Bonding in Metal Carbonyls

σ bond (Using the metal s, p_z and d_{z^2} orbitals)

dπ–pπ* back bond
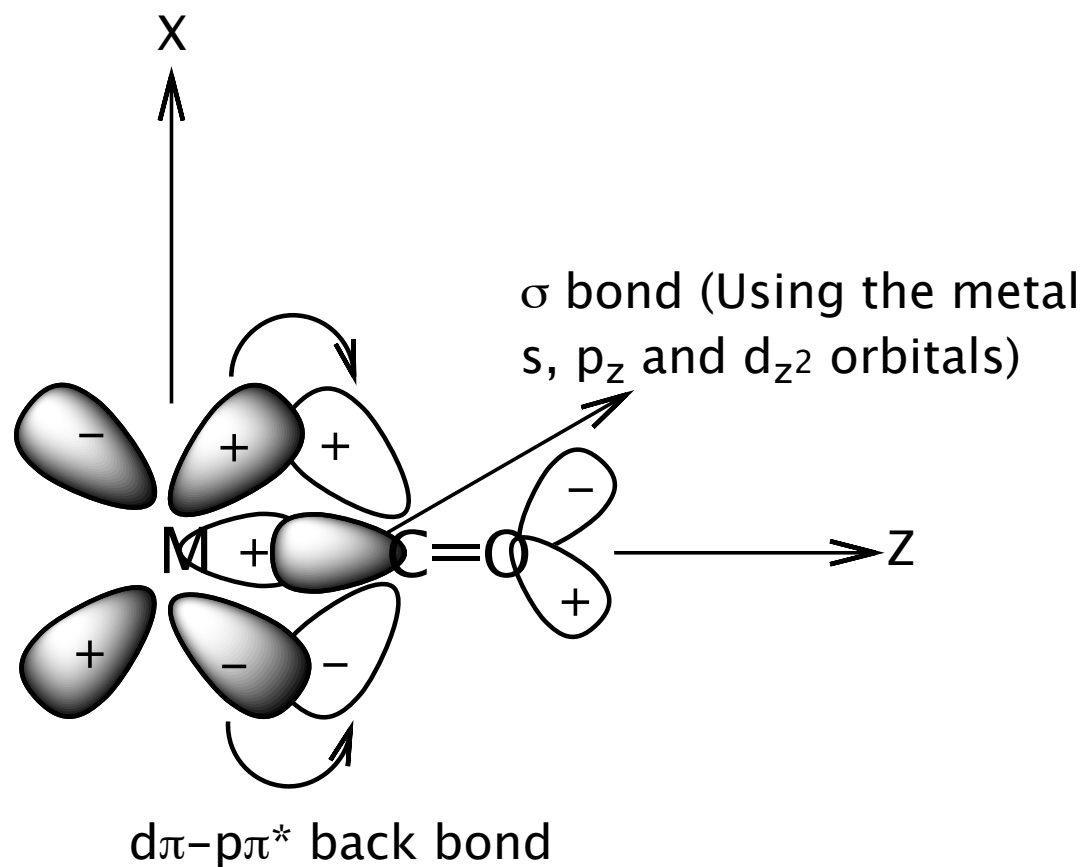
Metal-carbonyls: Bonding Modes

$$:O\equiv C:\longrightarrow M$$
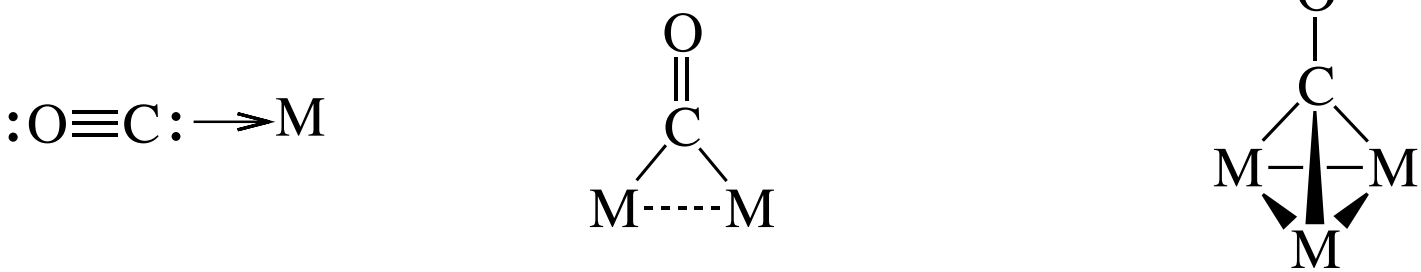
Terminal Mode
2e neutral donor

