiotopic sites will alternate.
  - Example: A metallocene with Cp on top and fluorene on bottom.
- C_1: Binding sites are diastereomers.
  - Generates hemiisotactic polypropylene.
  - Example: A metallocene with Cp$-$R on top and fluorene on bottom.

- To make this work, the Cp rings are often tethered to prevent rotation.

  - However, rotation can be harnessed to make stereoblock copolymers.

- Note that stereoblock copolymers can also be synthesized with two isotactic catalysts, relying on chain transfer.

- Late-metals: Chain walking.

  - A chain can grow or it can chain walk (do β-H elimination followed by a $2, 1$-insertion).
  - If it chain walks, we'll create a branch.

- We see this with late metals.

  - Early metals are terrible backbonders, so they will prefer to be on the alkyl side of the equilibrium.
  - Late metals can backbond, and will more readily form an olefin adduct (a necessary intermediate to chain walking).

- Thus, we use late metals. . .

  - Because sometimes we want branching, specifically finely tuned branching to a certain degree.
    - Recall that random branching can be achieved via a radical mechanism.
  - SHOP process:
    - We react ethylene with a nickel PO-type catalyst (a nickel catalyst with a bidentate ligand that chelates through a phosphorous and an oxygen), an enolate, or related phosphorous/oxygen based donors.
    - This creates olefin-terminating oligomers. This doesn't use chain walking, but rather the chain transfer process, which is much faster with late metals.
    - Products: C_4-C_8 (41%), C_{10}-C_{18} (40.5%), and C_{20+} (18.5%).
    - The short ones and the long ones can be combined with Mo_2O_3/Al_2O_3 to do olefin metathesis, yielding internal and terminal olefins.
    - Then, throwing in the medium-length ones and treating with $HCo(CO)_4$ (our hydroformylation catalyst) and syn gas yields terminal aldehydes, which with enough hydrogen can give us terminal alcohols, which are commodity chemicals.
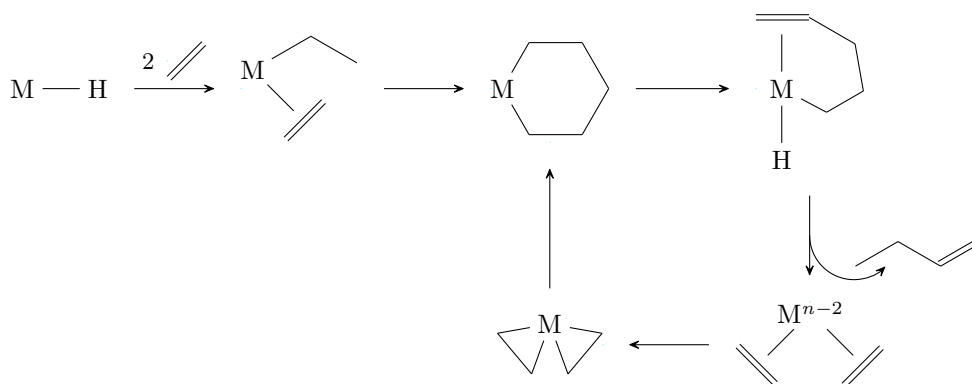
- Oligomerization mechanism:

Figure 5.4: Oligomerization mechanism.

  – A metathesis-like process.
  – Example with nickel.

- Polar monomer incorporation.

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

5.2   Office Hours (Anderson)

- Chain walking is when the metal bonds to a σ bond, moves to an adjacent carbon, moves to a double bond next, and on and on.

  – The terminal olefins are sterically favored, even though the internal ones are typically thermodynamically favored.
  – Early metals typically make linear polyolefins, while late metals prefer branched ones.

- What is the difference between a Chatt, distal, and alternating mechanism?

  – Chatt and distal mechanisms are the same thing (known as Chatt due to Eurocentrism).
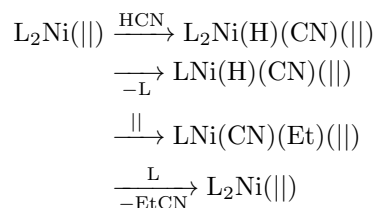
5.3 Discussion Section

5/11:
- HW5 is due 5/21/2021.

- Discussion recordings will be posted in the Panopto folder from now on, but there may be a delay.

- Point out dipole on CO in Homework 4.1a.

- Iron starts from Fe^I.

- Draws out and discusses the FeMoCO enzyme (which is actually an enzyme, not just iron, molybdenum, and a carbonyl ligand).

