Organometallic Chemistry

OF THE TRANSITION METALS

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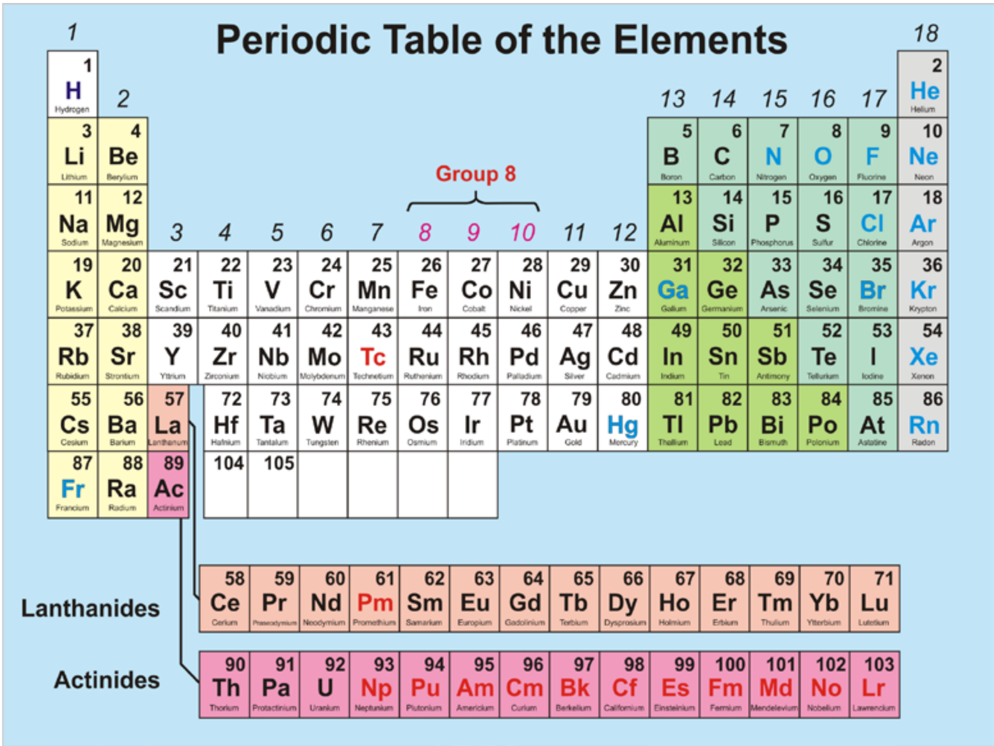
Organometallic Compounds

- *Organometallic Compounds*: *They contain direct metal-carbon bonds.*
- *Organometallic Compounds of the transition metals have unusual structures, and practical applications in organic synthesis and industrial catalysis.*

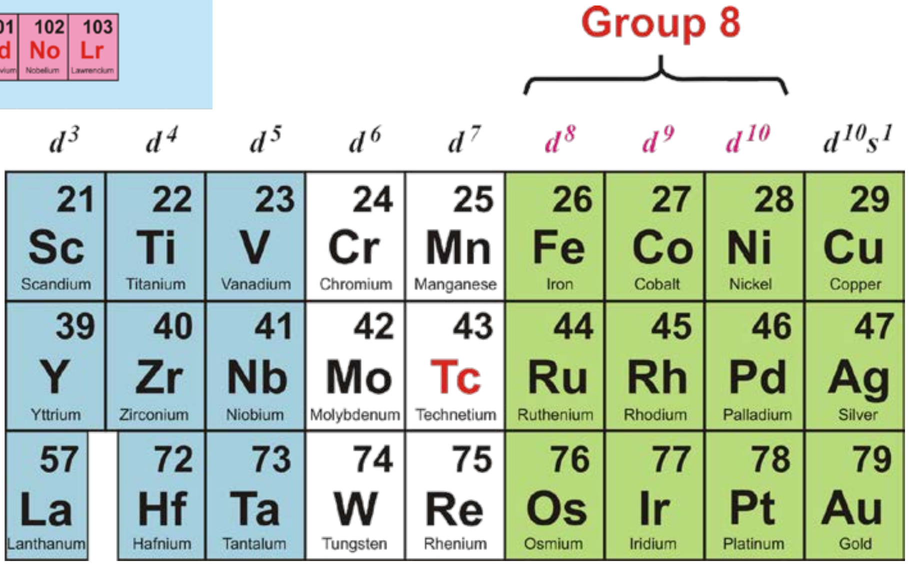


Periodic Table of the Elements

Group 8

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Berylium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104	105													

Lanthanides	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
Actinides	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium



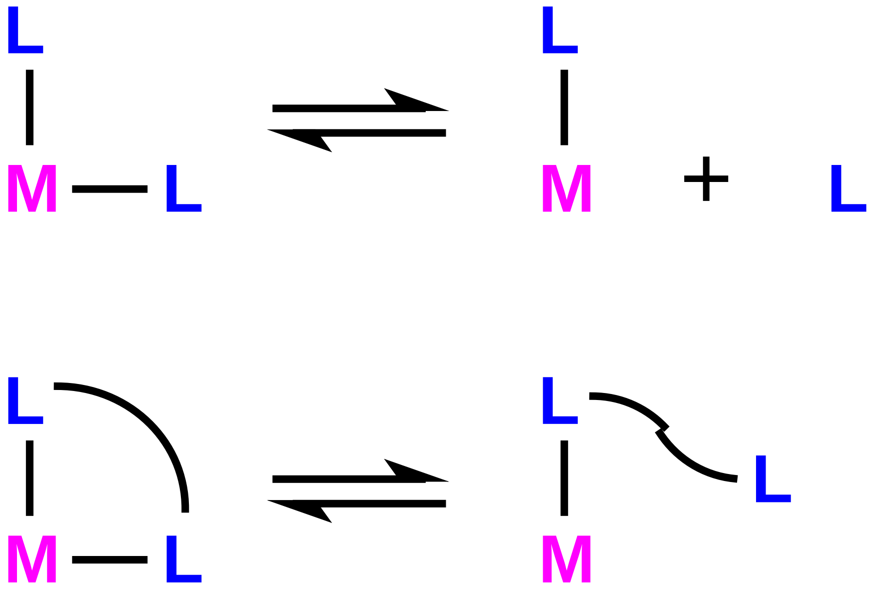
Group 8

d^{3}	d^{4}	d^{5}	d^{6}	d^{7}	d^{8}	d^{9}	d^{10}	$d^{10}s^{1}$
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Some Important Ligand Nomenclature

Chelate Effect: “chelate” is from the Greek meaning “claw”.

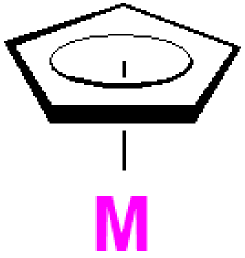
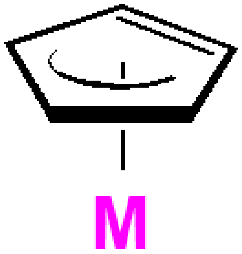
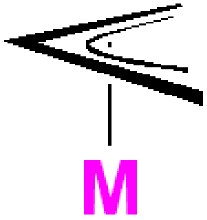
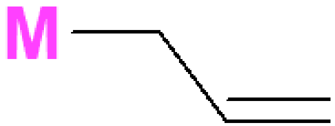
Since most metal-ligand bonds are relatively weak compared to C-C bonds, M-L bonds can often be broken rather easily, leading to dissociation of the ligand from the metal.



η^x

“eta-*x*” was originally developed to indicate how many ***contiguous*** donor atoms of a π-system were coordinated to a metal center.

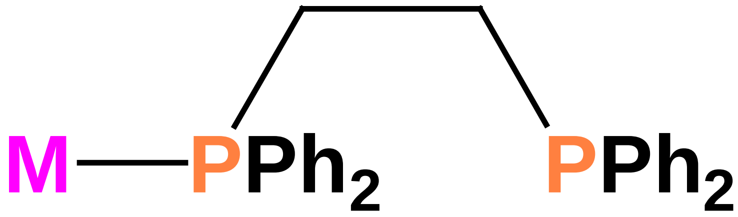
Hapticity is another word used to describe the bonding mode of a ligand to a metal center. An η^5-cyclopentadienyl ligand, for example, has all five carbons of the ring bonding to the transition metal center.

			
η^5-Cp	η^3-Cp	η^3-allyl	η^1-allyl

κ^x

“kappa-*x*” was developed to indicate how many *non*-*contiguous* donor atoms of a ligand system were coordinated to a metal center.

This usually refers to non-carbon donor atoms, but can include carbons.



A k^1-dppe ($Ph_2PCH_2CH_2PPh_2$) ligand, for example, has only one of the two phosphorus donors bonded to the transition metal center.

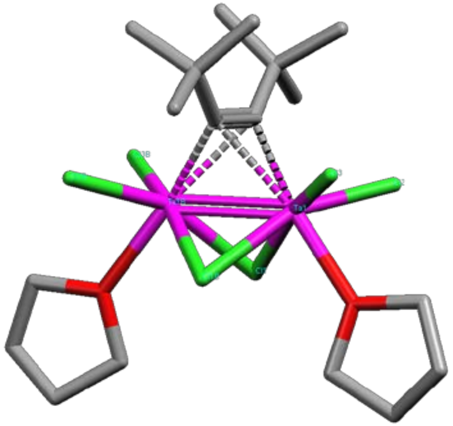
Nevertheless, most of the diphospines coordinate by the two phosphorus atoms, in a chelating way.

μ_x

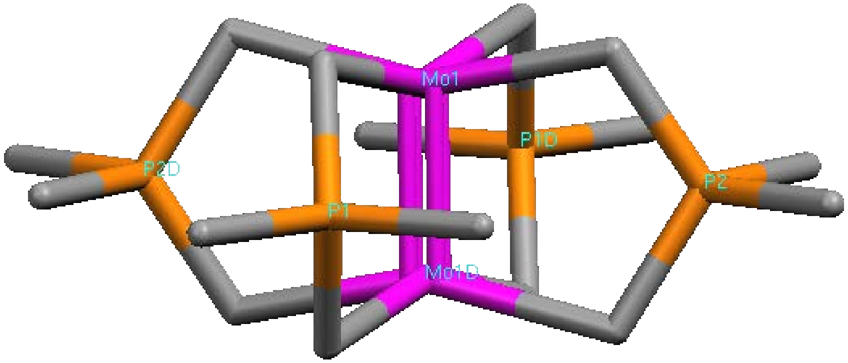
“mu-*x*” is the nomenclature used to indicate the presence of a **bridging ligand** between two or more metal centers. The *x* refers to the number of metal centers being bridged by the ligand. Usually most authors omit $x = 2$ and just use μ to indicate that the ligand is bridging the simplest case of two metals.

There are two different general classes of bridging ligands:

1) Single atom bridges
2) Two donor atoms separated by a bridging group (typically organic)
3) Two donor atoms bonded to one another (alkynes, O_2^{x-}, S_2^{x-}, allyl$^-$, etc)



Ta_2 (μ-*t*-Bu-C≡C-*t*-Bu) (μ-Cl)$_2$Cl$_2$(THF)$_2$



$Mo_2(\mu\text{-}CH_2P(Me)_2CH_2)_4$

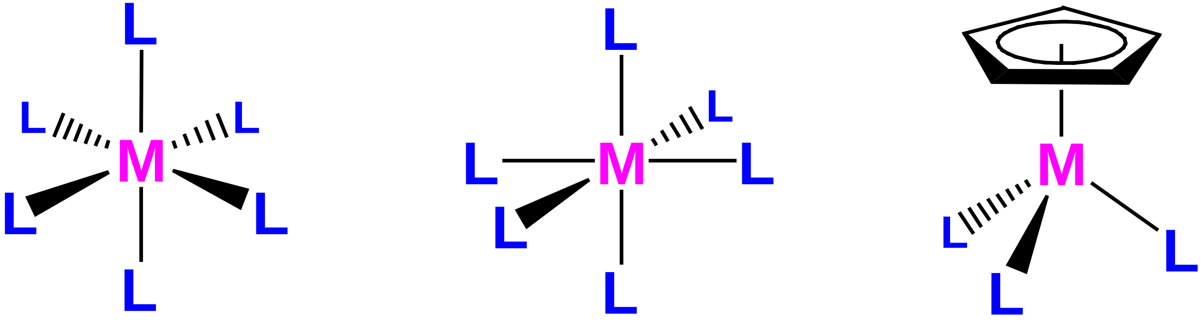
Nomenclature:

Inorganic/organometallic chemists generally do not use IUPAC naming rules. There are some qualitative rules that most authors seem to use in American Chemical Society (ACS) publications:

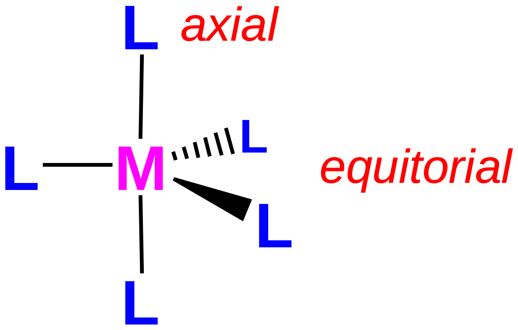
- in formulas with Cp (cyclopentadienyl) ligands, the Cp usually comes first, followed by the metal center: Cp_2TiCl_2
- other anionic multi-electron donating ligands are also often listed in front of the metal, e.g., trispyrazolylborate anion (Tp)
- in formulas with hydride ligands, the hydride is sometimes listed first. Rules # 1 & 2, however, take precedence over this rule: $HRh(CO)(PPh_3)_2$ and Cp_2TiH_2
- bridging ligands are usually placed next to the metals in question, then followed by the other ligands (note that rules 1 & 2 take precedence):
  $Co_2(\mu\text{-}CO)_2(CO)_6$, $Rh_2(\mu\text{-}Cl)_2(CO)_4$, $Cp_2Fe_2(\mu\text{-}CO)_2(CO)_2$
- anionic ligands are often listed before neutral ligands: $RhCl(PPh_3)_3$, $CpRuCl(=CHCO_2Et)(PPh_3)$ (neutral carbene ligand), $PtIMe_2(C\equiv CR)(bipy)$.

Common Coordination Geometries

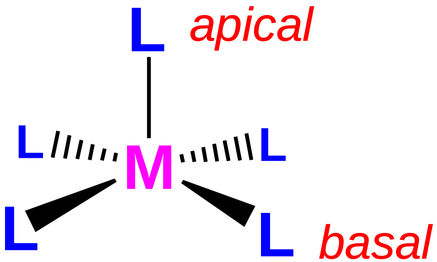
6-Coordinate: ***Octahedral*** **(90° & 180° angles)**



5-Coordinate: ***Trigonal Bypyramidal or Square Pyramidal***

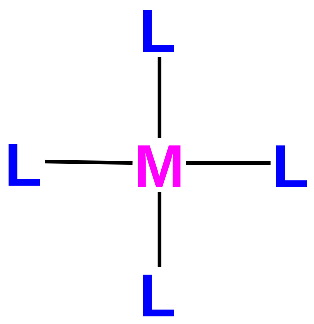


(90° & 120°)

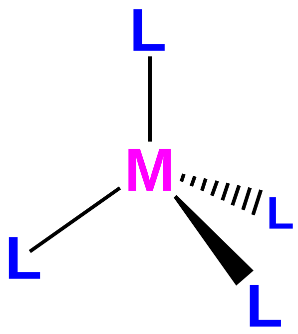


(~100° & 90°)

4-Coordinate: *Square Planar* *or* *Tetrahedral*



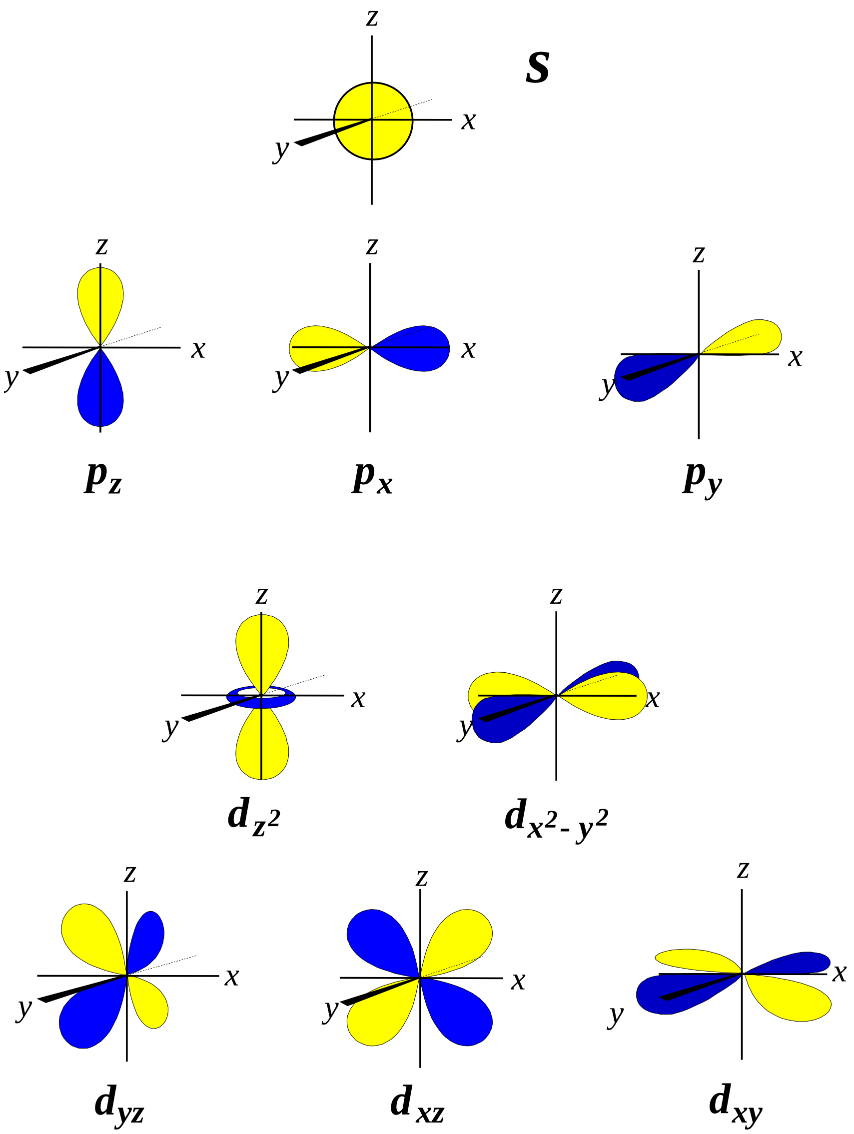
(90° & 180°)

