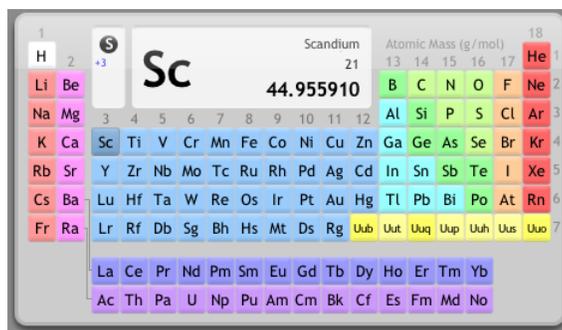


3.6: Simplifying the Organometallic Complex (Part 2)

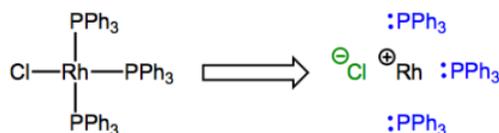
Now it's time to turn our attention to the metal center, and focus on what the deconstruction process can tell us about the nature of the metal in organometallic complexes. We'll hold off on a description of periodic trends of the transition series, but now is a good time to introduce the general characteristics of the transition metals. Check out groups 3-12 in the table below.



The transition metals are colored dark blue in this table.

The transition metals occupy the d-block of the periodic table, meaning that, as we move from left to right across the transition series, electrons are added to the d atomic orbitals. Just like organic elements, the transition metals form bonds using only their valence electrons. But when working with the transition metals, we need to concern ourselves only with the d atomic orbitals, as none of the other valence subshells contain any electrons. Although the periodic table may lead you to believe that the transition metals possess filled s subshells, we imagine metals in organometallic complexes as possessing valence electrons in d orbitals only! The reason for this is somewhat complicated, but has to do with the partial positive charge of complexed metals. Neutral transition metal atoms do, in fact, possess filled s subshells. Why, then, is it important to remember that the valence electrons of complexed metal centers are all d electrons? We will see that the number of d electrons possessed by a complexed metal is in many ways a useful concept. If you find that your counts are off by two, this common mistake is probably the culprit!

Let's turn our attention now to a new complex. I've gone ahead and deconstructed it for us.



Say hello to rhodium (Rh)! Don't fret; it's just a group 9 element.

The complex possesses one X-type and three L-type ligands, so the rhodium atom ends up with a formal charge of +1. The formal charge on the metal center after deconstruction has a very special name that you will definitely want to commit to memory: it's called the oxidation state. It's usually indicated with a roman numeral next to the atomic symbol of the metal (the "+" is implied). In the complex shown above, rhodium is in the Rh(I) or +1 oxidation state. Oxidation state is most useful because changes in oxidation state indicate changes in electron density at the metal center, and this can be a favorable or unfavorable occurrence depending on the other ligands around. We will see this principle in action many, many times! Get used to changes in oxidation state as everyday events in organometallic reaction mechanisms. Unlike carbon (with the exception of carbene...what's its oxidation state?!) and other second-row elements, the transition metals commonly exhibit multiple different oxidation states. More on that later, though. For now, training yourself to rapidly identify the oxidation state of a complexed metal is most important. Please note that when a complex possesses an overall charge, the oxidation state is affected by this charge!

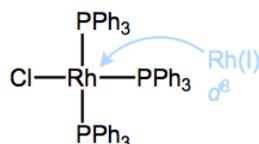
$$\text{oxidation state} = \text{number of X-type ligands bound to metal} + \text{overall charge of complex}$$

What of this number of d electrons concept? A very useful way to think about "number of d electrons" is as the "number of non-bonding electrons on the metal center," and you're probably familiar with identifying non-bonding electrons from organic chemistry. The numbers of valence electrons of each organic element are set in stone: carbon has four, nitrogen has five, et cetera. Furthermore, using this knowledge, it's straightforward to determine the number of lone pair electrons associated with an atom by subtracting its number of covalent bonds from its total number of valence electrons. E.g., for a neutral nitrogen atom in an amine NR₃, 5 - 3 = 2 lone pair electrons, typically. The extension to organometallic chemistry is natural! We can analyze complexed

metal centers in the same way, but they tend to have a lot more non-bonding electrons than organic atoms, and the number depends on the metal's oxidation state. For instance, the deconstructed rhodium atom in the figure above has 8 d electrons: 9 valence electrons minus 1 used for bonding to Cl. Dative bonds don't affect d electron count since both electrons in the bond come from the ligand.

$$\text{number of non-bonding electrons} = \text{number of d electrons} = \text{metal's group number} - \text{oxidation state}$$

Drawing all the non-bonding d electrons out as lone pairs would clutter things up, so they are never drawn...but we must remember that they're around! Why? Because the number of d electrons profoundly affects a complex's geometry. We will return to this soon, but the key idea is that the ligands muck up the energies of the d orbitals as they approach the metal (recall the "star-crossed lovers" idea), and the most favorable way to do so depends on the number of non-bonding electrons on the metal center.



Oxidation state and d electron count: two tools the OM chemist can't live without!

This post introduced us to two important bookkeeping tools, oxidation state and number of d electrons. In the final installment of the "Simplifying the Organometallic Complex" series, we'll bring everything together and discuss total electron count. We'll see that total electron count may be used to draw a variety of insightful conclusions about organometallic complexes.

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