M–P	2.218 Å	2.230 Å	**M–P**	2.146 Å	2.261 Å
P–R	1.846 Å	1.829 Å	**P–R**	1.598 Å	1.578 Å

P *d*   PR$_3$ σ*   P π acceptor MO   M-P backbonding interaction
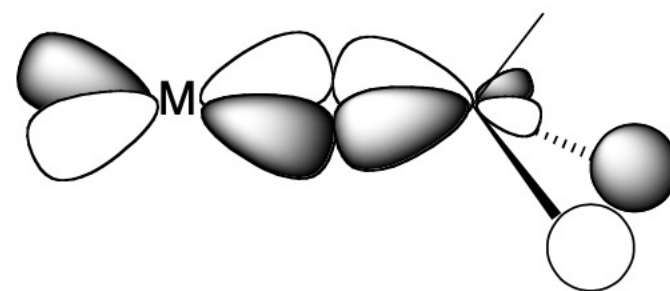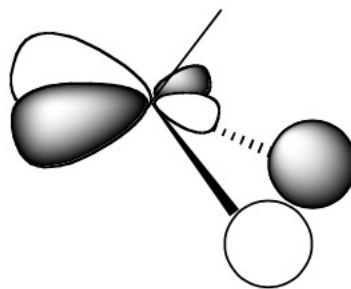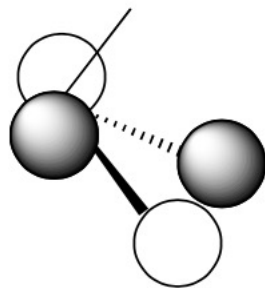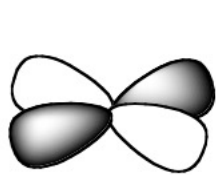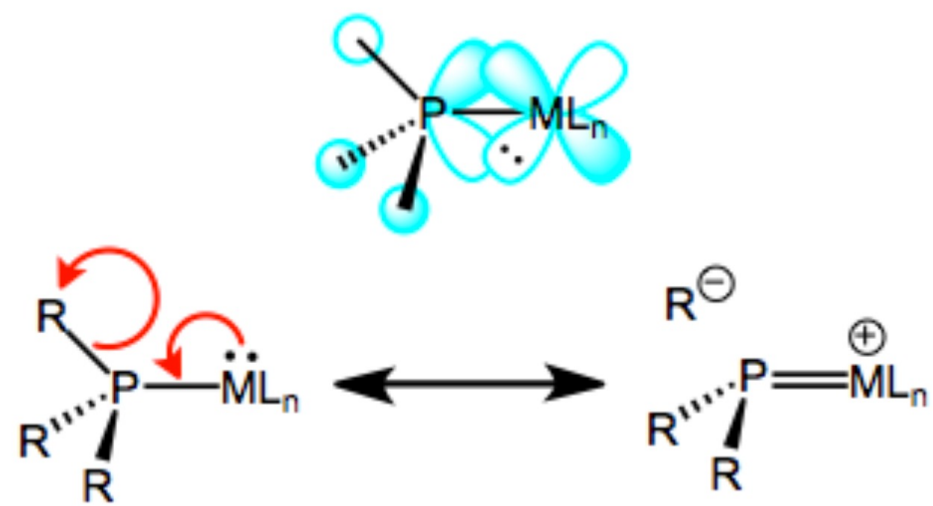
# Tolman's Cone Angle and Electronic Parameter

The **electron-donating ability** of a phosphine ligand was determined by measuring the ν_{CO} of a $Ni(CO)_3(PR_3)$ complex:

Lowest CO stretching frequency:

most donating phosphine
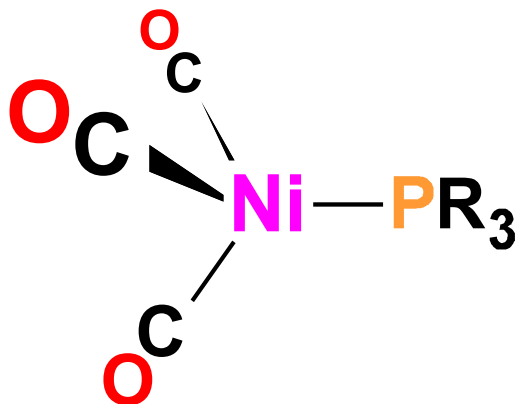
Highest CO stretching frequency:

least donating phosphine

(best π-acceptor)

