Unit 4

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4.1 Lecture 15: Nitrogen Fixation

- General form:
$$N_2 + 6\,H^+ + 6\,e^- \longrightarrow 2\,NH_3$$
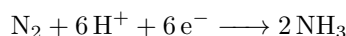
  - Alternatively, it could be $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$.
  - A simple reaction on paper, but in practice and mechanistically, very difficult.

- Nitrogen is one of the essential elements for life (CHNOPS), but we can't absorb it from the air in its elemental form as $N{\equiv}N$ gas. Indeed, we need it to be **fixed** before we can incorporate it (i.e., through food sources).

- Main pathways:

  - Lightning.
$$N_2 + O_2 \xrightarrow{h\nu} NO, NO_2{}^-, NO_3{}^-$$

    - 4-10 million tons per year.
    - Nitrate can be used by organisms; converted into useful nitrogen.
  - Natural enzymatic fixation.
    - 100-300 million tons per year (probably closer to the 100 side).
    - 40/60 ocean/land ratio.
    - Done by the enzyme nitrogenase, with FeMoCO[1] as a cofactor.
  - Mankind.
    - About 190 million tons per year.
    - Thus, mankind is currently fixing more nitrogen than all natural sources combined by a fair amount right now. This is what allows us to feed the planet at its current population.
    - Accomplished by the **Haber-Bosch process**.

- **Haber-Bosch process**: Humanity's primary method of fixing nitrogen.
$$N_2 + 3\,H_2 \underset{Fe/Mg}{\overset{\Delta, P}{\rightleftharpoons}} 2\,NH_3$$
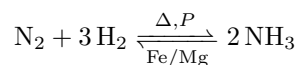
  - $-92\,kcal/mol$ (thermodynamically favored but kinetically difficult).
 - $200\,atm$ of pressure (pushes the equilibrium to the right via Le Châtelier's principle).

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[1]Literally pronounced as its written, i.e., "fih-MOH-koh."

- – 400 °C (required for the rate).
- – Potassium is an activator.

- 2 Nobel prizes for this: Fritz Haber (1918) and Carl Bosch (1931).

  - – Controversial at the time because the process facilitated the explosives industry and Haber was a Nazi.
  - – World War I and II would not have been sustainable for Germany without this process.

- Mechanism:

  - – On the surface of the iron catalyst, the pressure binds H_2 gas as hydrides and N_2 gas as bridging nitrides (between various iron atoms at the surface). It follows in a statistical and thermodynamic manner that amine ligands will be formed on the surface attached to the iron. These can then break off into ammonia gas.
  - – A solid state heterogeneous process.
  - – Nobel Prize (2007) to Gerhard Ertl for this mechanism.

- This process is highly efficient, but very energy intensive as well.

  - – As such, there is a race to find a less energy-intensive catalytic alternative.

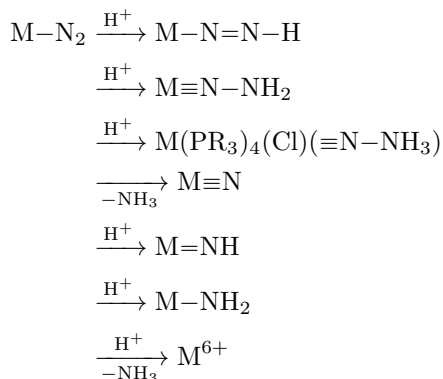- Molecular systems: The nitrogenase enzyme.

$$N_2 + 8\,H^+ + 8\,e^- \xrightarrow{\text{ATP}} 2\,NH_3 + H_2$$
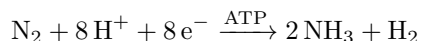
  - – Other extant cofactors include FeVCO and FeFeCO, but they are less common.
  - – Since ATP is used, this is still a very energy-intensive process.
  - – N_2 bonds to metal centers in many ways:
    - ■ Linear, bent, side-on, bridging linear, bridging side-on, multi-metal center bridging, etc.
  - – N_2 complexes are much less common than CO complexes since N_2 is a terrible ligand.
    - ■ The HOMO in N_2 makes it a σ donor, but CO's negative formal charge on the carbon makes it a better σ donor.
    - ■ Additionally, CO is a much better π acid due to its polarization.

