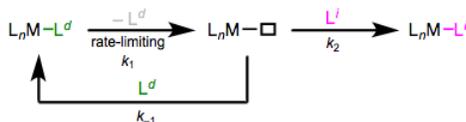


4.3: Dissociative Ligand Substitution Reactions

Associative substitution is unlikely for saturated, 18-electron complexes—coordination of another ligand would produce a 20-electron intermediate. For 18-electron complexes, dissociative substitution mechanisms involving 16-electron intermediates are more likely. In a slow step with positive entropy of activation, the departing ligand leaves, generating a coordinatively unsaturated intermediate. The incoming ligand then enters the coordination sphere of the metal to generate the product. For the remainder of this post, we'll focus on the kinetics of the reaction and the nature of the unsaturated intermediate (which influences the stereochemistry of the reaction). The reverse of the first step, re-coordination of the departing ligand (rate constant k_{-1}), is often competitive with dissociation.



A general scheme for dissociative ligand substitution. There's more to the intermediate than meets the eye!

Reaction Kinetics

Let's begin with the general situation in which k_1 and k_{-1} are similar in magnitude. Since k_1 is rate limiting, k_2 is assumed to be much larger than k_1 and k_{-1} . Most importantly, we need to assume that variation in the concentration of the unsaturated intermediate is essentially zero. This is called the steady state approximation, and it allows us to set up an equation that relates reaction rate to observable concentrations. Hold onto that for a second; first, we can use step 2 to establish a preliminary rate expression.

$$\text{rate} = k_2[\text{LnM}-\diamond][\text{Li}] \quad (1)$$

Of course, the unsaturated complex is present in very small concentration and is unmeasurable, so this equation doesn't help us much. We need to remove the concentration of the unmeasurable intermediate from (1), and the steady state approximation helps us do this. We can express variation in the concentration of the unsaturated intermediate as (processes that make it) minus (processes that destroy it), multiplying by an arbitrary time length to make the units work out. All of that equals zero, according to the SS approximation. The painful math is almost over! Since Δt must not be zero, the other factor, the collection of terms, must equal zero.

$$\Delta[\text{LnM}-\diamond] = 0 = (k_1[\text{LnM}-\text{L}^d] - k_{-1}[\text{LnM}-\diamond][\text{L}^d] - k_2[\text{LnM}-\diamond][\text{Li}])\Delta t \quad (2)$$

$$0 = k_1[\text{LnM}-\text{L}^d] - k_{-1}[\text{LnM}-\diamond][\text{L}^d] - k_2[\text{LnM}-\diamond][\text{Li}] \quad (3)$$

Rearranging to solve for $[\text{LnM}-\diamond]$, we arrive at the following.

$$[\text{LnM}-\diamond] = k_1 \frac{[\text{LnM}-\text{L}^d]}{(k_{-1}[\text{L}^d] + k_2[\text{Li}])} \quad (4)$$

Finally, substituting into equation (1) we reach a verifiable rate equation.

$$\text{rate} = k_2 k_1 \frac{[\text{LnM}-\text{L}^d][\text{Li}]}{(k_{-1}[\text{L}^d] + k_2[\text{Li}])} \quad (5)$$

When k_{-1} is negligibly small, (5) reduces to the familiar equation (6), typical of dissociative reactions like S_N1 .

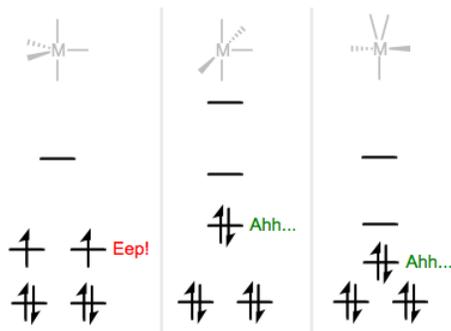
$$\text{rate} = k_1[\text{LnM}-\text{L}^d] \quad (6)$$

Unlike the associative rate law, this rate does not depend on the concentration of incoming ligand. For reactions that are better described by (5), we can drown the reaction in incoming ligand to make $k_2[\text{Li}]$ far greater than $k_{-1}[\text{L}^d]$, essentially forcing the reaction to fit equation (6).