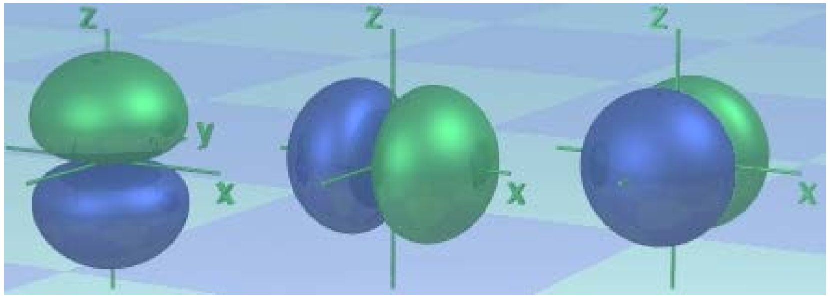


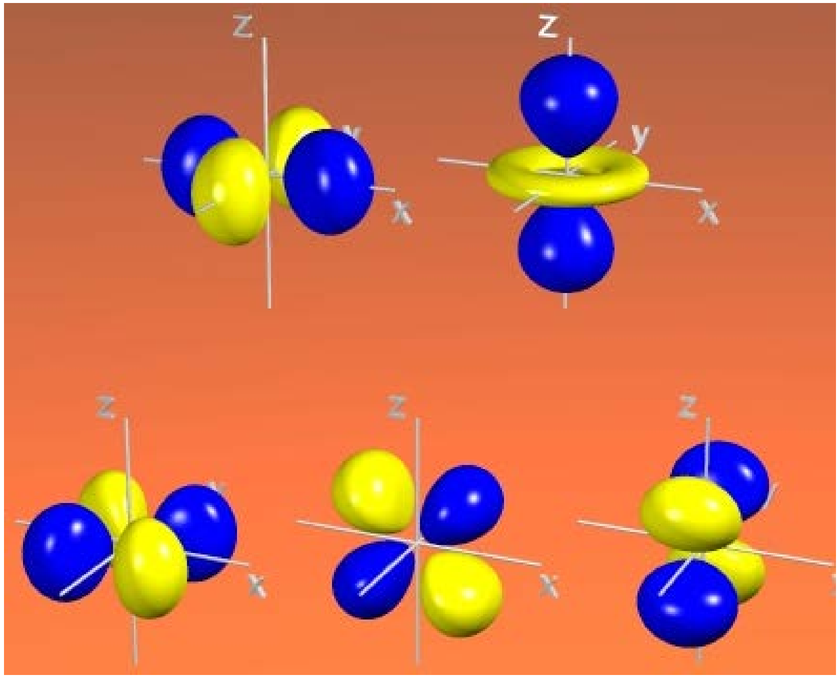
(109°)

Square planar geometry is generally limited to Rh, Ir, Ni, Pd, Pt, and Au in the d^8 electronic state when coordinated to 2e- donor ligands.

Bonding and Orbitals







18-Electron "Rule"

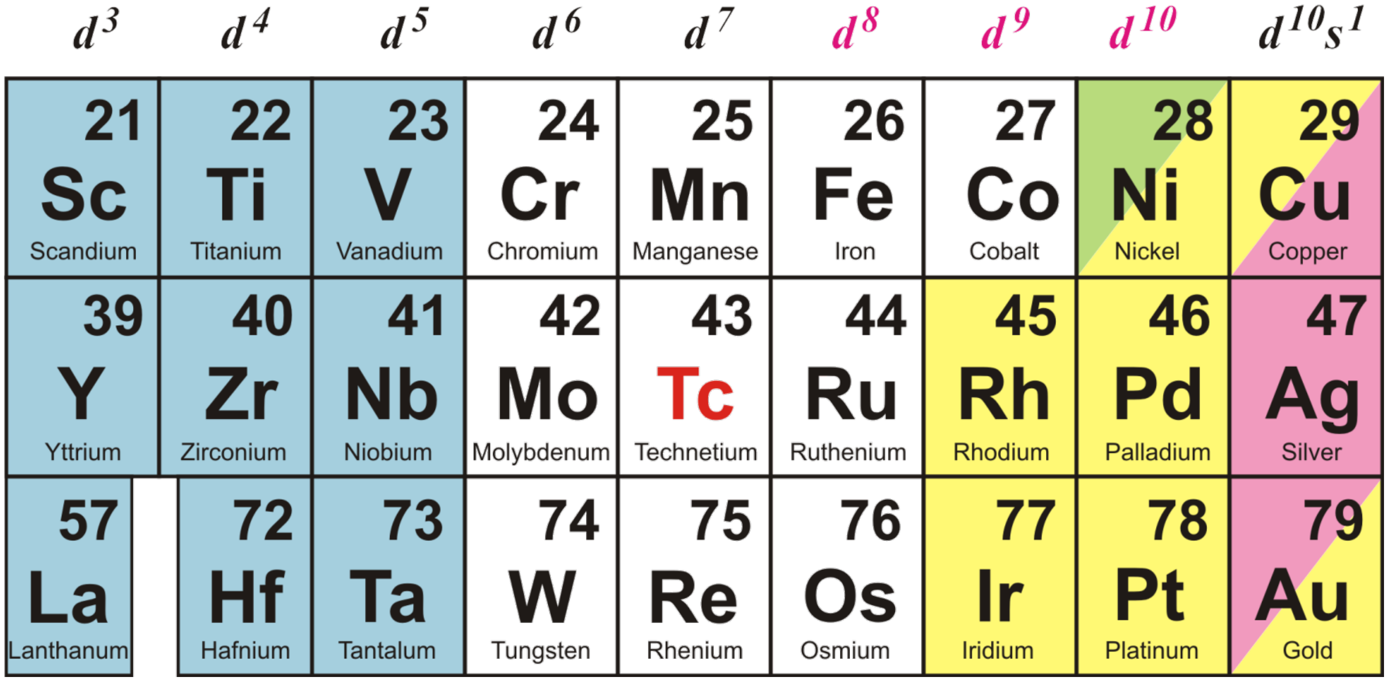
The vast majority of stable diamagnetic organometallic compounds have 16 or 18 valence electrons due to the presence of the five ***d*** orbitals which can hold 10 more electrons.

Electron counting is the process of determining the number of valence electrons about a metal center in a given transition metal complex. To figure out the electron count for a metal complex:

1) Determine the oxidation state of the transition metal center(s) and the metal centers resulting *d*-electron count. To do this one must:
    a) note any overall charge on the metal complex
    b) know the charges of the ligands bound to the metal center (ionic ligand method)
    c) know the number of electrons being donated to the metal center from each ligand (ionic ligand method)
2) Add up the electron counts for the metal center and ligands

18 e- counts are referred to as *saturated*, because there are no empty low-lying orbitals to which another incoming ligand can coordinate. Electron counts lower than 18e- are called *unsaturated* and can electronically bind additional ligands unless the coordination site is sterically blocked.

Exceptions to the 18-Electron “Rule”



d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum 72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	

Early Transition Metals

16e- and sub-16e- configurations are common

Coordination geometries higher than 6 relatively common

Middle Transition Metals

18e- configurations are common

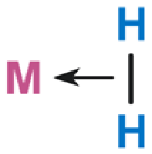
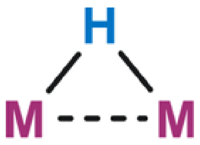
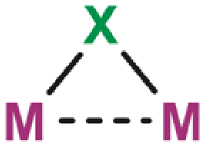
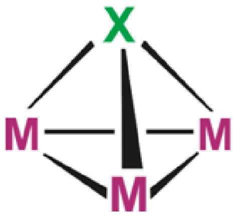
Coordination geometries of 6 are common

Late Transition Metals

16e- and sub-16e- configurations are common

Coordination geometries of 4 and lower are common: square planar

Ligands, Bonding Types, Charges, and Donors

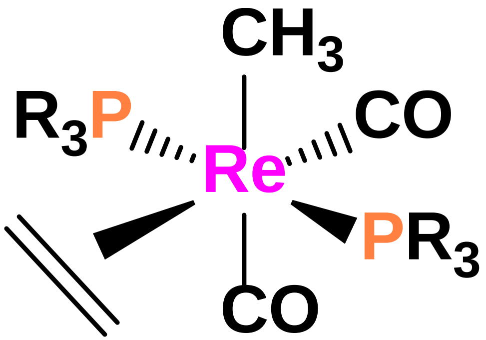
Ligand Name	Bonding Type	Formal Charge	Electrons Donated
Molecular Hydrogen: H_2		0	2
Hydride: H^-	M-H	-1	2
Hydride: H^-		-1	2
Halide: X^-	M-X	-1	2
Halide: X^- **μ bridging**		-1	4 (2 to each M)
Halide: X^- **μ_3 bridging**		-1	6 (2 to each M)

Ligands, Charges, and Donors

Ionic Method of electron-counting
Versus Covalent Method

Cationic 2e- donor:	NO^+ (nitrosyl)
Neutral 2e- donors:	PR_3 (phosphines), CO (carbonyl), $R_2C{=}CR_2$ (alkenes), $RC{\equiv}CR$ (alkynes, can also donate 4 e-), $N{\equiv}CR$ (nitriles)
Anionic 2e- donors:	Cl^- (chloride), Br^- (bromide), I^- (iodide), CH_3^- (methyl), CR_3^- (alkyl), Ph^- (phenyl), H^- (hydride) *The following can also donate 4 e- if needed, but initially count them as 2e- donors (unless they are acting as bridging ligands):* OR^- (alkoxide), SR^- (thiolate), NR_2^- (inorganic amide), PR_2^- (phosphide)
Anionic 4e- donors:	$C_3H_5^-$ (allyl), O^{2-} (oxide), S^{2-} (sulfide), NR^{2-} (imido), CR_2^{2-} (alkylidene) *and from the previous list:* OR^- (alkoxide), SR^- (thiolate), NR_2^- (inorganic amide), PR_2^-
Anionic 6e- donors:	Cp^- (cyclopentadienyl), N^{3-} (nitride)

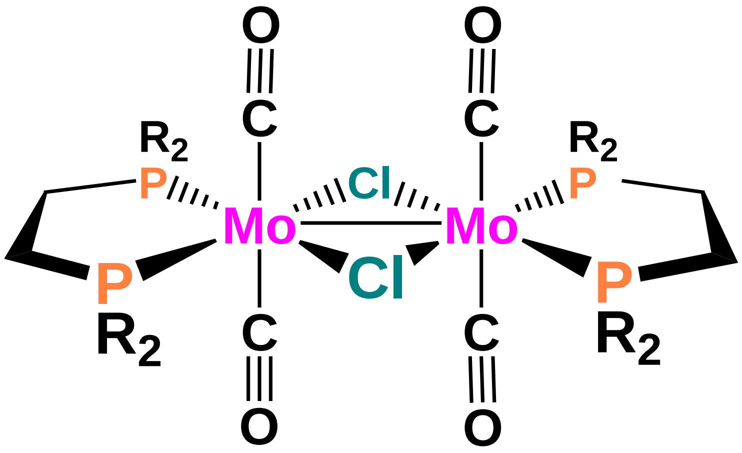
e-counting Examples: Simple



1) There is no overall charge on the complex
2) There is one anionic ligand (CH_3^-, methyl group)
3) The Re metal atom must have a +1 charge to compensate for the one negatively charged ligand. So the Re is the in the +1 oxidation state. We denote this three different ways: Re(+1), Re(I), or Re^I.

Re(+1)	d^6
2 PR_3	4e-
2 CO	4e-
CH_3^-	2e-
CH_2=CH_2	2e-
Total:	18e-

e-counting Examples: M-M Bonded System

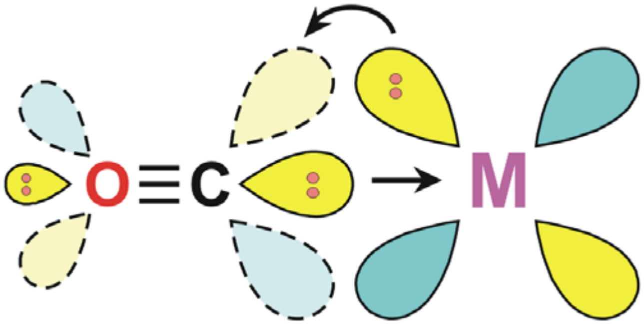


Mo(+1)	**d^5**
$2PR_3$	**4e-**
2CO	**4e-**
2μ-Cl^-	**4e-**
Sub-total:	***17e-***
Mo-Mo	**1e-**
TOTAL:	**18e-**

1) Generally treat metal-metal (M-M) bonds to be simple covalent bonds with each metal contributing 1e- to the bond. If you have two metal atoms next to one another and each has an odd electron-count, pair the odd electrons to make a M-M bond.
2) Bridging ligands, like halides, with at least 2 lone pairs almost always donate 2e- to each metal center.
3) Oxidation state determination: Total of two anionic ligands for two metal centers (overall complex is neutral). Thus each metal center needs to have a +1 oxidation state to balance the anionic ligands.

Common Ligands

Carbonyl Ligands - C≡O



empty π-acceptor orbitals on carbonyl*

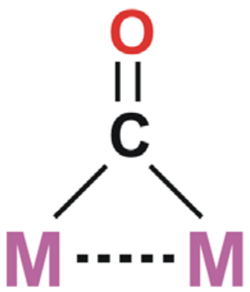
powerful π-acceptor ligand!

excellent ligand, therefore, for stabilizing electron-rich low-valent metal centers

Standard Bonding Modes:

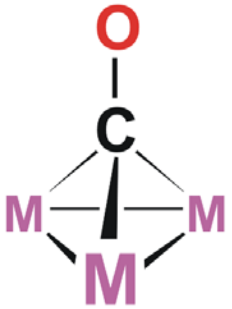
terminal mode

2e$^-$ neutral donor



μ_2- bridging mode

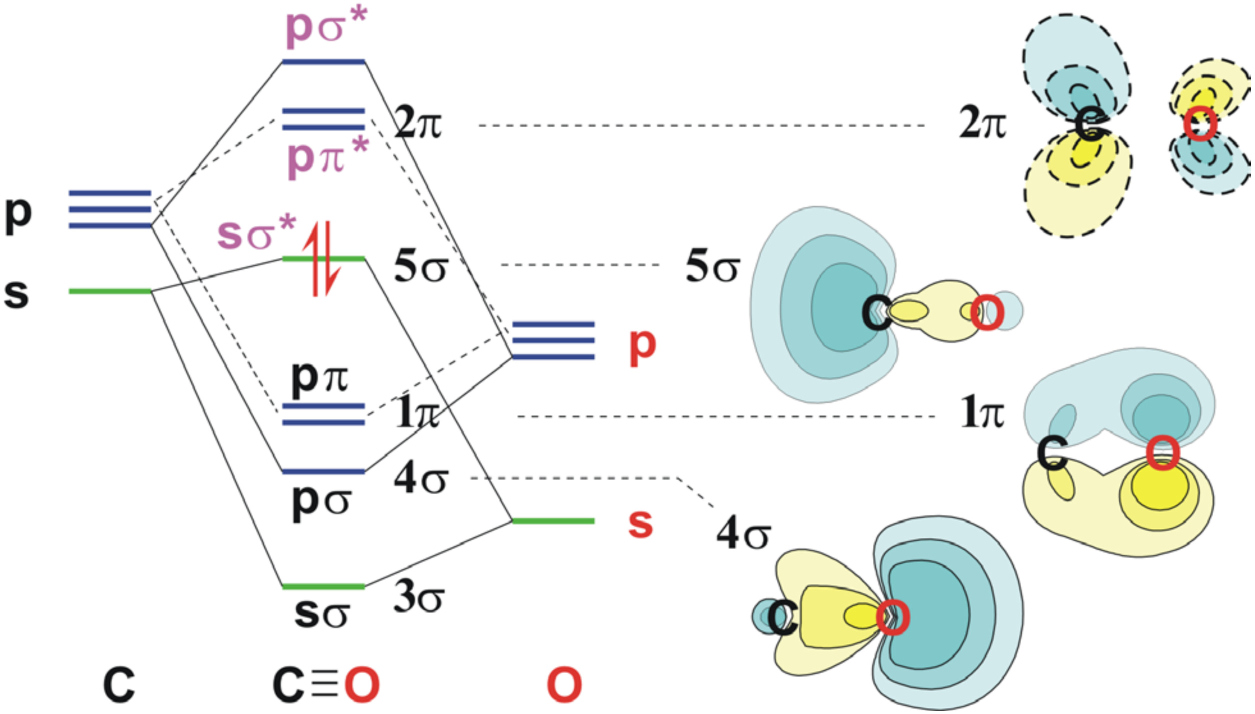
2e$^-$ neutral donor



μ_3- bridging mode

3e$^-$ neutral donor

Molecular Orbital (MO) Diagram



M-CO Bonding

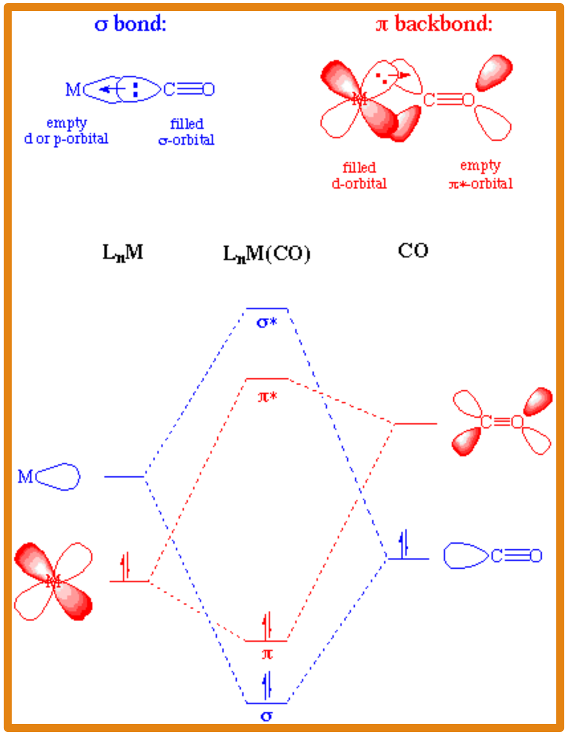
- M (σ) ← CO (σ)