  - FeMoCO possibly binds to CO in bidentate fashion through two irons.
    - This could support a Chatt mechanism since it would be easier to delocalize the higher oxidation state across two irons.
  - The iron in the center of FeMoCO that forms six partial bonds and doesn't really make any sense is sometimes called a **Texas iron**.

- Considers the 4-membered transition state and arrow-pushing for ROMP.

- It's good to know what the end groups are for the purposes of NMR.

- Goes over Figure 4.8 and Homework 4.4 in a bit more detail.

- Goes over Homework 3.

5.4 Lecture 19: Oxidative Olefin Functionalization

5/12:
- More fine molecule synthesis than industrial, although there are industrial applications.

- General form:
$$R-\equiv \xrightarrow[\text{cat}]{\text{HX}} R-=-X + R-CX=$$

  - Can also start from a double bond and make singly bonded products.

- Hydrocyanation:
$$R-= + HCN \xrightarrow{\text{cat}} R---CN$$

  - HCN is really toxic, so surrogates are used in some cases.
  - Used in the synthesis of adiponitrile, which becomes nylon.

- Controlling selectivity w/ catalysts:

  - $Ni(P(o\text{-}Tol)_3)_4$[2]: Selects for the terminal product, especially with sterically encumbered (i.e., geminal) olefins.
  - Styrene: Selects for the branched product.

- Mechanism:
$$L_2Ni(||) \xrightarrow{\text{HCN}} L_2Ni(H)(CN)(||)$$
$$\xrightarrow[-L]{} LNi(H)(CN)(||)$$
$$\xrightarrow{||} LNi(CN)(Et)(||)$$
$$\xrightarrow[-EtCN]{L} L_2Ni(||)$$

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[2] o-Tol is an ortho-tolyl group.

- The precatalyst is L_3Ni, and is activated when ethylene kicks out a ligand.
- The reductive elimination step is hard and requires a Lewis acid and a ligand to kick out ethyl cyanide.
- Can also have chain walking.

- Hydrosilylation:
$$R-= + HSiR_3 \xrightarrow{\text{cat}} R---SiR_3$$

  - Note that our starting material can also be $R-=X$ (where X can be oxygen, for instance), giving us $R-CH(SiR_3)-XH$ as a product.
  - Industrially important for making non-stick coatings.

- Common catalysts: Pd^0 and Karstedt's catalyst (a bridging mess of siloxanes bound to olefins and chelating).
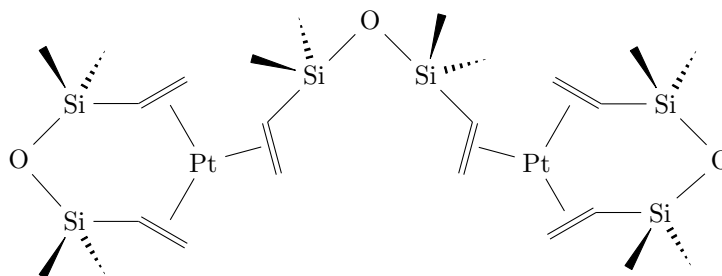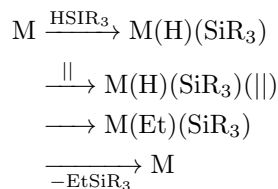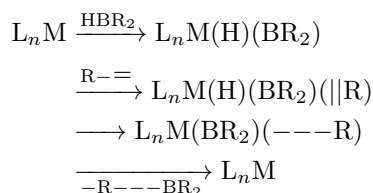

Figure 5.5: Karstedt's catalyst.

- H_2PtCl_6 also works (known as Speier's catalyst).

- We can also observe chain walking to bond a silyl away from where the olefin originally was.

- Mechanism:
$$M \xrightarrow{\text{HSIR}_3} M(H)(SiR_3)$$
$$\xrightarrow{||} M(H)(SiR_3)(||)$$
$$\longrightarrow M(Et)(SiR_3)$$
$$\xrightarrow[-\text{EtSiR}_3]{} M$$

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

- Hydroboration:
$$R-= + R_2BH \longrightarrow R---BR_2$$
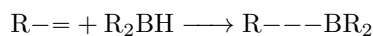
  - We need a catalyst because otherwise we're stuck at the mercy of the electronics of this reaction.
  - A catalyst is necessary for less electron-rich boranes.

- Mechanism:
$$L_nM \xrightarrow{\text{HBR}_2} L_nM(H)(BR_2)$$
$$\xrightarrow{R-=} L_nM(H)(BR_2)(||R)$$
$$\longrightarrow L_nM(BR_2)(---R)$$
$$\xrightarrow[-R---BR_2]{} L_nM$$

- We could also get from the second intermediate to $L_nM(H)(--C(H)(BR_2)(R))$, from which we can reductively eliminate to get $Me-C(H)(BR_2)(R)$ or β-H eliminate to get $=C(BR_2)(R)$.

