

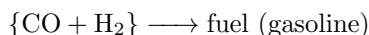
Unit 6

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6.1 Lecture 20: Fischer-Tropsch

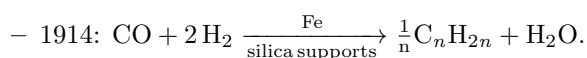
5/19:

- Industrial process mainly, but also has applications to renewable energy.
- Mechanism of the industrial catalysis in the first video; more on the molecular chemistry in the second video.
- General form:

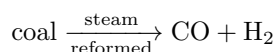


- Clearly, the reactants are Syn gas.
- Thermodynamics of $\text{CO} + x \text{H}_2 \longrightarrow \text{stuff}$.
 - As x increases, ΔH and ΔG decrease.
 - Conclusion: The more C–H bonds you make, the more thermodynamically favorable the process is.
 - A lot of this comes from the thermodynamic reducing power of hydrogen.

- History:

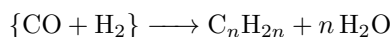


- The ratio of the reactants can be tuned.
- Iron is a solid-state catalyst here. Note that other metals can be used, but iron was the most common.
- The products are a mixture of medium to long chain alkanes, alkenes, and methane.
- The challenge and limitation of this process is that it yields a mixture (a Schultz-Flory distribution) of products.
- This means that there is no real selectivity, although C_7 is most common.
- This is also why chemists became interested in homogeneous catalysis for this area, because in principle it could give you better selectivity here.
- Industrially:



- This is commonly done in South Africa because they have a lot of coal.
 - CH_4 can also be used as a reactant.
- The ratio of the product gasses can be tuned by the water-gas shift reaction (see Lecture 17), which is $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$ (in the forward direction).

- CO₂ can then be removed.
- One potentially interesting exciting direction that's not been industrially accomplished due to cost is the reverse water-gas shift reaction, which is just the reverse direction.
- The reverse water-gas shift reaction is interesting because if you could convert CO₂ into CO + H₂O and remove the water, you could feed the CO back into the original process to make gasoline.
- Challenges:
 - Selectivity in the Fischer-Tropsch process.
 - Source of H₂ (right now we get it from fossil fuels). There is research into how to reduce CO₂ into fuels, but if we can get H₂ from somewhere other than fossil fuels, it's a solved problem.
- Conditions (for the following reaction):



- High temperatures (150-300 °C).
 - Favor faster rates and better conversion yield percentages, but more methane (the least valuable product).
- High pressure (1-30 atm).
 - Favors longer chain alkanes and better conversion since methane is a gas (lower likelihood of eliminating it).
- Optimal CO / H₂ concentration.
 - Cobalt catalysts use 1 : 2.
 - Iron catalysts should have relatively more CO.
- Product (Schultz-Flory) distribution:

$$\frac{W_n}{n} = (1 - \alpha)^2 \alpha^{n-1}$$

- $\frac{W_n}{n}$ is the average molecular weight?
- W_n is the weight fraction of hydrocarbons containing n carbon atoms and α is the chain growth probability (controlled by the catalyst and the conditions).
- If $\alpha < 0.5$, then methane dominates.
- However, as $\alpha \rightarrow 1$, the methane fraction decreases relative to the sum of heavy products.
- Sasol (a South African company) mediates this process.
- We can use the products for a variety of different things (heptane for fuel, heavier ones for wax [you can buy Sasol wax], etc.).
- If we were going to do this globally for fuel, we'd have a lot of wax as a byproduct, which we neither have a place to store nor can afford to do since it's so wasteful. Thus, there is great interest in selectivity for C₆, C₇, C₈, or even butene, from which we could do olefin metathesis to make hexanes.
- Two necessary things to use this process for renewable energy:
 1. Find a good source of hydrogen so that we could run the reverse water-gas shift reaction.
 - The reaction might need to be optimized a bit as well, but in principle that can be done; hydrogen is the real problem.
 2. Improve the selectivity of the Fischer-Tropsch chemistry.
- As with the Haber-Bosch process, this is solid support chemistry.
- Mechanism (initial proposal):

