

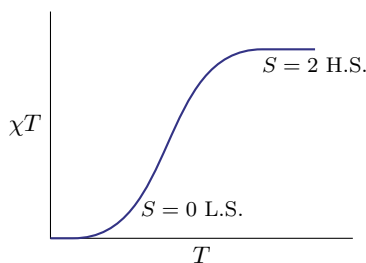
Unit 1

???

1.1 Lecture 1: Introduction/Key Trends

- 3/29:
- Largely asynchronous, but synchronous discussions, office hours, and tests.
 - Refer to the Canvas site for all information; it's the class hub.
 - To understand transition metal trends and properties, start with *atomic* properties and trends.
 - **Electronegativity:** The energy that an atom will gain when it gains an electron.
 - Fluorine really wants to gain an electron; thus, it has high electronegativity.
 - Do you mean electron affinity?
 - Increases across a row; decreases down a column.
 - Transition metals, in general, are an exception to this rule.
 - This is because of the **lanthanide contraction**.
 - Discontinuities in the transition metals (Mn and Ni) correspond to half-filled and filled *d* shells, respectively.
 - Extra stability means less of a desire to gain an electron.
 - **Ionization potential:** The energy required to remove an electron.
 - Varies with the identity of an element *and* its oxidation state.
 - Increases across a row; decreases down a column.
 - Size:
 - Many different definitions (depending on the specific thing you're interested in, one may be more useful than another). For example,
 - Atomic radius: Specific to an element.
 - Ionic radius: Specific to an oxidation state; as in salts and coordination complexes.
 - Covalent radius: Distance that one would expect for a bond; varies with bond order.
 - Decreases across a row; increases down a column (a notable exception to the latter trend follows from the lanthanide contraction).
 - Things that affect size:
 - Oxidation state.
 - Spin state (high spin [larger; this is because the e_g orbitals are antibonding, and antibonding electrons both push the bounds of the atom and weaken bonds, increasing the covalent radius] vs. low spin [smaller]).

- **Lanthanide contraction:** In the transition metals, there is a small/no increase in size between the second and third rows.
 - This is because the shell added in between contains the f orbitals, which are small, do not extend past the noble gas core, and do not provide good shielding.
 - Z goes up a lot with little shielding, so the $5d$ orbitals are contracted; thus, $4d/5d$ orbitals are similar in size.
- **Oxidation state:** The number of electrons a metal center is below its valence.
 - Typically, the maximum oxidation state is defined by the d -count for the 0-valent metal.
- Having discussed four trends, how are they related?
 - As oxidation state increases, “electronegativity” and ionization potential will increase, and the radius will decrease.
 - This is because removing an electron \Rightarrow reduces shielding \Rightarrow higher positive charge \Rightarrow all orbitals decrease in energy \Rightarrow all orbitals decrease in size (hence radius decreases, too).
 - Watch out for discontinuities such as Mn^{2+} .
- **Magnetic properties:** Unique to the transition metals and the f block.
 - Consider $\text{Fe}^{\text{II}}\text{L}_6^{2+}$ (d^6).
 - Possible states: Low spin ($S = 0$), intermediate spin ($S = 1$; rare), and high spin ($S = 2$).
 - We predict which state dominates by the:
 - **Pairing energy.**
 - **Ligand field stabilization energy.**
- **Pairing energy:** The energy cost of putting two electrons in the same orbital. *Also known as PE.*
 - Trends with orbital size/radius.
 - Decreases down a column.
- **Ligand field stabilization energy:** *Also known as LFSE.*
 - Can be thought of in terms of crystal field theory.
 - Extra thoughts on Figure VI.10 of Labalme (2021): Donating negative charge to a free metal ion in a spherically symmetric fashion uniformly raises the energy of the d orbitals by increasing repulsions and size.
 - Low-spin LFSE: $6 \cdot -4 \text{ Dq} + 3 \text{ PE} = -24 \text{ Dq} + 3 \text{ PE}$.
 - Intermediate-spin LFSE: $5 \cdot -4 \text{ Dq} + 1 \cdot 6 \text{ Dq} + 2 \text{ PE} = -14 \text{ Dq} + 2 \text{ PE}$.
 - High-spin LFSE: $4 \cdot -4 \text{ Dq} + 2 \cdot 6 \text{ Dq} + 1 \text{ PE} = -4 \text{ Dq} + 1 \text{ PE}$.
 - Thus, the energy difference between the low-spin and high-spin configurations is $20 \text{ Dq} + 2 \text{ PE}$. It follows that if $10 \text{ Dq} > 1 \text{ PE}$, then the complex will be low spin; and if $10 \text{ Dq} < 1 \text{ PE}$, then the complex will be high spin.
 - This also explains why the intermediate spin state is rare: if Δ_o is large enough to make $10 \text{ Dq} > 1 \text{ PE}$, then it will likely take the complex all the way to a low-spin configuration (and vice versa for high spin).
 - Lastly, this means that Fe^{II} is a good **spin-crossover** ion.
- **Spin-crossover (ion):** An ion that can have both high- and low-spin states.
 - The graph of the magnetic moment χT of Fe^{II} vs. temperature T (see Figure 1.1) moves from $S = 0$ at the bottom left to $S = 2$ at the top right.
 - d^2 ions are never spin-crossover ions: $-8 \text{ Dq} + 0 \text{ PE}$ for high spin vs. $-8 \text{ Dq} + 1 \text{ PE}$ for low spin.

