

Unit 5

???

5.1 Lecture 18: Olefin Polymerization

5/10:

- 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:

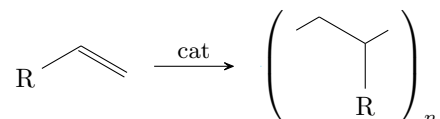
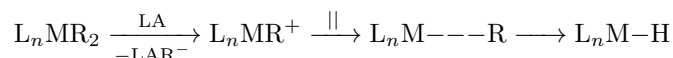


Figure 5.1: The general form of olefin polymerization.

- If $\text{R} = \text{H}$, we have polyethylene.
- If $\text{R} = \text{Me}$, 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 molecular weight x and M_x is x . Also known as M_N .

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



- 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:**
 - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-AlR_4^-]{AlR_3/MAO} L_nMe^+$.
 - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-MeBAr^F_4]{BAr^F_3} L_nMe^+$.
 - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-CH_4]{HBAr^F_4} L_nMe^+$.
 - 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:

- $\text{MR}(\text{||}) \longrightarrow \text{M}---\text{R} \xrightarrow{\text{||}} \text{M}(\text{||})(---\text{R}) \longrightarrow \text{M}---\text{R} \longrightarrow \longrightarrow \longrightarrow .$
- 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 : $\text{L}_n\text{M}-\text{pl} \xrightarrow{\text{H}_2} \text{L}_n\text{M}-\text{H} + \text{H}-\text{pl}$, where pl is a polymer^[1].
 - β -H elimination: $\text{L}_n\text{M}---\text{pl} \longrightarrow \text{L}_n\text{M}(\text{H})(\text{||pl}) \longrightarrow \text{L}_n\text{M}-\text{H} + =-\text{pl}$.
 - β -H abstraction: $\text{M}(\text{||})(---\text{pl}) \longrightarrow \text{M}(\text{Et})(\text{||pl}) \longrightarrow \text{MEt} + =-\text{pl}$.

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

- K_p is the rate of growth/propagation; K_t is the rate of termination.
- K_p vs. K_t dictates the product.
- $K_p \gg \gg K_t$ 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**.
- $K_t \gg K_p$ 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.

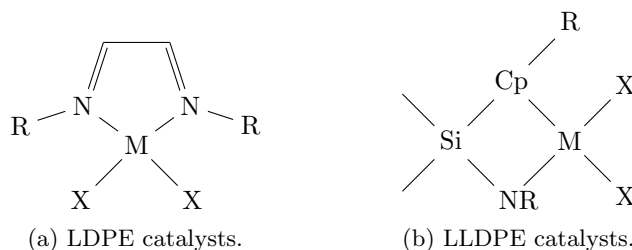


Figure 5.2: Polyethylene-type catalysts.

- 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:
 - $\text{TiCl}_x + \text{AlR}_x \longrightarrow$ a heterogeneous catalyst that's super active ($> 10^9$ kg of polymer per gram of catalyst).
 - Note that $x = 3$ or 4.
 - Alternate catalysts: $\text{Cr}^{\text{III}} + \text{silica} \xrightarrow{\text{O}_2, \Delta} \text{CrO}_4 \xrightarrow{\text{||}} \text{reduced Cr center (the active catalyst)}.$

¹Be 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 , $16 e^-$ 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 crystalline, highest melting point material.
- **Atactic** (polypropylene): Every methyl group is random.
 - The least crystalline, 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:

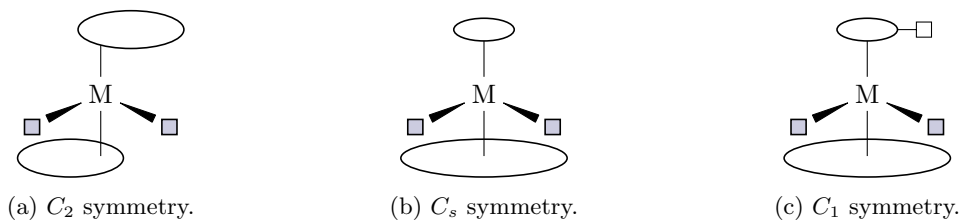


Figure 5.3: Polypropylene-type catalysts.

