Unit 5

More Catalytic Processes 2

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.
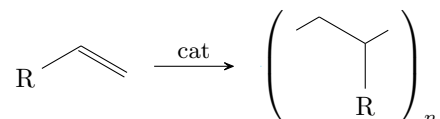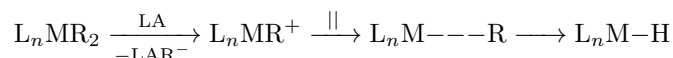
- General form:

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:

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

  - $\mathrm{L}_n\mathrm{MCl}_2 \xrightarrow{\mathrm{AlR}_3/\mathrm{MAO}} \mathrm{L}_n\mathrm{MMe}_2 \xrightarrow[-\mathrm{MeBAr^F_4}{}^-]{\mathrm{BAr^F}_3} \mathrm{L}_n\mathrm{Me}^+$.

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

  - 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.
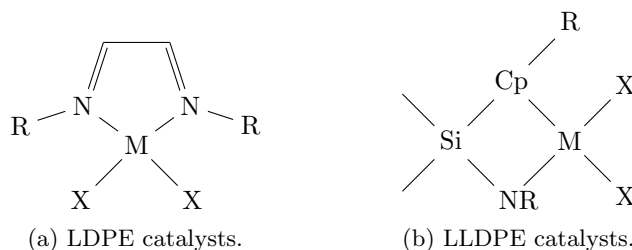
Figure 5.2: Polyethylene-type catalysts.

- 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 ($> 1 \times 10^9$ 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:

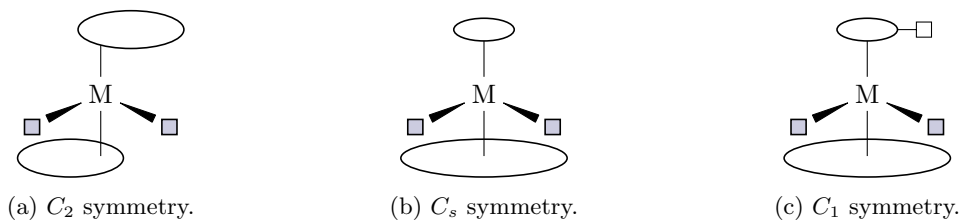(a) C_2 symmetry.   (b) C_s symmetry.   (c) C_1 symmetry.

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.
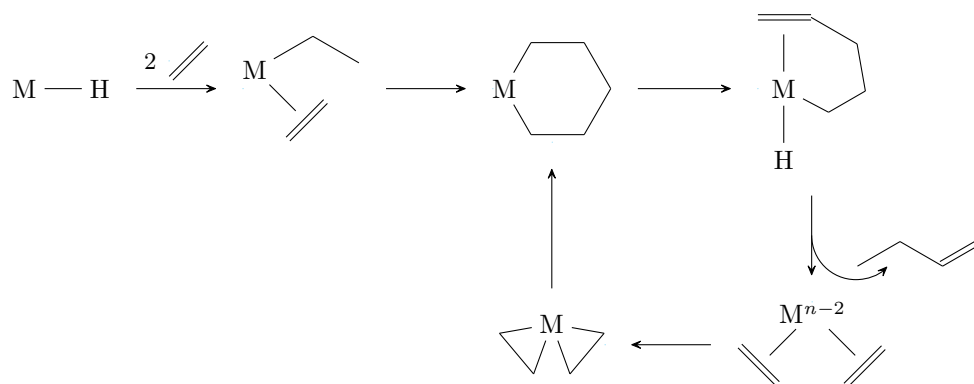
- Oligomerization mechanism:

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.
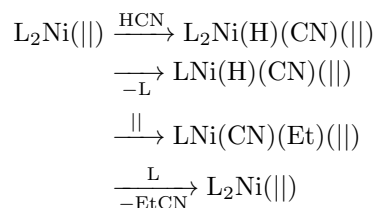
5.2   Office Hours (Anderson)

- 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:

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

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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).
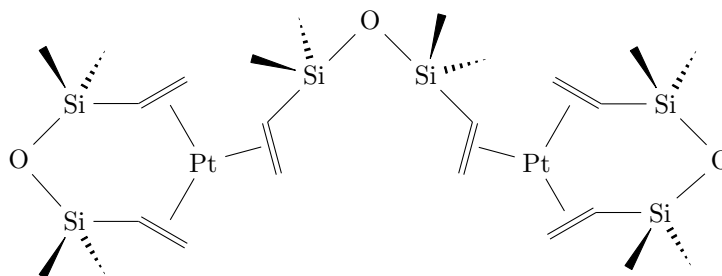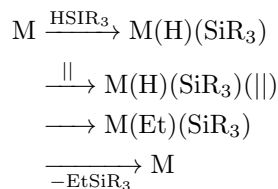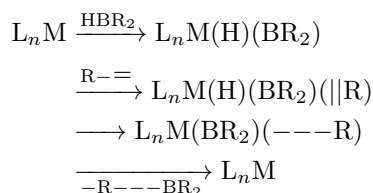

Figure 5.5: Karstedt's catalyst.