  Bonding: M-C

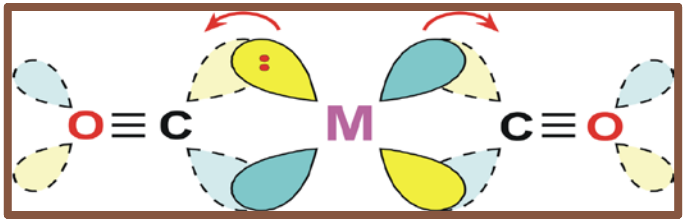
- M (π) → CO (π*)

  Backbonding:

  M-C bond: increases
  C-O bond: decreases
  υ_{CO} freq: decreases



Experimental Evidence of Multiple Bond M—C—O



Complex	νCO 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

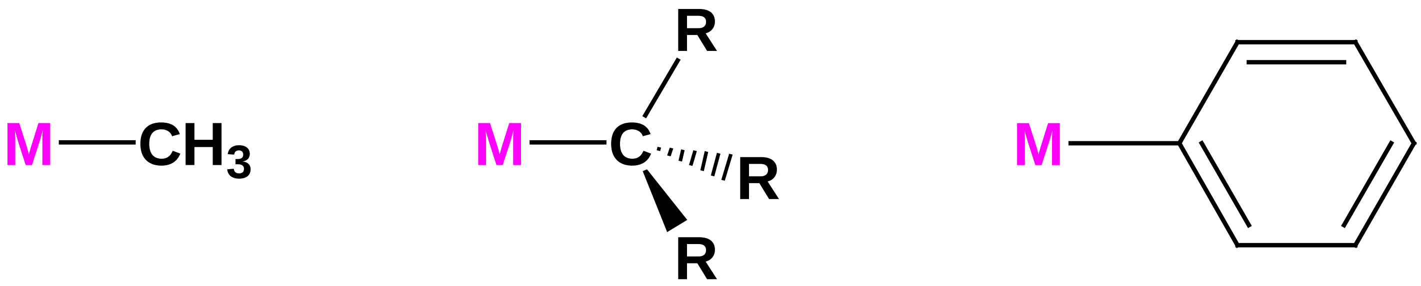
$CO > PF_3 > PCl_3 > P(OR)_3 > PR_3 > NH_3$

Electronic Effects on ν_{CO}

As the electron density on a metal center increases, more π-backbonding to the CO ligand(s) takes place. This further weakens the C-O bond by pumping more electron density into the formally empty carbonyl π* orbital. This increases the M-CO bond strength making it more double-bond-like, i.e., the resonance structure M=C=O assumes more importance.

d^x	Complex	ν_{CO} cm^{-1}
	free CO	2143
d^{10}	$[Ag(CO)]^+$	2204
	$Ni(CO)_4$	2060
	$[Co(CO)_4]^-$	1890
	$[Fe(CO)_4]^{2-}$	1790
d^6	$[Mn(CO)_6]^+$	2090
	$Cr(CO)_6$	2000
	$[V(CO)_6]^-$	1860

Alkyls and Aryls Ligands



Anionic 2 e- donors

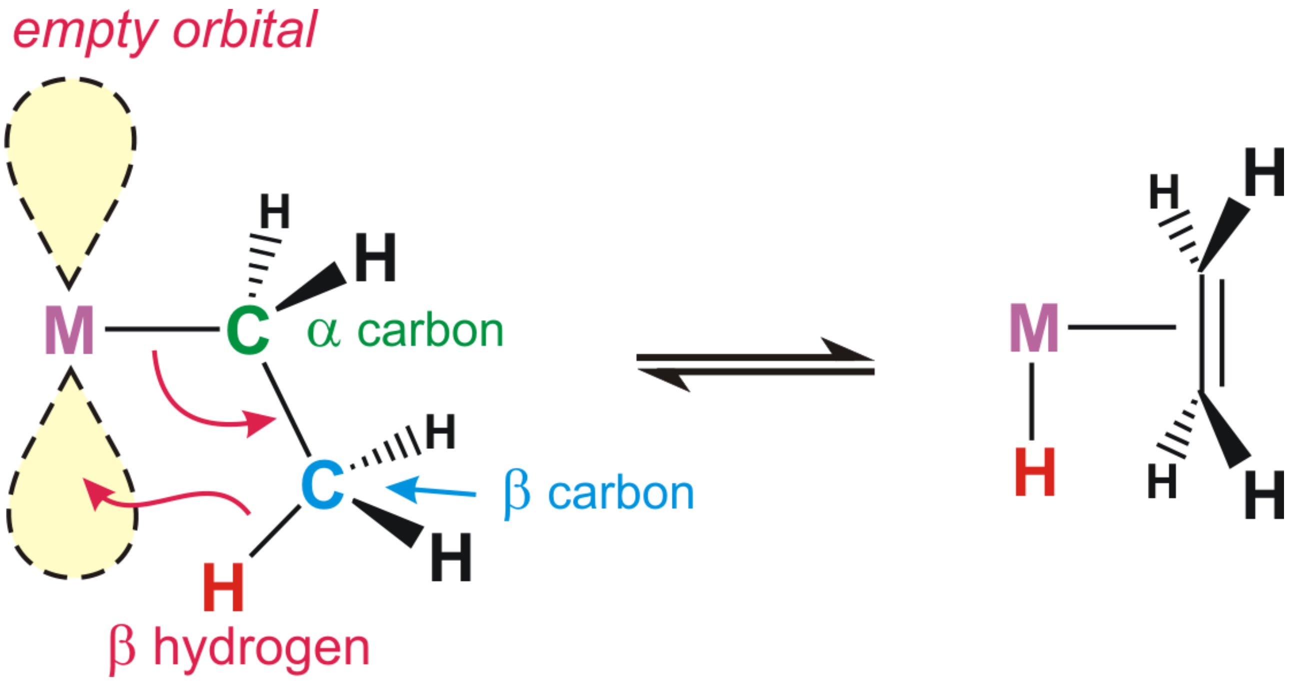
Alkyls are typically very **strong** mono-anionic σ-donors, second only to hydrides. They have virtually no π-acceptor ability unless a π-system is present.

Increasing the carbon substitution (replacing hydrogens with hydrocarbon groups such as methyl, ethyl, isopropyl) usually increases the donor strength, but steric factors can come into play and weaken the metal-alkyl bond (e.g., t-butyl groups are often too sterically hindered to bind well).

Replacing the hydrogens with fluorine atoms (very electron withdrawing) dramatically reduces the donor ability of the alkyl (aryl). For example, CF_3^- and $C_6F_5^-$ are not very strong donors. $C_6F_5^-$ could act as a weak to moderate π-acceptor due to its empty π* orbitals.

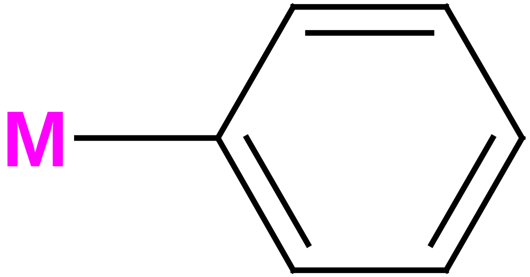
Metal alkyls are also typically quite to extremely reactive to molecular O_2, water, and a variety of other ligands and reagents. As with hydrides, they play a very important and active role in catalysis.

β-Hydride Elimination



Note that in order to have a β-hydride elimination you MUST have a empty orbital on the metal cisoidal (next) to the alkyl ligand. You also must have β-hydrogens present on the alkyl.

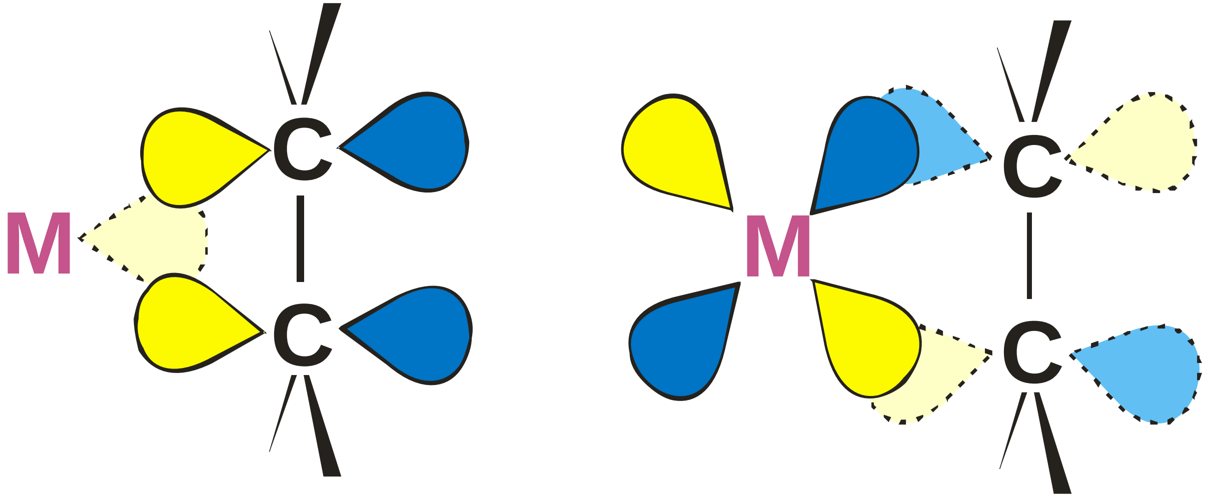
Aryl Ligands



Aryl ligands are relatively strong anionic two electron donors, like alkyls. Since they cannot easily β-hydride eliminate metal-aryls are relatively stable.

Aryls do have the potential for both π-donation and π-backbonding through the filled aryl π-orbitals and empty π* antibonding orbitals.

Alkenes/Alkynes



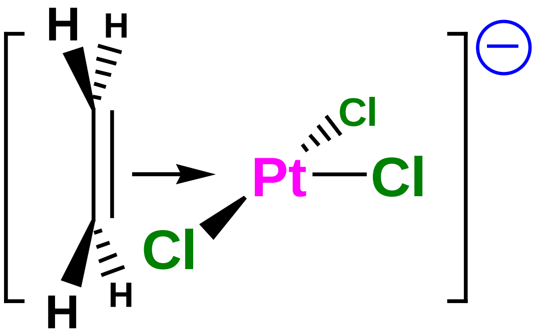
σ-donation via the
filled alkene π-system

π-back donation via the
empty alkene π^*-system

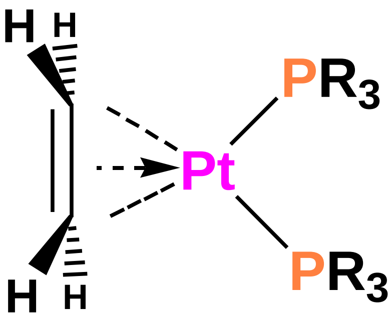
Dewar-Chatt-Duncanson bonding model (1953)

Alkenes are typically relatively weakly coordinating ligands. They are also extremely important substrates for catalytic reactions. The strongest alkene-metal bonds occur with third row metals (as with almost all ligands) and when one can get more π-backbonding to occur.

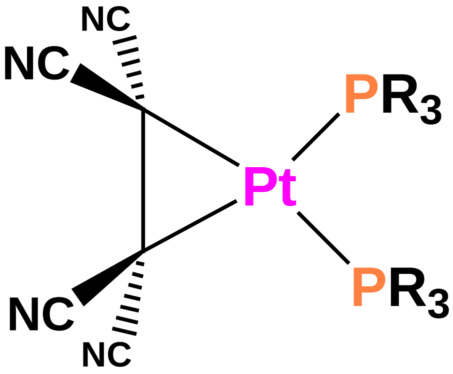
The amount of π-backbonding depends strongly on how electron-rich the metal center is and whether or not there are electron-withdrawing groups on the alkene to make it a better acceptor ligand.



Pt(2+)
C=C = 1.37Å
Zeiss's Salt



Pt(0)
C=C = 1.43Å

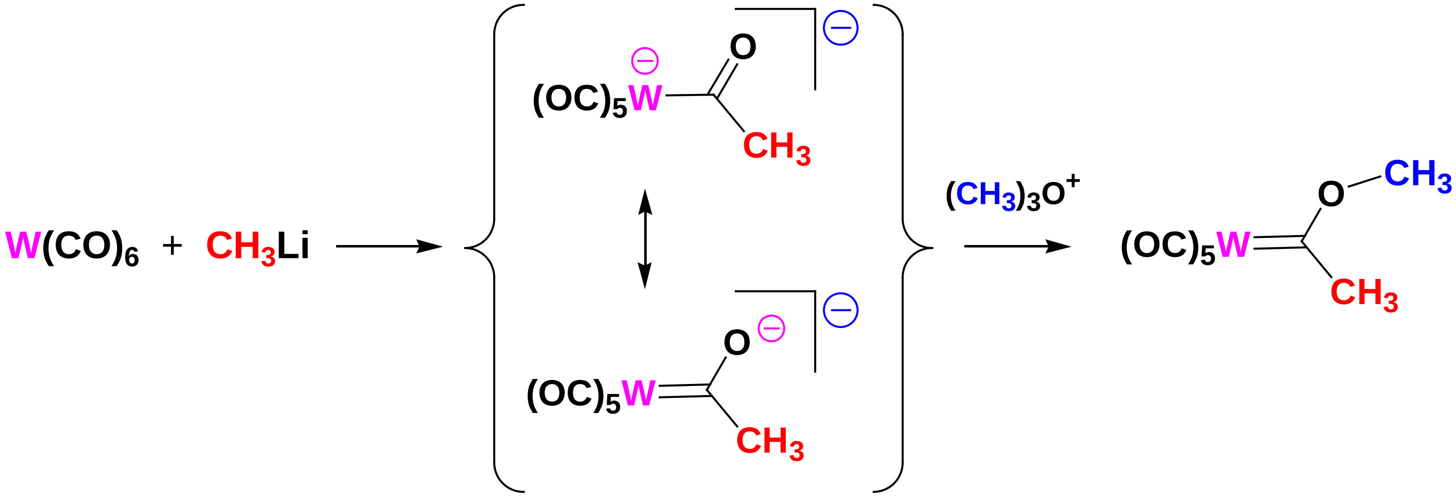


Pt(+2)
C--C = 1.49Å
metallocyclopropane

If the metal is electron-rich enough and/or if there are electron-withdrawing groups on the alkene, one can actually get a formal oxidation of the metal via the transfer of 2e- to the alkene to form a dianionic metallocyclopropane ligand that is now coordinated via two anionic alkyl σ-bonds (thus the assignment of Pt(+2)).

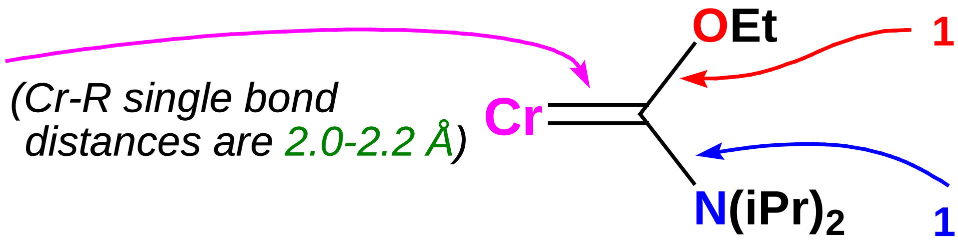
Fischer Carbenes and Carbines

In 1964 Fischer's group prepared the first transition metal carbon double bond, which he called a carbene, after the very reactive neutral organic CR2 fragment.



