Chemistry 424

Organometallic Chemistry

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424 –chem Course
Dr. Waed Z Al-Kayali
First term, 1435-36
Department of Chemistry
King Saud University

Class Meeting: theory **(Sun, Tues)(10-11)** and **(sun 8-9)**
Semester credit hours: 3.0 credits, second term. 1435-1436
Total Contact Hours: 39 hr.
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Office Hours: Sun.11-1
First Mid Term: **Sunday 2/1 (10-11)** Second Mid Term: **Sunday 7/2 (10-11)**

Chemistry 424 - Organometallic Chemistry Syllabus

This course covers the organometallic chemistry of the transition metals with emphasis on basic reaction types and the natural extensions to the very relevant area of homogeneous (and heterogeneous) catalysis.

I. Ligand Systems and Electron Counting

1. Oxidation States, *d* electron configurations, 18-electron *"rule“*
2. Carbonyls, Phosphines & Hydrides
3. σ bound carbon ligands: alkyls, aryls
4. σ/π-bonded carbon ligands: carbenes, carbynes
5. π -bonded carbon ligands: alkene, allyl, cyclobutadiene, arenes, cyclopentadienyl
6. Metal-Metal bonding

II. Reaction chemistry of complexes

1. Reactions involving the gain and loss of ligands
2. Reactions involving modifications of the ligand
3. Catalytic processes by the complexes

Recommended Book: ***"The Organometallic Chemistry of the Transition Metals"*** **by Robert Crabtree (4th Edition, Wiley).**

Reference Book: ***"The Principles and Applications of Transition Metal Chemistry"*****, by Collman, Hegedus, Norton and Finke**

Study Groups: The class will form study groups of 3 students to work together on the homework (each student hands in their own copy of the HW) and to answer questions in class (work alone on quizzes & exams).

Course Construction:

Two 50 min Exams: 2/1, 7/9	40%
Final Exam (2 hrs):	40%
Homeworks:3-5 homeworks	10%
Quizzes: Two quizess	10%

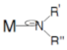
Organometallic Chemistry

Definition: *Definition of an organometallic compound*

Anything with M–R bond R = C, H (hydride)

Metal (of course) Periodic Table – down & left electropositive element (easily loses electrons)

NOT:



- Complex which binds ligands via, N, O, S, other M- carboxylates, ethylenediamine, water
- M–X where complex has organometallic behavior, reactivity patterns e.g., low-valent

oxidation State

d^n for compounds of transition elements n***d < (n+1) s or (n+1) p in compounds***

e.g., 3***d < 4s or 4p***

I. Ligand Systems and Electron Counting

Fundamentals You Need to Know:

- **Electronegative/Electropositive concepts**

Where do the partial positive and negative charges in a molecule reside? This is important for determining how much electron (e-) density will be donated from a ligand to a metal and where a nucleophile or electrophile will likely attack for chemical reactions.

- Lewis dot structures and valence electron counts

- Important for determining the number of electrons on a ligand and what the charge of the ligand is.
- We almost always deal with ligands with **even #'**s of electrons.
- If a ligand has an **odd #** of electrons we **add additional** electrons to get to an even #, usually to form a closed shell electron configuration with a formal negative charge(s).
 Exception = Boron.

- **Oxidation States of the central atom (metal)**
- **Organic line notation for drawing structures**

Electron Density is the presence of higher energy valence electrons around an atom.

Electrons are represented by a probability distribution spread out over a region of space defined by the

orbital: *s*, *p*, *d*, *f*, and/or

hybrid orbitals such sp^3, sp^2, *sp*, etc.

Atoms with quite a few valence electrons such as Pt(0) d^{10} and/or contracted orbitals have a ***high electron density*.**

Atoms with fewer valence electrons (e.g., Na^+) and/or diffuse orbitals (electrons spread out over a larger region of space) can be considered to have ***low electron densities***.

**** Do not confuse electron density with electronegativity**.

Electron-rich: Atoms that are willing to readily donate electron pairs to other atoms are called electron rich.

Ease of ionization is another property associated with electron-rich atoms.

