# MIGRATORY INSERTION: 1,2-INSERTIONS

Insertions of π systems into M-X bonds are appealing in the sense that they establish two new σ bonds in one step, in a stereocontrolled manner. As we saw in the last post, however, we should take care to distinguish these fully intramolecular migratory insertions from intermolecular attack of a nucleophile or electrophile on a coordinated π-system ligand. The reverse reaction of migratory insertion, β-elimination, is not the same as the reverse of nucleophilic or electrophilic attack on a coordinated π system.

1,2-Insertion is dinstinct from nucleophilic/electrophilic attack on coordinated ligands.
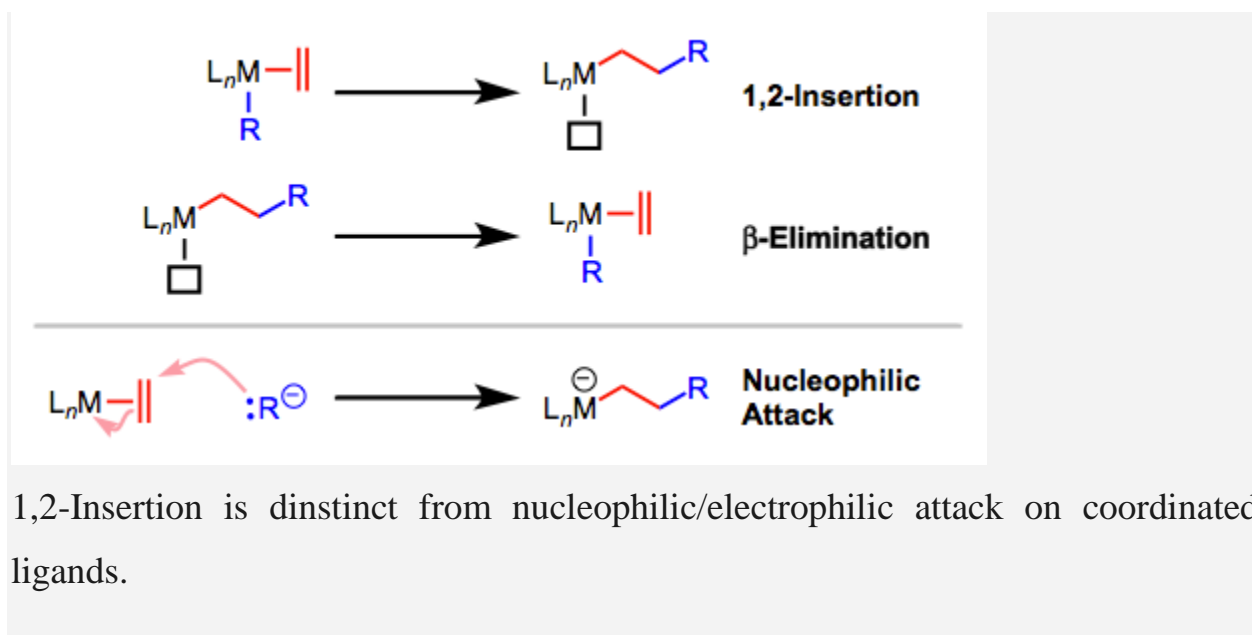
Like 1,1-insertions, 1,2-insertions generate a vacant site on the metal, which is usually filled by external ligand. For unsymmetrical alkenes, it's important to think about site selectivity: which atom of the alkene will end up bound to metal, and which to the other ligand? To make predictions about site selectivity we can appeal to the classic picture of the M–X bond as M^+X^-. Asymmetric, polarized π ligands contain one atom with excess partial charge; this atom hooks up with the

complementary atom in the M–R bond during insertion. Resonance is our best friend here!
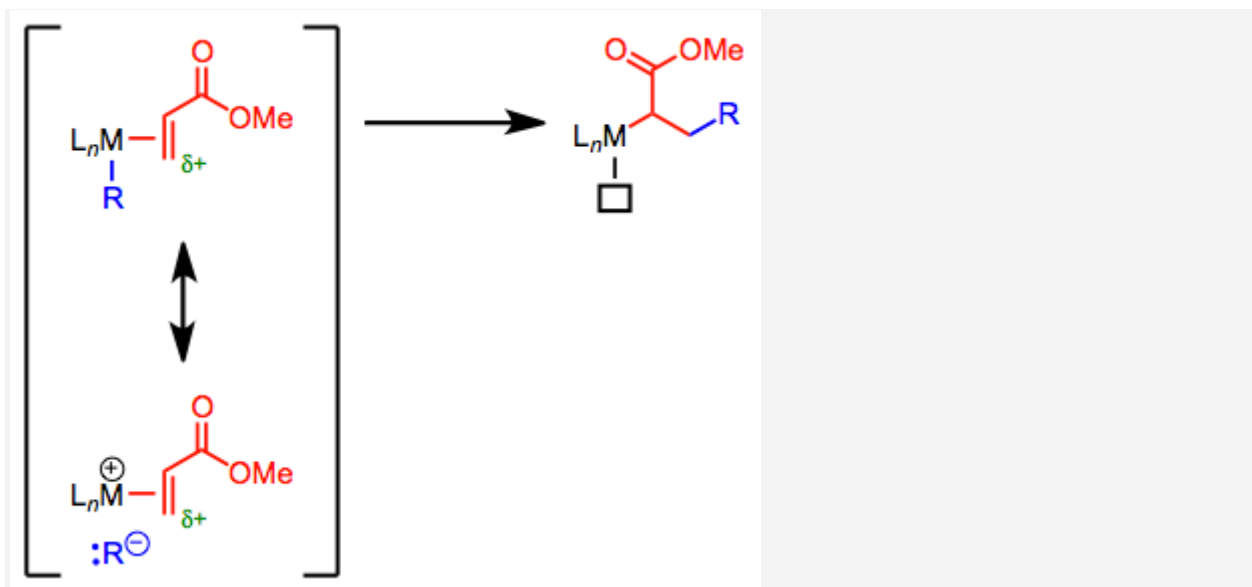
The site selectivity of 1,2-insertion can be predicted using resonance forms and partial charges.