Ernst O. Fischer
Technical University of Munich,
Germany

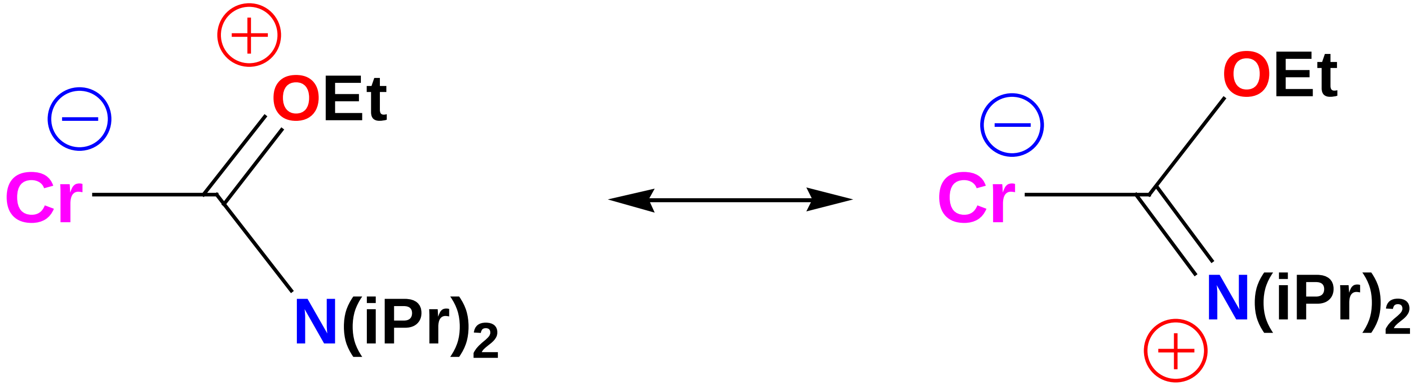
Structure on $(OC)_5Cr{=}C(Et)[N(i\text{-}Pr)_2]$



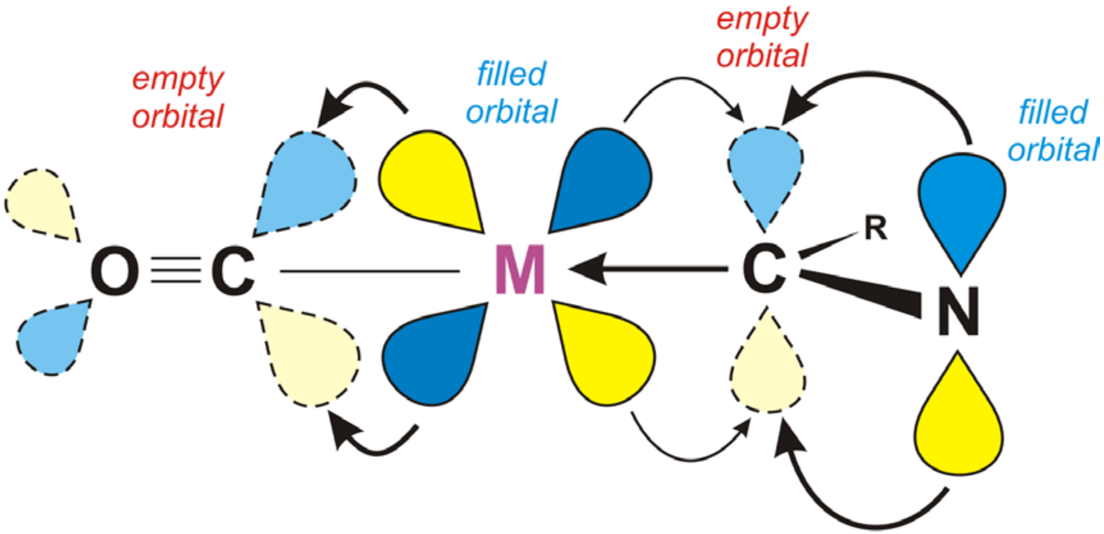
2.13 Å *(Cr-R single bond distances are 2.0-2.2 Å)*

1.35 Å *(normal distance should be 1.41 Å, a 0.06 Å shortening)*

1.33 Å *(normal distance should be 1.45 Å, a 0.12 Å shortening)*



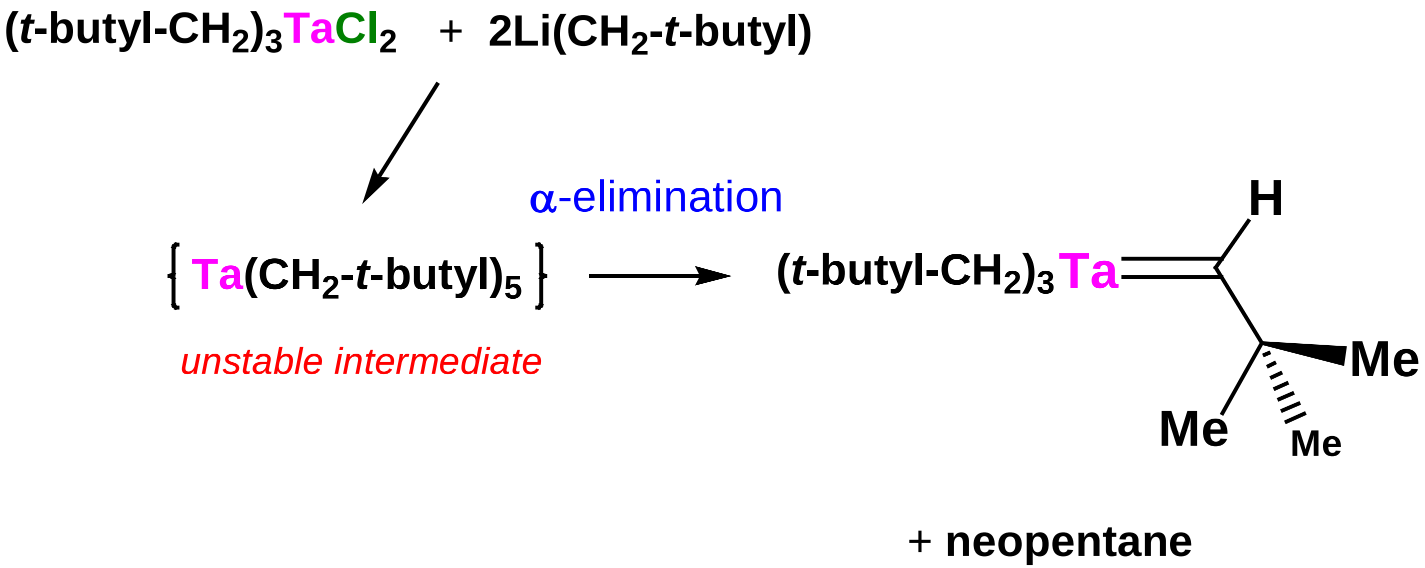
Fischer Carbenes are usually treated as neutral 2e- donor ligands that typically only makes a single bond to the metal (BUT, ***we often draw it as a double bond***!!).



competition for π-backbonding from the metal and the lone pair orbital(s) on the functional group(s) to the carbene empty orbital (N and S the best, then O, Ph, and other π-donating or lone pair containing groups)

Schrock Alkylidenes

In 1973 Richard Schrock, while working at DuPont central research, prepared the first early transition metal complex with a M=C double bond:



$(t\text{-butyl-}CH_2)_3TaCl_2 + 2Li(CH_2\text{-}t\text{-butyl})$

$\{Ta(CH_2\text{-}t\text{-butyl})_5\}$ $\xrightarrow{\alpha\text{-elimination}}$ $(t\text{-butyl-}CH_2)_3Ta{=}$

unstable intermediate

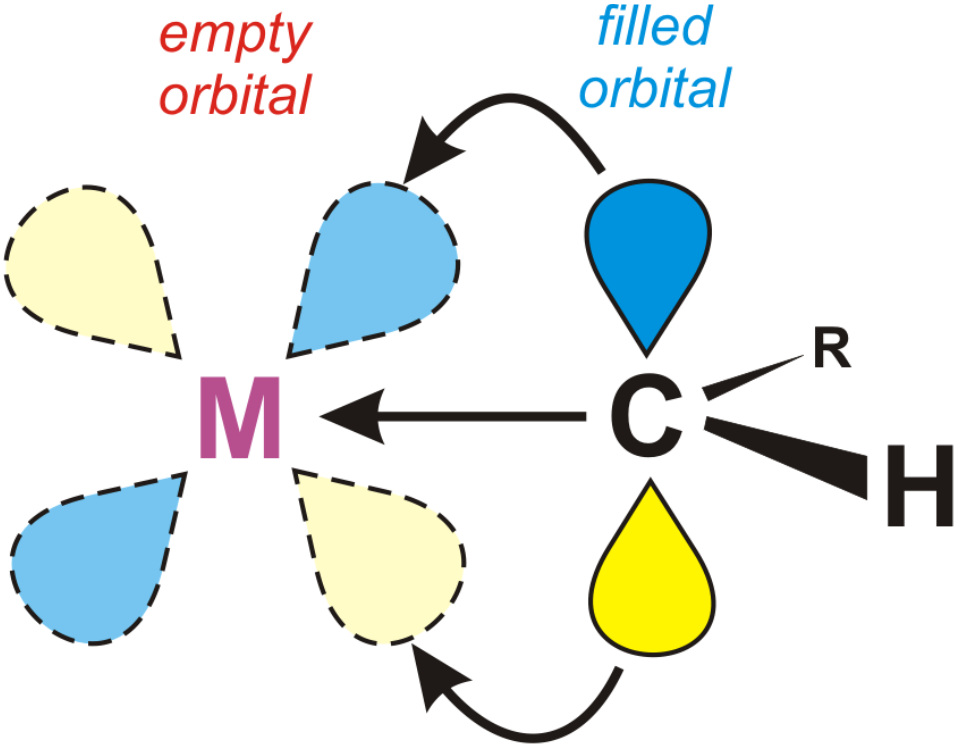
+ **neopentane**

Richard Schrock

MIT

Nobel Prize in 2005

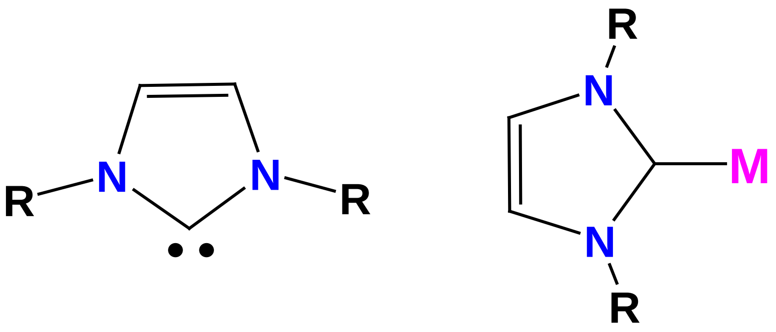
The bonding description commonly used to describe Schrock Alkylidenes is to treat the alkylidene as a dianionic 4e- donor ligand, which is what the electron counting and valence rules from the first chapter would indicate.

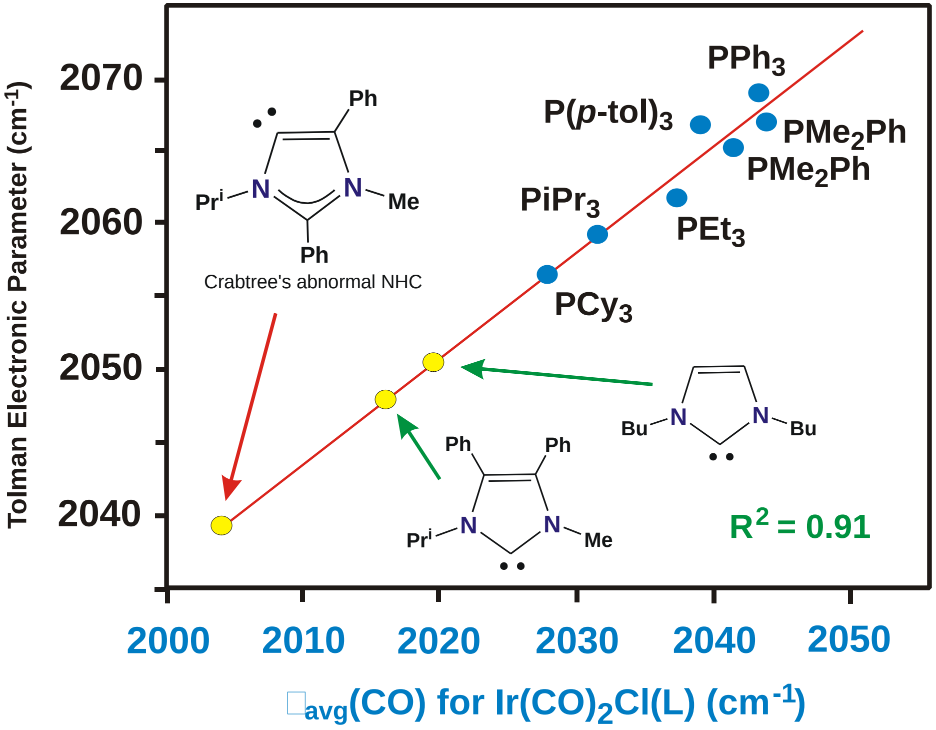


both the sp^2 and p orbitals on the alkylidene are filled (thus the -2 charge) and both can strongly donate to the empty orbitals on the early transition metal (only one empty d orbital is shown)

The “Hot” Carbene: N-Heterocyclic Carbenes (NHC’s)

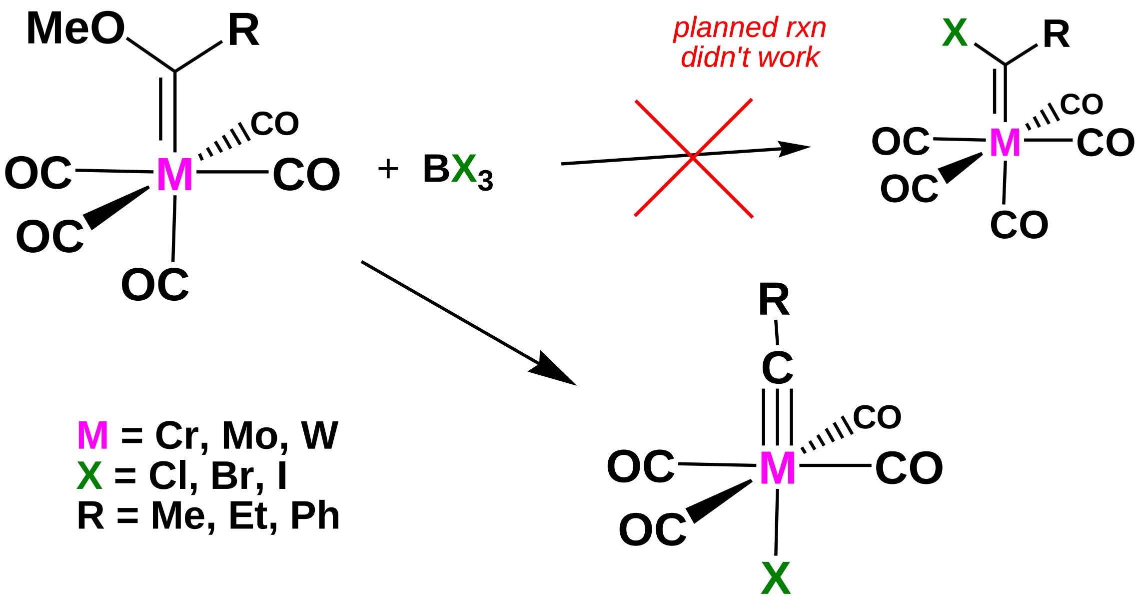
The hottest “new” ligands are imidazole-based N-heterocyclic carbenes (NHC’s). NHC’s are usually strong σ-donors, often exceeding the donor ability of an alkylated PR_3 ligand





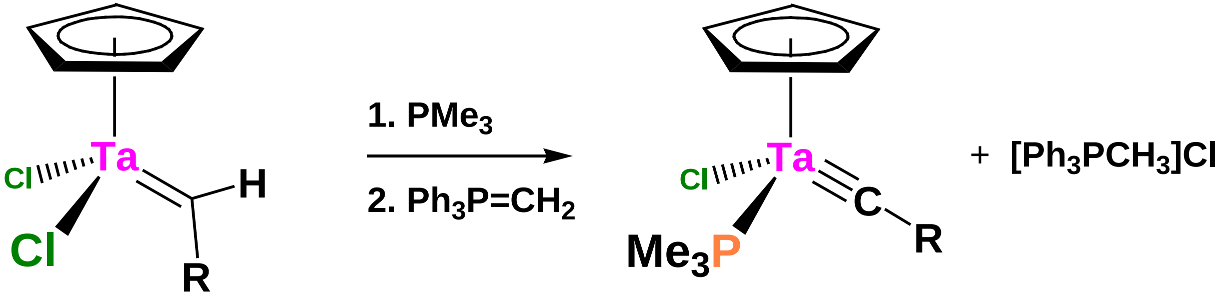
Carbynes/Alkylidynes

E. O. Fischer accidentally prepared the first M≡C-R triple bonded compound in 1973:

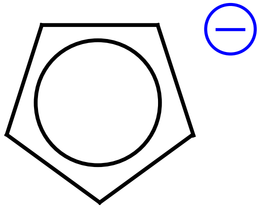


M = Cr, Mo, W
X = Cl, Br, I
R = Me, Et, Ph

Early transition metal versions were prepared first by Schrock in 1978 via α-deprotonation of the alkylidene:

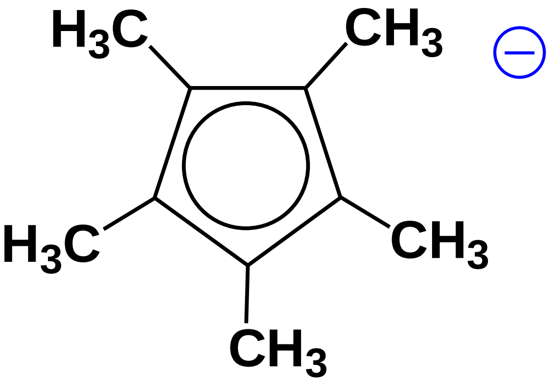


Cyclopentadienyl ligands



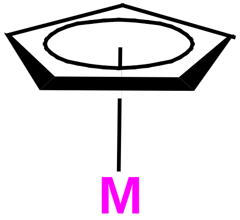
6e-
strong
donor

Cp

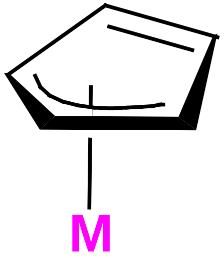


6e- stronger donor
bulky ligand

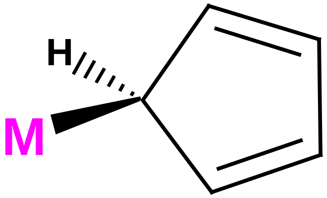
Cp*



η^5



η^3



η^1

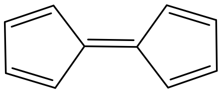
Brief History of Ferrocene:

1901 Synthesis of KC_5H_5 from K and C_5H_6

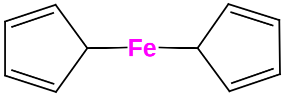
1951 Miller, Tebboth & Tremaine
Sythesis of $Fe(C_5H_5)_2$ from the reaction of C_5H_6 with freshly reduced Fe at 300ºC

1951 Keally & Pauson

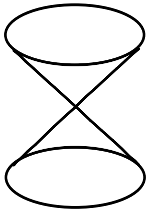
$3C_5H_5MgBr + FeCl_3 \longrightarrow Cp_2Fe +$ fulvalene $+ 3MgBrCl$



They were trying to make fulvalene!
They proposed that they had made:

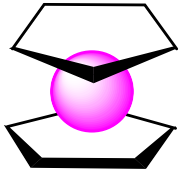


1952 E. O. Fischer proposes a *"Double-cone structure"*
X-ray structural data
Diamagnetism
Chemical behavior



1952 Geoffrey Wilkinson & Robert Woodward: *" Sandwich Structure"*
IR spectroscopy
Diamagnetism
Dipole moment = 0

Woodward noted that the Cp rings were susceptible towards electrophillic substitutions, similar to the aromatic behavior of benzene.