Figure 1.1: Magnetic moment vs. temperature for the Fe^{II} ion.

- Dq and PE values depend on:

- Ligand field strength.

- ΔO_h increases as σ donation increases.
- ΔO_h increases as π acceptance increases.
- ΔO_h decreases as π donation increases.
- To what extent do we need to have the spectrochemical series memorized?

- Metal center.

- Larger, more diffuse metals (i.e., second- and third-row transition metals) have better overlap with the ligands, giving rise to larger ΔO_h .
- Note that pairing energy decreases in second- and third-row transition metals (due to the larger orbitals).
- These two factors imply that second- and third-row transition metals are almost always low spin.

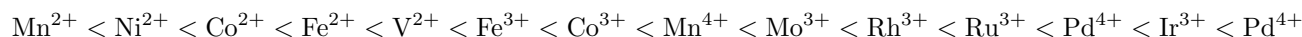
- Oxidation state.

- As oxidation state increases, ΔO_h increases (due to better energy matching, higher “electronegativity,” the role of electrostatics, and the electron configuration [d^5 is almost always high spin, and d^6 is often low spin]).
- Why do d^5 and d^6 exhibit the above behavior? Shouldn’t the stabilized orbitals be split more?
- See the below spectrochemical series for metals.

- Geometry.

- In a σ -only sense, lower coordination numbers tend to have smaller LFSEs.
- $T_d < C_{4v} \approx D_{3h} < O_h < D_{4h}$.
- $\Delta_{\text{sq. pl.}} \approx 1.74 \Delta O_h$.

- Spectrochemical series for metals (not as precise as the one for ligands, but a decent approximation):



- Hard/soft acid-base theory:

- Common Lewis acids:

- Proton: H^+ .
- Molecules with no octet: AlCl_3 , BR_3 (boranes), BeH_2 .
- Metal cations: Na^+ , Ti^{4+} .
- π acids: CO_2 , CO , PR_3 .

- Common Lewis bases:

- Carbanions: CR_3 .

- Hydrides: KH, NaH, LiAlH₄.
 - Amines, amides, and phosphines: NH₃, PR₄, NH₂⁻.
 - OH₂, SR₂, OH⁻.
 - Halides: F⁻, Cl⁻, Br⁻.
 - Carbonyl: CO (means CO is amphoteric).
 - Olefins: C₂H₄.
- Distinguishes hard vs. soft^[1].