- 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:

$$M \xrightarrow{\text{HSIR}_3} M(H)(SiR_3)$$
$$\xrightarrow{\text{||}} M(H)(SiR_3)(||)$$
$$\longrightarrow M(Et)(SiR_3)$$
$$\xrightarrow[-EtSiR_3]{} M$$

  - 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:

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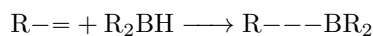
  - We need a catalyst because otherwise we're stuck at the mercy of the electronics of this reaction.
  - A catalyst is necessary for less electron-rich boranes.

- 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:

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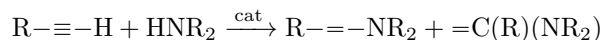
  - Can also be done from a doubly bonded reactant (remove the double bond from each product).

• 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. $2+2$: $L_nM=NR \xrightarrow{||} \begin{array}{c} L_nM \text{ —— } NR \\ \rule{0pt}{1em} \lfloor \qquad \rfloor \end{array} \xrightarrow{H_2NR} L_nM(NRH)(NREt) \xrightarrow[-EtNRH]{} L_nM=NR$.

    - Goes through a 4-membered $2+2$ transition state in the first step, as in Figure 3.17.

• Oxidative olefin functionalization.

• Wacker oxidation:

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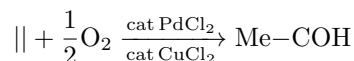
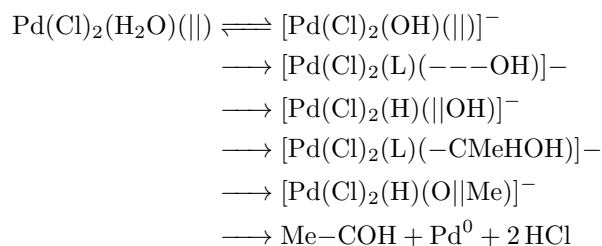 - Millions of tons per year; acetaldehyde feeds into a lot of processes.

• 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, $2\,CuCl + \frac{1}{2}O_2 + 2\,HCl \longrightarrow 2\,CuCl_2 + H_2O$.
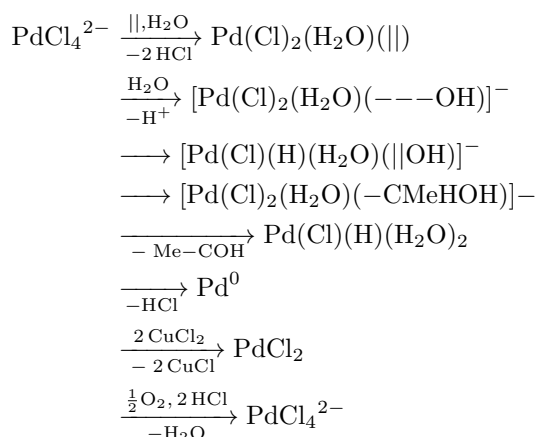 - Summing these three reactions, we have $|| + \frac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} Me-COH$.

• 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."

5.6   Discussion Section

5/18:
- Homework 5 today.

- Next Tuesday's discussion section might get moved to this coming Saturday at 1:00 PM CT.

- Sophie will publish a list of midterm 2 topics.

- Homework 5.2:

    - Early metal resting state: Metal alkyl.
        - Insertion of olefin is very fast so a bound oleffin is almost never observed for these systems.
        - Favors linear polyethylene.

    - Late metals: Metal-olefin adduct.
        - Olefins are more likely to dissociate.
        - Insertion of an olefin is not as fast; this helps lead to more chain transfer.
        - Late metal catlysts are more susceptible to β-H elimination so chain walking is also more common than with early metals.
        - Favors branched polyethylene via the chain transfer and chain walking mechanisms.

    - Chain transfer mechanism:
        - Termination mechanisms.
        - β-H elimination to form a metal-olefin adduct, and then the olefin dissociates from the metal.
        - If you react with ethylene time and time again to create a polymer, there's no reason you can't suddenly interact with another polymer in solution.