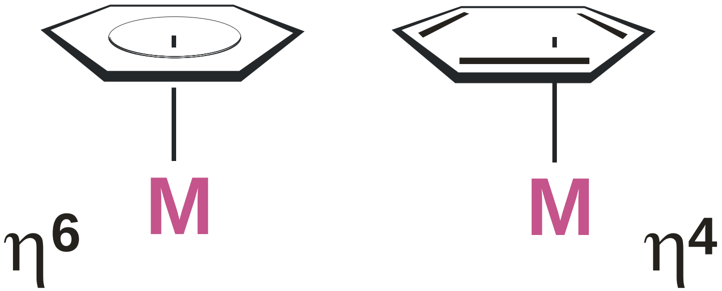


Thus the common name: **ferrocene**

1973 Fischer & Wilkinson receive the Nobel Prize in Chemistry for their "discovery" of ferrocene, which played a key role in opening up the new area of organometallic chemistry.

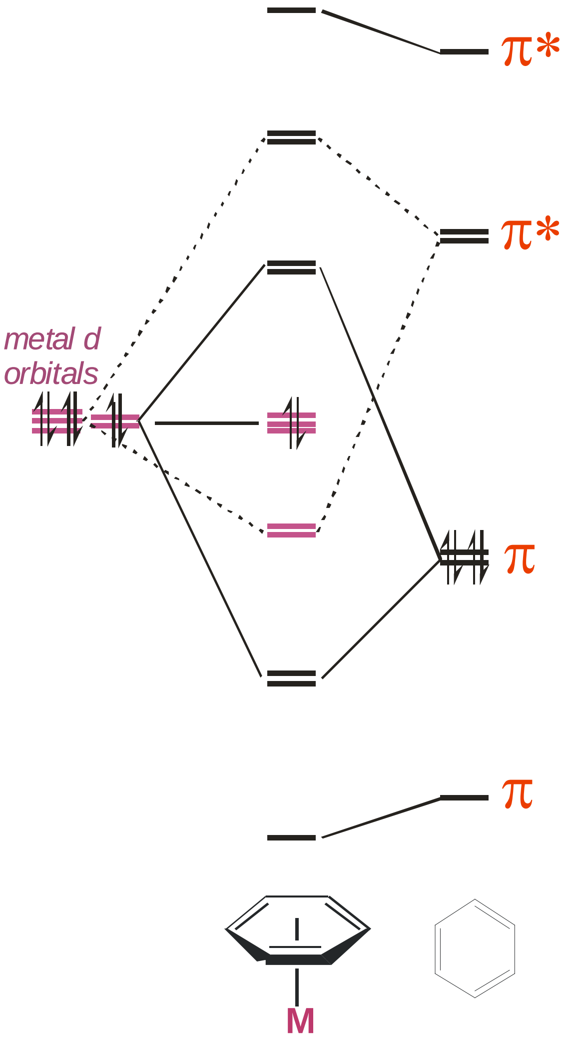
Arenes

Arenes (benzene being the simplest member of this family) typically coordinate in an $\eta 6$ fashion and as such are **neutral 6 e- donors**, although they can adopt lower coordination modes (η^4 and η^2).

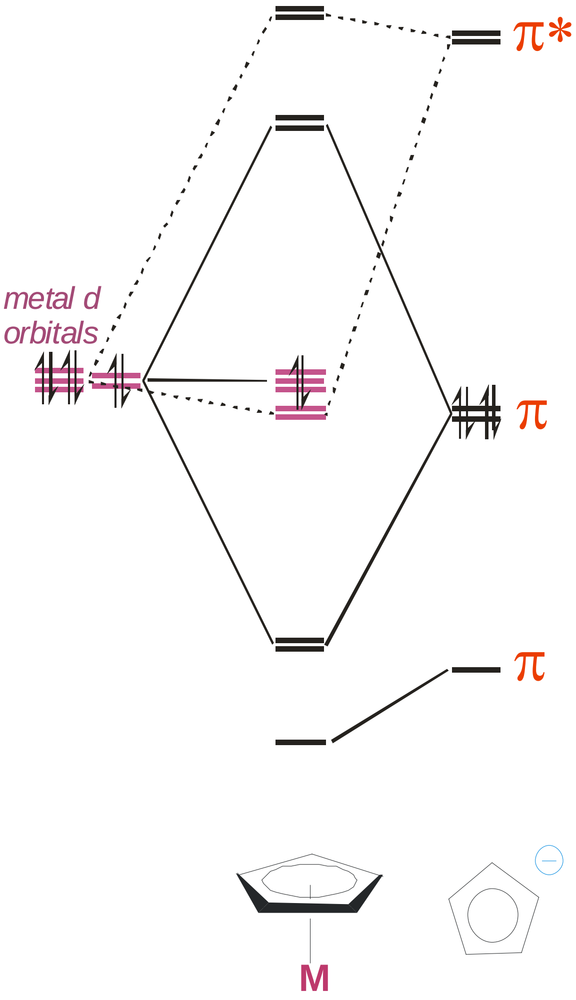


MO Comparison of Cp$^-$ vs. Arene Ligands

Benzene-Metal Complex

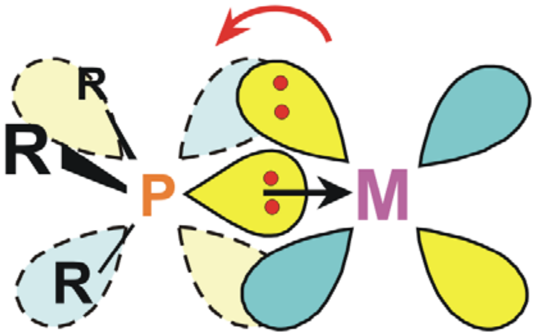


Cyclopentadienyl-Metal Complex



Phosphine Ligands – PR$_3$

empty d orbitals on phosphine can act as π-acceptor orbitals } not very important unless R-groups are electron-withdrawing



neutral 2e⁻ donor

Phosphine ligands

excellent soft-donor ligands with a wide variety of easily adjusted steric and electronic factors

R = carbon groups {
phosphine (US)
phosphane (Germany/Europe)

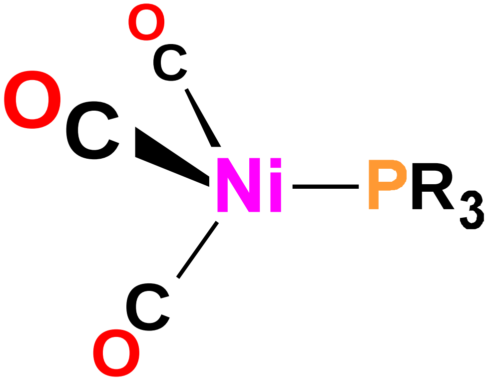
R = OR groups ⟶ phosphite

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

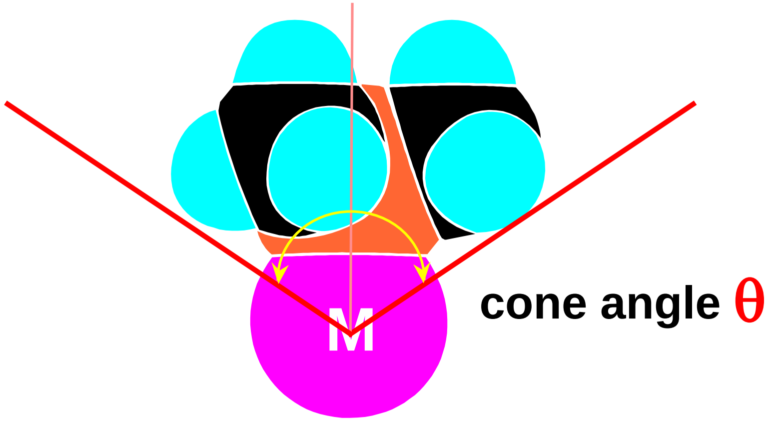


Highest CO stretching frequency:

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:



Reactivity

Ligand Substitution Reactions

> ***"A mechanism is a theory deduced from the available experimental data. The experimental results are facts; the mechanism is conjecture based on those facts"***

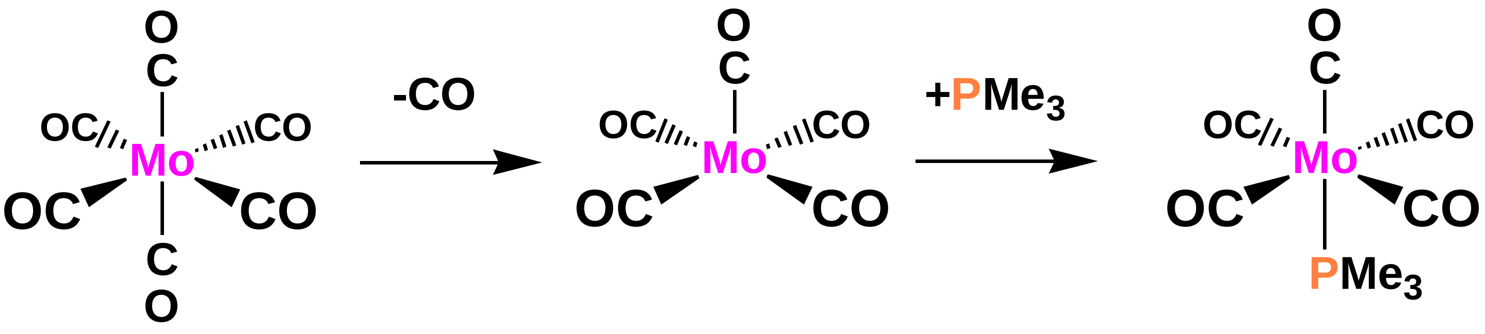
> ***"You can never prove that your mechanism is right - only wrong."***

$$\mathbf{ML}_{n} + x\mathbf{P} \rightleftharpoons \mathbf{ML}_{n-x}\mathbf{P}_{x} + x\mathbf{L}$$

The mechanism of this substitution will almost always depend on whether the parent ML_n complex is coordinatively saturated or not!

A **ligand substitution** can occur either by an ***associative*** or ***dissociative*** route. The exact mechanism depends in large part on the electron-count of the metal complex undergoing the ligand substitution. The simplest case is when one is dealing with an **18e-** metal complex.

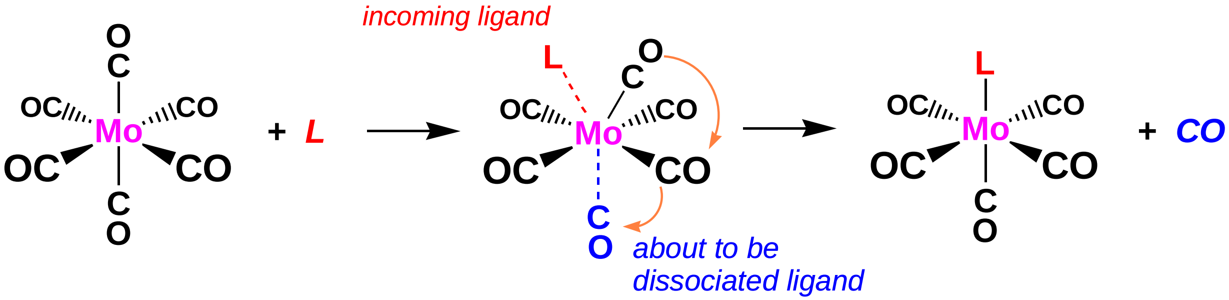
In this case one almost always has a ***dissociative substitution***.



18e- saturated complex

16e- unsaturated complex

18e- saturated complex



incoming ligand

about to be dissociated ligand

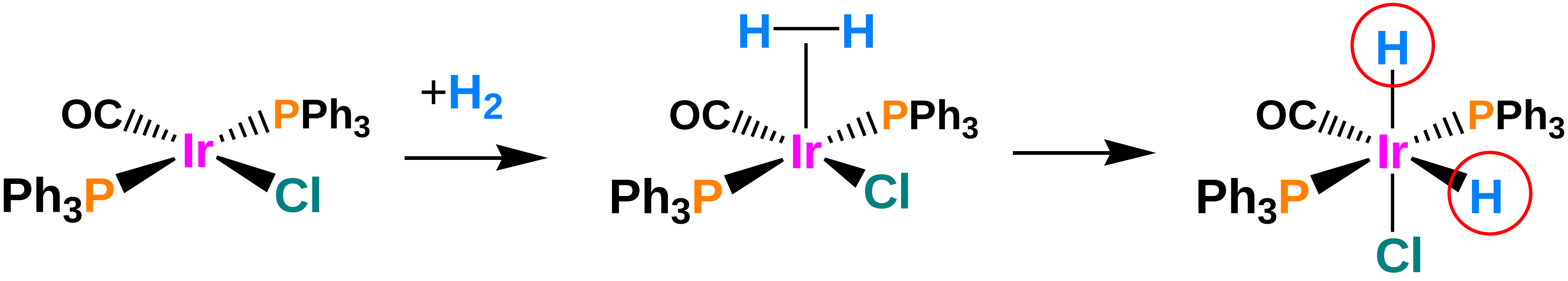
18e- complex

20e- transition state with added ligand

18e- complex

Oxidative Addition/Reductive Elimination

two new anionic hydride ligands



Ir(+1)
16e-

Ir(+1)
18e-

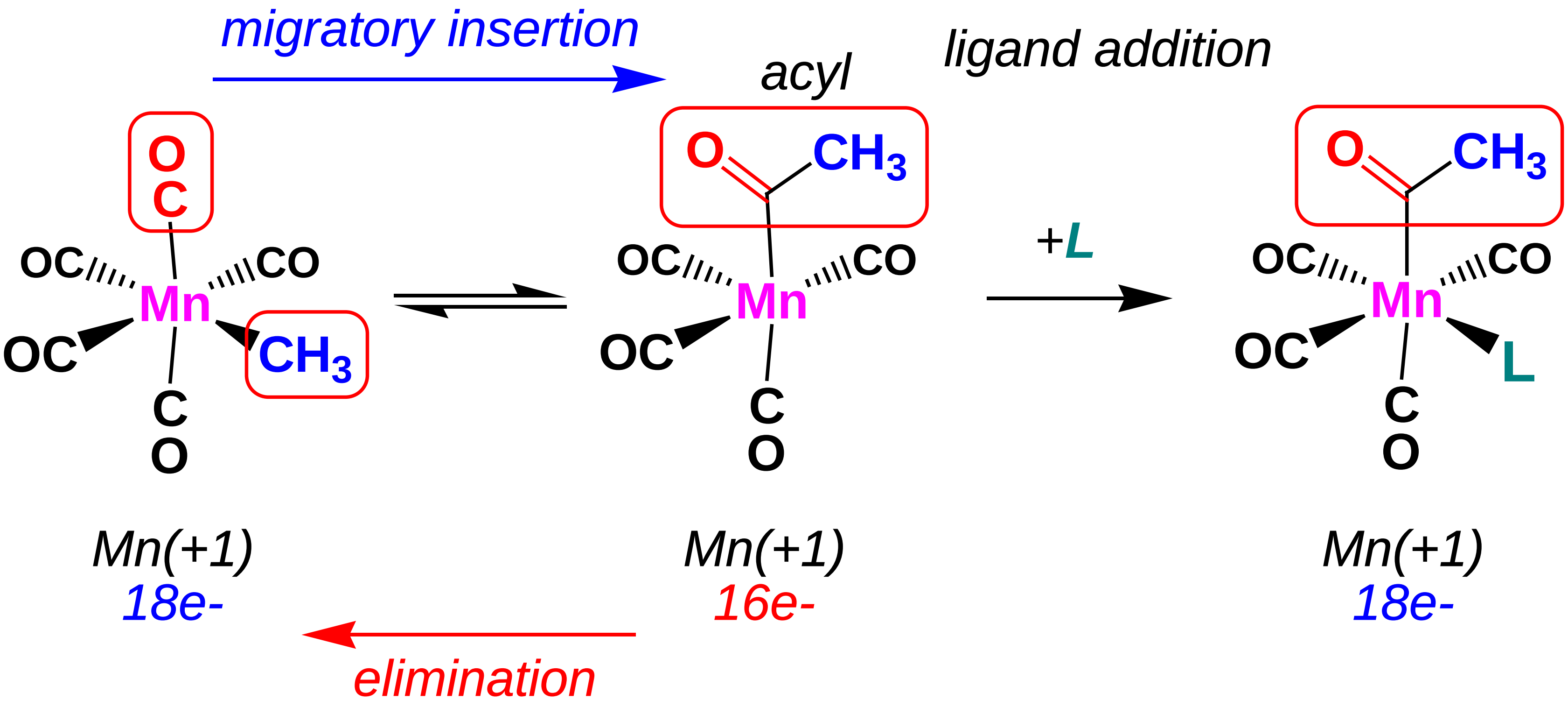
Ir(+3)
18e-

d^0 metals can ***NOT*** do ***oxidative additions***!!

