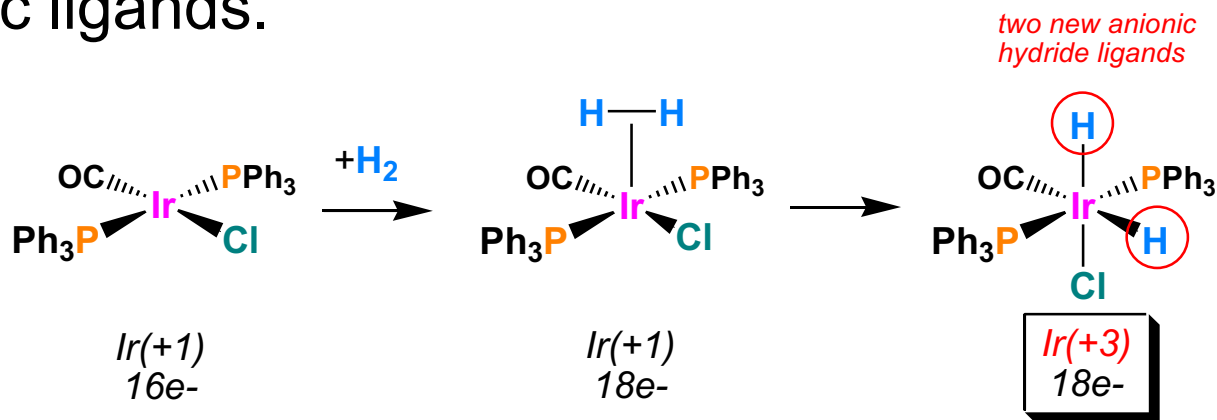


# Oxidative Addition

An **oxidative addition** reaction is one in which (usually) a neutral ligand adds to a metal center. In doing so it oxidizes the metal, typically by  $2e^-$ .

After oxidative addition, the co-ordination number of the metal typically increases by 2.

Generally, transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands.



# Oxidative Addition

Three main types of molecules (substrates) can perform oxidative additions to metal centers:

Non-electrophillic,

Non-electrophillic “intact”,

Electrophillic.

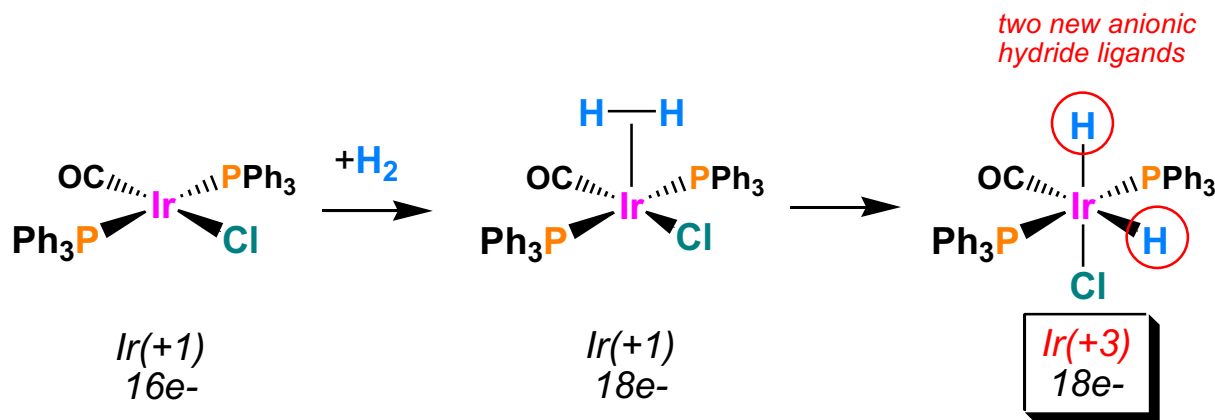
# Oxidative Addition - *Non-electrophillic*:

These molecules do NOT contain electronegative atoms and/or are not good oxidizing agents.

H<sub>2</sub>, C-H bonds, Si-H bonds, S-H bonds, B-H bonds, N-H bonds, S-S bonds and C-C bonds.

