CHEM 30400 (Organometallic Chemistry) Notes

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Weeks

Week 1

???

1.1 Reactions 1

3/21:
- 3 grade components: 2 exams (midterm and second midterm at official time slot), 2 hw sets to prepare you for the tests (for completion), 2 paper critiques (on some recent organometallic paper in the literature, and then we write a 2-page review; goal is not to trash the paper, but to say what you found interesting and what specifically could have been done better, e.g., "they missed this specific substrate that would be good to show").

  – Exams will be closed book and closed notes.
  – No further reminders on deadlines, so stay on top of it yourself!

- No textbook, just Anderson's notes. Loosely based off of John Hartwig's book *Organometallic Chemistry from Bonding to Catalysis*.

  – S+M is a good undergraduate text for beginners. They have it at the library.

- We're assuming a fair amount of knowledge, specifically, counting electrons.

  – If you don't feel proficient in this, start reading S+M now (I should review my 202 notes!).
  – There will be questions on HW1 on this.

- Anderson will be gone giving a seminar this Thursday, so we should watch the video on Canvas.

- Overall plan for the course: Reaction types, ligand types, catalysis.

- This course should be a bit different than Dong's version, since Dong is a hardcore organic chemist. Anderson will focus a bit more on transition metals.

- Today: Basic reactions of transition metal complexes.

- Association and dissociation reactions.

  – Recall S_N1 and S_N2 reactions.
  – These are both ligand substitutions.
  – Because of the diverse coordination environments of TMs, we have a few more flavors of this than with pure organic compounds.

- In this kind of the reaction, there is no change ($\Delta = 0$) in. . .

  – Oxidation state.
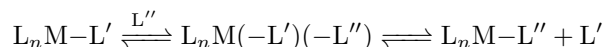 – Electron count.
  – Coordination number.

- Dissociative reactions.

- General form.

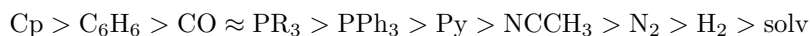$$L_n M{-}L' \rightleftharpoons L_n M + L' \xrightarrow{L''} L_n M{-}L'' + L'$$
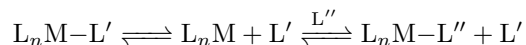
- Notes.

  - Analogous to S_N1.
  - More likely in highly coordinated complexes.
  - You rarely have "true" dissociative mechanisms.

- Associative reactions.

- General form.

$$L_n M{-}L' \xrightleftharpoons{L''} L_n M({-}L')({-}L'') \rightleftharpoons L_n M{-}L'' + L'$$

- Notes.

  - Analogous to S_N2.
  - More likely in square planar complexes.

- BDEs can help differentiate which mechanism takes place.

$$Cp > C_6H_6 > CO \approx PR_3 > PPh_3 > Py > NCCH_3 > N_2 > H_2 > solv$$

  - An associative reaction may be more likely with a more active ligand, displacing a less active one.
  - Sterics matter: PPh_3 may want to dissociate because its so bulky.

- Can a true dissociative mechanism exist?

  - A lot of work has been done on Pt^{II}. It's third-row and hence slow, so its kinetics are easier to study.
  - Can a square planar Pt^{II} center lose a ligand to become T-shaped?
  - An important experiment was done by Rafaelle Romeo (Chem Comm 1984, 542 and IC 1989, 28, 1939 and JACS 1989, 111, 8161)
  - Main compound considered: $PtPh_2(DMSO)_2$, DMSO is a Z-type ligand bonding through the oxygen. We trap the T-shaped ligand with a hyperpolarized DMSO molecule. That's something we can monitor the rate of.
  - Solvent that this is done in is deuterobenzene (C_6D_6).
  - Does the rate depend on the amount of incoming hyperpolarized DMSO? If no, then it's true dissociative.
  - Though even if it is "pure dissociative," you may get complications from η^2-DMSO species.
  - If you measure the rates as a function of temperature, you can get what you want.
  - $\Delta H^{\ddagger} = 84 \pm 26$ kJ/mol and $\Delta S^{\ddagger} = 0.5 \pm 78$ eu (entropy units). The larger error makes this basically zero. This all comes from the Eyring-Pulani (??) equation:

$$K = \frac{k_B T}{h} \exp(-\frac{\Delta G^{\ddagger}}{RT}) = \frac{k_B T}{h} \exp(\Delta S^{\ddagger}) \exp(-\frac{\Delta H^{\ddagger}}{RT})$$

  - ■ It follows that

$$\ln \frac{k_{obs}}{T} = -\frac{\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \frac{\ln(k_B)}{h} + \frac{\Delta S^{\ddagger}}{R}$$

  - ■ The wider the temperature range, the better your data and surer your conclusion.
  - You can also do a volume analysis.