1.2 Office Hours (Whitmeyer)

- 3/30:
- Electron affinity, not electronegativity, for the periodic trend?
 - At higher levels, people don't really distinguish between the two.
 - To what extent do we need to have the spectrochemical series memorized?
 - You don't need to memorize them, but it's good to know some of them off the top (exams are open note, but there are time constraints).
 - In connection with oxidation state, Prof. Anderson mentioned that d^5 is almost always high spin, and d^6 is often low spin. Why? Shouldn't the stabilized orbitals be split more?
 - 5 d electrons each in their own orbital minimizes the pairing energy.
 - 6 d electrons all occupy the lower orbitals to minimize antibonding contributions.
 - Using the textbook:
 - The lectures are essential in this course, and if you don't understand something in the lecture, ask Sophie or John or read the textbook.
 - If it's in those chapters, it could be asked about, but it probably won't be if John doesn't talk about it.

1.3 Lecture 2: Electron Counting, 18e⁻ Rule

- 3/31:
- Organometallic chemistry: Strictly speaking, compounds containing metal-carbon bonds. More broadly, it's homogeneous transition metal chemistry ([frequently diamagnetic] metals bonded to light atoms).
 - Deeply related to catalysis (both fine and bulk chemical synthesis, and biology).
 - Transition metal trends:
 1. Early transition metals tend to have higher oxidation states.
 - It's easier to remove electrons from less electronegative elements (electronegativity increases across a period).
 2. Size: 1st row < 2nd row \approx 3rd row.
 3. M–L bond strengths increase down a column.
 - Two reasons: Size (larger, more diffuse orbitals have better overlap) and electronegativity (increases down a column; this trend is unique to the transition metals).
 4. Higher coordination numbers are found for heavier metals.
 5. More high-spin species in the first row.
 6. First row transition metals prefer 1e⁻ coupled.

¹Hard vs. soft is the basis for the solubility rules!

– Why?

7. More difficult to reduce as you go down a triad (column).

• Common structures:

– 4 coordinate:

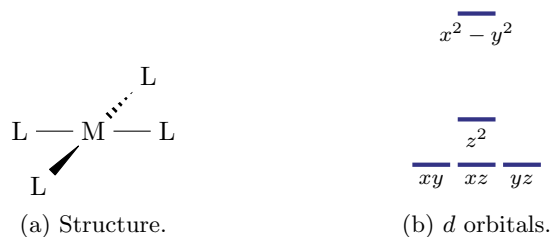


Figure 1.2: Square planar information.

- Square planar (note that the z^2 orbital can swap with the three degenerate orbitals beneath it fairly easily; what's important is that $x^2 - y^2$ is higher).



Figure 1.3: Tetrahedral information.

- Tetrahedral (much smaller splitting energy than some of the others).

– 5 coordinate:

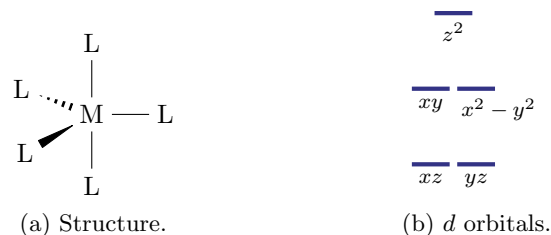


Figure 1.4: Trigonal bipyramidal information.

- Trigonal bipyramidal (the axial ligands push d_{z^2} high in energy, d_{xy, x^2-y^2} are degenerate by the threefold D_{3h} symmetry, and $d_{xz, yz}$ are nonbonding and thus lowest in energy; note also that this geometry has **fluxional ligands**).

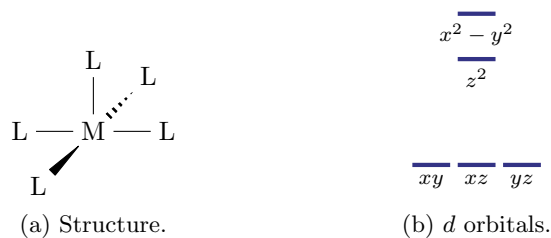


Figure 1.5: Square pyramidal information.

- Square pyramidal (think of it either as square planar with an axial ligand on top, or as octahedral missing one axial ligand on the bottom; thinking of it this way also rationalizes Figure 1.5b as the mean of Figures 1.2b and 1.6b).
- 6 coordinate.