μ_2-bridging mode
2e neutral donor

μ_3-bridging mode
3e neutral donor

4	5	6	7	8	9	10	11
Ti	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$	$Ni(CO)_4$	Cu
Zr	Nb	$Mo(CO)_6$	$Te_2(CO)_{10}$	$Ru(CO)_5$ $Ru_3(CO)_{12}$	$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	Pd	Ag
Hf	Ta	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_3(CO)_{12}$	$Ir_4(CO)_{12}$	Pt	Au

Metal-carbonyls: Evidence for Bonding
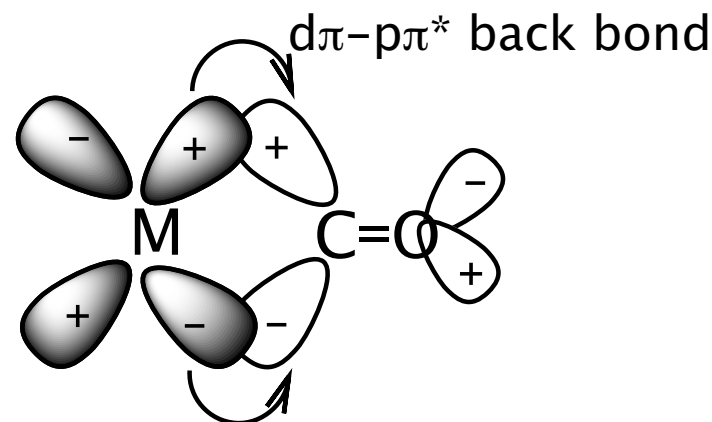
General observation is in line with model

Weakened C-O bond

Lower carbonyl stretching frequency
(compared to free CO)

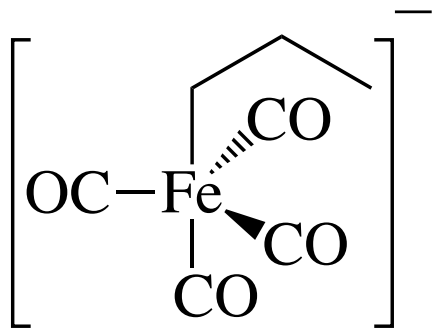Point to decrease in C-O bond order

C-O bond $\quad C \equiv O \quad$ 1.13 Å

$\quad H_2C = C = O \quad$ 1.17 Å

$\quad M \cdots C \cdots O \quad$ 1.13 – 1.16 Å

Metal-carbonyls: Evidence for Bonding

Fe-propyl = 2.20 Å

Fe-CO = 1.75 Å

Covalent bond radius; C(sp^3) = 0.77 Å and C(sp) = 0.70 Å
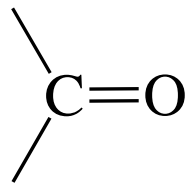
Confirms the formation of M-C multiple bond

Chemische Berichte **1975**, *108*, 1373-83.

Carbonyl IR Stretching Frequencies

1. The **position** of the carbonyl bands in the IR depends mainly on the bonding mode of the CO (terminal, bridging) and the amount of electron density on the metal being pi-backbonded to the CO.

2. The **number** (and intensity) of the carbonyl bands one observes depends on the number of CO ligands present and the symmetry of the metal complex.
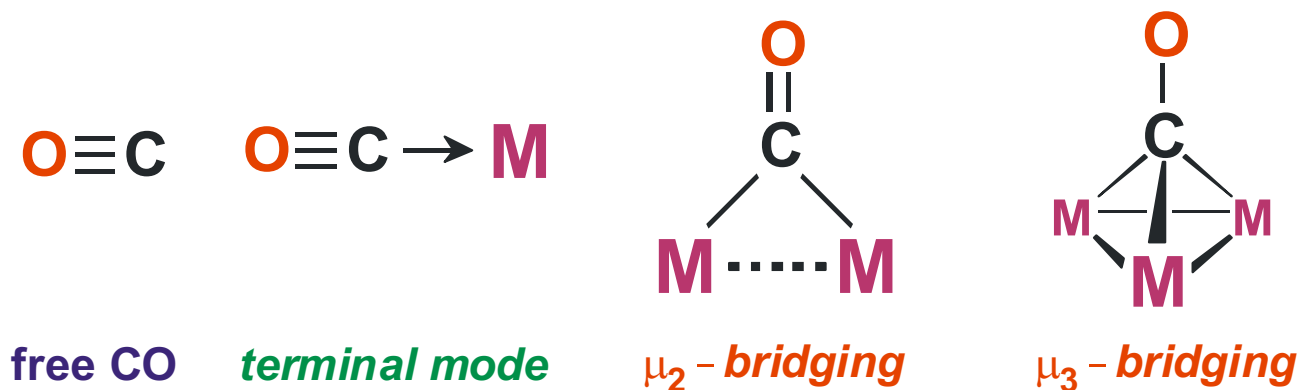
Metal-carbonyls: Evidence for Bonding