- 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:

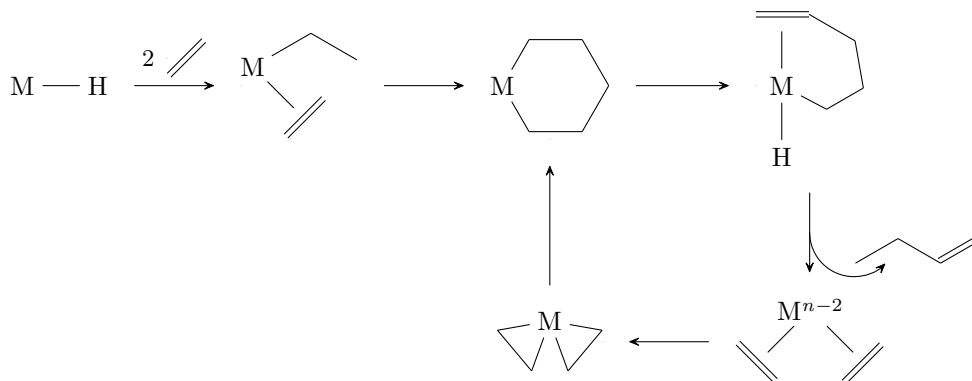


Figure 5.4: Oligomerization mechanism.

- 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

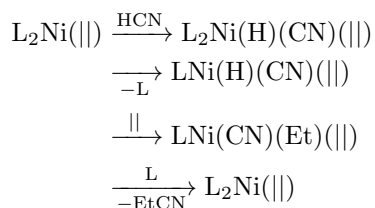
- 5/11:
- HW5 is due 5/21/2021.
 - Discussion recordings will be posted in the Panopto folder from now on, but there may be a delay.
 - Point out dipole on CO in Homework 4.1a.
 - Iron starts from Fe^I.
 - Draws out and discusses the FeMoCO enzyme (which is actually an enzyme, not just iron, molybdenum, 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:

$$\text{R}-\equiv \xrightarrow[\text{cat}]{\text{HX}} \text{R}-\text{X} + \text{R}-\text{CX}=\text{}$$
 - Can also start from a double bond and make singly bonded products.
 - Hydrocyanation:

$$\text{R}-\text{CH}=\text{CH}_2 + \text{HCN} \xrightarrow{\text{cat}} \text{R}-\text{CH}_2-\text{CH}_2-\text{CN}$$
 - 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-Tol)₃)₄^[2]: Selects for the terminal product, especially with sterically encumbered (i.e., geminal) olefins.
 - Styrene: Selects for the branched product.
 - Mechanism:



²o-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:

$$R- = + HSiR_3 \xrightarrow{cat} R- - SiR_3$$
 - 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).

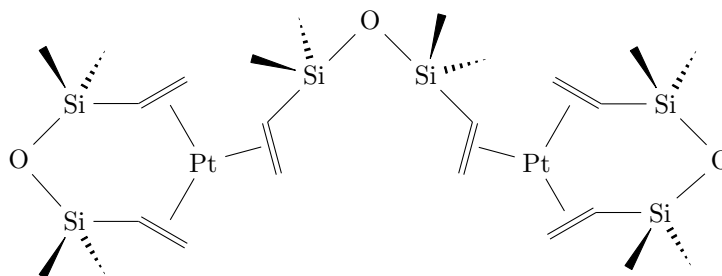
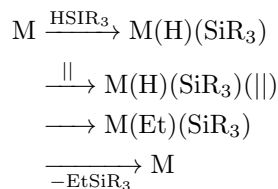
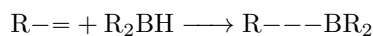


Figure 5.5: Karstedt's catalyst.

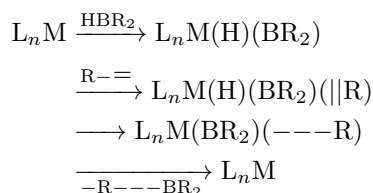
- H_2PtCl_6 also works (known as Speier's catalyst).
- We can also observe chain walking to bond a silyl away from where the olefin originally was.
- Mechanism:



- 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:

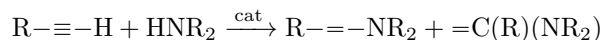


- We need a catalyst because otherwise we're stuck at the mercy of the electronics of this reaction.
- A catalyst is necessary for less electron-rich boranes.
- Mechanism:



- 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: $L_nRh(||R)(BR_2) \xrightarrow{-R---BR_2} L_nRh(||R)(BR_2) \xrightarrow{R_2BH} L_nRh(H)(BR_2)(CRH---BR_2) \xrightarrow{-R---BR_2} L_nRh(H)(BR_2)(---R) \xrightarrow{-R---BR_2} L_nMH$.
- With early metals: $L_nMH \xrightarrow{||R} L_nM(H)(||R) \xrightarrow{---R} L_nM---R \xrightarrow{HBR_2} L_nM(H)(BR_2)(---R) \xrightarrow{-R---BR_2} L_nMH$.
- Done to avoid oxidative addition type processes.