Often considered to be “*non-reactive*” substrates (except H<sub>2</sub>).

Generally require the presence of an **empty orbital** on the metal center in order for them to pre-coordinate prior to being activated for the oxidative addition reaction



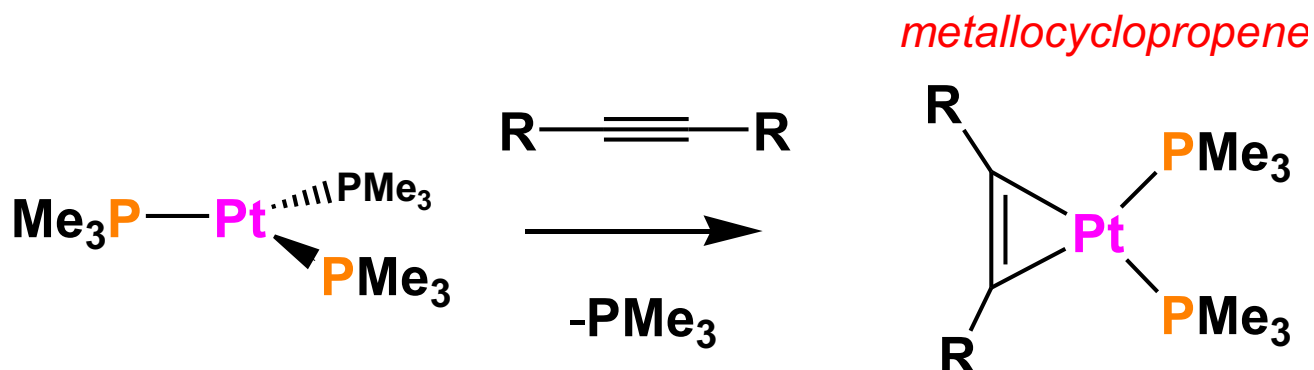
# Oxidative Addition –

## *Non-electrophillic “Intact”:*

The neutral molecules may or may not contain electronegative atoms, but do need to have a **double** or **triple bond**.

One needs a metal center with an **empty orbital** (16e- or lower count) in order to pre-coordinate the ligand before the oxidative addition occurs.

alkenes, alkynes, and O<sub>2</sub>



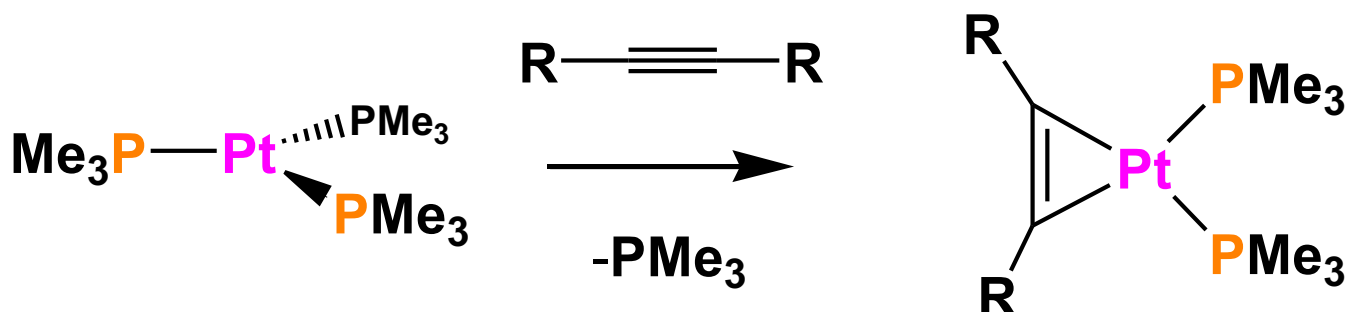
# Oxidative Addition –

## *Non-electrophillic “Intact”:*

Unlike most of the other substrate molecules that break a single bond and form two separate **anionic** ligands upon the oxidative addition, these ligands have double or triple bonds and only **one** of the  $\pi$ -bonds is broken leaving the  $\sigma$ -bond intact.