    - Chain walking was discussed last week.

- Homework 5.3:

    - Some catlysts polymerize ethylene to HDPE that contain a few long branches (ca. 1-2 per chain). Explain how long the branches might form. What distribution of branch lengths do you expect for your mechanism?

    - Which of the two branch forming pathways does the product here most resemble?
        - Chain transfer.

    - What kind of catalysts lead to this selectivity?
        - Open sterics, but maybe still some early metals to make sure you don't get shorter chains, maybe CGCs — can bind sterically crowded α-olefins competitively with ethylene.
        - Likely need high temp to keep polymer in solution.

- Homework 5.5:

    - Wacker-type reactions: Generally alkene to ketone, but there are variants with other heteroatoms and other levels of reduction (e.g., allylIN and allylO, C=N and C=O).

- Alternate Wacker oxidation mechanism (for an alcohol; see Figure 5.6):

    - Look back at the traditional mechanism but be aware of such derivatives. Know the similarities. The starting material should drive you toward the product.

    - Does it matter when the ligands are being lost and coordinated.
        - Not really.
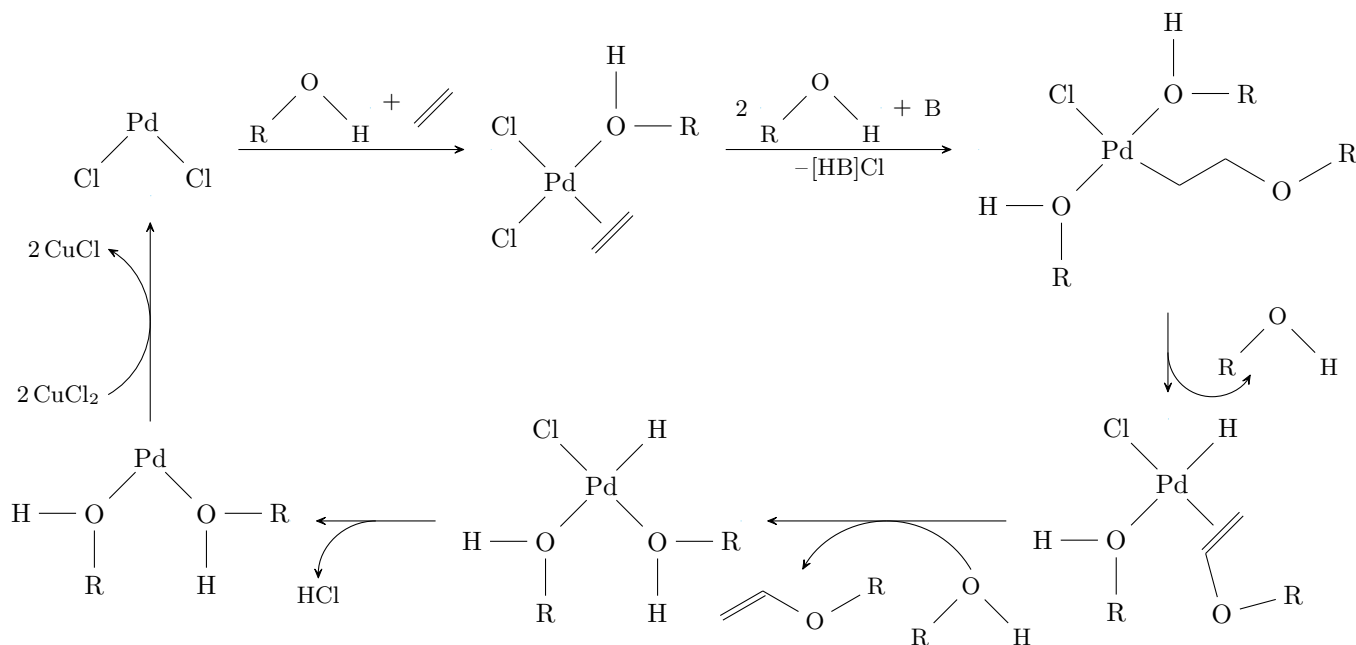   - Anderson's way is probably a bit more realistic.

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

- Brookehart type nickel- and palladium-based polymerization catalysts are introduced in Section 11.3.3 of the text. These catalysts differ from metallocene catalysts in that (1) the resting state is the (diimine)MR(ethylene)+ adduct 1, (2) chain walking is much faster than chain growth, (3) ethylene insertion into secondary alkyl metal species is fast, and (4) a hyper branched polyethylene is producced (ca. 100 branches at $1\,000\,°C$).

