So far, we’ve seen how deconstruction can reveal useful “bookkeeping” properties of organometallic complexes: number of electrons donated by ligands, coordination number, oxidation state, and d electron count (to name a few). Now, let’s bring everything together and discuss total electron count, the sum of non-bonding and bonding electrons associated with the metal center. Like oxidation state, total electron count can reveal the likely reactivity of OM complexes—in fact, it is often more powerful than oxidation state for making predictions. We’ll see that there is a definite norm for total electron count, and when a complex deviates from that norm, reactions are likely to happen.

Let’s begin with yet another new complex. This molecule features the common and important cyclopentadienyl and carbon monoxide ligands, along with an X-type ethyl ligand.

What is the total electron count of this Fe(II) complex?

The Cp or cyclopentadienyl ligand is a polydentate, six-electron L2X ligand. The two pi bonds of the free anion are dative, L-type ligands, which we’ll see again in a future post on ligands bound through pi bonds. Think of the electrons of the pi bond as the source of a dative bond to the metal. Since both electrons come from the ligand, the pi bonds are L-type binders. The anionic carbon in Cp is a fairly standard, anionic X-type binder. The carbon monoxide ligands are interesting examples of two-electron L-type ligands—notice that the free ligands are neutral, so these are considered L-type! Carbon monoxide is an intriguing ligand that can teach us a great deal about metal-ligand bonding in OM complexes…but more on that later.

After deconstruction, we see that the Fe(II) center possesses 6 non-bonding d electrons. The total electron count is just the d electron count plus the number of electrons donated by the ligands. Since the d electron count already takes overall charge into account, we need not worry about it as long as we’ve followed the deconstruction procedure correctly.

\[ \text{total electron count} = \text{number of d electrons} + \text{electrons donated by ligands} \]

For the Fe(II) complex above, the total electron count is thus \( 6 + (6 + 2 + 2 + 2) = 18 \). Let’s work through another example: the complex below features an overall charge of +1. Water is a dative ligand—that “2″ is very important!

Note that the overall charge is lumped into the oxidation state and d electron count of Mo.
The oxidation state of molybdenum is +2 here...remember that the overall charge factors in to that. When everything is said and done, the total electron count is \(4 + (6 + 2 + 2 + 2 + 2) = 18\).

What's up with 18?! As it turns out, 18 electrons is a very common number for stable organometallic complexes. So common that the number got its own rule—the 18-electron rule—which states that stable transition-metal complexes possess 18 or fewer electrons. The rule is analogous to organic chemistry's octet rule. The typical explanation for the 18-electron rule points out that there are 9 valence orbitals (1 s, 3 p, 5 d) available to metals, and using all of these for bonding seems to produce the most stable complexes. Of course, as soon as the rule left the lips of some order-craving chemist, researchers set out to find counterexamples to it, and a number of counterexamples are known. Hartwig describes the rule as an "empirical guideline" with little theoretical support. In fact, theoretical studies have shown that the participation of p orbitals in complex MOs is unlikely. I know that's not what you want to hear—but hang with me! The 18-electron rule is still a very useful guideline. It's most interesting, in fact, when it is not satisfied.

One last example...how would you expect the complex below to react?

![Cobaltocene: jonesing for chemical change.](image)

If we assume that the 18-electron rule is true, then cobaltocene has a real problem. It possesses \(7 + (6 + 6) = 19\) total valence electrons! Yet, we can also reason that this complex will probably react to relieve the strain of not having 18 electrons by giving up an electron. Guess what? In practice, cobaltocene is a great one-electron reducing agent, and can be used to prepare anionic complexes through electron transfer.

\[
[\text{CoCp}_2 + \text{ML}_n \rightarrow [\text{CoCp}_2]^+ + [\text{ML}_n]^{\text{an}}]
\]

This post described how to calculate total electron count and introduced the power of the 18-electron rule for predicting whether a complex will donate or accept electrons. We will definitely see these ideas again! But what happens when the electron counts of two complexes we're interested in comparing are the same? We'll need more information. In the next post, we'll explore the periodic trends of the transition series. Our goal will be to make meaningful comparisons between complexes of different metals.

**Contributors**

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