The willingness to share or donate electron pairs is related to

lower electronegativity,

larger numbers of valence electrons,

good donor groups on the atom in question,

negative charges,

or some combination of these factors.

Using organic terminology I would consider an electron-rich atom to be a good **nucleophile** (electron pair donating).

Electron-deficient (poor): Atoms that are NOT willing to donate or share electron pairs to other atoms are called electron deficient (poor).

These atoms typically have

lower lying empty orbitals that can accept electron pairs from other atoms.

The un-willingness to donate or share electron pairs could be caused by:

high electronegativity,

cationic charge(s),

lack of electron pairs,

or some combination of these.

I would consider many (but not all) electron-deficient atoms/molecules to be good **electrophiles** (electron-pair accepting) and certainly poor donors.

Fluoride anion, F^-:

This anion has **high electron density** due to

the negative charge,

filled octet of electrons,

and **small size.**

But NOT electron-rich, meaning not good electron donor.

The extremely **high electronegativity** of a fluorine atom means that it desperately wants to pick up an extra electron to form the fluoride anion, which is extremely stable.

The **filled valence orbitals are fairly low in energy** for F^- and generally **poor donors**.

It is certainly **not electron-deficient** as it doesn't have any **low-lying empty orbitals** and does not want to accept any more electrons. It is **not electron-rich** either since it is a **very poor nucleophile** and generally a **poor ligand** for most metals

Methyl anion, CH_3^-: This anion is very **electron-rich** and a **powerful nucleophile**. The electron-richness comes from:

the **lower electronegativity** of carbon,

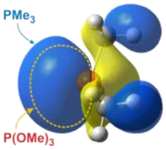
and the **high energy** of the anionic ***sp^3***-hybridized lone pair that makes it a strong donor group.

PMe_3 vs. $P(OMe)_3$:

The **methyl groups** are considered to be **electron donating** making the P center more electron-rich.

The **methoxy groups** are **electron-withdrawing** due to the electronegative oxygen atoms, making the P center more electron deficient.

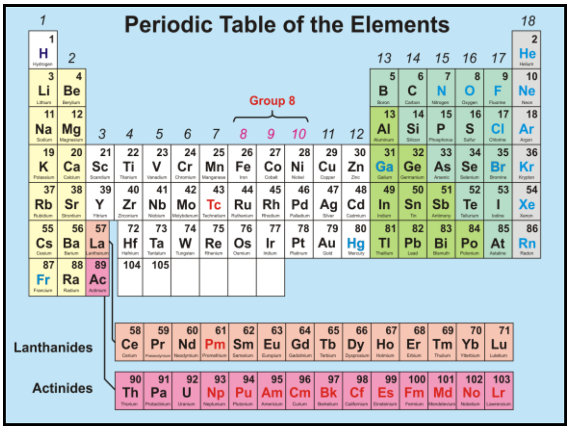
Note the **higher energy** of the P lone pair (highest occupied molecular orbital, HOMO), **greater spatial extent** (generally better overlap with metal d-orbitals), and **lower positive charge** on P for PMe_3 relative to $P(OMe)_3$.



MO plot of the lone pair orbital (HOMO) for PMe_3. Dashed outline indicates the spatial extent of the lone pair for $P(OMe)_3$.

PMe_3
HOMO = –5.03 eV
Charge on P = +0.22

$P(OMe)_3$
HOMO = –7.40 eV
Charge on P = +0.75



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																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104	105													

Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

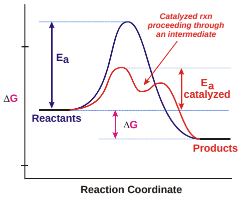
Transition Metal Catalysis

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

A catalyst is a substance that increases the rate of rxn without itself being consumed (but it is involved!) in the reaction.