The **size** or **steric bulk** of a phosphine ligand was determined from simple 3-D space-filling models of the phosphine ligand coordinated to a Ni atom:

cone angle θ

OXIDATIVE ADDITION
REDUCTIVE ELIMINATION
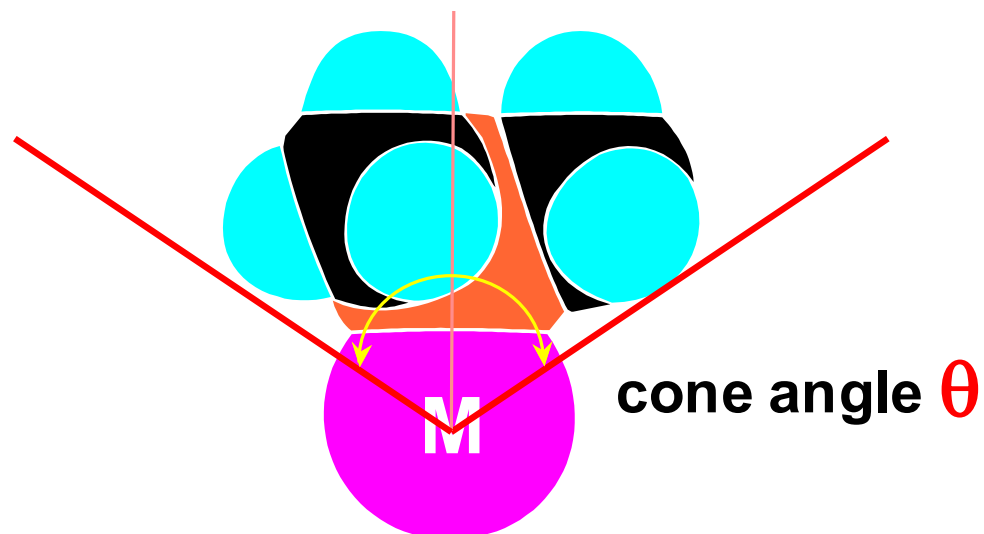
$$L_nM \ + \ A-B \longrightarrow L_nM^{n+2} \begin{smallmatrix} \diagup A \\ \diagdown B \end{smallmatrix} \quad \text{Oxidative addition}$$
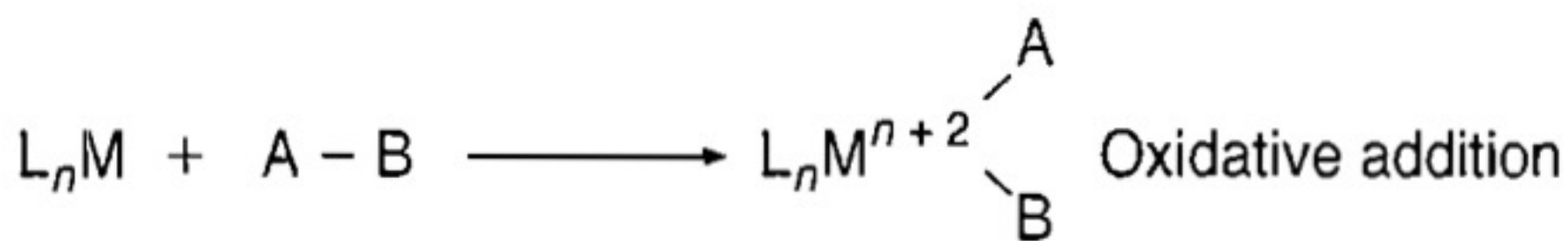
X valence electrons at M
m d-electrons
n oxidation state of M

$X+2$ valence electrons at M
$m-d$-electrons
$n+2$ oxidation state of M

$$L_nM^{n+2} \begin{smallmatrix} \diagup A \\ \diagdown B \end{smallmatrix} \longrightarrow L_nM^n \ + \ A-B \quad \text{Reductive elimination}$$