- Alternate mechanism: $L_nRh(||R)(BR_2) \longrightarrow L_nRh-CRH--BR_2 \xrightarrow{R_2BH} L_nRh(H)(BR_2)(CRH--BR_2)$ $\xrightarrow[-R---BR_2]{} L_nRh(||R)(BR_2)$.

- With early metals: $L_nMH \xrightarrow{||R} L_nM(H)(||R) \longrightarrow L_nM---R \xrightarrow{HBR_2} L_nM(H)(BR_2)(---R) \xrightarrow[-R---BR_2]{}$ L_nMH.
    - Done to avoid oxidative addition type processes.

- Hydroamination:
$$R-\equiv-H + HNR_2 \xrightarrow{cat} R-=-NR_2 + =C(R)(NR_2)$$
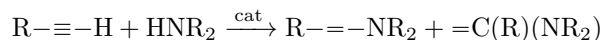
    - Can also be done from a doubly bonded reactant (remove the double bond from each product).

- Mechanisms:

    1. Nucleophilic attack: $L_nM \longrightarrow L_nM-|| \xrightarrow{RNH_2} M---NH_2R \xrightarrow[-EtNRH]{} L_nM$.

    2. Insertion: $L_nM-NHR \xrightarrow{||} L_nM(||)(NHR) \longrightarrow L_nM---NRH \xrightarrow[-EtNRH]{RNH_2} L_nM-NRH$.

    3. $2+2$: $L_nM=NR \xrightarrow{||} \begin{array}{c} L_nM \text{---} NR \\ \square \end{array} \xrightarrow{H_2NR} L_nM(NRH)(NREt) \xrightarrow[-EtNRH]{} L_nM=NR$.
        - Goes through a 4-membered $2+2$ transition state in the first step, as in Figure 3.17.

- Oxidative olefin functionalization.

- Wacker oxidation:
$$|| + \frac{1}{2}O_2 \xrightarrow[cat\,CuCl_2]{cat\,PdCl_2} Me-COH$$
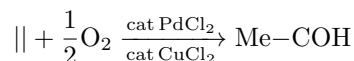
    - Millions of tons per year; acetaldehyde feeds into a lot of processes.
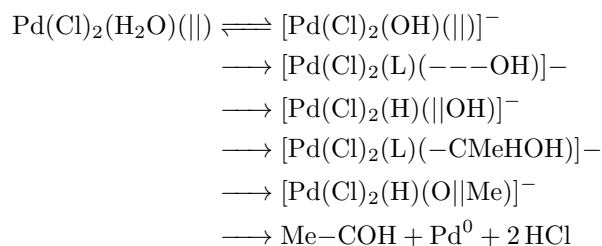
- Stoichiometry:

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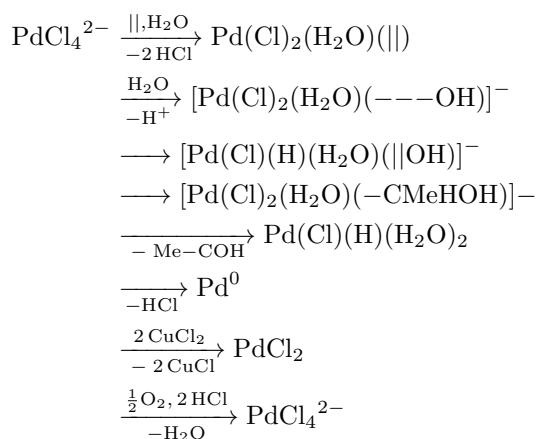
- Mechanism:

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

$$Pd(Cl)_2(H_2O)(||) \rightleftharpoons [Pd(Cl)_2(OH)(||)]^-$$
$$\longrightarrow [Pd(Cl)_2(L)(---OH)]-$$
$$\longrightarrow [Pd(Cl)_2(H)(||OH)]^-$$
$$\longrightarrow [Pd(Cl)_2(L)(-CMeHOH)]-$$
$$\longrightarrow [Pd(Cl)_2(H)(O||Me)]^-$$
$$\longrightarrow Me-COH + Pd^0 + 2\,HCl$$

2. External attack at a ligand: React the starting compound with OH^- to produce $[Pd(Cl)_2(H_2O)(---OH)]-$, which then feeds into the third intermediate.

3. Water nucleophilic attack: React the starting compound with H_2O and remove a proton to produce $[Pd(Cl)_2(H_2O)(---OH)]-$, which then feeds into the third intermediate.