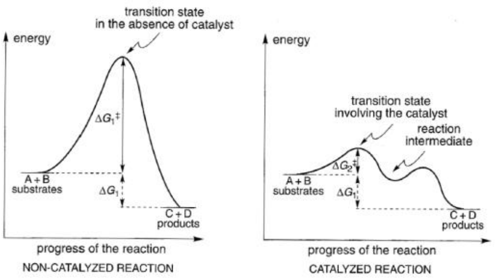
A catalyst speeds up the rate at which a chemical reaction reaches equilibrium.

The overall thermodynamics of the rxn is ***NOT*** changed by the catalyst. Therefore, very endothermic (*non-spontaneous*) reactions are usually NOT suitable for catalytic applications.



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 rxn. An excellent catalyst will lower the activation energy the most.

A Catalyst Significantly Lowers the Reaction Activation Energy



Products of un-catalyzed and catalyzed reactions may be different

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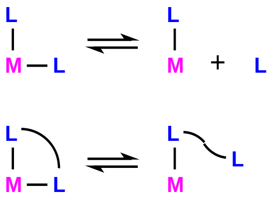
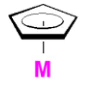
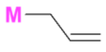
Chelate Effect: "chelate" is from the Greek meaning "claw" or to grab on to. Since most metal-ligand bonds are relatively weak compared to C-C bonds. M-L bonds can often be broken rather easily, leading to dissociation of the ligand from the metal.



From a ***kinetic viewpoint***, if one of the ligands dissociates, it will remain close enough to the metal center to have a high probability of re-coordinating before another ligand can get in an bind. From a ***thermodynamic*** *viewpoint*, by tethering two donor ligands together, one removes most of the entropic driving force for dissociating a ligand and thus making more particles in solution (more disorder).

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.

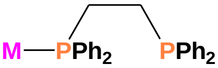
η^x values for all-carbon based ligands where the x value is odd usually indicate *anionic* carbon ligands (e.g., η^5-Cp, η^1-CH_3, η^1-allyl or η^3-allyl, η^1-$CH=CH_2$). The # of electrons donated (ionic method of electron counting) by the ligand is usually equal to $x + 1$. Even η^x values usually indicate *neutral* carbon π-system ligands (e.g., η^6-C_6H_6, η^2-$CH_2=CH_2$, η^4-butadiene, η^4-cyclooctadiene). The # of electrons donated by the ligand in the even (*neutral*) case is usually just equal to *x*.

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



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)

Ordering in Formula

- Formulas with Cp (cyclopentadienyl) ligands, the Cp usually comes first, followed by the metal center: Cp_2TiCl_2

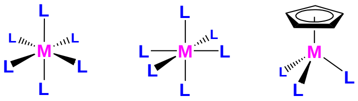
- Formulas with hydride ligands, the hydride is sometimes listed first, $HRh(CO)(PPh_3)_2$ and Cp_2TiH_2

- Bridging ligands are usually placed next to the metals in question, then followed by the other ligands:
$Co_2(\mu\text{-}CO)_2(CO)_6$, $Rh_2(\mu\text{-}Cl)_2(CO)_4$, $Cp_2Fe_2(\mu\text{-}CO)_2(CO)_2$

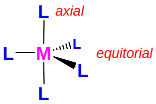
- Anionic ligands are often listed before neutral ligands: $RhCl(PPh_3)_3$, $CpRuCl(=CHCO_2Et)(PPh_3)$ (neutral carbene ligand), $PtMe_2(C{\equiv}CR)(bipy)$.

Common Coordination Geometries

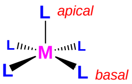
6-Coordinate: ***Octahedral*** **(90° & 180° angles)**



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

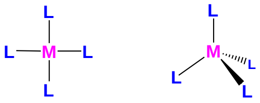


(90° & 120°)



(~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.