- Allen and Senoff (in 1965) reported the first dinitrogen complex.

$$RuCl_3 \cdot 3\,H_2O + N_2H_4 \cdot H_2O \longrightarrow [Ru^{II}(N_2)(NH_3)_5]^{2+}[Cl_2]^{2-}$$
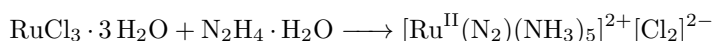
  - – N_2H_4 is hydrazine (rocket fuel), and is much more stable as a hydrate.
  - – The product is d^6 with $18\,e^-$ and has $\mu_{N_2} = 2170\text{-}2115\,\text{cm}^{-1}$ (the range depends on the anion).
  - – For reference, free N_2 has a stretching frequency of $2331\,\text{cm}^{-1}$.

- Yamamoto gives the first example of a dinitrogen complex formed from free N_2 ($HCo(PPh_3)_3(N_2)$).

- Joe Chatz, George Leigh, and Dilworth in Sussex (of the British/American camp), and Hidai and Nishibayashi (of the Japanese camp) became interested in nitrogen fixation following Yamamoto's work.

  - – Second and third row Group 6 complexes such as molybdenum were the focus.
  - – Example: $MoX_4L_2 \xrightarrow[\text{Na/Hg}]{N_2,\,L} Mo(N_2)_2L_4$.
    - ■ L is typically a phosphine.
    - ■ With various phosphine ligands, you can get different geometries.

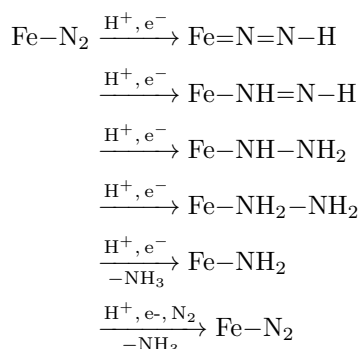- – Another example: $cis-\mathrm{W(N_2)_2(PMe_2Ph)_4} \xrightarrow[\mathrm{MeOH}]{\mathrm{H_2SO_4}} 2\,\mathrm{NH_3 + N_2 + W^{VI}(oxo)}$.

  - ■ Works with molybdenum, too, but tungsten gives a better yield.
  - ■ The overall reaction is $\mathrm{W^0 + 6\,H^+ + N_2 \longrightarrow 2\,NH_3 + W^{VI}}$.
  - ■ Some important subreactions/steps are $\mathrm{N_2 + 4\,e^- \longrightarrow N_2H_4}$ and $\mathrm{N_2 + 2\,e^- \longrightarrow N_2H_2}$.

- Mechanism (by Chatt):

$$\mathrm{M-N_2} \xrightarrow{\mathrm{H^+}} \mathrm{M-N{=}N-H}$$
$$\xrightarrow{\mathrm{H^+}} \mathrm{M{\equiv}N-NH_2}$$
$$\xrightarrow{\mathrm{H^+}} \mathrm{M(PR_3)_4(Cl)({\equiv}N-NH_3)}$$
$$\xrightarrow[\mathrm{-NH_3}]{} \mathrm{M{\equiv}N}$$
$$\xrightarrow{\mathrm{H^+}} \mathrm{M{=}NH}$$
$$\xrightarrow{\mathrm{H^+}} \mathrm{M-NH_2}$$
$$\xrightarrow[\mathrm{-NH_3}]{\mathrm{H^+}} \mathrm{M^{6+}}$$

  - – Very few compounds in the form of the first intermediate (diazene) are known. These compounds are very susceptible to β-H elimination from water, though.
  - – The second intermediate has a hydrazido ligand.
  - – The fourth intermediate has a nitride.
  - – The fifth intermediate has an imide.
  - – The sixth intermediate has an amide ligand.

- Hidai uses silanes: $\mathrm{M(N_2)_2(PR_3)_4} \xrightarrow{\mathrm{TMSI}} \mathrm{TMS-N{=}N-MI(PR_3)_4} \xrightarrow[\mathrm{N_2}]{\mathrm{Na,\,THF}} \mathrm{M(N_2)_2(PR_3)_4 + NH(TMS)_2 +}$ $\mathrm{NH_3 + NaNH_2 + NaNH(TMS)}$, etc.

- Yandulov and Schrock (2003) creates a well-defined catalyst for nitrogen fixation.

