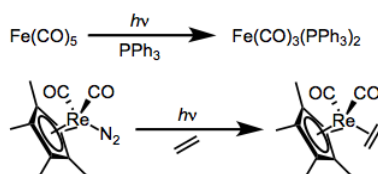


4.10: Quirky Ligand Substitutions

Over the years, a variety of “quirky” substitution methods have been developed. All of these have the common goal of facilitating substitution in complexes that would otherwise be inert. It’s an age-old challenge: how can we turn a stable complex into something unstable enough to react? Photochemical excitation, oxidation/reduction, and radical chains all do the job, and have all been well studied. We’ll look at a few examples in this post—remember these methods when simple associative or dissociative substitution won’t get the job done.

Photochemical Substitution

Substitution reactions of dative ligands—most famously, CO—may be facilitated by photochemical excitation. Two examples are shown below. The first reaction yields only monosubstituted product without ultraviolet light, even in the presence of a strongly donating phosphine.

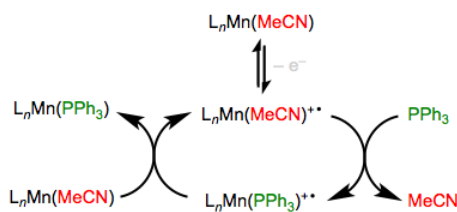


Dissociative photochemical substitutions of CO and dinitrogen.

All signs point to dissociative mechanisms for these reactions (the starting complexes have 18 total electrons each). Excitation, then, must increase the M–L antibonding character of the complex’s electrons; exactly how this increase in antibonding character happens has been a matter of some debate. Originally, the prevailing explanation was that the LUMO bears M–L antibonding character, and excitation kicks an electron up from the HOMO to the LUMO, encouraging cleavage of the M–L bond. A more recent, more subtle explanation backed by calculations supports the involvement of a [metal-to-ligand charge-transfer](#) state along with the “classical” ligand-field excited state.

Oxidation/Reduction

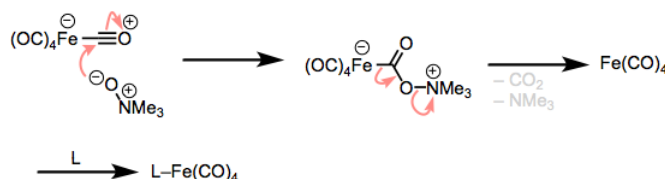
Imagine a screaming baby without her pacifier—that’s a nice analogy for an odd-electron organometallic complex. Complexes bearing 17 and 19 total electrons are much more reactive toward substitution than their even-electron counterparts. Single-electron oxidation and reduction (“popping out the pacifier,” if you will) can thus be used to efficiently turn on substitution. As you might expect, oxidation and reduction work best on electron-rich and electron-poor complexes, respectively. The Mn complex in the oxidative example below, for instance, includes a strongly donating MeCp group (not shown).



Oxidation accelerates substitution in electron-rich complexes through a chain process.

Reduction works well for electron-poor metal carbonyl complexes, which are happy to accept an additional electron.

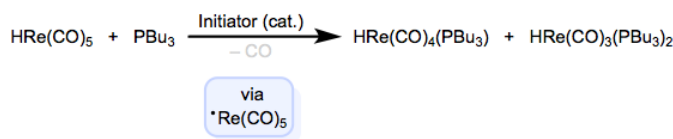
There is a two-electron oxidation method that’s also worth knowing: the oxidation of CO with amine oxides. This nifty little method releases carbon dioxide, amine, and an unsaturated complex that may be quenched by a ligand hanging around. The trick is addition to the CO ligand followed by elimination of the unsaturated complex. As the oxidized CO₂ and reduced amine float away, the metal complex finds another ligand.



Oxidation of CO with amine oxides. A fun method for dissociative substitution of metal carbonyls!

Radical Chain Processes

Atom abstraction from 18-electron complexes produces neutral 17-electron intermediates, which are susceptible to ligand substitution via radical chain mechanisms. The fact that the intermediates are neutral distinguishes these methods from oxidation-based methods. First-row metal hydrides are great for these reactions, owing to their relatively weak M–H bonds. One example is shown below.



Radical-chain substitution involving atom abstraction.

After abstraction of the hydrogen atom by initiator, substitution is rapid and may occur multiple times. Propagation begins anew when the substituted radical abstracts hydrogen from the starting material to regenerate the propagating radical and form the product. These quirky methods are nice to have in your back pocket when you're backed into a synthetic corner—sometimes, conventional associative and dissociative substitution just won't do the job. In the next post, we'll press on to oxidative addition.

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