Problem: **Sketch structures for the following:**

a) CpRuCl(=$CHCO_2Et$)(PPh_3)

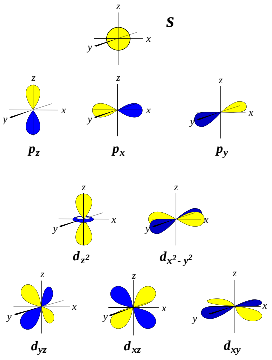
b) $Co_2(\mu\text{-}CO)_2(CO)_6$ (Co-Co bond, several possible structures)

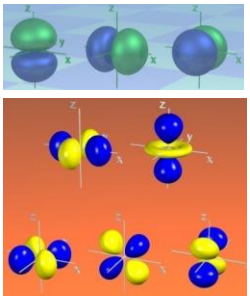
c) trans-HRh(CO)$(PPh_3)_2$ [Rh(+1) = d^8]

d) $Ir_2(\mu\text{-}Cl)_2(CO)_4$ [Ir(+1) = d^8]

e) Cp_2TiCl_2

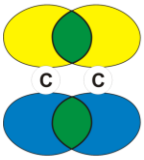
Bonding and Orbitals



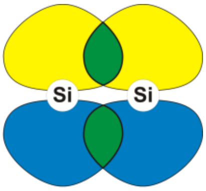


Overlap Efficiency

The strength of a chemical bond (covalent or dative) is related to the amount of overlap between two atomic (or hybrid) orbitals. The overlap efficiency can be thought of as the orbital overlap area divided by the non-overlapping area. The smaller this ratio, the weaker the bonding.



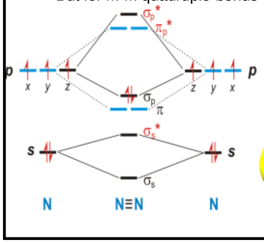
ethylene, $H_2C{=}CH_2$
C=C = 1.35Å

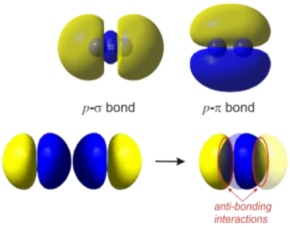


silylene, $H_2Si{=}SiH_2$
Si=Si = 2.06Å

Overlap efficiency

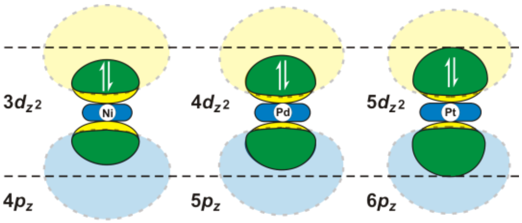
Overlap efficiency also applies to σ-bonds between atoms.
Dihalogen bond strengths increase $F_2 < Cl_2 < Br_2 < I_2$.
But decrease as one goes from C-C > Si-C > Ge-C > Sn-C > Pb-C.
For most transition metal M-M single bonds the trend is fairly consistent:
first row < second row < third row.
But for M-M quadruple bonds one has: Cr-Cr << Mo-Mo > W-W.



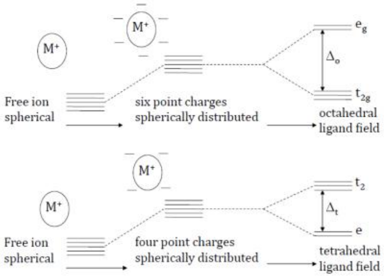


Square Planar

Square planar complexes typically have ***d*⁸** (sometimes ***d*⁹**) electronic configurations and are usually limited to the following elements: **Rh, Ir, Ni, Pd, Pt, Cu, & Au**.



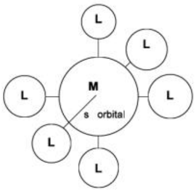
d^6 Octahedral maximum of 6 coordinate

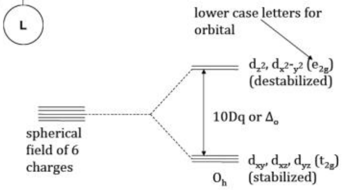


Picture of Octahedral Complex

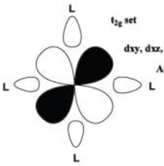
Various representations

(ignore "s orbital"





The five d-orbitals form a set of two bonding molecular orbitals (**e_g set** with the **dz^2** and the **dx^2-y^2**), and a set of three non-bonding orbitals (**t_{2g} set** with the **dxy, dxz,** and the **dyz orbitals**).