- $\Delta V^{\ddagger} = 5.5\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$.
      - You won't see this very often, though.
      - Here, we look at the rate as a function of pressure, which is related back to volume by the ideal gas law.

- Associative reactions (that are disguised as dissociative reactions). *picture*

  - Example from JACS 2003, 125, 8870.
  - Consider the above compounds.
  - Goal: Consider electrostatic effects between a borate and a silane.
  - Reaction: React these compoudns with benzene to substitute the CH_3 and yield CH_4 as a byproduct. You lose the methane via C-H activation.
  - Eyring analysis to measure the activation energies again.
  - Here, we get $\Delta S^{\ddagger} = -30.2$ eu and $\Delta H^{\ddagger} = 19$ kcal/mol for a, and $\Delta S^{\ddagger} = 0.2 \pm 5$ eu and $\Delta H^{\ddagger} = 16 \pm 1$ kcal/mol for b.
  - What's proposed is an **anchiomeric pathway**.

- What Anderson's doing is introducing two reactions, providing examples, and then providing examples of how they're still being investigated, complicated, and convoluted by the literature.

- Next up: Oxidative additions and reductive eliminations.

- General form.
$$L_nM + A{-}B \rightleftharpoons L_nM({-}A)({-}B)$$
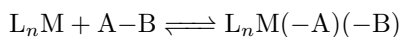
- Notes.

  - In the forward direction. . .
      - Oxidation state increase by 2.
      - Electron count increases by 2.
      - Coordination number increases by 2.
  - Reductive elimination is the opposite.

- Reductive elimination must occur from a *cis* arrangement.

  - Example: No reductive elimination from *trans* ligands in a square planar complex.

- Reductive elimination is uncommon for early TM metals (which tend to be more reducing, i.e., don't like to go down to lower oxidation states; these early TMs just do oxidative addition in general)

- Reductive elimination is faster for electron poor metals (e.g., Pd tends to do reductive elimination more quickly than nickel).

- H_2 is fast to reductively eliminate.

- Oxidative addition does not need to be *cis*, i.e., it can yield *trans* products. This is because association tends to be easier than dissociation.

- Example: Vaska's complex, named after Lorrie Vaska, who was a UChi grad student at the time. *structure*

  - React with MeI to get a *cis* addition, where L abbreviates PPh_3.
  - React with H_2 to get another *cis* product.
 - React with O_2 to get a bidentate chelating species.

- ■ Here, we've gone from an oxygen, cleaved a π bond, and formed a peroxide. It is a nonclassical oxidative addition.
  - We go $\text{Ir}^{\text{I}} \longrightarrow \text{Ir}^{\text{III}}$ in all three.
  - This compound (as well as PFAS's) have been explored as synthetic blood substitutes because of their ability to reversibly bind O_2. Fluorinated solvents show potential nowadays; this is a hard problem, but an important one.

- Different kinds of oxidative addition.

- Concerted mechanism.

- General form. *picture; pull image from 202 notes*

- Notes.

  - We make the adduct with orbital interactions. The filled σ orbital donates into the metal d orbitals. Similarly, the metal d-orbitals donate into the antibonding orbitals of $A-B$, cleaving that.

- S_N2.

- General form.
$$M: + R-X \longrightarrow M-R^+ + X^- \longrightarrow X-M-R$$

- Notes.

  - No clear preference for *cis/trans*.
  - Can also be reversible.

- Radical chain.

- General form.

$$M + I_n \longrightarrow MI_n \cdot \xrightarrow{\text{R}-\text{X}} I_nM-X + R \cdot \xrightarrow{\text{M}} R-M \cdot + X-R \longrightarrow R-M-X + R \cdot \longrightarrow \cdots$$

- Notes.