Oxidative Addition/Reductive Elimination

$$L_nM^z + \underbrace{H^{\oplus}}_{\text{Cationic}} \longrightarrow [L_nM^{z+2}-\underbrace{H}_{}]^{\oplus} \quad \text{Anionic}$$

$$L_nM^z + \underbrace{O_2}_{\text{Neutral}} \longrightarrow L_nM^{z+2}\begin{array}{c} O \\ \| \\ \underbrace{O}_{} \end{array} \quad \text{Dianionic}$$
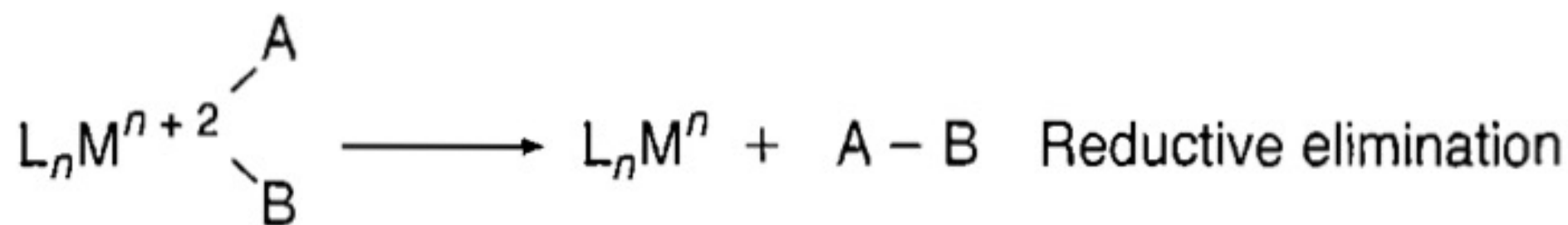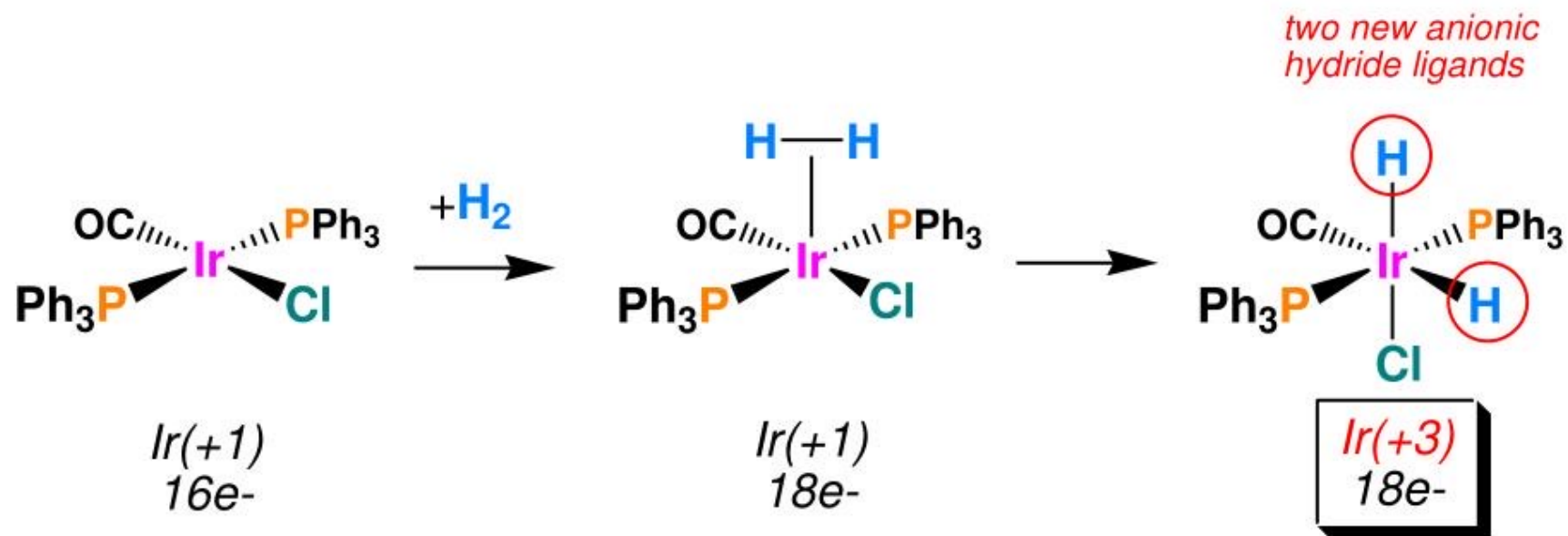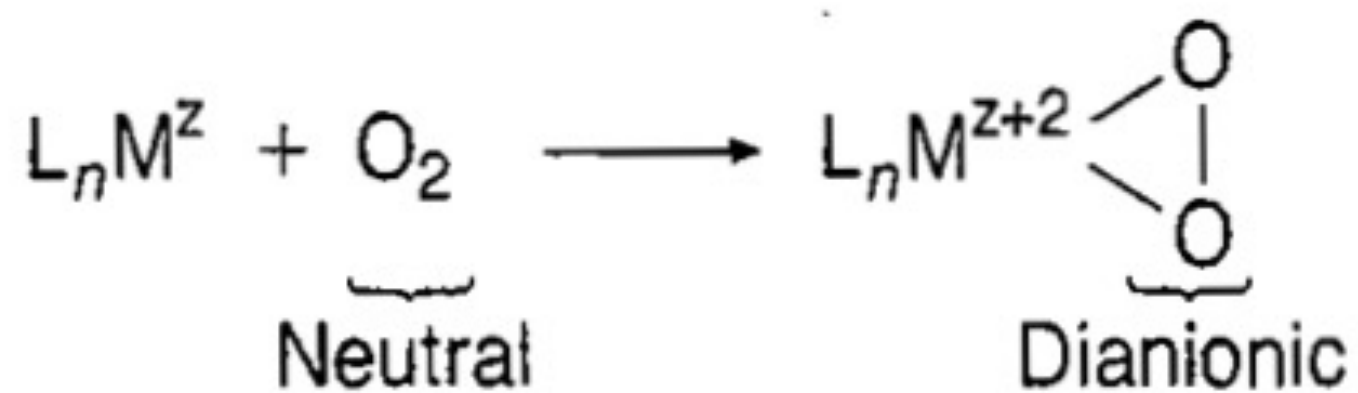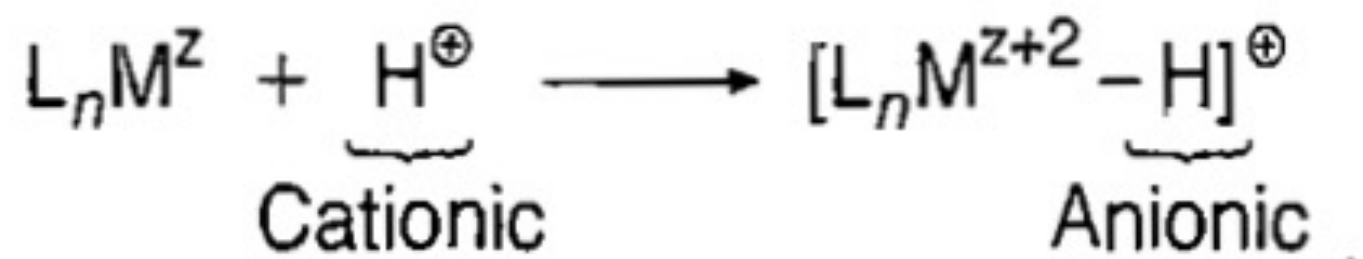
1. *Oxidative addition to more electron-rich metal centers tends to be more favorable than oxidative addition to more electron-poor metal centers.*[12] Although the actual charges at the metal change much less than the oxidation states during oxidative addition, the tendency of oxidative addition to occur more