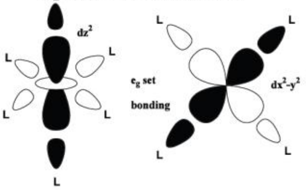
e_g orbitals point at ligands (antibonding)

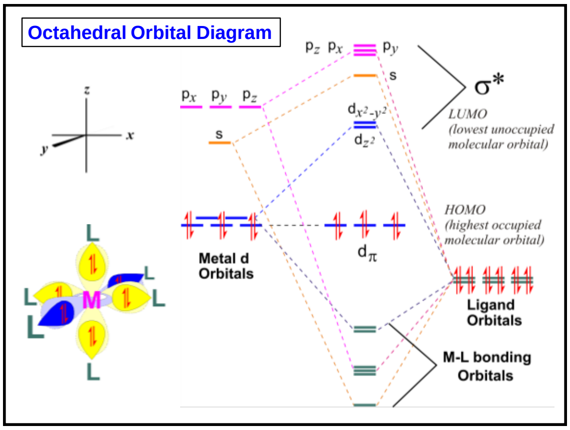
appropriate symmetry for σ-bonds to ligands

σ-bonds will be six d^2sp^3 hybrids

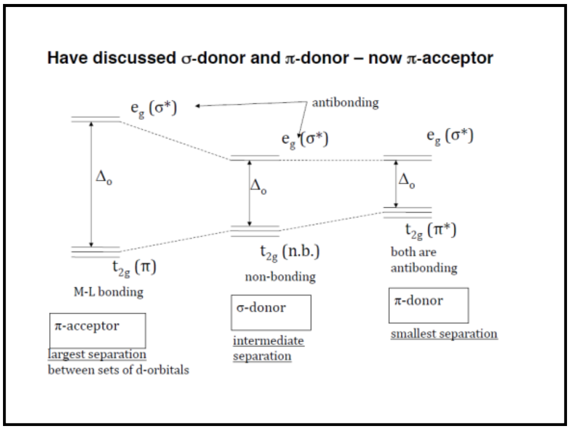
nd_z2, $nd_{x}2_{-y}2$, (n+1)s, $(n+1)p_x,p_y,p_z$

t_{2g} orbital set left as non-bonding

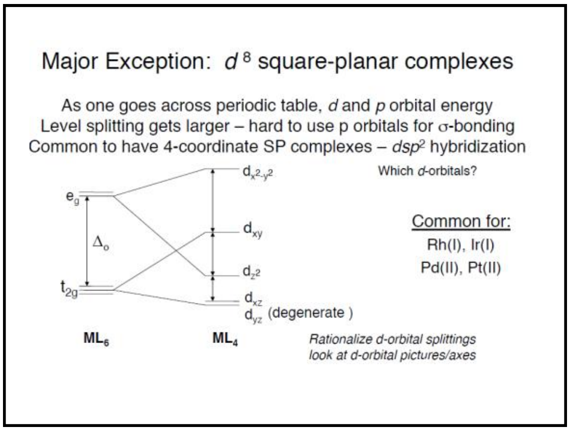




Octahedral Orbital Diagram



Have discussed σ-donor and π-donor – now π-acceptor



Major Exception: d^8 square-planar complexes

As one goes across periodic table, *d* and *p* orbital energy
Level splitting gets larger – hard to use p orbitals for σ-bonding
Common to have 4-coordinate SP complexes – *dsp*^{2} hybridization

Which *d*-orbitals?

Common for:
Rh(I), Ir(I)
Pd(II), Pt(II)

Rationalize d-orbital splittings
look at d-orbital pictures/axes

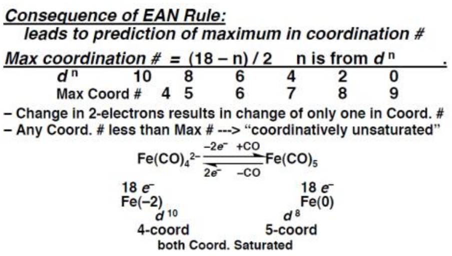
18-Electron "Rule"

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 relative to C, O, N, etc.