IR Data $\nu_{CO} = \dfrac{1}{2\pi c}\sqrt{\dfrac{k}{\mu_{co}}}$ k and hence $\boldsymbol{\nu}$ is a measure of bond strength

Molecule	ν_{CO}
$H_3C\!-\!O\!-\!CH_3$	$1000\ cm^{-1}$
$C\!=\!O$	$1720\ cm^{-1}$
$C\!\equiv\!O$	$2143\ cm^{-1}$
$H_3B\!\leftarrow\!C\!\equiv\!O$	$2165\ cm^{-1}$

Bonding Modes:

As one goes from a terminal CO-bonding mode to μ_2-bridging and finally μ_3-bridging, there is a relatively dramatic drop in the CO stretching frequency seen in the IR.

|	free CO	terminal mode	μ_2 – bridging	μ_3 – bridging
ν_{CO} IR (cm^{-1})	2143	2120 - 1850	1850 - 1720	1730 - 1500

(for neutral metal complexes)

Bridging carbonyls tend to have weaker and broader IR bands.

Effect of Electron Density on Metal in Homoleptic Complexes

Weaking of the CO bond can be correlated to the back-donation of metal e density to CO

| Molecule	ν_{CO}	Molecule	ν_{CO}
$Mn(CO)_6^+$	2090 cm^{-1}	free CO	2143
$Cr(CO)_6$	2000 cm^{-1}	$[Ag(CO)]+$	2204
$V(CO)_6^-$	1860 cm^{-1}	Ni(CO)4	2060
$Ti(CO)_6^{2-}$	1750 cm^{-1}		
$Ni(CO)_4$	2046 cm^{-1}		
$Co(CO)_4^-$	1883 cm^{-1}		
$Fe(CO)_4^{2-}$	1788 cm^{-1}		
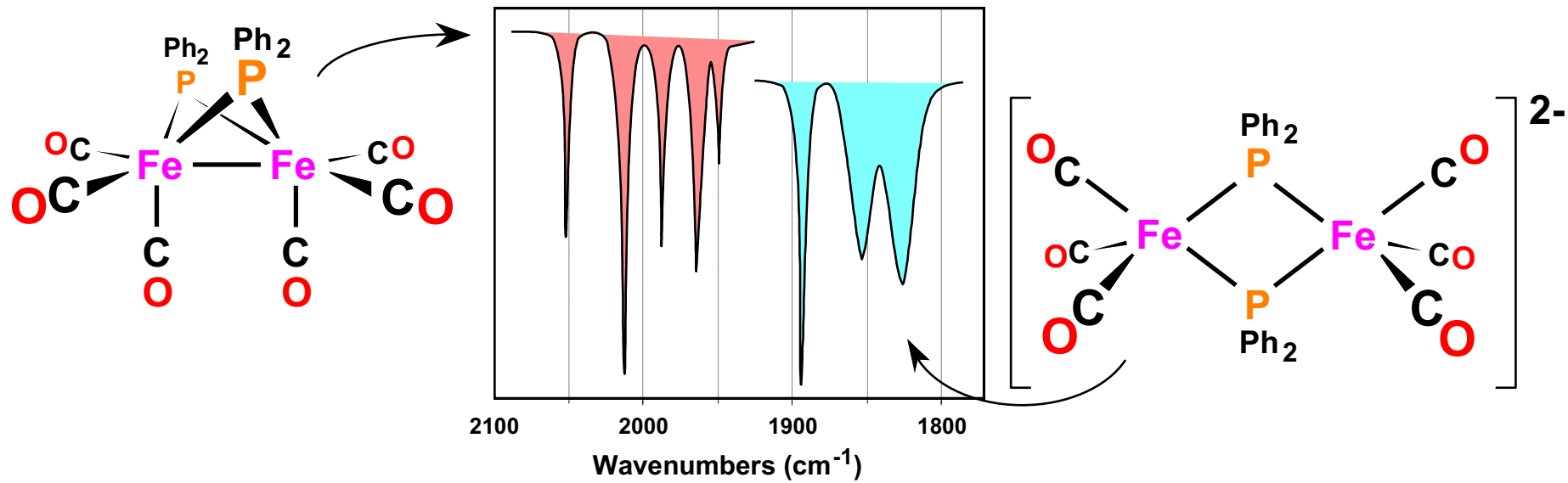
Ligand Donation Effects:

Ligands that are *trans* to a carbonyl can have a particularly large effect on the ability of the CO to effectively pi-backbond to metal.

Two *trans* **π**-backbonding ligands will partially compete for same *d*-orbital electron density and weakens each others net M-L bond

Trans σ-backbonding ligands strengthens the M-CO bond
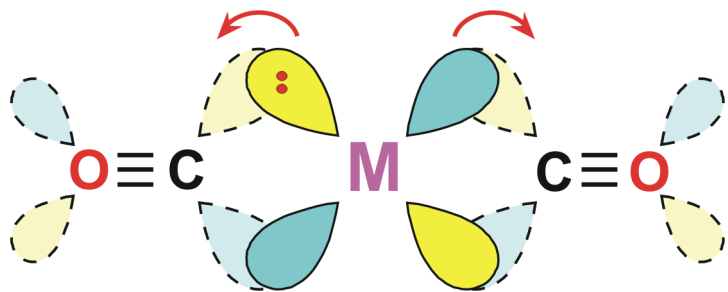
Pyridines and amines –
Weak σ-donors and
worse **π**-acceptors. CO has no competition for **π**-acceptance

Complex	ν_{CO} cm^{-1}
$Mo(CO)_3(PF_3)_3$	2090, 2055
$Mo(CO)_3(PCl_3)_3$	2040, 1991
$Mo(CO)_3[P(OMe)_3]_3$	1977, 1888
$Mo(CO)_3(PPh_3)_3$	1934, 1835
$Mo(CO)_3(NCCH_3)_3$	1915, 1783
$Mo(CO)_3(triamine)_3$	1898, 1758
$Mo(CO)_3(pyridine)_3$	1888, 1746

Based on CO IR stretching frequencies, the following ligands can be ranked from **best** π-acceptor to **worst**:

$$NO^+ > CO > PF_3 > RN{\equiv}C > PCl_3 > P(OR)_3 > PR_3 > RC{\equiv}N > NH3$$
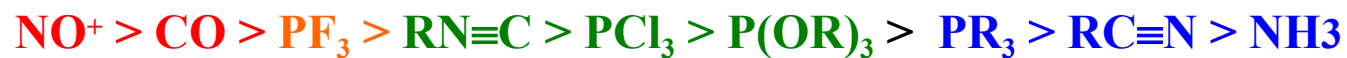
Oxidative Addition

An ***oxidative addition*** reaction is one in which (usually) a neutral ligand adds to a metal center and in doing so oxidizes the metal, typically by 2e-. Co-ordination number of the metal typically increases by 2. The transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands.
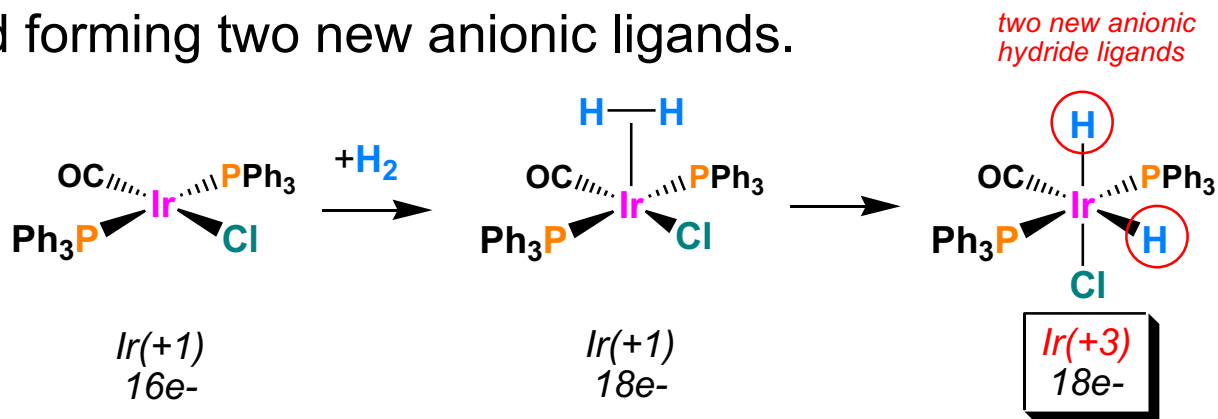
There are three main classes of molecules (substrates) that can perform oxidative additions to metal centers:

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_2, C-H bonds, Si-H bonds, S-H bonds, B-H bonds, N-H bonds, S-S bonds, C-C bonds, etc.

Often considered to be *"non-reactive"* substrates (except H_2).

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

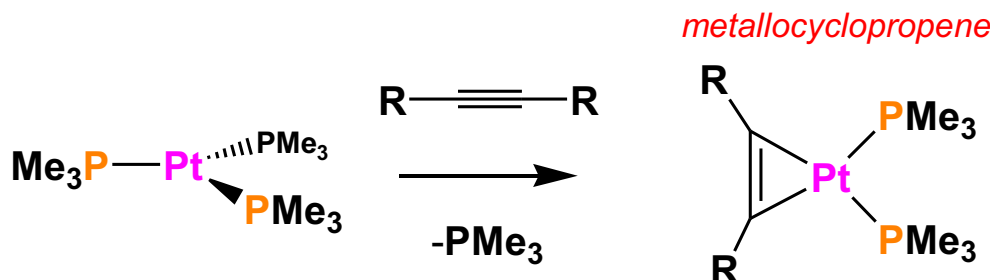# Oxidative Addition –

Non-electrophillic "Intact":

May or may not contain electronegative atoms, but do need to have a **double** or **triple bond** present.

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

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 <u>one</u> of the **π**-bonds is broken leaving the σ-bond intact.

