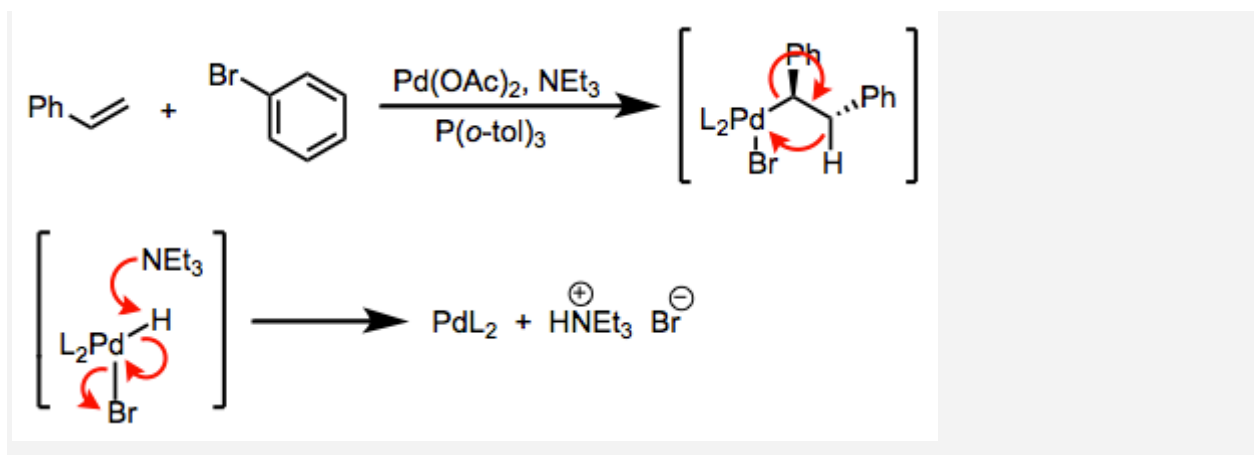


EPIC LIGAND SURVEY: METAL ALKYLs – III

In this last post on alkyl ligands, we'll explore the major modes of reactivity of metal alkyls. We've discussed β -hydride elimination in detail, but other fates of metal alkyls include reductive elimination, transmetalation, and migratory insertion into the M–C bond. In a similar manner to our studies of other ligands, we'd like to relate the steric and electronic properties of the metal alkyl complex to its propensity to undergo these reactions. This kind of thinking is particularly important when we're interested in controlling the relative rates and/or extents of two different, competing reaction pathways.

Reactions of Metal Alkyl Complexes

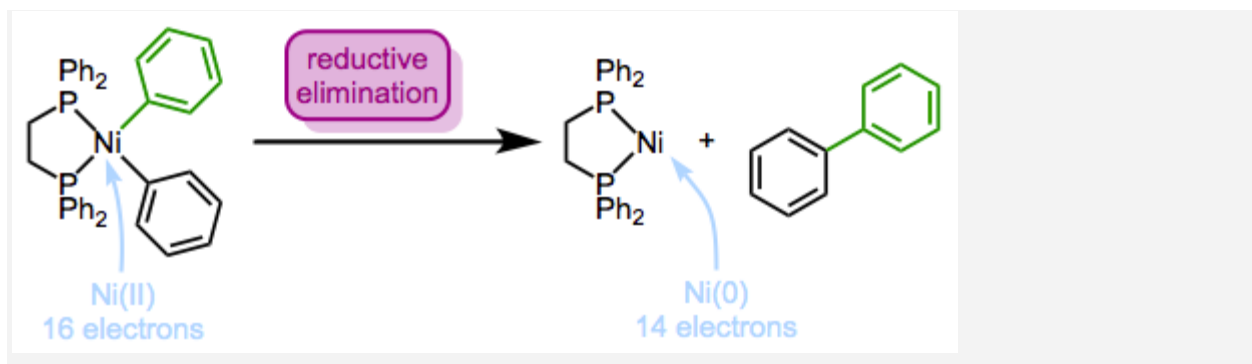
Recall that **β -hydride elimination** is an extremely common—and sometimes problematic—transformation of metal alkyls. Then again, there are reactions for which β -hydride elimination is desirable, such as the Heck reaction. Structural modifications that strengthen the M–H bond relative to the M–C bond encourage β -hydride elimination; the step can also be driven by trapping of the metal hydride product with a base (the Heck reaction uses this idea).