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.



Consequence of EAN Rule:

leads to prediction of maximum in coordination #

Max coordination # = (18 – n) / 2   n is from d ⁿ

d ⁿ	10	8	6	4	2	0
Max Coord #	4	5	6	7	8	9

– Change in 2-electrons results in change of only one in Coord. #

– Any Coord. # less than Max # ---> "coordinatively unsaturated"

$$Fe(CO)_4^{2-} \underset{2e^-\ \ -CO}{\overset{-2e^-\ \ +CO}{\rightleftharpoons}} Fe(CO)_5$$

18 e^-, Fe(−2), d^{10}, 4-coord

18 e^-, Fe(0), d^8, 5-coord

both Coord. Saturated

Eighteen-Electron Rule - Examples

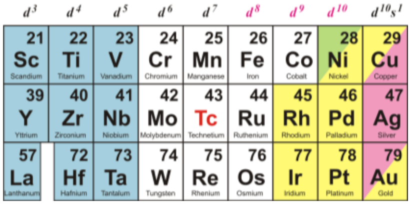
$Co(NH_3)_6^{3+}$ $Cr(CO)_6$

Obey 18-electron rule for different reasons

Carbonyl Compounds in Metal-Metal Bonded Complexes less straightforward

$Fe_2(CO)_9$ $[\pi\text{-}Cp)Cr(CO)_3]_2$ $Co_2(CO)_8$ (2 isomers)

Exceptions to the 18-Electron "Rule"



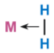
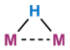
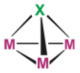
Early Transition Metals
16e- and sub-16e- configurations are common
Coordination geometries higher than 6 relatively common

Middle Transition Metals
18e- configurations are common
Coordination geometries of 6 are common

d^6

Late Transition Metals
16e- and sub-16e- configurations are common
Coordination geometries of 5 and lower are common: d^8 = square planar

Ligands, Bonding Types, Charges, and Donor #'s

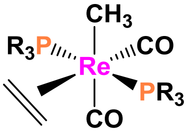
Ligand Name	Bonding Type	Formal Charge	Electrons Donated
Molecular Hydrogen: H_2		0	2
Hydride: H^-	M-H	-1	2
Hydride: H^-		-1	2
Halide: X^-	M-X	-1	2
Halide: X^- μ bridging		-1	4 (2 to each M)
Halide: X^- μ_3 bridging		-1	6 (2 to each M)

Ligands, Charges, and Donor #'s

Ionic Method **of electron-counting**

Cationic 2e- donor:	NO^+ (nitrosyl)
Neutral 2e- donors:	PR_3 (phosphines), CO (carbonyl), $R_2C{=}CR_2$ (alkenes), RC≡CR (alkynes, can also donate 4 e-), N≡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)

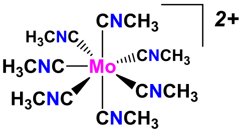
e-counting Examples: Simple



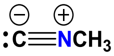
1) There is no overall charge on the complex
2) There is one anionic ligand (CH_3^-, methyl group)
3) The Re metal atom must have a +1 charge to compensate for the one negatively charged ligand. So the Re is the in the +1 oxidation state. We denote this three different ways: Re(+1), Re(I), or Re^I.

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

e-counting Examples: Simple *(but semi-unusual ligand)*



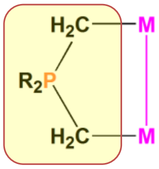
1) There is a +2 charge on the complex
2) The $CNCH_3$ (methyl isocyanide) ligand is neutral, but lets check the Lewis Dot structure to make sure that is correct:



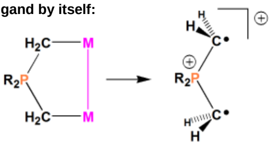
3) Because there is a +2 charge on the complex and all neutral ligands present, the Mo has a +2 charge & oxidation state.