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

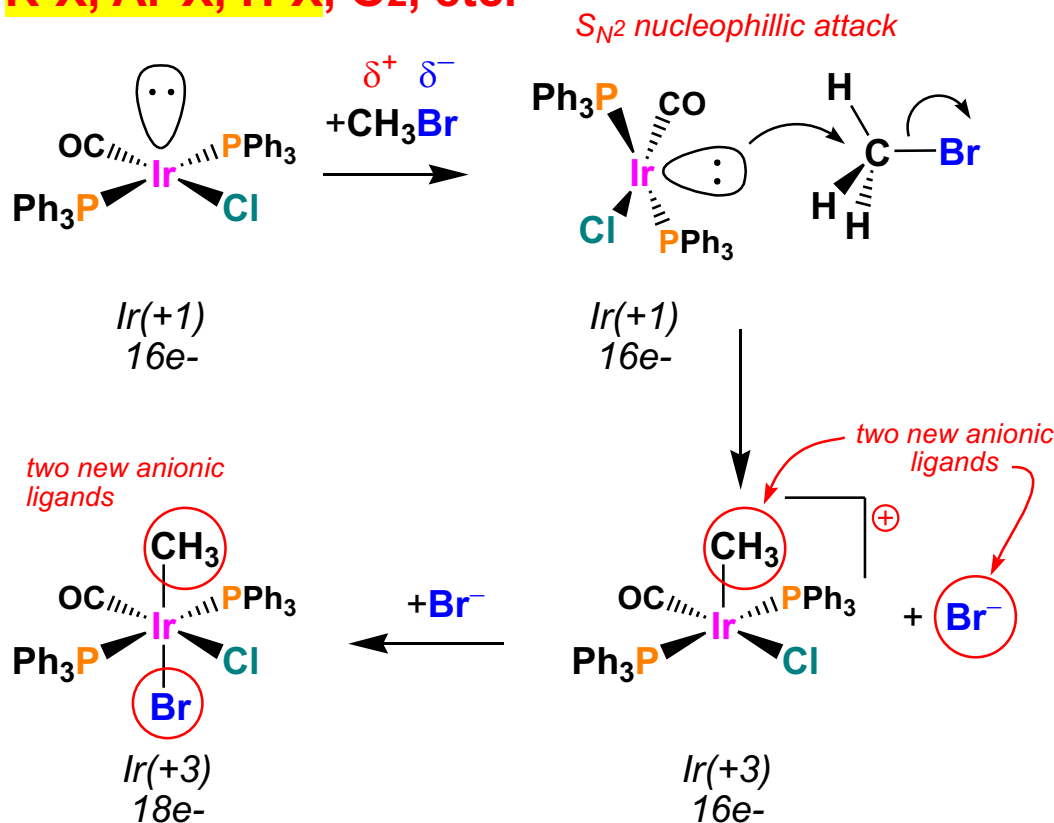**alkenes, alkynes, and O2**

metallocyclopropene

Oxidative Addition – *Electrophillic:*

These molecules **_do_** contain electronegative atoms and are good oxidizing agents. They are often considered to be *"reactive"* substrates. These molecules do **_NOT_** require the presence of an **empty orbital** (18e- is OK) on the metal center in order to perform the oxidative addition rxn.

X$_2$ (X = Cl, Br, I), R-X, Ar-X, H-X, O$_2$, etc.

S_{N2} nucleophillic attack

δ^+ δ^-
+CH$_3$Br

Ir(+1)
16e-

Ir(+1)
16e-

two new anionic ligands

+Br$^-$

two new anionic ligands

+ Br$^-$

Ir(+3)
18e-

Ir(+3)
16e-

General Features of Oxidative Additions

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

So in comparing two or more metal complexes to see which will be the most reactive towards a particular substrate for oxidative addition you would pick the metal center with the strongest donor ligands, fewest p-acceptor ligands, or most negative charge.

Also remember that the non-electrophillic ligands (Class A) and "intact" ligands (Class C) usually require that there is an empty orbital (16e- or lower) on the metal center in order to react.
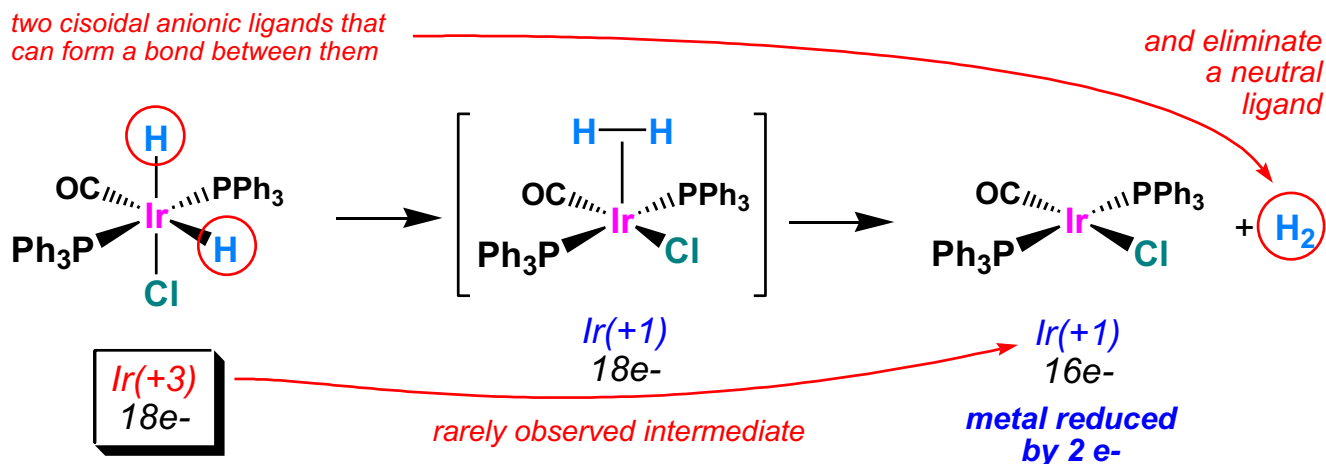
Reductive Elimination

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.

Each anionic ligand pushes one electron back onto the metal center (in the case of a monometallic complex) to reduce it by 2e-.