So always electron count the starting and final metal complexes to check out the overall electron-count, metal oxidation state and *d*-electron count!

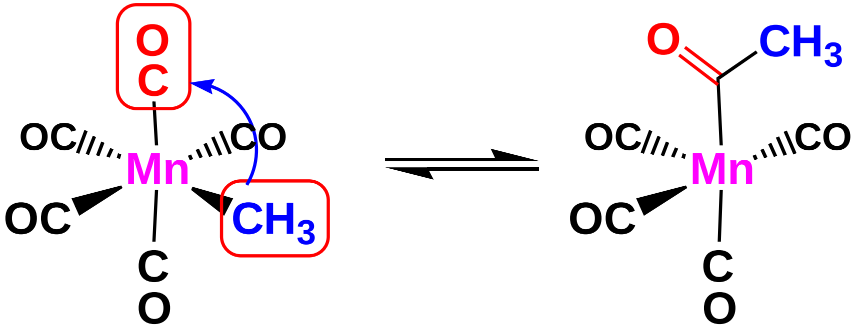
Migratory Insertion & Elimination Reactions

A *migratory insertion* reaction is when a cisoidal anionic and neutral ligand on a metal complex couple together to generate a new coordinated anionic ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another. *There is NO change in the oxidation state or d electron-count of the metal center.*



Migration vs. Insertion

Migration

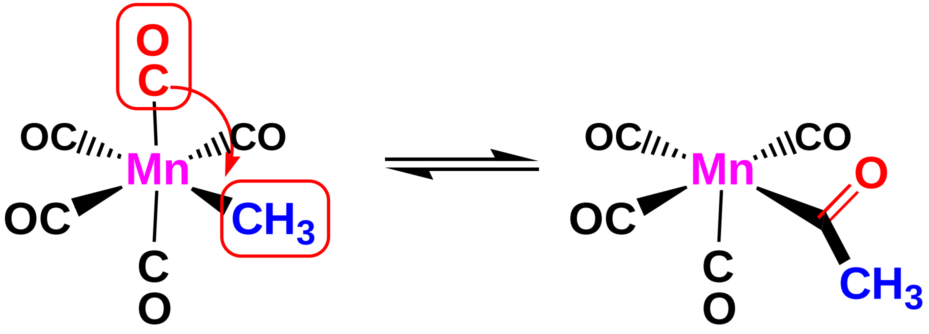


Mn(+1)
18e-

Mn(+1)
16e-

a MIGRATION rxn involves the anionic ligand doing a nucleophillic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

Insertion

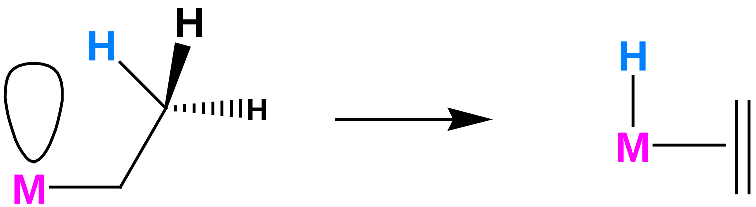


Mn(+1)
18e-

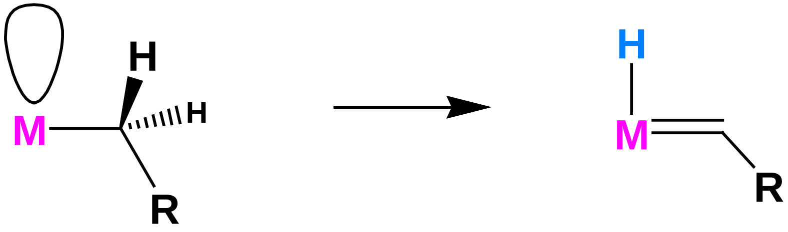
Mn(+1)
16e-

an INSERTION rxn involves the neutral ligand moving over to where the anionic ligand is coordinated and "inserting" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind from where the neutral ligand originally was located.

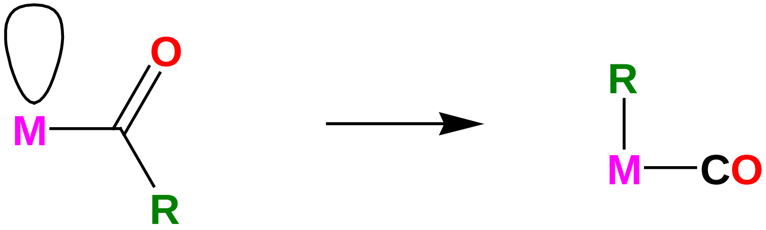
Eliminations



β-hydride elimination



α-hydride elimination



carbonyl elimination
or decarbonylation

The key points are:

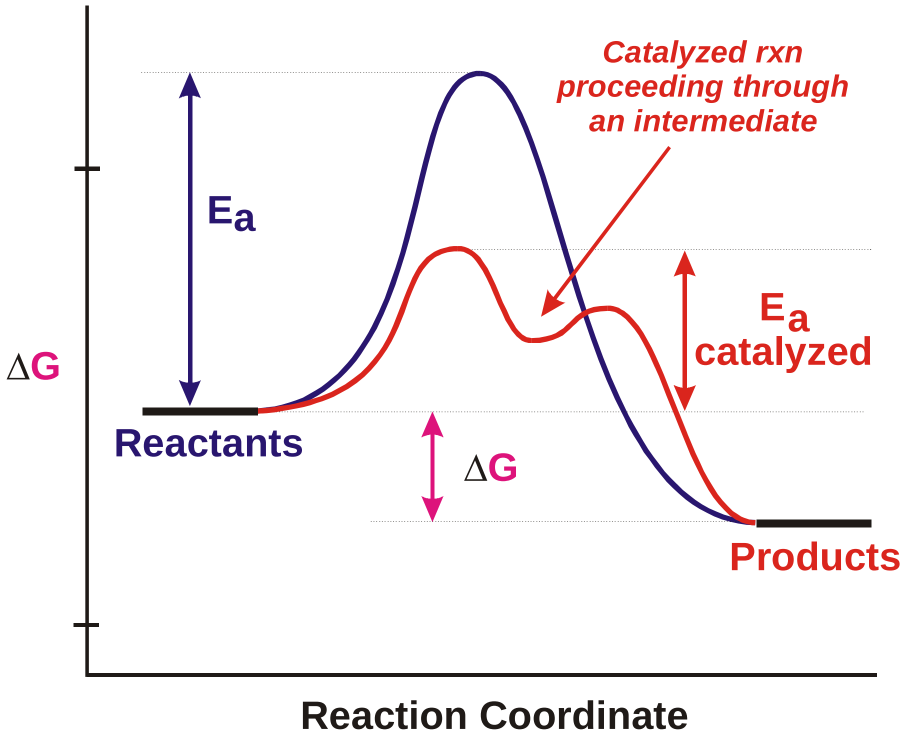
1) **No change in formal oxidation state (exception: alkylidenes)**
2) **You must have an empty orbital that is cisoidal to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.**

Homogeneous Catalysis

Transition Metal Catalysis

$$A + B \xrightarrow{[catalyst]} C$$

A catalyst is a substance that increases the rate of reaction without itself being consumed (but it is involved!) in the reaction. A catalyst speeds up the rate at which a chemical reaction reaches equilibrium. The overall thermodynamics of the reaction is *NOT* changed by the catalyst.



A catalyst provides an alternate mechanism (or pathway) for the reactants to be transformed into products. The catalyzed mechanism has an activation energy that is lower than the original uncatalyzed reaction. An excellent catalyst will lower the activation energy the most.

Some Catalysis Terminology

Turnover (TO) -- one loop through the catalyst cycle. Typically one equivalent of reactant is converted to one equivalent of product (per equivalent of catalyst).

Turnover Frequency (TOF) or Turnover Rate -- the number of passes through the catalytic cycle per unit time (typically sec, min or hrs). This number is usually determined by taking the # of moles of product produced, dividing that by the # of moles of catalyst used in the reaction, then dividing that by the time to produce the given amount of product.

Turnover Number (TON) -- the absolute number of passes through the catalytic cycle before the catalyst becomes deactivated.

Academic chemists sometimes report only the turnover number when the catalyst is very slow (they don't want to be embarassed by reporting a very low TOF), or decomposes quite rapidly.

Industrial chemists are interested in both TON and TOF. A large TON (e.g., 10^6 - 10^{10}) indicates a stable, very long-lived catalyst. TON is defined as the amount of reactant (moles) divided by the amount of catalyst (moles) times the % yield of product.

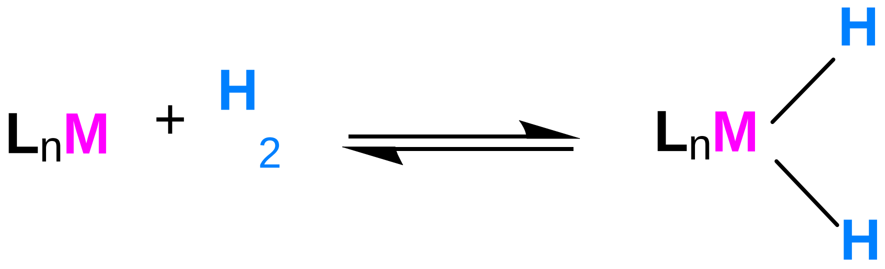
Authors often report mole % of catalyst used. This refers to the fraction of catalyst used relative to the amount of limiting reactant present.

***ee* (enantioselectivity)** – this defines the enantioselectivity of an asymmetric catalyst that produces more of one optically active enantiomer (*R* enantiomer, for example) than the other (*S* enantiomer). **ee** is defined as:

$$ee = \frac{|R - S|}{R + S} \times 100\%$$

A catalyst that makes an equal amount of *R* and *S* enantiomers has 0% ee (a *racemic* mixture). 85% or higher is generally considered a good ee, although that depends on what the best known catalyst can do relative to that being reported.

Hydrogenation



$$L_nM + H_2 \rightleftharpoons L_nM(H)(H)$$

oxidative addition

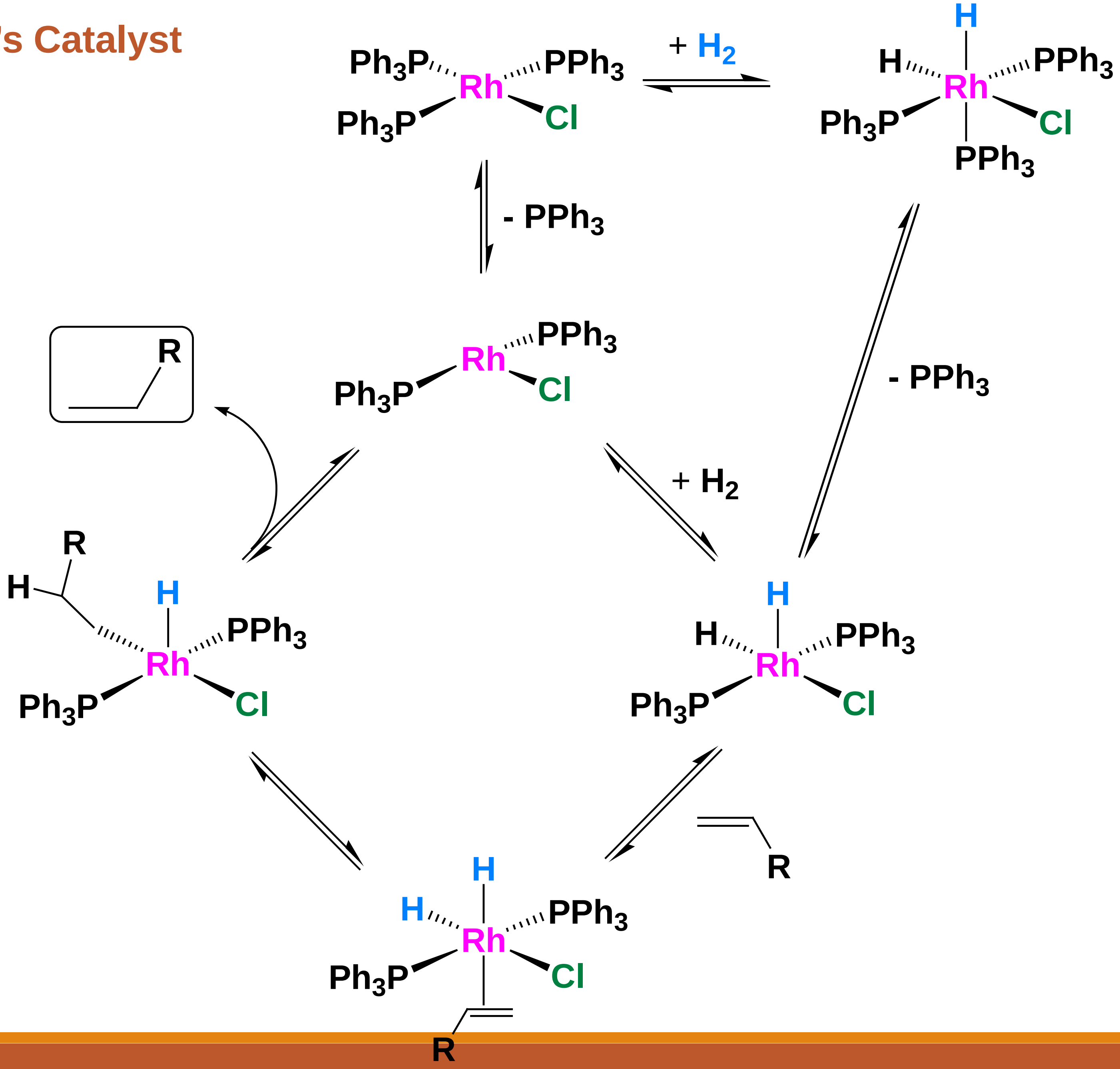
$$L_nM\text{-}X + H_2 \rightleftharpoons L_nM\text{-}H + HX$$

hydrogenolysis

$$L_nM + H_2 + B: \rightleftharpoons [L_nM\text{-}H]^- + H^+{:}B$$

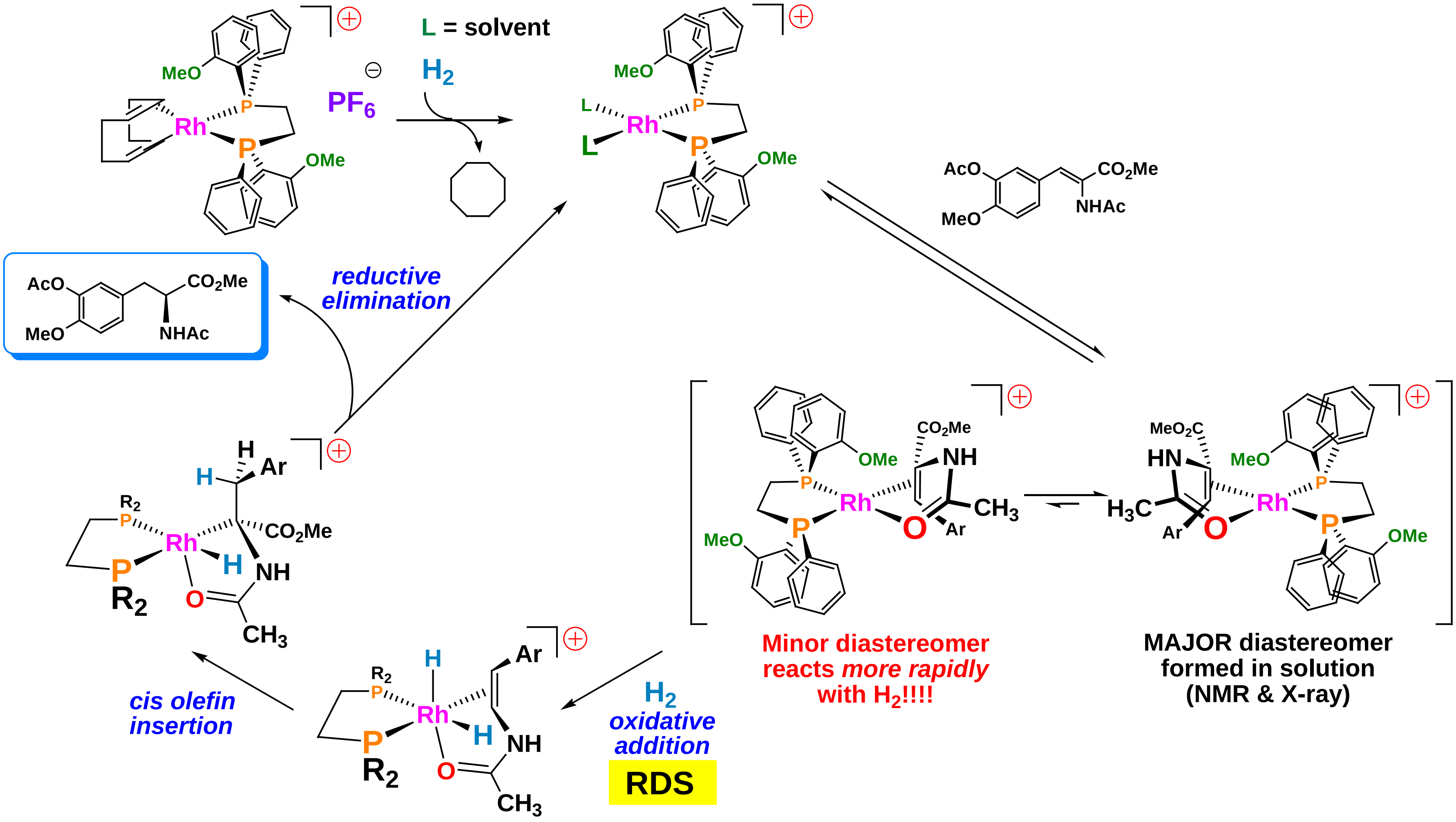
heterolytic cleavage

Wilkinson’s Catalyst



Asymmetric Hydrogenation

Halpern *Science* **1982**, *217*, 401



L = solvent

H_2

reductive elimination

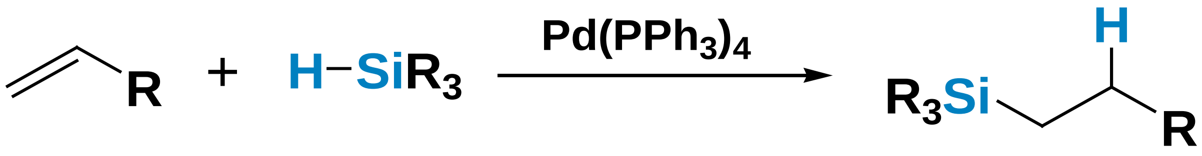
cis olefin insertion

H_2
oxidative addition
RDS

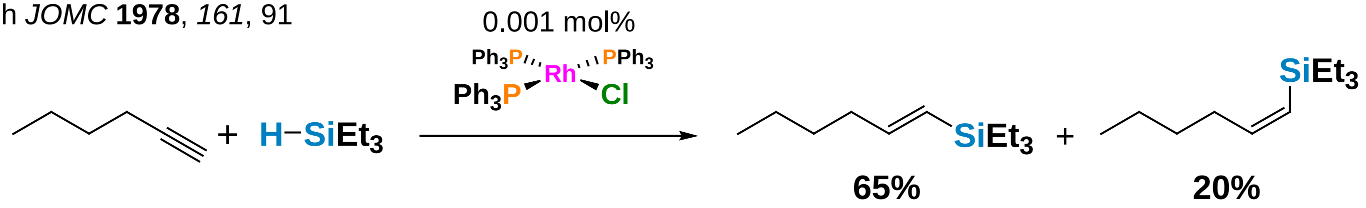
Minor diastereomer reacts *more rapidly* with H_2!!!!