The Unsaturated Intermediate & Stereochemistry

Dissociation of a ligand from an octahedral complex generates an unsaturated ML_5 intermediate. When all five of the remaining ligands are L-type, as in $\text{Cr}(\text{CO})_5$, the metal has 6 d electrons for a total electron count of 16. The trigonal bipyramidal geometry

presents electronic problems (unpaired electrons) for 6 d electrons, as the figure below shows. The orbital energy levels come from [crystal field theory](#). Distortion to a square pyramidal or a distorted TBP geometry removes the electronic issue, and so five-coordinate d6 complexes typically have square pyramidal or distorted TBP geometries. This is just the [geometry prediction](#) process in action!



TBP geometry is electronically disfavored for d6 metals. Distorted TBP and SP geometries are favored.

When the intermediate adopts square pyramidal geometry (favored for good π -acceptors and σ -donors...why?), the incoming ligand can simply approach where the departing ligand left, resulting in retention of stereochemistry. Inversion is more likely when the intermediate is a distorted trigonal bipyramid (favored for good π -donors). As we've already seen for associative substitution, fluxionality in the five-coordinate intermediate can complicate the stereochemistry of the reaction.

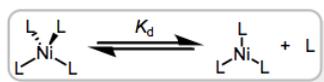
Encouraging Dissociative Substitution

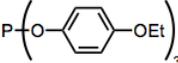
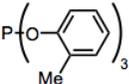
In general, introducing structural features that either stabilize the unsaturated intermediate or destabilize the starting complex can encourage dissociative substitution. Both of these strategies lower the activation barrier for the reaction. Other, quirky ways to encourage dissociation include photochemical methods, oxidation/reduction, and ligand abstraction.

Let's begin with features that stabilize the unsaturated intermediate. Electronically, the intermediate loves it when its d electron count is nicely matched to its crystal field orbitals. As you study organometallic chemistry, you'll learn that there are certain "natural" d electron counts for particular geometries that fit well with the metal-centered orbitals predicted by [crystal field theory](#). Octahedral geometry is great for six d electrons, for example, and square planar geometry loves eight d electrons. Complexes with "natural" d electron counts—but bearing one extra ligand—are ripe for dissociative substitution. The classic examples are d8 TBP complexes, which become d8 square planar complexes (think Pt(II) and Pd(II)) upon dissociation. Similar factors actually stabilize starting 18-electron complexes, making them less reactive in dissociative substitution reactions. d6 octahedral complexes are particularly happy, and react most slowly in dissociative substitutions. The three most common types of 18-electron complexes, from fastest to slowest at dissociative substitution, are:



Destabilization of the starting complex is commonly accomplished by adding steric bulk to its ligands. Naturally, dissociation relieves steric congestion in the starting complex. Chelation has the opposite effect, and tends to steel the starting complex against dissociation.



L	Cone Angle	K_d
P(OEt) ₃	109	$< 10^{-10}$
	128	$6 \cdot 10^{-10}$
P(O <i>i</i> -Pr) ₃	130	$2.7 \cdot 10^{-5}$
	141	$4 \cdot 10^{-2}$
PPh ₃	145	huge

As steric bulk on the ligand increases, dissociation becomes more favorable.

I plan to cover the “quirky” methods in a post of their own, but these include strategies like N-oxides for CO removal, photochemical cleavage of the metal–departing ligand bond, and the use of silver cation to abstract halide ligands. Oxidation and reduction can also be used to encourage substitution: 17- and 19-electron complexes are much more reactive toward substitution than their 18-electron analogues.

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