  - Even when it looks like clean 2-electron chemistry, we can still have active radical mechanisms. This is a downside of the TM mantra that they "can do a lot of things."
  - I_n is an initiator.

- Electron transfers.

- General form.

$$M^Q + R-X \longrightarrow M^{\cdot +} + R-X^{\cdot -} \longrightarrow M^{\cdot +} + R \cdot + X^- \longrightarrow M-R^+ + X^- \longrightarrow X-M-R$$

- Notes.

  - Common in cross-coupling chemistry and with palladium.

- Examples of these different flavors and how one probes between them.

- Jack Halpern.

  - We'll talk about Halpern a lot because he did a lot of seminal work on mechanistic organometallic chemistry, and he did it here. He was on the short list for a Nobel prize but didn't get it. He was a grumpy old guy.

- JACS 1966, 88, 354

- $L_2IrCl(CO) + MeX$ usually yields a *trans* product. You start with a d^8 16 e- compound and end with a d^6 18 e- complex which is very stable. Thus, you get the kinetic product (trans, super stable and inert, will not rearrange into thermodynamic product), not the more stable thermodynamic product.

- Rate trend: $MeI > MeBr \gg MeCl$.

- Rate law: $k[MeI][Ir]$. $\Delta S^\ddagger = 43$ eu.

- Strong solvent polarity effect: The general reaction is $L_nIr + CH_3-X \longrightarrow [L_nIrMe^+][X-] \longrightarrow L_nIr(CH_3)(X)$. Proposition: You form an initial 5-coordinate species, and then the anion snaps down.

- Bimolecular oxidative addition.

- General form.
$$2\,L_nM + R-X \longrightarrow L_nM-R + L_nM-X$$
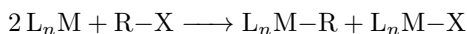
- This is another Halpern example: JACS 1965, 87, 5361.
  - Took $2\,Co^{II}(CN)_5{}^{3-} + MeI \longrightarrow [(CN)_5Co-Me]^{3-} + (CN)_5CoI^{3-}$.
  - We get $2\,L_nM + 2\,R-X \longrightarrow 2\,L_nM-X + R-R$. Ullmann couplings are thought to go through this pathway.
  - Another example where this crops up is Cp_2^*Yb Yb so its a strong one-electron reductant that wants to get to 3+, so mixing $Cp_2^*Yb + CH_2Cl_2 \longrightarrow Cp_2^*Yb-Cl + H_2ClC-CH_2Cl$.

- Another classic example by Whitesides: JACS 1974, 96, 2814. *picture*
  - This is an isotopically labeled electrophile reacted with Fp ($CpFe(CO_2)^-$).
  - Looking at this as a Newman projection, we have *cis*-hydrogens. Looking at J_{H-H} tells us if they're *cis* or not. Do we investigate this coupling constant with NMR like in 302??
  - This yields what's drawn above. It follows that this is a true S_N2-type reaction with inversion.
  - Variation: Insert palladium into the $C-OTs$ bond and then a phenyl anion to get get reductive elimination, which *preserves* the stereochemistry.
    - Takeaway: Concerted implies conservation of the carbon stereochemistry.

- One other example with the Fp anion: Probing for radical reactions with Fp^- plus cyclopropyl radical clocks. The idea is that one radical opens extremely rapidly to form another one $(10^8\,s^{-1})$. Bromide gives you the same thing with Fp nearly perfectly, meaning that this is perfect S_N2. Doing this with iodide means that you do have a competitive radical mechanism.

- This answers the question of if you can have competitive mechanisms with the same kind of reaction.

- Last note for today: The *trans* effect and *trans* influence.

- **Trans influence**: A ground state effect.
  - Essentially, if you look at the bond lengths of the $Pt-P$ bonds in different *cis/trans* isomers, they're different.
  - $2.25\,Å$ vs. $2.31\,Å$.
  - Phosphorus is stronger *trans*-influencing, so they weaken bonds *trans* to them.
  - What is a stronger *trans* influencing ligand? Look at the spectrochemical series. Essentially the same.

- **Trans effect**: A kinetic effect.
  - The Cl^- that will substitute first is the one that is *trans* to the stronger trans-influencing ligand (which is likely higher in the spectrochemical series).

- There's more in the notes that we will not cover, or maybe next lecture.