Notably, the ligand does pick up **two electrons** from the metal and becomes a **dianionic** ligand.

alkenes, alkynes, and  $O_2$

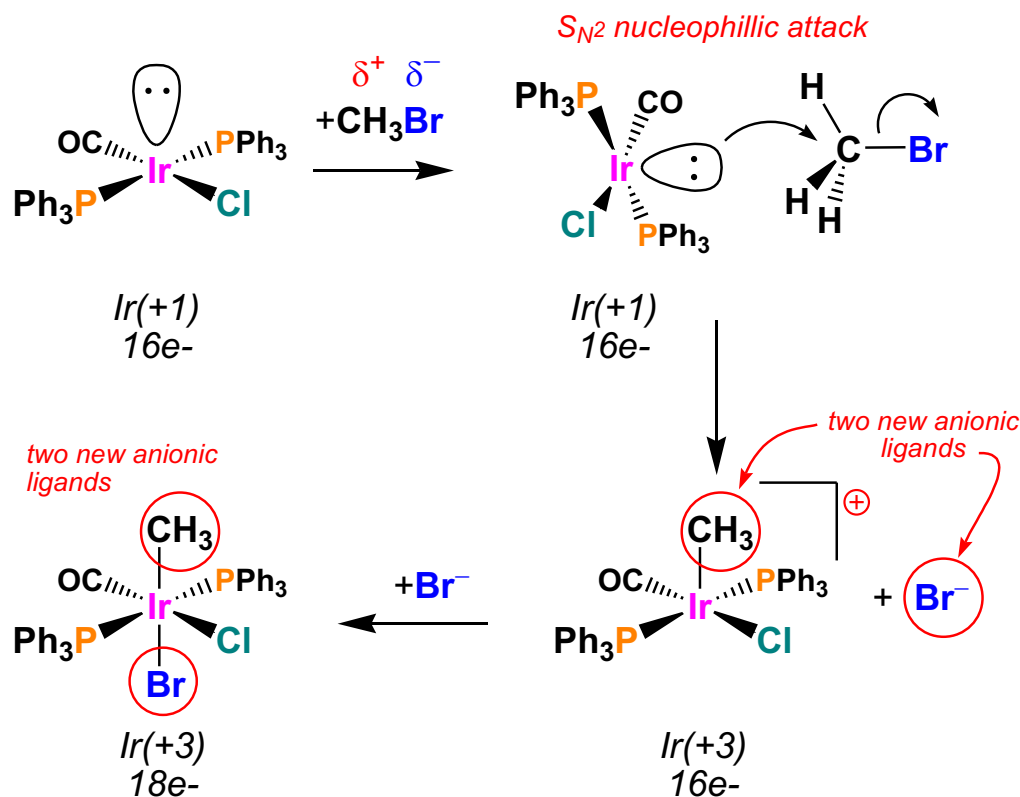


# Oxidative Addition – *Electrophillic*:

These molecules **do** contain electronegative atoms and are good oxidizing agents.

They are often considered to be “*reactive*” substrates.

**X<sub>2</sub> (X = Cl, Br, I), R-X, Ar-X, H-X**



# Oxidative Addition – *General Features:*

Oxidative addition involves oxidation (removal of electrons) of the metal center. Hence, the more **electron-rich** the metal, the more easier is the oxidative addition to the metal center.

In comparing two or more metal complexes to see which will be the most reactive towards a particular substrate for oxidative addition, one would pick the metal center with the *strongest donor* ligands, fewest  *$\pi$ -acceptor* ligands, or most **negative** charge.