A nice study by Yu and Spencer illustrates these effects in homogeneous palladium- and rhodium-catalyzed hydrogenation reactions. Unactivated alkenes generally exhibit lower site selectivity than activated ones, although steric differences between the two ends of the double bond can promote selectivity.
Reactivity Trends in 1,2-Insertions

The thermodynamics of 1,2-insertions of alkenes depend strongly on the alkene, but we can gain great insight by examining the structure of the product alkyl. Coordinated alkenes that give strong metal-alkyl bonds after migratory insertion tend to undergo the process. Hence, electron-withdrawing groups, such as carbonyls and fluorine atoms, tend to encourage migratory insertion—remember that alkyl complexes bearing these groups tend to have stable M–C bonds.

Insertions of alkenes into both M–H and M–R (R = alkyl) are favored thermodynamically, but the kinetics of M–R insertion are much slower. This observation reflects a pervasive trend in organometallic chemistry: M–H bonds react more rapidly than M–R bonds. The same is true of the reverse, β-elimination. Even in cases when both hydride and alkyl elimination are thermodynamically favored, β-hydride elimination is much faster. Although insertion into M–R is relatively slow, this elementary step is critical for olefin polymerizations that form polyalkenes (Ziegler-Natta polymerization). This reaction deserves a post all its own!

As the strength of the M–X bond increases, the likelihood that an L-type π ligand will insert into the bond goes down. Hence, while insertions into M–H and M–C are relatively common, insertions into M–N and M–O bonds are more rare. Lanthanides and palladium are known to promote insertion into M–N in some cases, but products with identical connectivity can come from external attack of nitrogen on a coordinated π ligand. The diastereoselectivity of these reactions provides mechanistic insight—since migratory insertion is *syn* (see below), a *syn* relationship between Pd and N is to be expected in the products of migratory insertion. An *anti* relationship indicates external attack by nitrogen or oxygen.
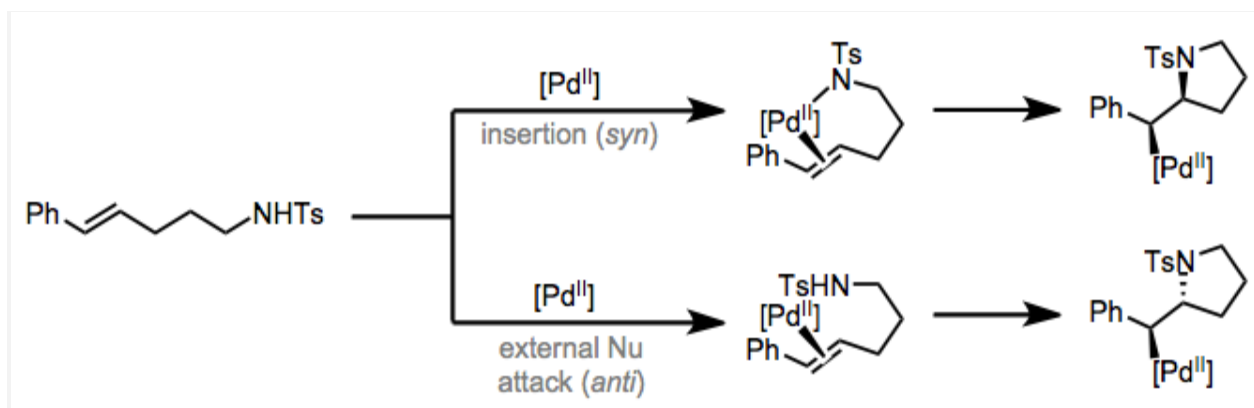
The diastereoselectivity of formal insertions provides insight about their mechanisms.