  - – The catalyst is molybdenum bound to dinitrogen and a tridentate TREN scaffold anion (with hexaisopropal $tert$-phenyl (HIPT) aryl groups).
  - – They add eight equivalents of cobaltocene ($\mathrm{CoCp_2}$), seven equivalents of lutidinium (a pyridinium acid), and the bulky, noncoordinating counteranion $[\mathrm{BAr^F_4}]^-$.
  - – They fish out $\mathrm{Mo-NH_3 + NH_3}$. Reducing the former product gives $\mathrm{Mo^{III}(N_2)}$ with a weak reductant.
    - ■ If you use a slightly stronger reductant (decamethylchromocene; $\mathrm{CrCp_2^*}$) and a slow addition of acid, you get approximately 8 turnovers.
  - – This is not a great yield, but the important part is that it exists and they can observe all of the intermediates.
    - ■ Observing said intermediates verified the mechanism proposed by Chatt and Hidai.
  - – To reiterate, this is the Chatt/Distal[2] cycle they observed: $\mathrm{Mo-N{\equiv}N} \xrightarrow{\mathrm{H^+,\,e^-}} \mathrm{M-N{=}N-H} \xrightarrow{\mathrm{H^+,\,e^-}}$ $\mathrm{M{\equiv}N-NH_2} \xrightarrow{\mathrm{H^+,\,e^-}} \mathrm{M{\equiv}N} \xrightarrow{\mathrm{H^+,\,e^-}} \mathrm{M{\equiv}NH} \xrightarrow{\mathrm{H^+,\,e^-}} \mathrm{M-NH_2} \xrightarrow[\mathrm{-NH_3}]{\mathrm{H^+,\,e\text{-},\,N_2}} \mathrm{Mo-N{\equiv}N}$.
    - ■ Note that molybdenum starts in the 3+ oxidation state at $\mathrm{M-N{\equiv}N}$ and goes up to 6+ at $\mathrm{Mo{\equiv}N}$ before cycling back down.

- Shilov had a number of systems, but they were poorly defined.

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[2]Note that Chatt and Distal are interchangeable synonyms.

- Other selected examples.

  - Zirconium can do this catalysis in some cases.
  - Laplaza and Cummins (1995) find that molybdenum trisannelides and dinitrogen can go through a kinked transition state to yield two equivalents of $L_3Mo\equiv N$.

- Iron:

  - Present in all enzymatic cofactors that mediate nitrogen fixation.
    - Until 10-15 years ago, they thought it wasn't directly involved though.
  - $(PR_3)_4Fe(N_2) \xrightarrow{\text{XS H}^+}$ only trace amounts of NH_3.
  - Yuki et al. (2012) finds that simple iron salts and even substituted ferrocenes react with a strong reductant, sodium, and TMSCl to make $N(TMS)_3$ (which is catalytic and can be transformed into ammonia). The yield is about 25 equivalents per iron.
    - This shows that iron can do this chemistry.
  - Dr. Anderson's thesis work with Jonas Peters finds that $Fe(N_2)(B(PR_2Ph)_3) \xrightarrow[\text{XS HBAr}^F_4]{\text{XS KC}_8} NH_3$[3] (Anderson et al., 2013).
    - Seven equivalents per iron. More recent tinkering has brought it up to nearly 100 equivalents per iron.
    - Mechanism: $L_3FeN_2^- \xrightarrow{2\,H^+} L_3Fe\equiv N-NH_2^+ \longrightarrow \longrightarrow \longrightarrow NH_3$.
    - Suggests a Chatt/Distal mechanism.
  - Differing mechanistic proposal: Alternating mechanism.

$$
\begin{aligned}
Fe-N_2 &\xrightarrow{H^+,\,e^-} Fe=N=N-H \\
&\xrightarrow{H^+,\,e^-} Fe-NH=N-H \\
&\xrightarrow{H^+,\,e^-} Fe-NH-NH_2 \\
&\xrightarrow{H^+,\,e^-} Fe-NH_2-NH_2 \\
&\xrightarrow[-NH_3]{H^+,\,e^-} Fe-NH_2 \\
&\xrightarrow[-NH_3]{H^+,\,e\text{-},\,N_2} Fe-N_2
\end{aligned}
$$

    - This doesn't require as many oxidation states as the Chatt mechanism (which favors iron, which doesn't easily form oxidation states other than 2+ and 3+).
    - We also don't see a nitride or imide intermediate, but we do see a diazene, hydrazido $1-$, and hydrazine adducts.
    - Enzyme data supports this mechanism.

4.2 Office Hours (Anderson)

- How much strain is needed for ROMP to proceed?

  - Norbornene is a common one.
  - 4 membered rings.
  - 7- and 8-membered rings are usually not sufficiently strained.

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[3]Note that the reactant is the same compound discussed in problem 3 of Homework 1.

- Cyclopropene does exist, and it does do ROMP, but it polymerizes so quickly that you can't do much with it.
  - If it's cold and you throw in a metathesis catalyst, it will probably work.
  - Recall that it also participates in Diels-Alder reactions.