– The β-H elimination step can also occur by a Cl^--assisted process where the chloride abstracts the H^+ from the alcohol.

– All four hydrogens in acetaldehyde come from ethylene.

- Stereochemical experiments:

  – Draws a mechanism yielding stereochemistry consistent with mechanisms 2 and 3, but not 1. This means it's probably actually external attack at a ligand.

  – If $[Cl^-]$ is high, we activate the following pathway: $[Pd(Cl)_2(L)(---OH)]- \longrightarrow [Pd(Cl)_3(---OH)]^{2-} \longrightarrow Cl---OH$.

  – Rate $= \frac{[PdCl_4{}^{2-}][C_2H_4]}{[Cl-][H^+]}$.

  – Therefore, we'll make the chlorinated pathway more than the productive pathway if we add a bunch of chloride.

- Overall mechanism:

$$PdCl_4{}^{2-} \xrightarrow[-2\,HCl]{||, H_2O} Pd(Cl)_2(H_2O)(||)$$

$$\xrightarrow[-H^+]{H_2O} [Pd(Cl)_2(H_2O)(---OH)]^-$$

$$\longrightarrow [Pd(Cl)(H)(H_2O)(||OH)]^-$$

$$\longrightarrow [Pd(Cl)_2(H_2O)(-CMeHOH)]-$$

$$\xrightarrow[-\,Me-COH]{} Pd(Cl)(H)(H_2O)_2$$

$$\xrightarrow[-HCl]{} Pd^0$$

$$\xrightarrow[-\,2\,CuCl]{2\,CuCl_2} PdCl_2$$

$$\xrightarrow[-H_2O]{\frac{1}{2}O_2,\,2\,HCl} PdCl_4{}^{2-}$$

- Other applications:

  – Higher olefins: $R-= + \frac{1}{2}O_2 \xrightarrow{Pd^{II},\,CuCl_2,\,H_2} R-COH$.

  – The nucleophile need not be H_2O:

  ■ $|| + ROH \longrightarrow ||OR$.

  ■ $|| + [COOR]^- \longrightarrow C(O)(R)(O||)$.

  – Draws out another few useful processes.

  – Useful chemistry with dienes.

  ■ Cyclohexadiene can become cyclohexene with para-acetates.

  ■ Useful applications of the above reaction in total synthesis: Setting stereochemistry with a catalytic attack, as used in the synthesis of paenilactane B.

  – This chemistry also works with nitrogen-based nuleophiles.

5.5 Office Hours (Anderson)

5/17:
- Which molecules are anionic in the carbonylation mechanism and why?
  - They're all anions.
- What is M_x in the definition of number averaged molecular weight?
  - N_x is number of chains with x number of monomers. M_x is the molecular weight of a chain with x monomers.
  - From the perspective of the video, you could think of N_x as the number of chains with molecular weight M_x.
- Can you explain the oligomerization mechanism?
  - Oligomerization is baby polymerization (potentially more useful).
  - In principle, it could go through a regular insertion mechanism.
  - If you have competitive elimination of polymers, your polymers will be shorter on average.
  - Butene is a higher value product than oligomers.
  - Use half-type mechanisms to balance the stoichiometry. Necessitates bimolecular chemistry in real life.
- Olefin polymerization catalysts are classically Group 4, d^0 metals.
- Homework 5.3:
  - Use chain walking or chain transfer.
  - You'll have a statistical mixture of branches if you're chain walking, so it's not this.
- Is the catalyst resting state always the one before the step with the highest energy of activation?
  - The precatalyst can't technically be the resting state because it's an off-cycle intermediate.
  - Homework: It's the major species in solution; the other enantiomer being bound.
    - Each pathway could have a different resting state.
    - Recognize what state of the catalyst is sitting in the mixture; draw the two cycles and decide.
- **Principle of microscopic reversibility**: To be mechanistically allowed, a reaction must be irreversible to *some* extent.
- Homework 5.6:
  - Use either Chalk-Herrod or modified Chalk-Herrod.
- Midterm 6:
  - NR_2^- is a σ donor and a π donor because it has filled π orbitals on the nitrogen.
  - Phosphines are π acids.
  - Cp is all three.
  - Methyl is a pure σ donor.
  - Cyclobutadiene is both.
  - O_2^- is a π donor.
  - Draw out like a Lewis structure – two lone pairs on NR_2^- means filled σ and π orbitals; CH_3 has only filled σ orbitals.
  - Orbital diagrams.
  - If he wants an MO diagram, he'll say "MO diagram."