- A mechanism for polymerization showing how branches are formed (see Figure 5.7).

  - We start from a precatalyst and go through a couple of activation steps.
  - Then we show three possible pathways.

    - ■ The top one creates no branches but leaves the possibility open for a chain transfer.
    - ■ The middle one creates a methyl branch.
    - ■ The bottom one creates an ethyl branch.

  - Note that if R contains more carbons, we ccan see even more chain walking, leading to longer branches and our ultimate hyperbranched product.

- What property or properties give rise to the differences in polymerization behavior between (diimine)PdR$^+$ and Cp$_2$ZrR catalysts?

  - It's Zr(IV) as a cation.
  - Palladium(II) is d^8 and soft, while zirconium(IV) is d^0 and hard. While both are poor backbonders, the soft character of the former leads to stronger metal olefin coordination. This enables β-H elimination of (diimine)PdCH$_2$CH$_2$R$^+$ to form (diimine)PdHCH$_2$=CHR$^+$ to compete with trapping by ethylene to form the resting state, and thus enables chain walking to compete with growth.
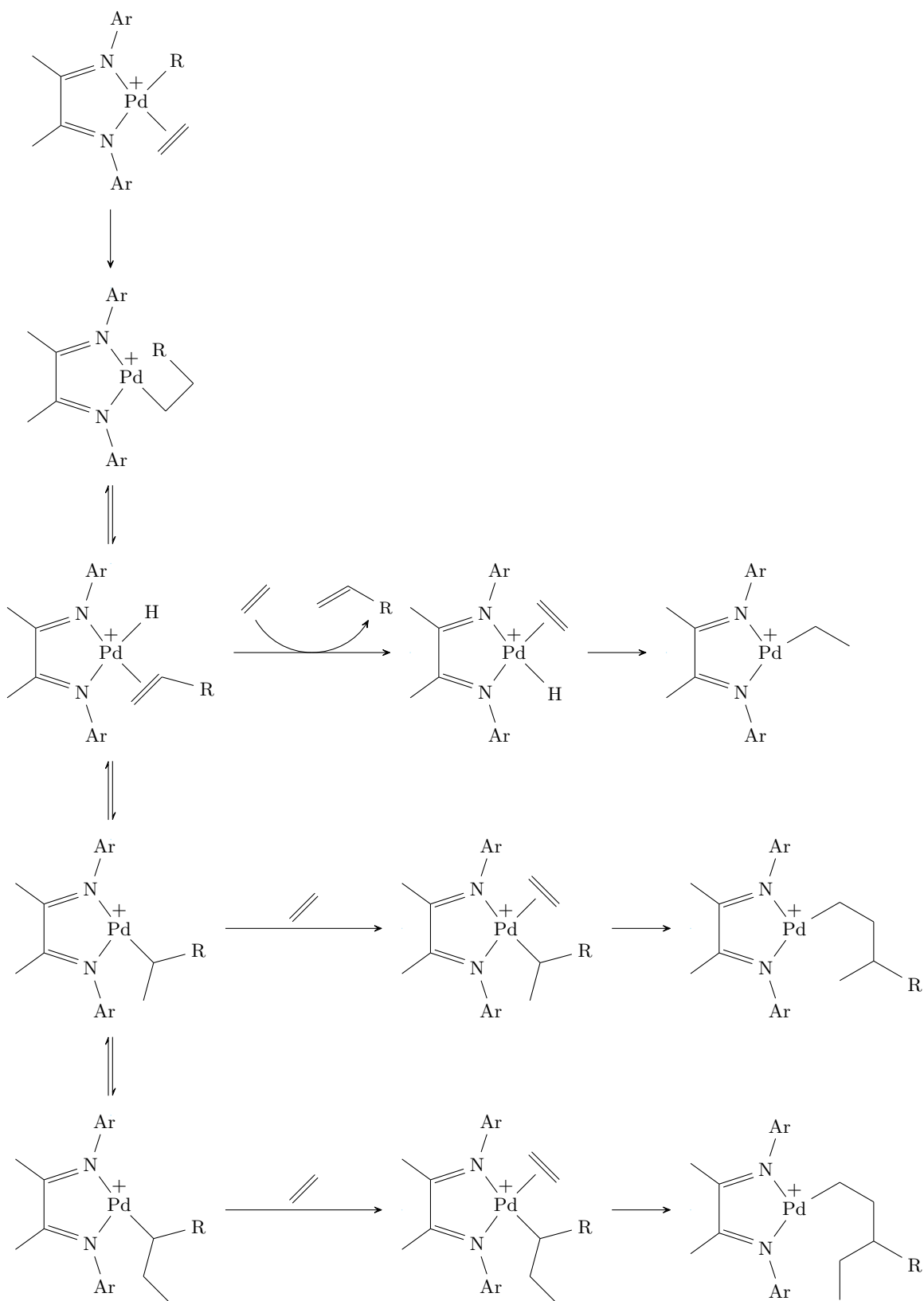 - Palladium is a much better backbonder because it *has* d electrons.