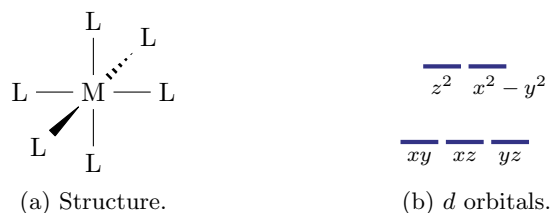


Figure 1.6: Octahedral information.

- Octahedral ($d_{xy,xz,yz}$ are nonbonding in a σ -only framework, but can take on bonding character when π interactions are considered).

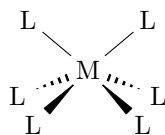


Figure 1.7: Trigonal bipyramidal information (structure).

- Trigonal bipyramidal (each pyramid is eclipsed, rather than staggered as in octahedral; Pfenig and Seppelt (1996) explores this geometry in greater depth).
- **Fluctional ligands:** A set of ligands that readily exchange positions around the molecular center via a **Berry pseudorotation**.
- Ligand types (see Labalme (2021, p. 93)).
- **X-type** (ligand): Typically anionic, covalent donors.
- **L-type** (ligand): Typically neutral. *Also known as dative donor*.
- **Z-type** (ligand): Typically neutral, but can be cationic (no electrons to donate; these are acceptors).
- Note that a carbonyl group can be both an L- and a Z-type ligand (L if it participates in σ donation, and Z if it participates in π acceptance).
 - Similar to how Cl^- can be both a σ and π donor.
- On hard/soft matching: remember that harder ligands will prefer harder metals, and vice versa.
- Electron counting:
- Organic chemistry concerns itself with an octet.
- But the octet rule is really a large HOMO-LUMO gap rule; filling stable orbitals and leaving the unstable orbitals empty.
 - In CH_4 for example, we want to fill the σ and π MOs with all 8 electrons that they can hold, but leave σ^* and π^* unfilled (see Figure III.17 in Labalme (2021)).
 - However, in ML_6 for example (considering only d orbital/ligand σ orbital interactions), we have nine σ /nonbonding orbitals that are ok to fill up and two σ^* orbitals that we should try to avoid filling up (see Figure 1.6b as well as Figure VI.2 from Labalme (2021) for a decent approximation).

- The nine orbitals that are ok to fill up in an ML_6 compound can hold 18 electrons; this gives rise to the **18 electron rule**.
- **18 electron rule:** An octahedral ML_6 transition metal complex with 18 electrons is fairly energetically favorable.
- Low-spin square planar:
 - 4 σ /NB ligand orbitals plus 4 nonbonding metal d orbitals gives 8 σ /NB orbitals that can hold 16 electrons in total (see Figure 1.2b).
 - Figure VI.13 of Labalme (2021) says that *two* metal orbitals form bonding/antibonding orbitals with the ligand orbitals, so why does Dr. Anderson assert that only *one* does? Is it because of what he said about d_{z^2} being practically interchangeable with the $d_{xy,xz,yz}$ ligands in square planar complexes?
- **16 electron rule:** A square planar ML_4 transition metal complex with 16 electrons is fairly energetically favorable.
- Note that the 18 and 16 electron rules respectively imply that octahedral complexes prefer d^6 configurations and square planar complexes prefer d^8 configurations.
- Note also that since the HOMOs in both 18-electron octahedral and 16-electron square planar complexes are nonbonding, the 18/16 electron rules are more of a suggestion.
 - In general, these numbers are more of a maximum; lower counts can still be stable.
 - However, there are cases of 19 and 20 electron systems.
- 2 schools of thought on electron counting: the **ionic method** and the **covalent method**.
 - Dr. Anderson prefers the covalent method; he's of the opinion that it's a bit more foolproof.
 - Proponents of the ionic method argue that it's nice because it gives you the oxidation state of the metal center throughout the process, but it can run into snags with certain ligands (in step 1 below, it is not always clear what splitting electronegativity dictates).