favorably to complexes possessing more electron-rich metal centers results from the increase in partial positive charge at the metal center during most oxidative addition reactions. Therefore, faster addition to more electron-rich metal centers originates from a ground state or thermodynamic effect.
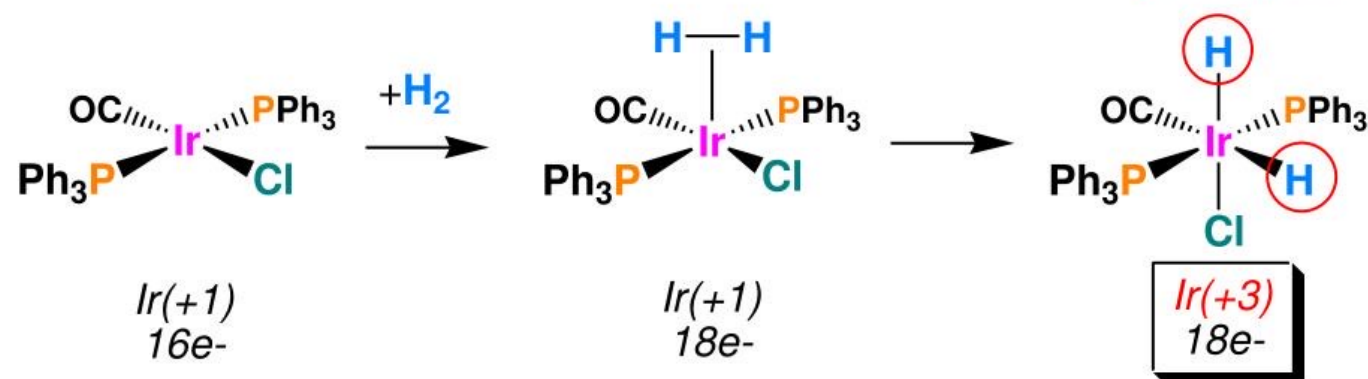
2. *Oxidative addition to less-hindered metal centers tends to be more favorable than oxidative addition to more-hindered metal centers.*[12−14] This trend can be understood by the changes in coordination number that occur during oxidative addition. The more hindered the metal center, the more destabilized are the higher coordinate products from an oxidative addition. Thus, this steric effect, too, originates from ground state or thermodynamic properties.