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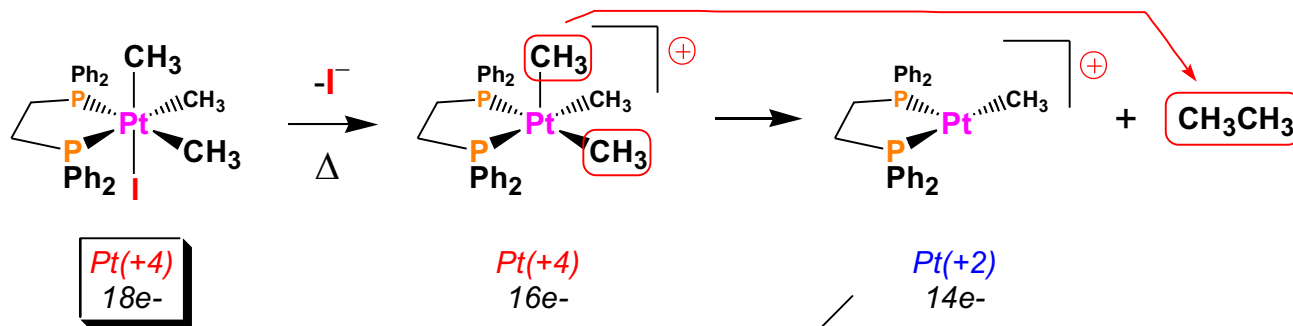
Reductive Elimination

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

Since **reductive elimination** involves pushing electrons back onto the metal center from two anionic ligands that are usually more electronegative than the metal center, it is best if the metal center is **electron deficient**.

This can be accomplished by having electron-withdrawing ligands (e.g., CO), cationic charge(s), and/or coordinative unsaturation (sub-18e- counts).

While reductive elimination can occur from saturated 18e- complexes (so 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.

CH₃ ... Pt(+4) 18e-

$-I^-$, Δ

Pt(+4) 16e- $\oplus$

Pt(+2) 14e- $\oplus$ + CH_3CH_3

The dissociation of the I- generates a cationic unsaturated complex. This is electron deficient enough to help promote the reductive elimination of ethane (CH_3CH_3).

$+I^-$

Pt(+2) 16e-
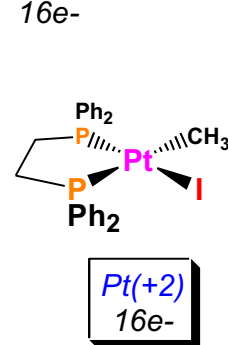
Goldberg, J. Am. Chem. Soc. ***1995**, 117, 6889-6896*

reductive elimination →

Pt(+4) 18e- ⇌ (Δ) Pt(+2) 16e- + CH_3I

← **oxidative addition**
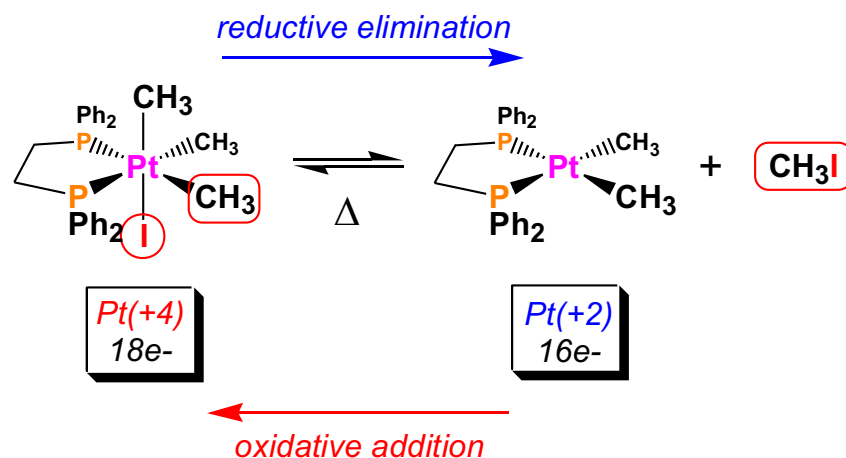
The reductive elimination of the CH_3I is kinetically favored. This is because the orbitals around the iodide anion are spherically symmetric and this makes it much easier to overlap with the alkyl group orbital to perform the reductive elimination. The sp^3 directed orbitals on the two CH_3 groups are more difficult to overlap in order to get the reductive elimination to occur. But the reductive elimination of the CH_3CH_3 is thermo-dynamically considerably more favorable and the back oxidative addition much more difficult.