Ionic Method	Covalent Method
1. Break all M–L bonds according to electronegativity (or accordingly, to form the most stable fragments). Note that M–L bonds split homolytically.	1. Draw a legitimate Lewis structure (no half bonds or circles [as in benzene]). Don't forget lone pairs.
2. The charge on the metal after step 1 is its oxidation state.	2. Assign formal charges (in a dative bond, these belong to the ligand).
3. From 2, assign a d -electron count.	3. The number of electrons that a given ligand donates is equal to its formal charge plus twice the number of dative bonds plus the number of covalent bonds.
4. The electron count equals the d^n count plus the ligand donors (typically 2 electrons per ligand).	4. The electron count is that d^n count for M^0 plus the sum of the ligand electron donations minus the charge on the complex.

- Gain familiarity with the d counts of common transition metals.
- A metal can actually have multiple oxidation states in resonance with each other, whereas the electron count is indisputable, i.e., the only number that you can definitively assign to a complex.
 - This is why it's better to use the covalent method; it goes straight to assigning the electron count, foregoing any possible issues with the oxidation state.

- If you apply each method correctly, they should both give the same answer.
- Examples (ligands):
 - A phosphine PR_3 .
 - The phosphine has a lone pair to donate to the metal center, forming a **dative bond**.
 - Alternatively, the formal charge on phosphorous in a $\text{M}-\text{PR}_3$ situation is +1 and there is 1 covalent bond.
 - Either way, the phosphine is a 2-electron donor; this is further confirmed by the fact that phosphines are L-type ligands.
 - CO.
 - We have multiple possible resonance structures for a $\text{M}-\text{C}\equiv\text{O}$ bond, but we can robustly treat this with the covalent method.
 - $\text{M}-\text{C}\equiv\text{O}^{\oplus}$ has a +1 formal charge and 1 covalent bond, suggesting that CO is a 2-electron donor.
 - $\text{M}=\text{C}=\text{O}^{\cdot\cdot}$ has no formal charge and 2 covalent bonds, suggesting that CO is a 2-electron donor.
 - $\text{M}\equiv\text{C}-\ddot{\text{O}}^{\ominus}$ has a -1 formal charge and 3 covalent bonds, suggesting that CO is a 2-electron donor.
 - $\text{M}\leftarrow\text{C}\equiv\text{O}^{\oplus}$ has a net 0 formal charge and 1 dative bond, suggesting that CO is a 2-electron donor.
 - NO.
 - If NO bonds linearly, it's a 3-electron donor (take $\text{M}-\text{N}\equiv\text{O}^{\oplus}$ as a possible resonance structure).
 - If NO bonds bent, it's a 1-electron donor (take $\text{M}-\ddot{\text{N}}=\ddot{\text{O}}^{\cdot}$ for example).
- **Dative bond:** A covalent bond between two atoms where one of the atoms provides both of the electrons that form the bond.
- Examples (metal complexes):
 - Ferrocene, a sandwich compound with an iron atom between two cyclopentadienyl (or Cp) groups (covalent method).
 - Each carbon atom forms a single covalent bond to iron. This gives each iron four covalent bonds (two to its neighbors in the ring, one to its hydrogen, and one to iron), so there are no formal charges.
 - Thus, each Cp ligand donates 5 electrons by the covalent method, and iron as a d^8 compound donates 8 electrons.
 - Therefore, this is an 18 electron complex.
 - Ferrocene (ionic method):
 - The cyclopentadienyl anion has a 1- charge, making it a 6π -electron aromatic system.
 - There are two of these anions, with a total charge of 2- between them, so iron must be in the Fe^{2+} oxidation state to compensate.
 - This makes iron d^6 , which plays well with 18 electron systems.
 - Hexamethyl tungsten $\text{W}(\text{CH}_3)_6$ (covalent method):
 - Each CH_3 ligand forms a single covalent bond with W without formal charge; thus, each donates 1 electron.
 - W is d^6 .
 - Thus, the d count is 12, making it a pretty reactive compound.
 - $\text{W}(\text{CH}_3)_6$ (ionic method):