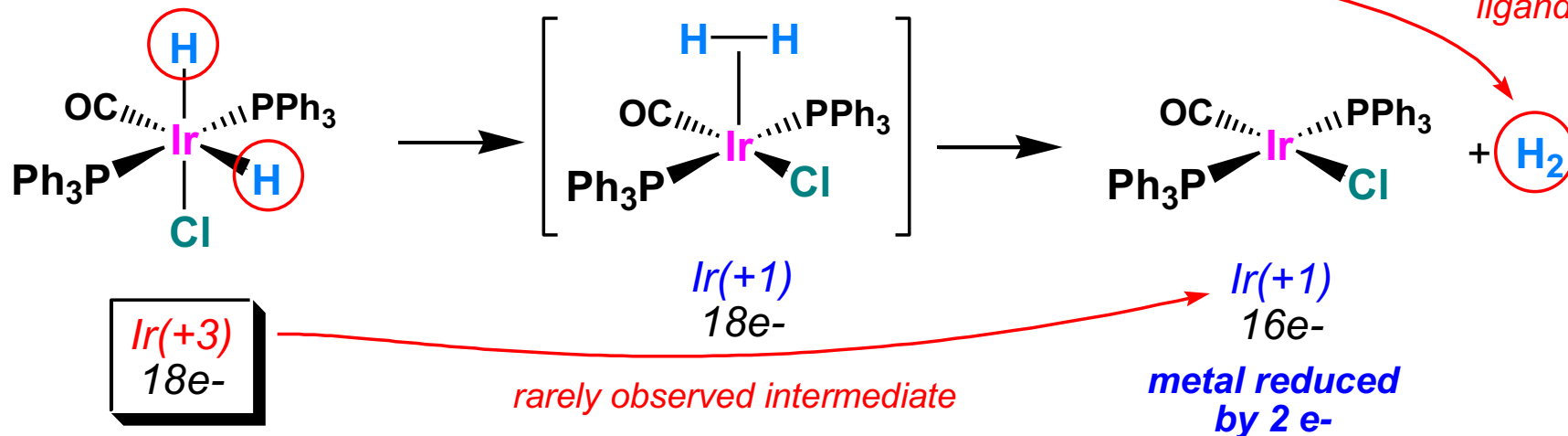
Note that the non-electrophilic ligands and “intact” ligands usually require that there is an *empty orbital* (16e<sup>-</sup> or lower) on the metal center in order to react.

# Reductive Elimination

A **reductive elimination** reaction is the reverse of an oxidative addition.

It is a reaction in which **two cisoidal anionic ligands** on a metal center couple together.

*two cisoidal anionic ligands that can form a bond between them*





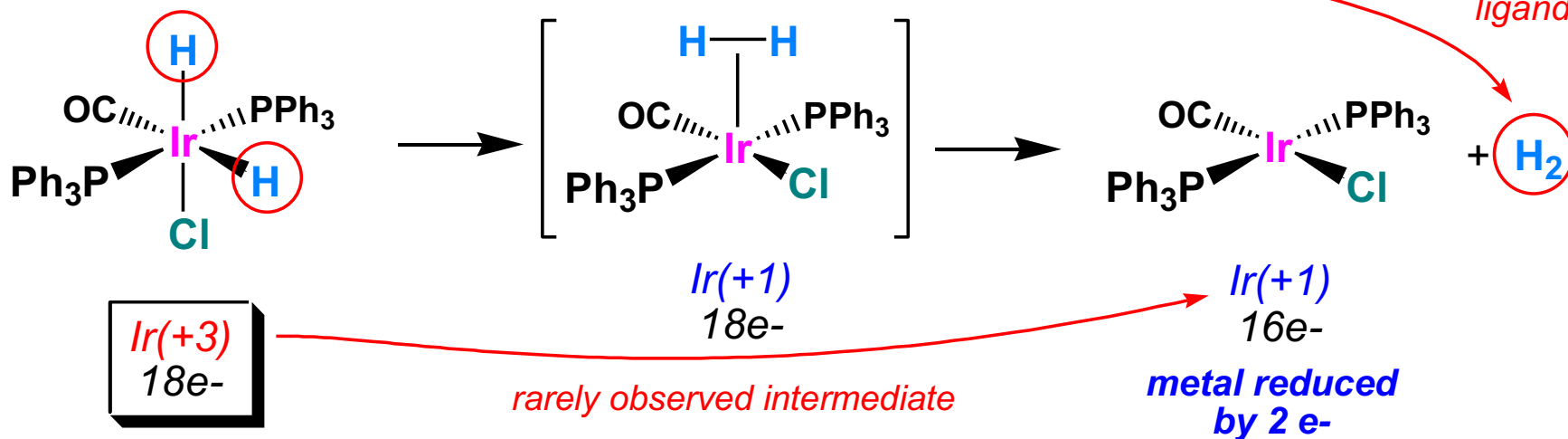
# Reductive Elimination

Each anionic ligand pushes one electron back onto the metal center to reduce it by  $2e^-$ .

