

4.4: Ligand substitution

Ligand substitution is the first reaction one typically encounters in an organometallic chemistry course. In general, ligand substitution involves the exchange of one ligand for another, with no change in oxidation state at the metal center. The incoming and outgoing ligands may be L- or X-type, but the charge of the complex changes if the ligand type changes. Keep charge conservation in mind when writing out ligand substitutions.

How do we know when a ligand substitution reaction is favorable? The thermodynamics of the reaction depend on the relative strength of the two metal-ligand bonds, and the stability of the departing and incoming ligands (or salt of the ligand, if they're X type). It's often useful to think of X-for-X substitutions like acid-base reactions, with the metal and spectator ligands serving as a "glorified proton." Like acid-base equilibria in organic chemistry, we look to the relative stability of the two charged species (the free ligands) to draw conclusions. Of course, we don't necessarily need to rely just on primal thermodynamics to drive ligand substitution reactions. Photochemistry, neighboring-group participation, and other tools can facilitate otherwise difficult substitutions.

Ligand substitution is characterized by a continuum of mechanisms bound by associative (A) and dissociative (D) extremes. At the associative extreme, the incoming ligand first forms a bond to the metal, then the departing ligand takes its lone pair and leaves. At the dissociative extreme, the order of events is opposite—the departing ligand leaves, then the incoming ligand comes in. Associative substitution is common for 16-electron complexes (like d8 complexes of Ni, Pd, and Pt), while dissociative substitution is the norm for 18-electron complexes. Then again, reality is often more complicated than these extremes. In some cases, evidence is available for simultaneous dissociation and association, and this mechanism has been given the name interchange (IA or ID).

Over the next few posts, we'll explore ligand substitution reactions and mechanisms in detail. We'd like to be able to (a) predict whether a mechanism is likely to be associative or dissociative; (b) propose a reasonable mechanism from given experimental data; and (c) describe the results we'd expect given a particular mechanism. Keep these goals in mind as you learn the theoretical and experimental nuts and bolts of substitution reactions.

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