Figure 5.7: Polymerization with Brookehart catalysts.

- The isopropal substituents on the aryl rings of the diimine ligand in catalyst 1 are critical for the generation of high molecular weight polymer. These aryl rings are oriented perpendiccular to the palladium square plane as indicated. Catalysts with small groups in these positions, such as 2, produce only low molecular weight oligomeric products. Rationalize the difference. Hint: Consider the mechanism of ligand substitution.

    - Large substituents inhibit chain transfer! They stop ethylene from knocking out the polymer.

    - Charge transfer requires β-H eliminatiom and substitution of $H_2C=CH_2$pl by $H_2C=CH_2$ to begin substitution at square planar complexes normally proceeds by an associative mechanism in which the incoming ligand binds at an axial site. Large substituents at the ortho positions of the $N-Ar$ rings of the Brookhart catalysts disfavor this process, leading to high molecular weight. The ortho-methyl substituents in 2 are too small to inhibit ligand substitution and hence chain transfer, and so a low molecular weight product is formed.

- Normal polypropylene, which contains only $(-CH_2CHMe-)$ units, contains 333 Me brancches per 1000 carbons. However, (α-diimine)PdR$^+$ catalysts polymerize polypropylene to a chain straightened polypropylene that contains only about 200 branches per 1000 carbons, indicating the presence of many $CH_2CH_2CH_2$ units. Explain these results. (Hint: Consider insertion regiochemistry.)

    - A 2,1-insertion followed by chain walking leads to a net 1,3 insertion, i.e., incorporation of a linear C_3 unit in the polymer. About a third of the time the catalyst undergoes 2,1-insertion, resulting in a chain-straightened polypropylene.

- CF$_3$ is a strong electron withdrawing group, and will affect the electrons of the phenyl group. $C-F$ bonds are also stronger than $C-H$ bonds. Fluorine makes organic compounds more lipophilic, and more hydrophobic.

5.7   Homework 5 One-On-One (Anderson)

- Homework 5.3:

    - What do you mean, "what distribution of branch lengths do you expect for your mechanism?"

        ■ Explain why your mechanism consistent with the expected distribution of branch lengths.

- Homework 5.4:

    - How exactly does the transfer take place? What attacks what? Where do the groups bend and why?

        ■ Use your hand as a propylene. When the methyl points away from the polymer, that's not good. We want the mathyl pointing towards the polymer. The face that is bound to the metal center is attacked by the alkyl group in matallocene catalysts. External nucleophiles in other reactions attack from the outside. This is very much related to σ-bond metathesis.

- Homework 5.5:

    - Activation step?

        ■ What I have is correct.

    - Charge on Pd?

        ■ Neutral.

    - Does MeCN bond datively?

        ■ Yes.

    - Ridiculous arrow pushing step?

        ■ It's ok to have so much stuff happen because it's a concerted reaction. It dooesn't have to be concerted, but it can be. Tertiary collisions are bad, but intramolecular is fine.

- 2-coordinate species?
    - Keep it tetrasolvated.
- Shannon Stahl is applying the Wacker oxidation to many things. Aerobic oxidations with palladium.

- Homework 5.6-**3**:
    - Alkynes?
        - Instead of reductive eliminations, use β-H elimination to get a dihydride metal species.

- Misc. test thoughts.
    - He likes bonus reactions. What bonds are being formed? Our Pd cycles from 0 to II. Think of it like a mathematical proof. You've got a toolbox of things that you can do and just see if it gets you closer. So (A) leave it to the end of the test and (B) just try to keep track of electrons, oxidative addition, reductive elimination, etc.

- Misc. thoughts on the class.
    - 201 is a class that builds up. 202 draws on a lot of background knowledge and chemical intuition that takes time to develop.

- Thoughts on PChem.
    - PChem is pretty self-contained. Talk with the instructors.