- For each ligand, we split to W^+ and CH_3^- .
- This makes the metal center oxidation state W^{VI} , with a resultant d^0 configuration.
- $\text{W}(\text{CO})_6$ (covalent method).
 - From above, CO is a 2-electron donor. Thus, the 6 CO's donate 12 electrons. This combined with the fact that W is d^6 makes this an 18 electron system, i.e., pretty stable.
- $\text{W}(\text{CO})_6$ (ionic method):
 - We split $\text{W}-\text{CO}$ into $\text{W}^0 + \text{CO}$.
- $\text{Pt}(\text{Cl})_4^{2-}$ (covalent method):
 - Each chloride forms 1 covalent bond (donates 1 electron).
 - Platinum is d^{10} (because it's chemically bound, the 6s electrons fall to the d orbitals; what would the d count of copper or zinc be? 10 as well?).
 - The charge on the complex is 2–, so the electron count is $4 \cdot 1 + 10 - (-2) = 16 \text{ e}^-$'s.
- $\text{Pt}(\text{Cl})_4^{2-}$ (ionic method):
 - $\text{Pt}-\text{Cl} \longrightarrow \text{Pt}^+ + \text{Cl}^-$.
 - Thus, we have Pt^{4+} . But the charge is 2–, so we actually have Pt^{2+} , which is d^8 , which plays well with the 16-electron system.
- An enzymatic cofactor (covalent method):

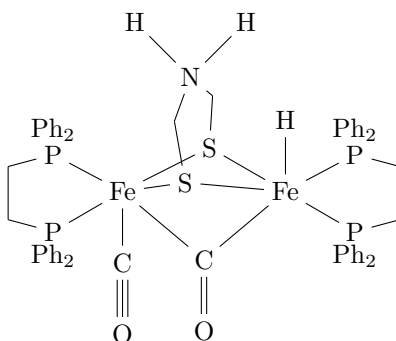


Figure 1.8: An enzymatic cofactor.

- Each phosphine and each carbonyl is a 2-electron donor.
- The hydride is an X-type ligand with a covalent bond, and thus a 1-electron donor.
- Now for the big bulky center bridging ligand: The sulfurs each carry a +1 formal charge and form two covalent bonds to the metal centers, so they each contribute three electrons. The nitrogen has an additional +1 formal charge, so the ligand overall is a $2 \cdot 3 + 1 = 6$ -electron donor.
- Summing all of this gives us 20 electrons.
- Now for the metal centers: Each iron is d^8 .
- Thus, that's 36 electrons in total, but divided over two iron centers.
- Therefore, the electron count for each iron is 18.
- Metal-metal bonds:
 - Assume that each metal will want to get to an electron count of 18.
 - Thus, the number of M–M bonds you would expect is

$$\# \text{ of M-M bonds} = (18 \text{ e}^- \text{'s} \cdot \# \text{ of metals} - \# \text{ of e}^- \text{'s from L's and M}^0 \text{'s})/2$$
 - Essentially, one M–M covalent bond contributes one electron to each M, or two electrons to the complex as a whole.

- As we can see, this number would be 0 for the enzymatic cofactor in Figure 1.8, which is why we'd expect no metal-metal bonding between the two iron centers.
- Bridging hydrides and halides:

– We can treat this by putting a +1 formal charge on the bridging atom: $M-\overset{\oplus}{X}-M$.

– Alternatively, we can recognize what the nature of the interaction is: $M-\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}-M$.

- From the above picture, it is clear that there is one covalent and one dative bond at play, making the bridging X-type ligand a 3-electron donor.

- We are now prepared to treat one final example:

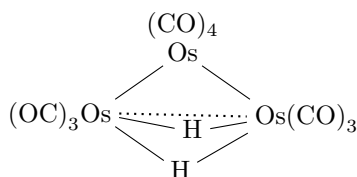
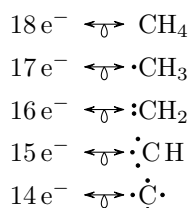


Figure 1.9: Electron counting for $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-H})_2$.