The coupled anionic ligands then usually fall off the metal center as a **neutral** molecule.

*two cisoidal anionic ligands that can form a bond between them*

*and eliminate a neutral ligand*



# Reductive Elimination - *General Features:*

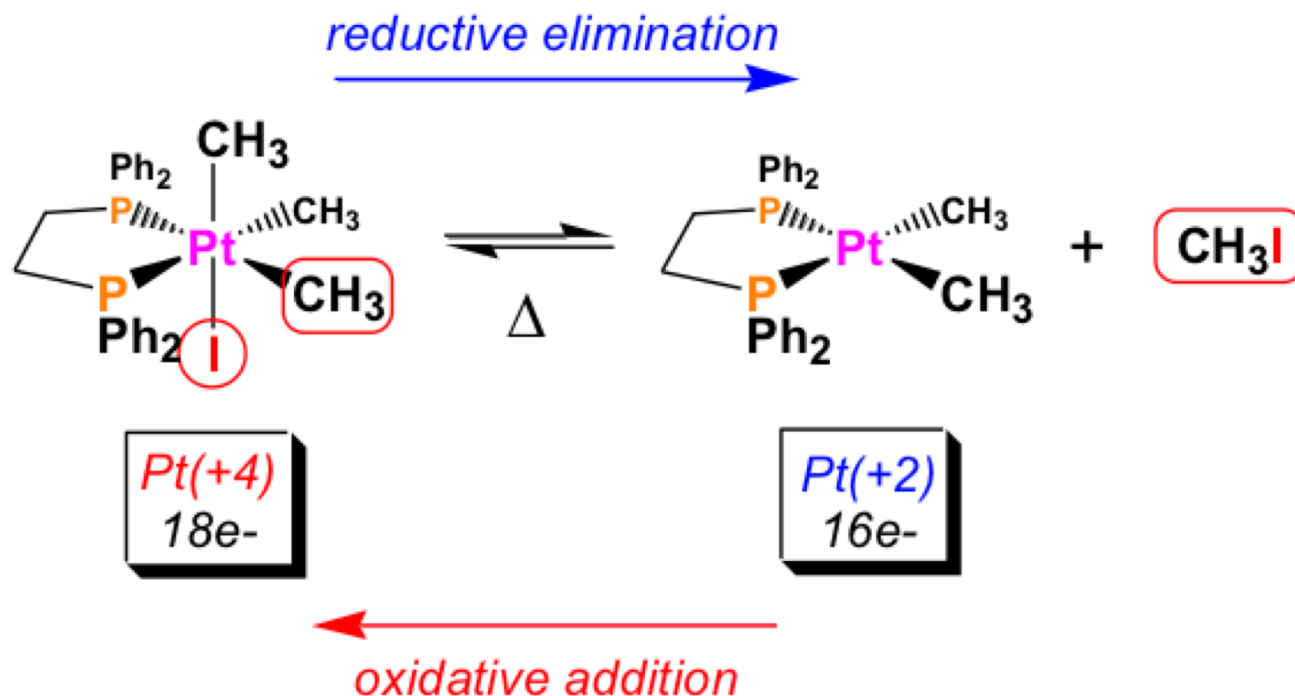
Since ***electron-rich*** metal complexes favor **oxidative addition**, the reverse is true for reductive elimination.

***Electron deficient*** metal centres favor reductive elimination.

This can be accomplished by having more  ***$\pi$ -acceptor*** ligands, cationic charge(s), and/or coordinative unsaturation (lower than 18e- count).

While ***reductive elimination*** can occur from saturated 18e- complexes (as long as the two ligands that you want to reductively eliminate are *cisoidal* to one another), it has been shown that reductive elimination can be promoted by a ligand dissociation generating an unsaturated and more electron-deficient metal center.

# Reductive Elimination – *Kinetic Preference:*



# Reductive Elimination – *Thermodynamic Preference:*