- Solid-state iron binds hydrides and CO on its surface, leading the formation of a formyl species before adding another hydrogen to go to a bound alcohol species, losing H₂O to go to a bound carbene (the carbene is important because it facilitates chain growth), and then proceeding to a bound methyl species. With enough methyl species, you could do other things.
- Gerhard Ertl proves this wrong.
- Mechanism (actual):
 - Solid-state iron binds hydrides and carbonyls on its surface. Next, we split CO to make bound carbides and bound oxides. With more H₂, we can mix and scramble the carbides, oxides, and hydrides, kicking out H₂O and making bound carbene species, which can then go on and form the product that we want as described in the initial proposal.
 - Proven with in situ studies performed on the surface of these materials.
- Another key contribution to the proof came from molecular chemistry, which showed that formyl species are generally unstable:

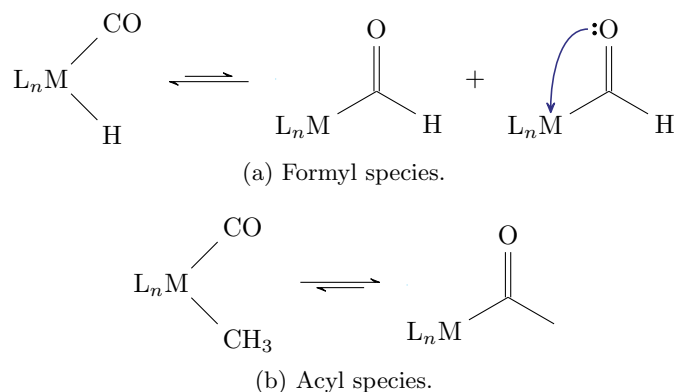
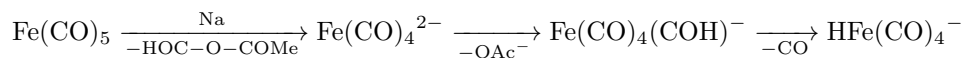
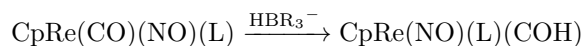


Figure 6.1: Stability of metal-carbonyl derivatives.

- In Figure 6.1a, the reactant is generally favored because it has two bonds instead of one, and metal-hydride bonds are highly thermodynamically favored over metal alkyl bonds.
- In Figure 6.1b, the product is generally favored.
- Think about the equilibrium in terms of the nucleophilicity of the X group. Hydrides are not nucleophilic, whereas alkyl species are.
- The synthesis of metal formyl species was pioneered by Jim Collman in 1973.

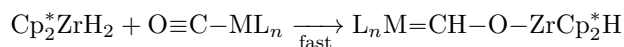


- The first step is ill defined, and the products of it are a messy mixture of carbon-containing products.
- The second intermediate (the formyl species) is unstable and will decompose over time to form the final product.
- Chuck Casey and John Gladys found stable formyl species (the product of the following reaction):



- The reactant is a chiral, 18 e⁻, d⁶ species.

- John Bercaw did more with metal-formyl species:



- The first species is an extremely hydridic metal hydride that has very similar properties to LiAlH. It is a $16e^-$, d^0 species.
- This chemistry is driven by the strength of the zirconium bond (≈ 130 kcal/mol).
- Note that although this is technically a formyl species, it's in practice more of a Fischer carbene structure.
 - The bonding is very different and the Lewis acid activation of that strong Zr^{IV} Lewis acid makes this more of a carbene structure.
 - This is useful in C–C coupling reactions.
- One example of ML_n is Cp_2W .
- Another one is $\text{Cp}_2\text{Nb}(\text{H})(\text{CO}) + \text{Cp}_2^*\text{ZrH}_2 \longrightarrow \text{Cp}_2\text{Nb}(\text{H})(\text{CH}-\text{O}-\text{ZrCp}_2^*\text{H}) \xrightleftharpoons{\text{fast}} \text{Cp}_2\text{Nb}(\text{H})(\text{CH}_2-\text{O}-\text{ZrCp}_2^*) \xrightarrow{\text{H}_2} \text{Cp}_2\text{NbH}_3 + \text{Cp}_2^*\text{Zr}(\text{H})(\text{OCH}_3) \xrightarrow{\text{no rxn}} \cdot$
 - Nb is niobium.
 - A major problem is once we form that extremely strong metal-oxygen bond, it will not break, so it's very hard to get H_2O off of these species.