- Hydroamination:



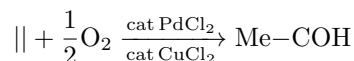
- Can also be done from a doubly bonded reactant (remove the double bond from each product).

- Mechanisms:

1. Nucleophilic attack: $L_nM \xrightarrow{RNH_2} L_nM-NH_2R \xrightarrow{-EtNRH} L_nM$.
2. Insertion: $L_nM-NHR \xrightarrow{||} L_nM(||)(NHR) \xrightarrow{---NRH} L_nM---NRH \xrightarrow{-EtNRH} L_nM-NRH$.
3. 2 + 2: $L_nM=NR \xrightarrow{||} \begin{array}{c} L_nM \text{ --- } NR \\ | \quad \quad | \\ \hline \end{array} \xrightarrow{H_2NR} L_nM(NRH)(NREt) \xrightarrow{-EtNRH} L_nM=NR$.
– Goes through a 4-membered 2 + 2 transition state in the first step, as in Figure 3.17.

- Oxidative olefin functionalization.

- Wacker oxidation:



- Millions of tons per year; acetaldehyde feeds into a lot of processes.

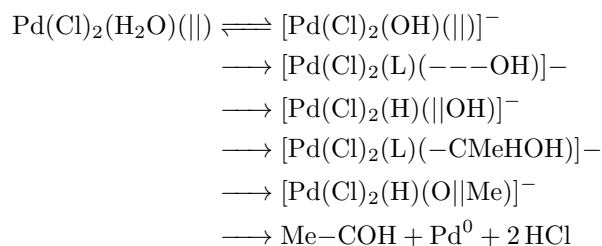
- Stoichiometry:

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

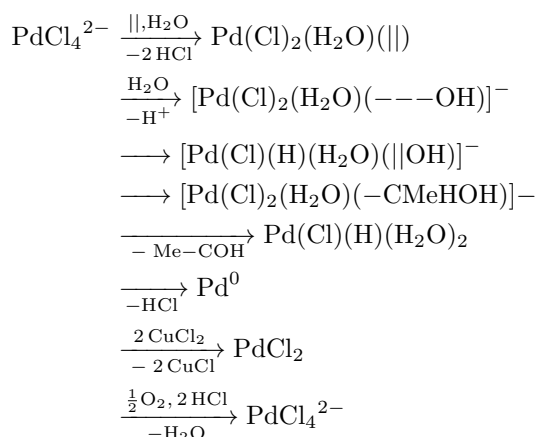
- Mechanism:

- 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:



2. External attack at a ligand: React the starting compound with OH^- to produce $[\text{Pd}(\text{Cl})_2(\text{H}_2\text{O})(---\text{OH})]^-$, which then feeds into the third intermediate.
 3. Water nucleophilic attack: React the starting compound with H_2O and remove a proton to produce $[\text{Pd}(\text{Cl})_2(\text{H}_2\text{O})(---\text{OH})]^-$, 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 $[\text{Cl}^-]$ is high, we activate the following pathway: $[\text{Pd}(\text{Cl})_2(\text{L})(---\text{OH})]^- \longrightarrow [\text{Pd}(\text{Cl})_3(---\text{OH})]^{2-} \longrightarrow \text{Cl}---\text{OH}$.
 - $\text{Rate} = \frac{[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-][\text{H}^+]}$.
 - Therefore, we'll make the chlorinated pathway more than the productive pathway if we add a bunch of chloride.
 - Overall mechanism:



- Other applications:
 - Higher olefins: $\text{R}-= + \frac{1}{2}\text{O}_2 \xrightarrow{\text{Pd}^{\text{II}}, \text{CuCl}_2, \text{H}_2} \text{R}-\text{COH}$.
 - The nucleophile need not be H_2O :
 - $|| + \text{ROH} \longrightarrow ||\text{OR}$.
 - $|| + [\text{COOR}]^- \longrightarrow \text{C}(\text{O})(\text{R})(\text{O}||)$.
 - 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 nucleophiles.