

[00:00] Hello everyone! My name is Vennela. I'm a senior at the University of Chicago, where I work in the Anderson Lab, developing a nickel catalyst for CO<sub>2</sub> utilization.

[00:10] So the larger problem I'm really trying to address here is that CO<sub>2</sub> emissions have been rising pretty rapidly, especially over the last 50 years or so. And this, with all this CO<sub>2</sub> in the atmosphere, really exacerbates climate change effects. So one way we can try to alleviate that is by incorporating atmospheric CO<sub>2</sub> into more useful chemicals.

[00:40] A good target for this is sodium acrylate, which we use to make these superabsorbent polymers that are actually in a lot of really common products. So this is a pretty large market that could be using carbon dioxide in its production.

[00:55] Currently sodium acrylate is made from sequential oxidations of propylene. If we want to use carbon dioxide, instead, we can envision this coupling of CO<sub>2</sub> and ethylene gas and build acrylate in this way. So this process is not spontaneous, and actually homogenous nickel catalysts have shown a lot of promise for enabling this coupling.

[01:25] So here I'm showing a pretty simple catalytic cycle for the overall process, which most of the reported catalytic systems seem to go through. You'll notice that after the initial oxidative coupling, you end up at this ringed intermediate, which is called a nickelalactone. So the thing about these nickelalactones is that this ring structure is actually pretty rigid, and that makes it very difficult to go through this opening productive reactivity to release sodium acrylate.

[02:00] For most of the reported catalytic systems, it appears that the main method of ring-opening is this deprotonation step, where you pull off a beta-proton from this carbon here, and then that helps you to move forward. However, these reported systems still suffer from pretty low efficiency, mainly due to the overall stability of these nickelalactones and the difficulty of this forward reactivity.

[02:30] So the goal of my project is to design a system where these nickelalactones can be destabilized, leading to more effective ring-opening and efficient catalysis.

[02:40] So the hypothesis I've been working on is essentially that the supporting ligand can include a steric bulk component positioned to disrupt this nickel-oxygen bond, and promote ring opening in that way. And then also pushing a lot of electron density into this metal center should also disfavor the nickel-oxygen bond and help ring-opening reactivity.

[03:05] So I've chosen to do this using these N-heterocyclic carbene-type ligands, where essentially this divalent carbene carbon center can provide a lot of electron density to the metal center. And then also these NHCs are very modular, so you can really tune the sterics as you need to.

[03:30] Specifically, I've been working with this bis(carbene) where two carbene centers provide a lot of electron donation. And then these bulky tert-butyl groups provide steric imposition in the plane of the nickelalactone.

[03:45] Experimentally, I've been able to synthesize a nickel(0) precatalyst, starting from this imidazole and then this bisimidazolium salt, followed by deprotonation and metalation to get this nickel(0) complex that should be able to react with ethylene and carbon dioxide.

[04:05] In small-scale studies of ethylene and CO<sub>2</sub> reactivity with this starting complex, I have produced this species that I've assigned as a nickelalactone. Although I haven't been able to isolate and purify the product. The assignment is supported by crude NMR, IR, and mass spec data.

[04:30] So here I'm showing the mass spectrum, where the main ion matches what the ionized mass of this nickelalactone should be. And the isotope pattern is also consistent.

[04:45] And then in this IR spectrum, with the blue being the starting complex and the red being the new product, you can see this very intense stretch at 1617 wavenumbers. And I believe that is this C–O stretch here, and it seems to be in the range of the many reported nickelalactones in the literature.

[05:10] So although this data is crude, I do believe that a nickelalactone has formed. And so the next step would be observing whether this can be done catalytically to produce acrylate.

[05:25] So I've tried a number of catalytic conditions. This being essentially the base conditions where I have the starting complex and I'm using this substituted phenoxide BHT, which has been used in the literature before. And essentially I'm pressurizing a THF solution of these with ethylene and then with carbon dioxide and heating it up.

[05:50] And actually, I observe sodium acrylate in none of these trials, which, based on the modifications I made to the base and the gas pressures, and then also some smaller-scale deprotonation studies with the nickelalactone material, I believe is due to a difficulty in deprotonating the bis(NHC) nickelalactone, perhaps because the two carbene centers make the nickelalactone too electron-rich.

[06:25] So to explain this a little further, I'd been working on this idea that pushing electronic density into the nickel center can help the ring-opening with this nickel-oxygen bond.

[06:35] But instead, I should consider also that pulling electron density away from this beta-hydrogen should make it more acidic, leading to easier deprotonation, while still pushing electron density into the nickel-oxygen bond should help the ring-opening. So really it's an asymmetric character of the ligand that I might want for this system.

[07:00] So to kind of investigate this a little more, I turned to this computational study using density functional theory, where in a very basic explanation, essentially I provide certain molecules in a particular geometry and then calculate essentially the optimized geometry for which the potential energy surface of this entire configuration is minimized. So for each scan, you essentially get a single point energy and an optimized geometry.

[07:35] So I did this for a variety of nickelalactones, where I fixed a phenoxide base with the oxygen a certain distance from the beta-hydrogen. And then I did a series of calculations incrementally decreasing that distance until I reached this value, which simulates a protonated phenoxide and a deprotonated beta-carbon here.

[08:00] And I will mention that at this point, this nickelalactone geometry does not look like the initial planar structure, as I've drawn here, but rather something twisted or at least changed from the initial planar geometry.

[08:20] I did these calculations for a number of systems, so here I'm showing three of them. So, one of these is the bis(NHC) nickelalactone that I've been working with experimentally. And then two of these are these phosphino-NHCs, where you can see the asymmetry really played out in the presence of two different lactone isomers.

[08:40] So this green system is actually one of the best catalytic systems for acrylate production in this way that has been reported, where they have this electron-withdrawing group on the NHC and an electron-donating group on the phosphine. And in this blue system I'm showing, I sort of switched that, where the electron-donating group is on the NHC and the electron-withdrawing group is on the phosphine. So that's further playing with that electronic asymmetry.

[09:10] On the right here in this graph, I'm essentially plotting the decreasing beta-hydrogen and phenoxide distances, with the initial geometry single-point energy set to zero and each subsequent energy plotted as a difference from that starting point, to kind of see what the energy barrier might look like.

[09:30] And you'll notice in this red line corresponding to the bis(NHC) system, there really is no peak in energy. And this supports the idea that the deprotonation is a pretty difficult process for this system.

[09:45] And in comparison with these phosphino-NHC systems, you'll see that the peaks seem to be around 10 kilocalories per mole, and significantly lower for this particular isomer, which supports the idea that this asymmetry really helps in this deprotonation process.

[10:05] These initial results do suggest that the electronic asymmetry is important, so I have started the synthesis of new ligands based on this design idea. But I also want to continue testing the bis(NHC) system to validate the idea that stronger bases are necessary to see that deprotonation occur.

**[10:25]** But definitely, computational investigation of a much wider variety of ligands with these varying properties can help me to see whether these trends that I've picked out might hold more globally, and whether further ligand design changes might be good to undertake.

**[10:45]** Essentially, I'm hoping that these NHC ligands can lead to the design of efficient catalysts coupling CO<sub>2</sub> and ethylene for acrylate production.

**[11:00]** So, I want to thank the entire Anderson group for their support, especially Professor Anderson and my mentor, Kate, and then also the University of Chicago and the Beckman Foundation for funding. And thank you all for listening!