Stereochemistry of 1,2-Insertions

1,2-Insertion may establish two stereocenters at once, so the stereochemistry of the process is critical! Furthermore, 1,2-insertions and β-eliminations are bound by important stereoelectronic requirements. An analogy can be made to the E2 elimination of organic chemistry, which also has strict stereoelectronic demands. For migratory insertion to proceed, the alkene and X-type ligand must be *syncoplanar* during insertion; as a consequence of this alignment, X and ML_n end up on the same face of the alkene after insertion. In other words, insertions into alkenes take place in a *syn* fashion. Complexes that have difficulty achieving a coplanar arrangement of C=C and M–X undergo insertion very slowly, if at all.
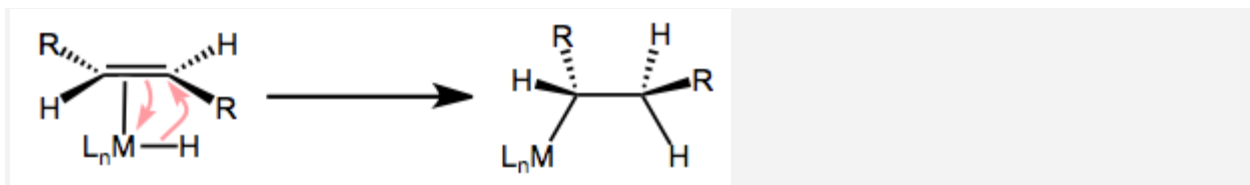

1,2-Insertions take place in a *syn* fashion. The metal and X end up bound to the same face of the alkene.

This observation has important implications for β-elimination, too—the eliminating X and the metal must have the ability to align *syn*.

Insertions of Other π Systems

To close this post, let's examine insertions into π ligands other than alkenes briefly. Insertions of alkynes into metal-hydride bonds are known, and are sometimes involved in reactions that I refer to collectively as "hydrostuffylation": hydrosilylation, hydroesterification, hydrogenation, and other net H–X additions across the π bond. Strangely, some insertions of alkynes yield *trans* products, even though *cis* products are to be expected from *syn* addition of M–X. The mechanisms

of these processes involve initial *syn* addition followed by isomerization to the *trans* complex via an interesting resonance form. The *cis* complex is the kinetic product, but it isomerizes over time to the more thermodynamically stable *trans* complex.
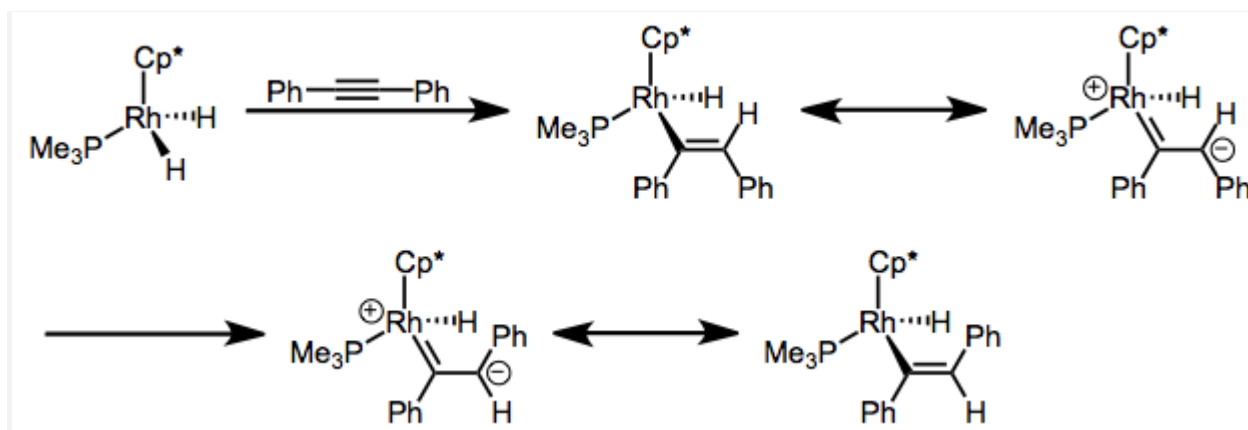
Migratory insertions of alkynes into M–H produce alkenyl complexes, which have been known to isomerize.

The strongly donating Cp* ligand supports the legitimacy of the zwitterionic resonance form—and suggests that the C=C bond may be weaker than it first appears!

Polyenes can participate in migratory insertion, and insertions of polyenes are usually quite favored because stabilized π-allyl complexes result. In one mind-bending case, a coordinated arene inserts into an M–Me bond in a *syn* fashion!

Have you ever stopped to consider that the addition of methyllithium to an aldehyde is a formal insertion of the carbonyl group into the Li–Me bond? It's true! We can think of these as (very) early-metal "insertion" reactions. Despite this precedent, migratory insertion reactions of carbonyls and imines into *late*-metal hydride and alkyl bonds are surprisingly hard to come by. Rhodium is the most famous metal that can make this happen—rhodium has been used in complexes for arylation and vinylation, for example. Insertion of X=C into the M–R bond is

usually followed by β-hydride elimination, which has the nifty effect of replacing H in aldehydes and aldimines with an aryl or vinyl group