- ROMP does *not* release ethylene.
  - Ring strain is the driving force.
  - Part (d) is a typo; ethylene gas is the common byproduct of *most* of these reactions. We should still show ROMP as is.

- How do metal d orbitals enable $2 + 2$ cycloaddition?
  - Butadiene plus ethylene requires ethylene to have filled π^* orbitals (these have the appropriate symmetry).
    - Diels-Alder $4 + 2$ cycloaddition is allowed.
  - The symmetry of the metal orbitals (esp. d_{z^2} and d_{xy}) enables $2 + 2$ cycloaddition.

- η and κ bonding?
  - IUPAC likes κ more now, but η is historical.
  - η indicates a continguous π system while κ simply indicates denticity.
  - Figure 2.23a is κ^2 as well.
  - Bidentate ligands bond in a κ^2 fashion.
  - Numbers on these as well as μ should exclusively be superscripts.
  - A metal bound face-on to a carboxylate would be η^3, but this is very atypical/nontexistent bonding. Side-on bonding (i.e., to both oxygens) would be κ^2.

4.3 Discussion Section

5/4:
- Midterm 2 is 5/25/2021.

- Final paper due 5/26/2021; Sophie has asked Dr. Anderson for more information.
  - Due at noon.
  - Sophie will post an example paper.
  - As the last assignment for this course, you will write a critical review of 1 of 6 availabble papers.
  - Some of these papers include material outside the scope of organometallic chemistry. Try to focus on topics relevant to this course. The reviews should be no longer than 700 words not including citations or fiugre captions, althouggh additional ccitations are not requried if you only use information presented in the paper or the class. The critique should be written with Times New Roman 12 point font and 0.5 inch margins.
  - General outline fofr the critiques:
    - 1 introduction paragraph.
    - 2 experimental summary paragraphs.
    - 3 discussion paragraphs.
    - 4 critique paragraphs.
    - Figures.
  - Sophie is willing to look over assignments (email them to her), but we have to get them to her by the 19th for her to take a look.
  - They should be professional but not excessively formal.

- A more detailed outline will be published later.
- A critique isn't necessarily a flaw, but more a suggestion of another experiment they could run or some other conclusion they could have drawn.

- Final is 6/3/2021.

- Midterm 1:
  - Biggest issues:
    - Running out of time.
    - Omitting parts of answers (generally not reading instructions in general). If it says draw orbitals, explain, or predict, you need to do that.
  - She'll talk to John about making it/the next one shorter.
  - Syntheses are only one point?
  - If we would like to know more feedback about our exams, we can reach out with specific questions about questions.
  - 1a: Reduce with Na or Hg metal and then throw in MeI. $\frac{1}{2} \text{Mn}_2(\text{CO})_{10} \xrightarrow[-2\,\text{NaCl}]{\text{Na/Hg}} \text{Na}[\text{Mn}(\text{CO})_5] \xrightarrow[-\text{NaI}]{\text{MeI}}$.
  - 3a: Like-signed lobes donate (*correct notes*?). You can also show either $d_{x^2-y^2}$ or d_{z^2} for σ donation.
  - 3b: We need charges on the metal in $\text{M}-\text{C}\equiv\text{O}^+$ resonance structures (-, 0, +).
  - 3c: Also identify the dominant resonance structure.
  - 4c: Cp can ring-slip to stabilize the electron count.
  - 4d: Cone angle starts at metal center and includes specifically the full van der Waals radii of the phosphine R groups at the base fo the cone. Most commonly forgotten: metal center, van der Waals radii.
  - 4f: H_2CrO_4 is Cr^{6+}, d^0, while $\text{Cr}(\text{CO})_4{}^{4-}$ is Cr^{4-}, d^{10}. The difference is different than you expect because they are actually very similar.
  - 5: First, backcalcculate out spin-state to determine $S = 1$ and $S = 0$. Second, luckily, they're 4-coordinate, so the simplest solutin is to loook for two geometries that ggive the two spin states. You interconvert the things in solution, giving a mixed magnetic moment. $\mu = 2\sqrt{S(S+1)}$.
  - 6: Cp^- is a π donor. Cyclobutadiene is both (the orbital drawing shows that you have a HOMO π donor and a LUMO π acceptor).
  - 7: No extra sites for a better bridge and only bad bridges present (if you draw them you can tell). Whenever you need to compare two ligands, think:
    1. Chelate? Neither ligand.
    2. Hard/soft affinity? Both hard.
    3. Strong field? Isocyanide much stronger, more likely all low spin.
    4. Trans effect? All the same ligand.