Ir(+1)
16e-

Ir(+1)
18e-

Ir(+3)
18e-
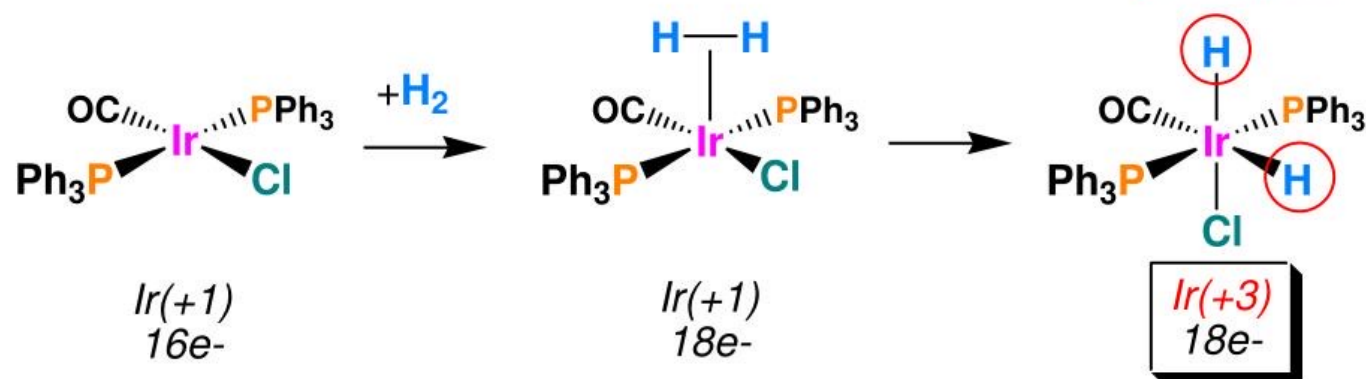
3. *Oxidative addition of nonpolar reagents requires a site of unsaturation and a d-electron count of 16 or less.* Because ligands are added to the metal center during an oxidative addition process, an open coordination site is needed to accommodate the incoming reagent. In addition, the two electrons of the bond of the nonpolar reagent are contained in the product of the oxidative addition. This increase in valence electron count requires that the metal complex in the elementary oxidative addition step possess a d-electron count of 16 or less to abide by the 18-electron rule. The site of unsaturation and an electron configuration that contains 16 or fewer valence electrons may be present in the starting material. Alternatively, the site of unsaturation may be generated by the dissociation of a ligand from the metal center prior to the elementary step of oxidative addition. In this case, oxidative addition can occur to an 18-electron complex, but the process must be initiated by ligand dissociation, and the free ligand must be one of the products of the reaction.