- How we think about the molecular systems that form C–C bonds.

- This is ultimately what happens on solid support surfaces in industrial catalysis.
- The challenge is that those industrial systems don't have selectivity; molecular systems could in principle provide this (this is an area of active research).

- To recap, we just talked about the potential of early metal hydrides to activate CO (Bercaw's niobium system took it all the way to a methanol equivalent).

- Bercaw (a titan of organometallic chemistry):

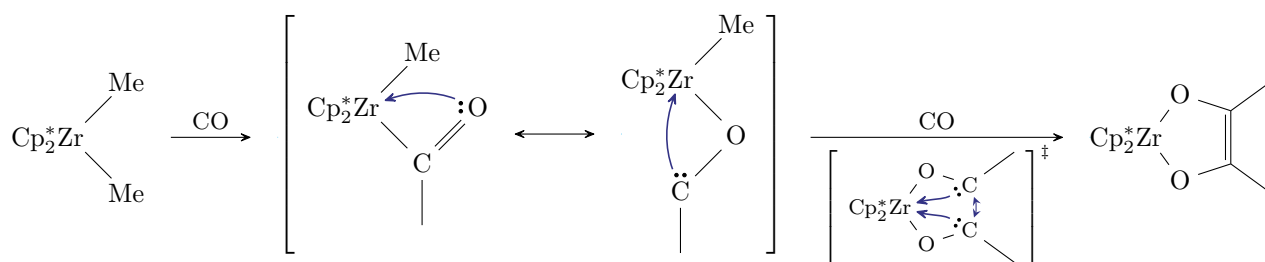


Figure 6.2: Bercaw's first C–C coupling.

- The first ever C–C coupling that was observed in a well-defined and pretty clean way from CO.
 - Using methyl groups makes it imperfect.
 - The mechanism isn't entirely clear.
- The second step proceeds from the second resonance structure.
- Additionally, Bercaw studied reactions with $\text{Cp}_2^*\text{ZrH}_2\text{CO}$, a compound with virtually no π back-bonding:
 - $\text{Cp}_2^*\text{ZrH}_2\text{CO} \xrightarrow{\text{H}_2} \text{Cp}_2^*\text{Zr}(\text{H})(\text{OCH}_3)$, where $-\text{OCH}_3$ is a methanol equivalent.
 - $\text{Cp}_2^*\text{ZrH}_2\text{CO} \xrightarrow{\text{CO}} \text{Cp}_2^*\text{Zr}(\text{H})-\text{O}-\text{O}-\text{Zr}(\text{H})(\text{Cp}_2^*)$. Here, we actually see C–C coupling.

- $\text{Cp}_2^*\text{ZrH}_2\text{CO} \xrightarrow{\text{CO}, \text{H}_2} \text{Cp}_2^*\text{Zr}(\text{H})-\text{O}-\text{O}-\text{Zr}(\text{H})(\text{Cp}_2^*)$. This is even closer to ethylene glycol, but the Zr-O bonds are still an issue.
 - $\text{Cp}_2^*\text{ZrH}_2 + \text{Cp}_2^*\text{Zr}(\text{CO})_2 \longrightarrow \text{Cp}_2^*\text{Zr}(\text{H})-\text{O}-\text{O}-\text{Zr}(\text{H})(\text{Cp}_2^*)$
- Similarly, Tobin Marks looked at $\text{Cp}_2^*\text{Th}(\text{OR})(\text{H})$ (thorium hydride alkoxides), where $\text{R} = \text{CH}(t\text{-Bu})_2$ is a pretty bulky super-isopropal ligand abbreviated $i\text{-Pr}^*$:

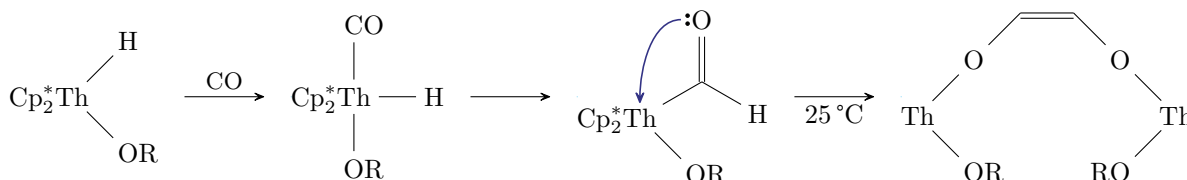


Figure 6.3: Marks' C-C coupling.

- The theme with early metals: If you can get to the Fischer carbene type structure, you can get coupling.
- Pete Wolczanski worked with tantalum silox complexes.
 - $\text{Ta}(\text{OSi}(t\text{-Bu})_3)_3 + 2 \text{CO} \longrightarrow 2 (\text{silox})_3\text{TaO} + (\text{silox})_3\text{Ta}=\text{C}=\text{C}=\text{Ta}(\text{silox})_3$.
 - This is C-C coupling *and* complete deoxygenation.
- Challenge with all of this chemistry: early-metal oxygen bonds are an extreme thermodynamic sink.
 - Unfortunately, the transition from metal-carbon bonds to metal-oxygen bonds is also the driving force of this reactivity.
 - We can get around this issue by trapping the oxygen with other electrophiles.
- Kit Cummins: $\text{MoL}_3 \xrightarrow{\text{CO}} \text{L}_3\text{MoCO} \xrightarrow{1 \text{ Na}} \text{Na}[\text{L}_3\text{MoCO}] \xrightarrow[\text{-NaCl}]{\text{Bu}^t-\text{COCl}} \text{L}_3\text{Mo}\equiv\text{C}-\text{O}-\text{COBu}^t \xrightarrow[\text{-CO}_2, \text{H}_2\text{C}=\text{CMe}_2]{\Delta} \text{L}_3\text{Mo}\equiv\text{C}-\text{H} \xrightarrow{\text{KBn}} [\text{L}_3\text{Mo}\equiv\text{C}]^-$.
 - $\text{L} = \text{N}(t\text{-Bu})(\text{xylyl})$.
 - The third step is more explained in organic chemistry, where an electrophile like the one added (pivaloyl chloride) should create an ester species and lose NaCl.
 - Note that KBn is benzyl potassium.
 - There are very few examples of terminal carbides, but note that this is similar to what happens on the surface of the solid state iron catalyst.
 - This isn't perfect because we're releasing CO_2 , but it is a step where the oxygen isn't trapped on the metal center.
- Theodor Agapie (with his graduate student Joshua Buss):

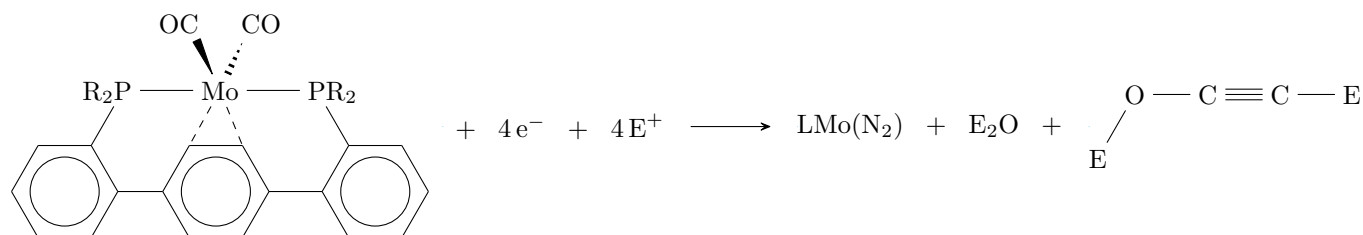


Figure 6.4: Agapie's C-C coupling.