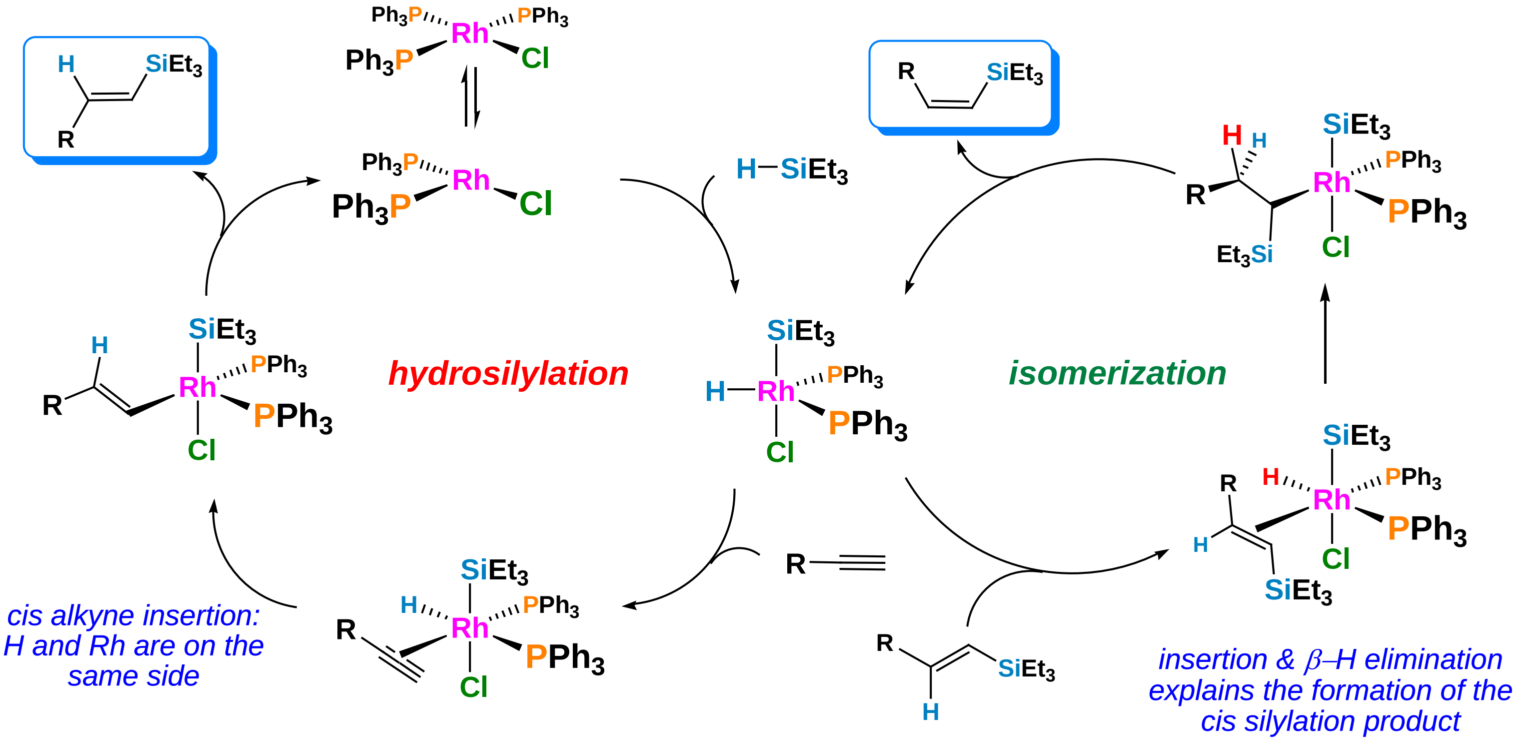
MAJOR diastereomer formed in solution (NMR & X-ray)

Other H-X additions: Hydrosilylation and Hydrocyanation



Parish *JOMC* **1978**, *161*, 91

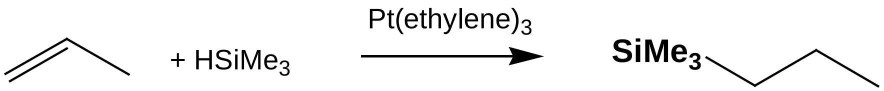




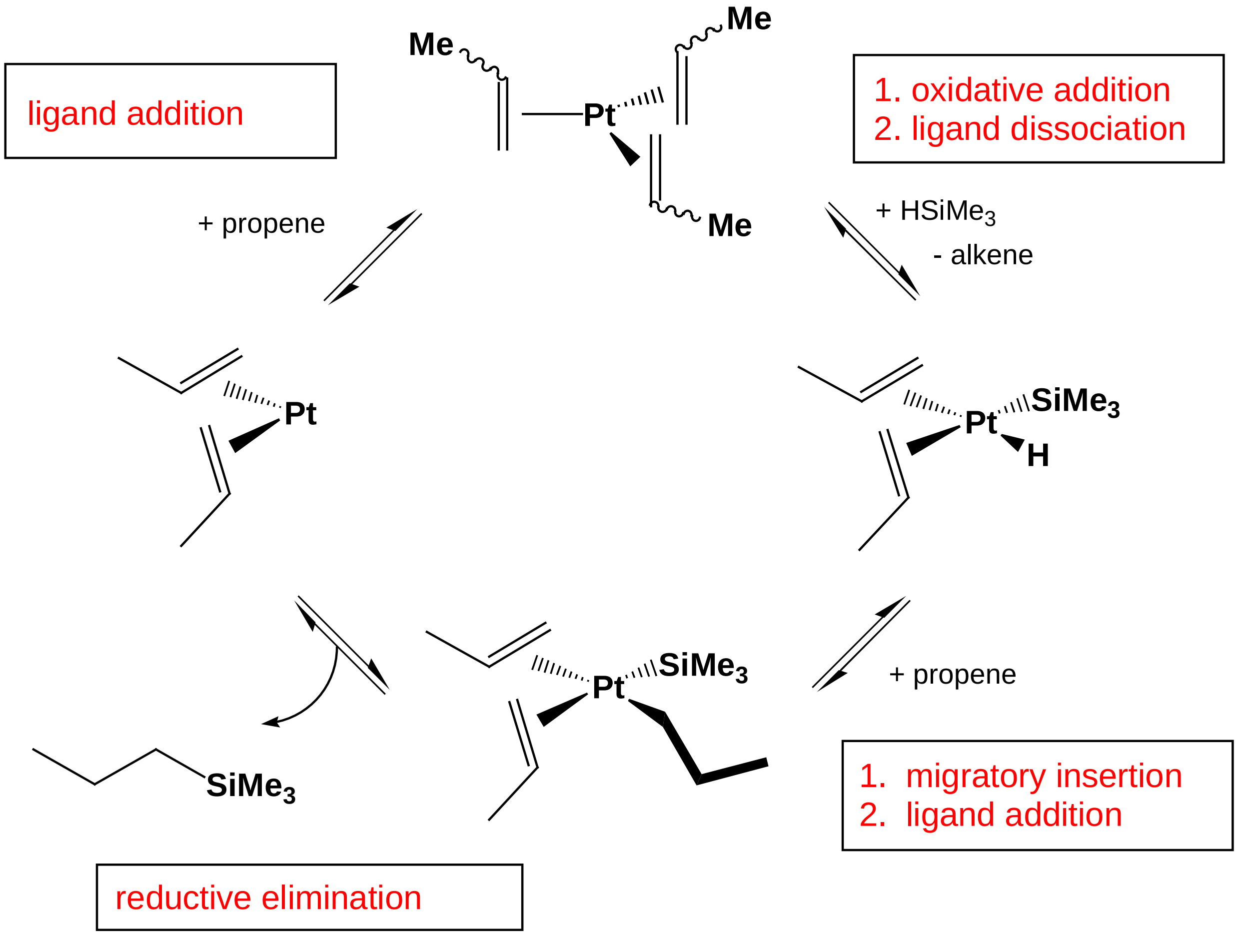
cis alkyne insertion:
H and Rh are on the
same side

insertion & β–H elimination
explains the formation of the
cis silylation product
(In fact, adding catalyst and HSiR$_3$
to the isolated trans product leads
to isomerization)

An example of a Pt-catalyzed reaction is shown below:



Hydrosilylation



ligand addition

1. oxidative addition
2. ligand dissociation

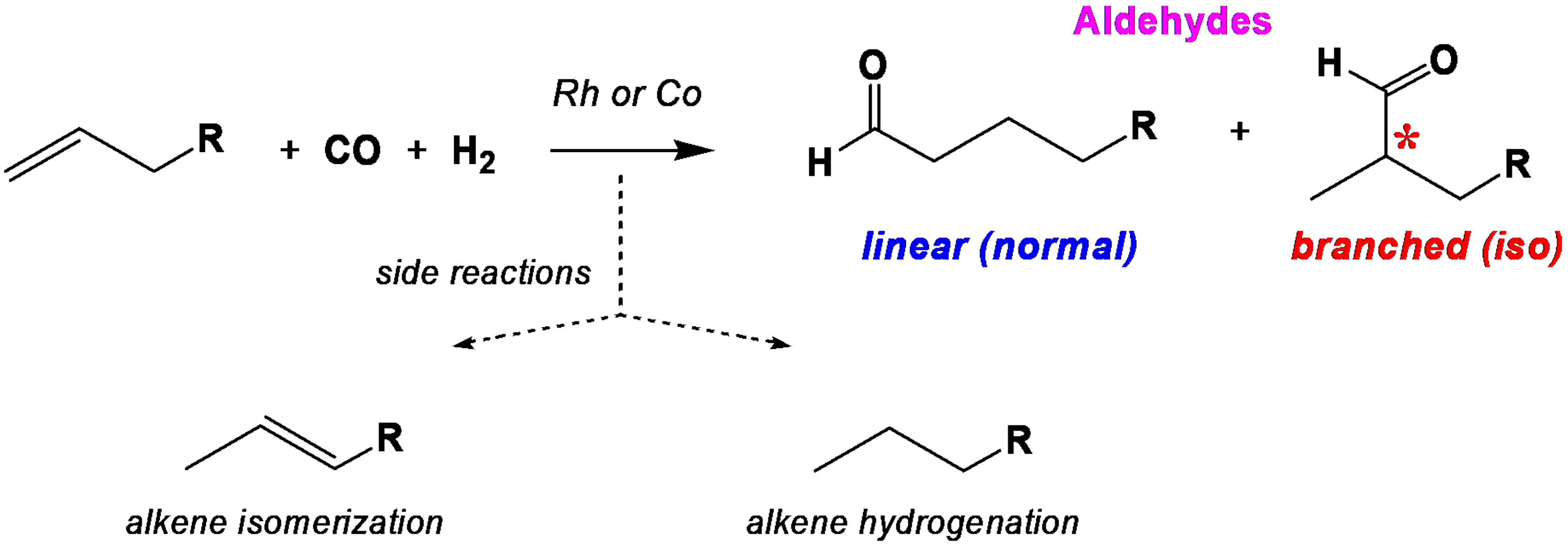
1. migratory insertion
2. ligand addition

reductive elimination

Note that there are different numbers of ligands on the metal. Too many is bad, too few is bad. How can you tell how many to use??

Electron counting is the key, which is presented later in this chapter.