Oxidative addition of polar electrophiles, such MeX or HX (X= halide, sulfonate, or related stable anion) need not occur to a 16-electron metal center if a cationic metal center is generated with an uncoordinated anion. In this "oxidative ligation" mentioned previously and shown in Figure 6.1, the electrons of the Me–X or H–X bond do not add to the electron count of the metal because they are contained in the free anion of the product.

Oxidative Addition/Reductive Elimination
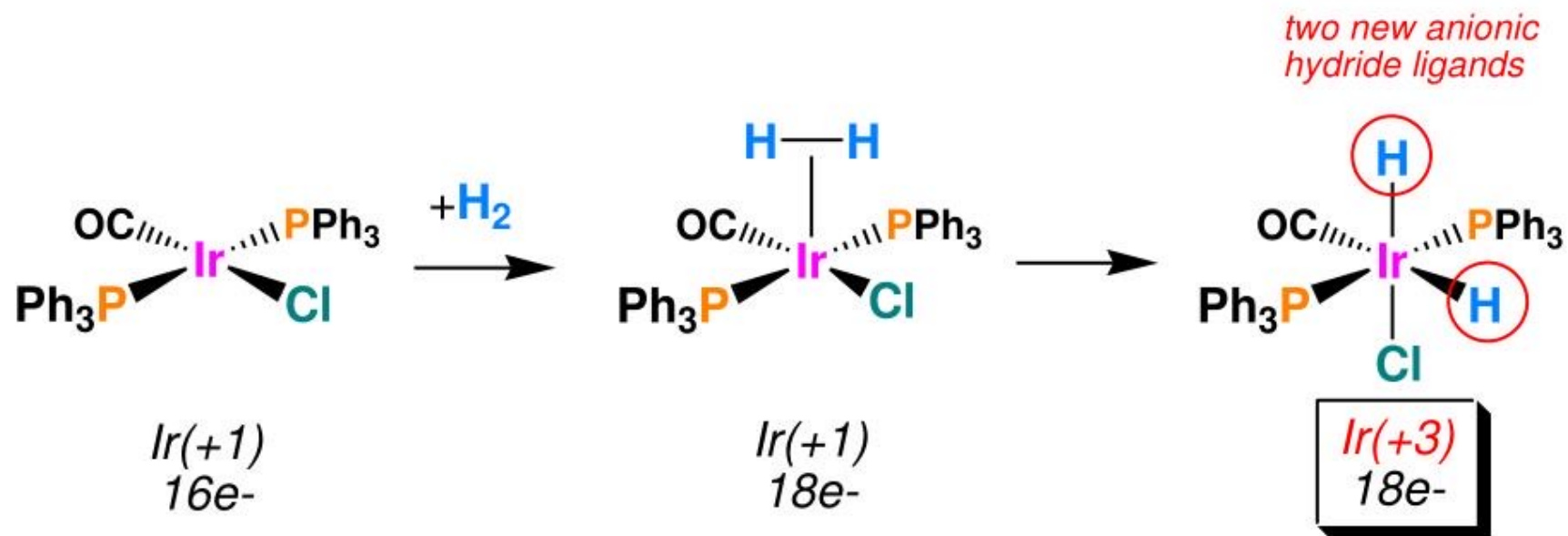
4. *Rates and equilibrium constants for ligand dissociation or association that occur prior to oxidative addition affect the rates of the overall addition processes.* Because oxidative addition is often preceded by ligand dissociation, the propensity of the starting complex to undergo dissociation of ligand affects the overall rate of oxidative addition.[15] For example, complexes containing tightly chelating bidentate ligands often undergo oxidative addition more slowly than analogous complexes containing monodentate ligands, and complexes containing strongly bound monodentate ligands are often less reactive toward addition than complexes containing weakly bound ligands.[16,17]

Reagents that are nonpolar or have low polarity:

H_2, RH, ArH, R_3SiH, R_3SnH, $R_3Sn–SnR_3$, R_2B-H, R_2BBR_2, RSSR, NC–CN, and Ph-PPh$_2$

Reagents that are highly polar:

HX, X_2, RCO_2H, RX, ROTs, RC(O)X, RSO_2X, $ROSO_2X$, RC(O)–OPh, HgX_2, and $SnCl_4$, $GeCl_4$, R_3SnCl, R_3PbCl

Reagents with medium polarity:

RSH, ROH, RNH_2, ArX, ArCN, CCl_4, and $CHCl_3$

Excess Et₃SiH