- Each carbonyl ligand is a 2-electron donor.
- Each bridging hydride is a 3-electron donor.
- Each Os–Os bond contributes 2 electrons.
- Thus, the ligands donate 30 electrons in total.
- Each osmium is d^8 .
- Thus, the metal centers donate 24 electrons in total.
- Therefore, the number of Os–Os bonds is $\frac{18 \cdot 3 - (30 + 24)}{2} = 0$, i.e., there are no Os–Os bonds.
- Now this question could just be a relic of my previous understanding of bonding, and the answer may just be “MO theory,” but I’m still gonna ask: Where do the electrons in all of the bonds come from? It seems like if the osmiums are giving electrons to Os–Os and Os–H bonds, and we still count osmium as d^8 , we are counting some electrons twice.
- Isolobal/isoelectronic analogy:
 - We can assume based on the fact that $\text{Cr}(\text{CO})_6$ has 18 electrons and is stable that the isoelectronic compounds $\text{V}(\text{CO})_6^-$ and $\text{Mn}(\text{CO})_6^+$ have identical electron counts and similar properties.
 - Note that all of these compounds are both isoelectronic and isolobal. What does isolobal mean?
 - We can do the same thing between $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{NO})(\text{CO})_3$, and $\text{Fe}(\text{NO})_2(\text{CO})_2$.
 - Also $\text{Mn}(\text{CO})_5$, $[\text{CpMn}(\text{CO})_2]^-$, and $\text{CpFe}(\text{CO})_2$ (these are isoelectronic, but not isolobal).
- We can also consider isolobal analogies between transition-metal-complex electron counts and organic fragments.
 - For example,



- We can also make analogies between other atoms/metal fragments: $\cdot\dot{\text{P}}\cdot \leftrightarrow \cdot\dot{\text{C}}\text{H} \leftrightarrow (\text{CO})_3\text{Co}$.
- Multiply bonded fragments can also work: $\text{M}=\text{O} \leftrightarrow \text{M}=\text{N}-\text{R} \leftrightarrow \text{R}_2\text{C}=\text{O}$ for double bonds, and for triple bonds: $\text{M}\equiv\text{O} \leftrightarrow \text{M}\equiv\text{N}-\text{R} \leftrightarrow [\text{R}-\text{C}\equiv\text{N}-\text{H}]^+$.
- **Oxidation state:** The number of electrons a metal has given up or acquired.
- **Chemical valence:** The number of electrons from the metal that are engaged in bonding.
- In many cases, the valence and oxidation state are the same, but they can differ.
 - They notably differ when M–M bonds and Z-type ligands are in play.
- Consider the structure formed by two dimerized fic (is this the right spelling? Does it have a charge by itself?) fragments (a fic fragment is $\text{CpFe}(\text{CO})_2$).

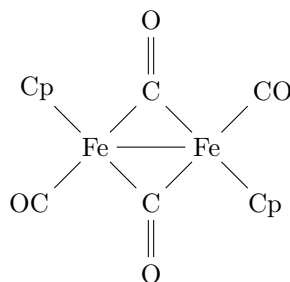


Figure 1.10: Two dimerized fic fragments.

- The oxidation state of each iron is Fe^{I} (since Cp is the only electronegative ligand).
- The valence of each iron is Fe^{II} (since Cp takes 1 electron and the Fe–Fe bond takes another).
- Note that as this is an 18-electron complex, it makes sense that the bound “iron ion” should be d^6 (Fe^{II}), not d^7 (Fe^{I}).
- Does the iron have tetrahedral or square planar geometry and why?
- Now consider the compound $[\text{CpFe}(\text{CO})_2\text{AlMe}_3]^-$.
 - The oxidation state of the iron is Fe^{II} .
 - The valence of the iron is Fe^{III} (confirm this?).
 - Here, unlike the last example, the oxidation state is a better descriptor (we can think of the iron as donating two electrons to AlMe_3).