- KC_8 yields the 4e^- .
- The electrophile E^+ is something like TMSCl , a silane, or another silyl electrophile.
- This also proceeds through carbides.
- Jonas Peters (on iron): $\text{Fe}\equiv\text{C}-\text{O} + \text{TMSCl} \longrightarrow \text{Fe}\equiv\text{C}-\text{OTMS}$.
 - We are trapping the oxygen with an oxygen-silicon bond, which thermodynamically are quite strong.
 - Problem: While a silyl electrophile is substantially better than trapping the metal center (which entirely precludes catalysis), the silyl electrophiles generate stoichiometric waste. We need to trap the oxygen with water, not a silyl ether.
 - Thus, what you ultimately want to do is use later metals (like iron), but use hydrogen instead.
- Dan Suess (graduate student of Jonas Peters):

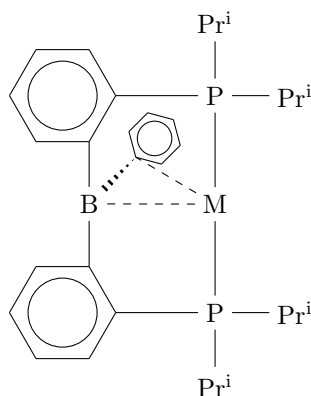


Figure 6.5: The DPB ligand.

- Investigates various reactions of DPB-bound irons.
- $\text{DPBFe}-\text{N}\equiv\text{N}-\text{FeDPBB} \xrightarrow{4\text{CO}} \text{DPBFe}(\text{CO})_2 \xrightarrow{\text{XS CO}} \text{FeP}_2\text{B}(\text{CO})_3$.
 - The product here is formally Fe^0 , but actually slightly higher than that.
- $\text{DPBFe}-\text{N}\equiv\text{N}-\text{FeDPBB} \xrightarrow{4\text{CO}} \text{DPBFe}(\text{CO})_2 \xrightarrow{\text{H}_2} \text{FeP}_2(\kappa^2\text{-BH})\text{H}(\text{CO})_2$.
- $\text{DPBFe}-\text{N}\equiv\text{N}-\text{FeDPBB} \xrightarrow{4\text{CO}} \text{DPBFe}(\text{CO})_2 \xrightarrow{1\text{K}^0} [\text{FeP}_2(\kappa^2\text{-PhB})(\text{CO})_2]^- \xrightarrow{\text{XS K}^0} [\text{FeP}_2\text{B}(\text{CO})_2]^{2-} \xrightarrow{2\text{TMSOTf}}$ a very weird product.
 - The third intermediate is highly activated and somewhat analogous to $\text{Fe}(\text{CO})_5^{2-}$.
 - The product has a $-\text{C}-\text{OTMS}$ substituent, as well as a tridentate derivative of the DPB ligand that still bonds through the two phosphines, but instead of partially bonding through the boron and the ipso-carbon of the phenyl ring, the boron binds to an additional $\text{C}-\text{OTMS}$ ligand through the carbon, which in turn binds back to the iron center.
 - This product has many resonance structures; one with particular merit is $\text{Fe}(\equiv\text{C}-\text{OTMS})_2$ with one of the triple bonds bonding datively to the boron, although it implies an Fe^{VI} oxidation state that is likely an overestimation, even though the iron is certainly high-valent here.
 - Note that if the product is treated with hydrogen, we selectively create (Z)- $\text{TMSO}-\text{C}\equiv\text{C}-\text{OTMS}$.
 - This is not catalytic, but it is one of the few examples where we don't generate an intractable metal-oxide, and we do generate a $\text{C}-\text{C}$ coupled product.
- Conclusion: There's a lot of interesting organometallic chemistry surrounding $\text{C}-\text{O}$ activation and getting that prepped for functionalization, specifically via $\text{C}-\text{C}$ bond formation.

- This is not a solved problems.
 - While molecular chemistry offers the promise of selectivity, there are real challenges with activating it and getting H_2O out instead of trapping the oxygen with silyl electrophiles.
 - Part of the issue is the stability of the molecular complexes (they're not as stable as a solid iron surface) and you need a lot of energy to split $\text{C}\equiv\text{O}$ bonds. On the other hand, if you apply that energy thermally, it will hurt your selectivity.
- There's some extra molecular chemistry in the notes.