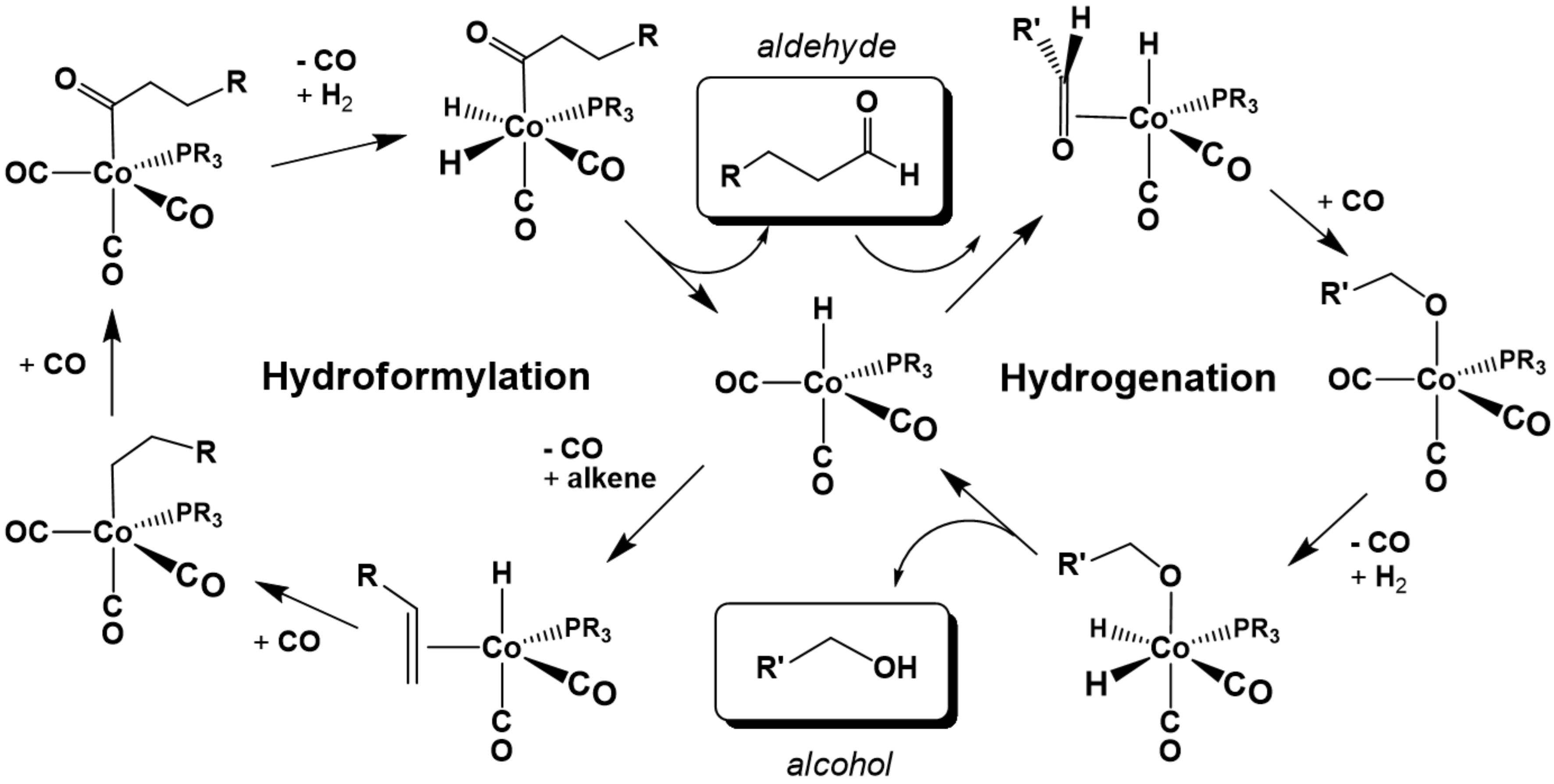
Hydroformylation



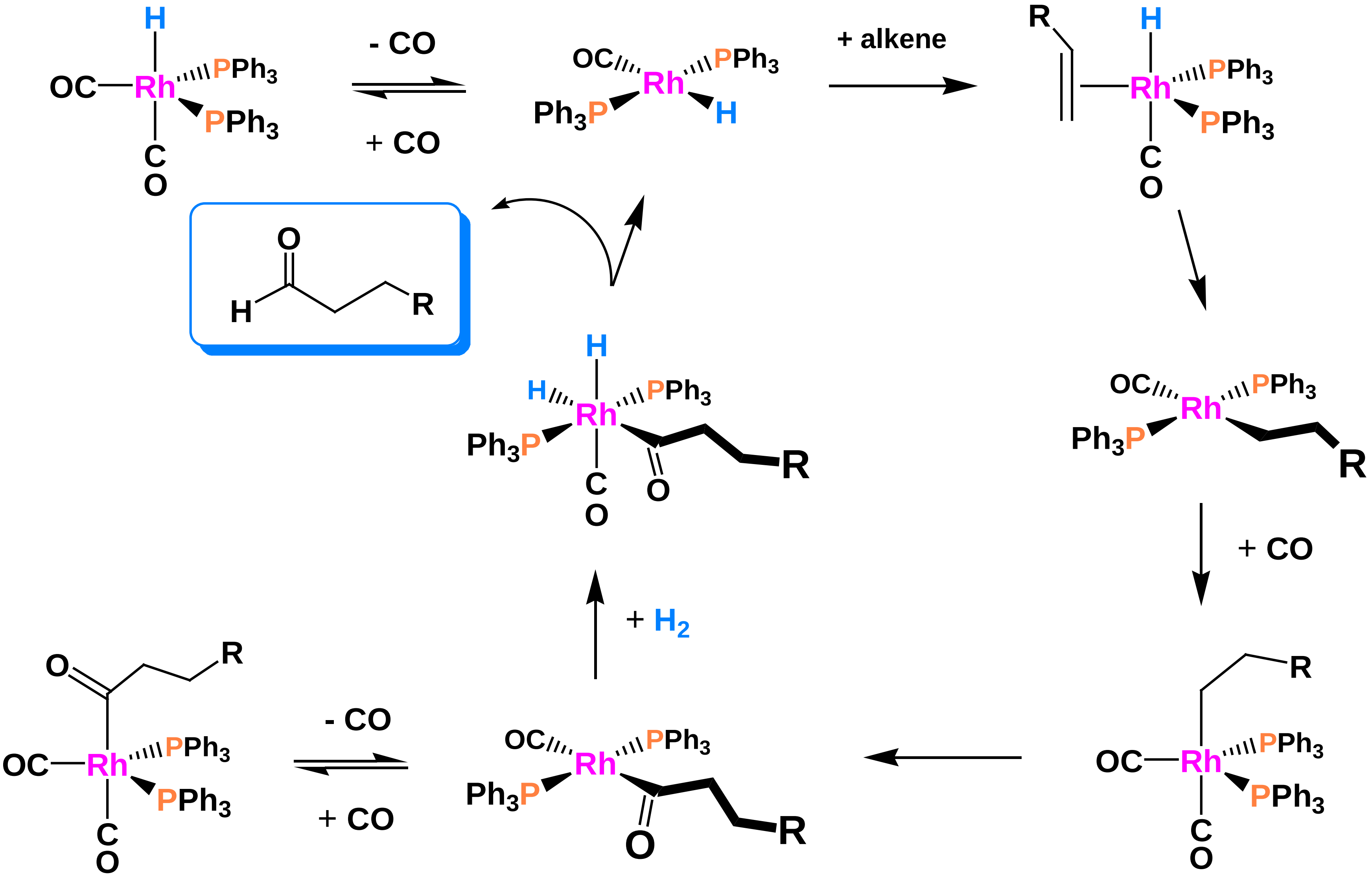
- *** Largest homogeneous catalytic process***
- *** > 15 billion pounds of aldehydes (alcohols) per year***
- ***Commercial catalysts are complexes of Co or Rh***
- ***Selectivity to linear (normal) aldehyde important***

$HCo(CO)_4(PR_3)$ Catalyst System – Phosphine Modified

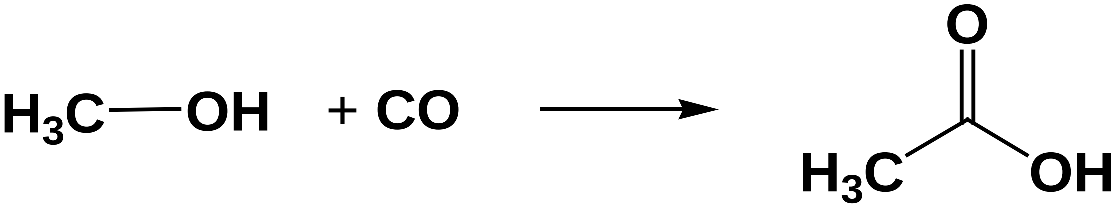
Lynn Slaugh and Richard Mullineaux; Shell Chemical Co.



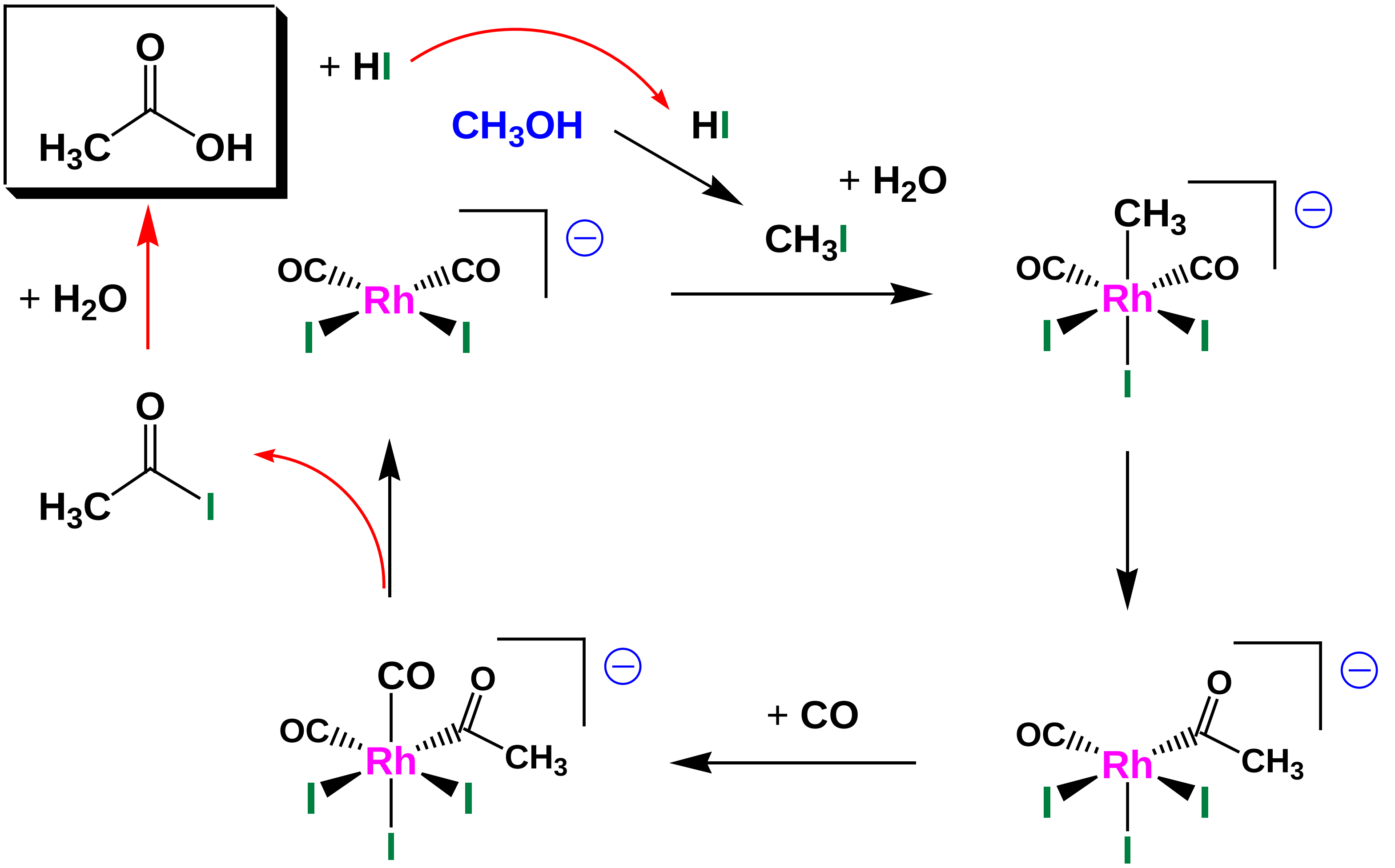
$HRh(CO)(PR_3)_2$ Catalyst System



Acetic Acid Process Monsanto/BP/Celanese



	Cobalt	**Rhodium**
Concentration	~ 10^{-1} M	~ 10^{-3} M
Temperature	~ 230°C	~180°C
Pressure	500-700 atm	30-40 atm
Selectivity	90%	> 99%
H_2 effect	CH_4, CH_3CHO, EtOH byproducts	no adverse effect

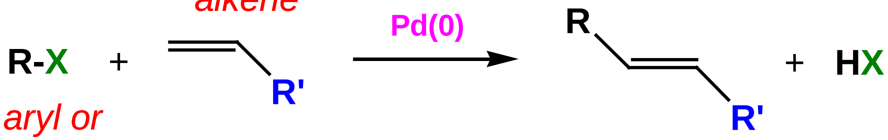


- The reaction is independent of CO pressure
- First order in both rhodium and MeI.
- Rate determining step is the oxidative addition of MeI to the $[Rh(CO)_2I_2]^-$ catalyst.

Pd-Catalyzed C-C Coupling Rxns

Heck reaction:

alkene



aryl or vinyl halide

Stille coupling:

organotin

$$R{-}X + R'{-}SnR_3 \xrightarrow{Pd(0)} R{-}R' + XSnR_3$$

aryl or vinyl halide

Negishi coupling:

organozinc

$$R{-}X + R'{-}ZnR \xrightarrow{Pd(0)} R{-}R' + XZnR$$

aryl or vinyl halide

Suzuki coupling:

organoboron

$$R{-}X + R'{-}B(OH)_2 \xrightarrow{Pd(0)} R{-}R' + XB(OH)_2$$

aryl or vinyl halide

Sonogashira coupling:

alkyne

$$R{-}X + {\equiv}{-}R' \xrightarrow{Pd(0)} R{-}{\equiv}{-}R' + HX$$

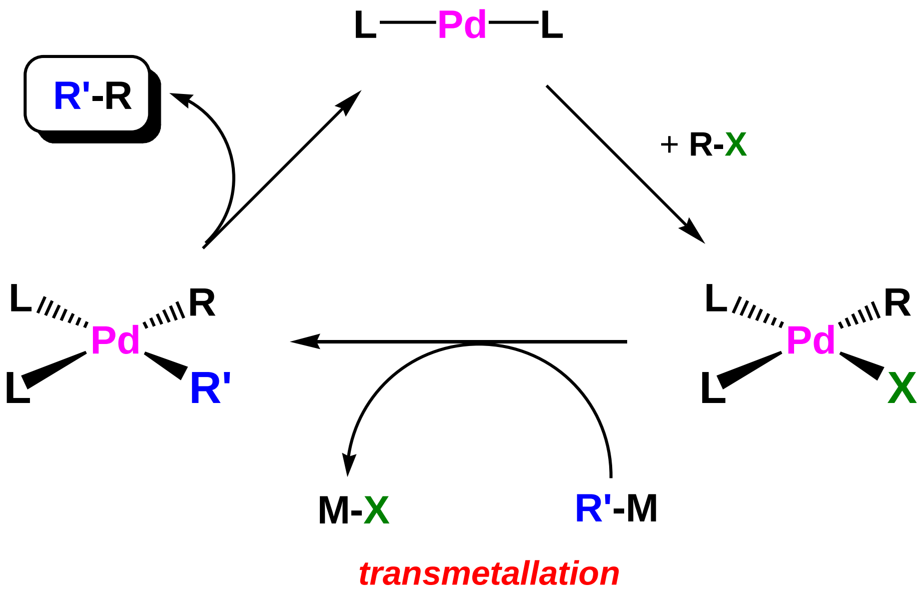
aryl or vinyl halide

Cross-Coupling of Organometallics and Halides

$$\mathrm{R\text{-}X} \quad + \quad \mathrm{R'\text{-}M} \xrightarrow{\mathrm{Pd(0)}} \mathrm{R\text{-}R'} \quad + \quad \mathrm{MX}$$

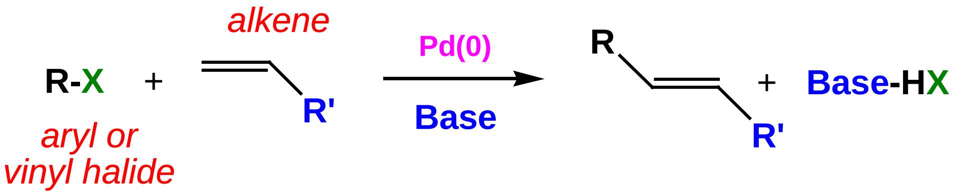
M = MgX, ZrCp$_2$Cl, ZnX, SnR$_3$, B(OR)$_2$, AlMe$_2$, SiR$_3$, Cu,…

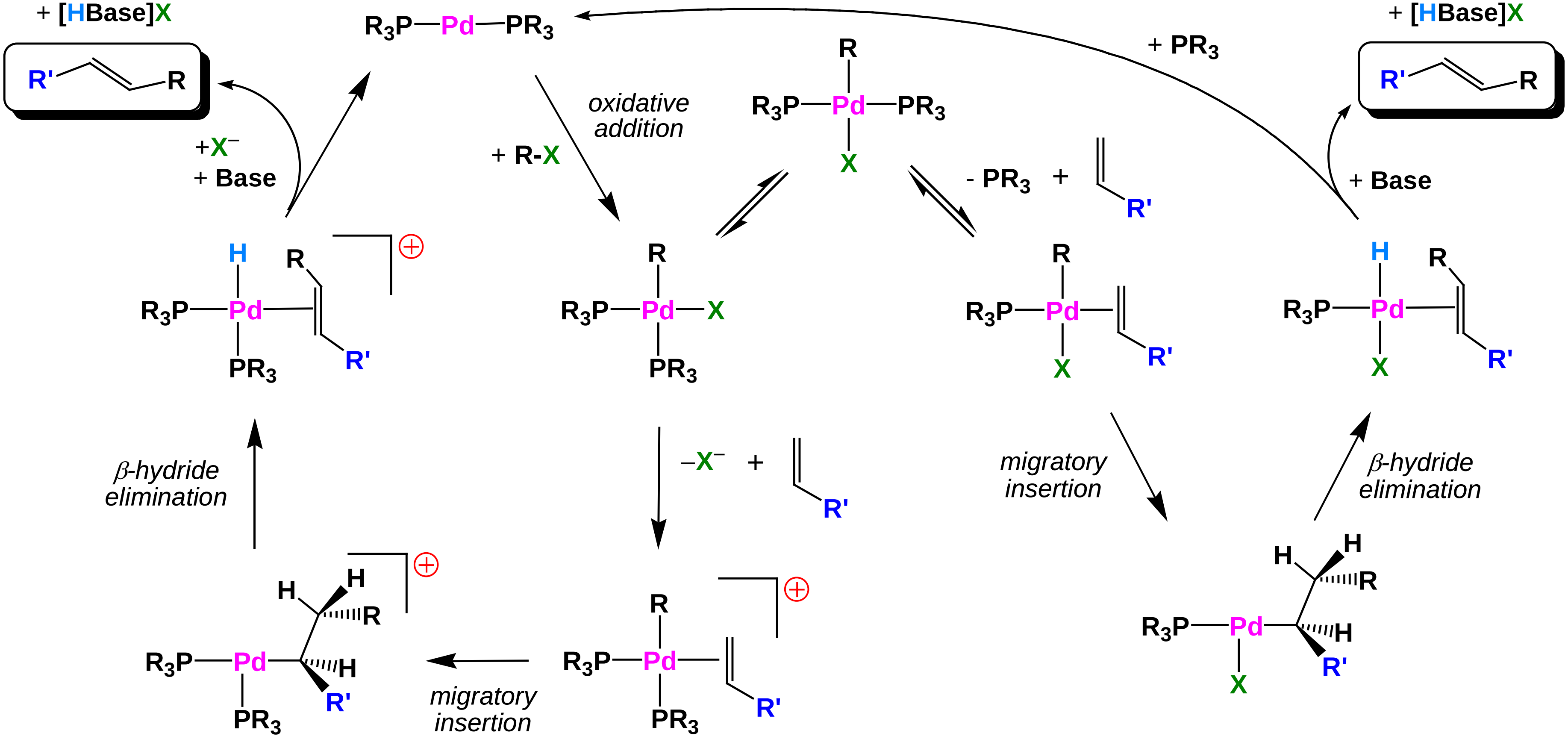
The mechanism involves oxidative addition of the halide or triflate to the initial Pd(0) phosphine complex to form a Pd(II) species. The key slow step is a **transmetallation**, so called because the nucleophile (**R'**) is transferred from the metal in the organometallic reagent to the palladium and the counterion (**X** = halide or triflate) moves in the opposite direction. The new Pd(II) complex with two organic ligands undergoes reductive elimination to give the coupled product and the Pd(0) catalyst ready for another cycle.



The halide partner (**R**–X) must be chosen with care, as β-hydride elimination would decompose the first intermediate during the slow transmetallation step. The choice for **R** is restricted to substituents without β-hydrogen atoms: vinyl, allyl, benzyl, and polyfluoroalkyl halides, triflates, and phosphates have all been coupled successfully.

Heck reaction:





Este material docente ha sido elaborado en el marco de una convocatoria de ayudas para el desarrollo de proyectos de innovación educativa y mejora de la calidad docente (convocado por el Vicerectorat de Polítiques de Formació i Qualitat Educativa de la Universitat de València, en el curso 2017-2018). Código: UV-SFPIE_RMD17-725369

Estas diapositivas forman una parte del contenido docente de la asignatura "Química Inorgánica Avanzada" del Máster Universitario en Química.