During the Heck reaction, beta-hydride elimination is driven by a base.

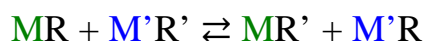
On the flip side, stabilization of the M–C bond discourages elimination and encourages its reverse: migratory insertion of olefins into M–H. Previously we saw the example of [perfluoroalkyl ligands](#), which possess exceptionally stable M–C bonds. The fundamental idea here—that electron-withdrawing groups on the alkyl ligand stabilize the M–C bond—is quite general. Hartwig describes an increase in the “ionic character” of the M–C bond upon the addition of electron-withdrawing groups to the alkyl ligand (thereby strengthening the M–C bond, since ionic bonds are stronger than covalent bonds). Bond energies from organic chemistry bear out this idea to an extent; for instance, see the relative BDEs of Me–Me, Me–Ph, and Me–CCH in [this reference](#). I still find this explanation a little “hand-wavy,” but it serves our purpose, I suppose.

Metal alkyls are subject to **reductive elimination**, the microscopic reverse of oxidative addition. The metal loses two covalent ligands, its formal oxidation state decreases by two units, total electron count decreases by two units, and an R–X bond forms. Reductive elimination is favorable when the R–X bond in the organic product is more stable than the M–R and M–X bonds in the starting complex (a thermodynamic issue). It should be noted, however, that the kinetics of reductive elimination depend substantially on the steric bulk of the eliminating ligands. Concerted reductive elimination of R–H usually possesses a [lower](#) activation energy than R–R elimination.

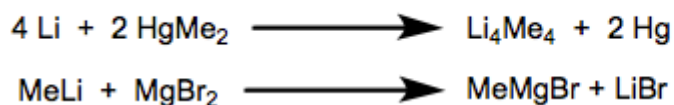


An example of reductive elimination. Intuitively, the electron density at the metal center increases as this step proceeds.

Transmetalation involves the transfer of an alkyl ligand from one metal to the other. An interesting problem concerns the relative reactivity of metal alkyls toward transmetalation. Assuming similar, uncomplicated ligand sets, which of two metal centers is more likely to hold on to an alkyl ligand? Consider the two situations below.



The first is a *bona fide* transmetalation; the second is really a double replacement reaction. The distinction is rarely drawn in practice, but it's important! The difference is that in the first case, a single-electron transfer of sorts must take place, while in the second case, no redox chemistry is necessary. Favorability in the first case is governed by the relative reduction potentials of M and M' (the reaction goes forward when M' is more easily oxidized than M); in the second case, the relative electropositivities of the metals is key, and other factors like lattice energies may be important. The distinction between transmetalation *per se* and double replacement explains the paradoxical synthetic sequence in the figure below. In practice, both are called "transmetalation." See [these slides](#) (page 6) for a summarizing reference.



Reaction	E° (V)
$\text{Hg}_2^{2+} + 2 \text{e}^- \longrightarrow 2 \text{Hg}(0)$	+0.85
$\text{Mg}^{2+} + 2 \text{e}^- \longrightarrow \text{Mg}(0)$	-2.37
$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}(0)$	-3.05

How are both of these reactions favorable? The first is a true transmetalation; the second is a double replacement.

This brings our extended look at metal alkyl complexes to a temporary close. Of course, metal alkyls are *everywhere* in organometallic chemistry...so seeing them again is pretty much inevitable! The next installment in the Epic Ligand Survey series concerns allyl, cyclopentadienyl, and other odd-membered pi systems. These L_nX -type ligands can, like arenes, pile as many as six electrons on the metal center at once.

Source : <http://organometallicchem.wordpress.com/2012/03/16/epic-ligand-survey-metal-alkyls-part-3/>