Mo(+2)	d^4
7 $CNCH_3$	14e-
Total:	18e-

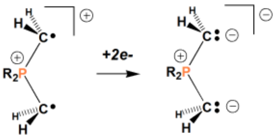
e-counting Examples: Ligand Analysis



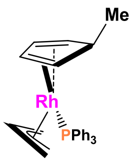
1) Remove the metal atom(s) and examine the ligand by itself:



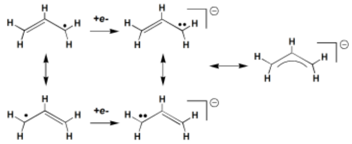
2) If the donor atoms have an odd # of e-'s, add enough to get an even # and (usually) a filled octet. As you add e-'s don't forget to add negative charges!!



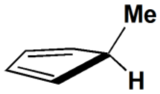
e-counting Examples: Tricky System

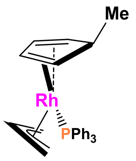


1) There is no overall charge on the complex
2) There is one anionic ligand ($C_3H_5^-$, allyl)



3) The top ligand is NOT a $MeCp^-$! It is a neutral diene that has a H attached to the methyl-substituted ring carbon. This is a neutral 4e- donor.





3) Because the complex is neutral and there is one anionic ligand present, the Rh atom must have a +1 charge to compensate for the one negatively charged ligand. So the Rh atom is in the +1 oxidation state.

Rh(+1)		d^8
PR_3		2e-
η^4-C_5H_5Me		4e-
η^3-$C_3H_5^-$		4e-
	Total:	18e-

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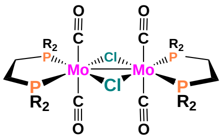
e-counting Examples: M-M Bonded System

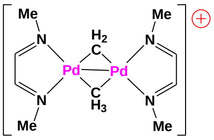


1) Generally treat metal-metal (M-M) bonds to be simple covalent bonds with each metal contributing 1e- to the bond. If you have two metal atoms next to one another and each has an odd electron-count, pair the odd electrons to make a M-M bond.
2) Bridging ligands, like halides, with at least 2 lone pairs 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.

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

Very Common Mistake: Students determining the oxidation state for complexes with 2 or more metal centers often add up all the anionic ligands and then figure out the oxidation state for only one of the metal centers based on this.

e-counting Examples: M-M Bonded System

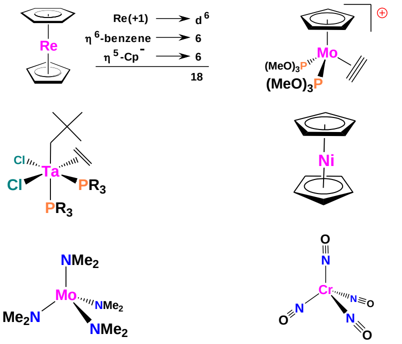


Ligand analysis: The chelating N ligand is a bis-imine, is neutral, with each N atom donating 2e-. Two different bridging ligands – an anionic CH_3^- (methyl group) and a dianionic CH_2^{2-} (carbene or alkylidene). The CH_3^- only has one lone pair of electrons, so it has to split these between the two metals (1e- to each). The CH_2^{2-} alkylidene ligand, on the other hand, has 2 lone pairs & donates 2e- to each M.

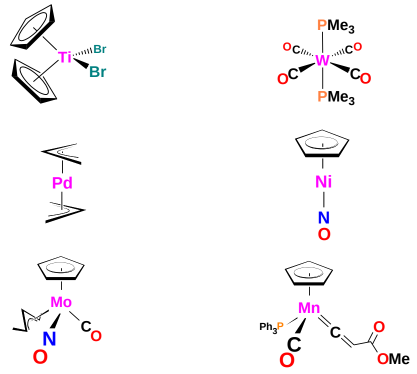
Oxidation state analysis: Total of 3 negative charges on the ligands (anionic methyl, dianionic alkylidene) and a positive charge on the complex. Therefore the two Pd centers must have a TOTAL of a +4 charge, or a +2 charge (oxidation state) on each.

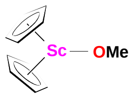
Pd(+2)	d^8
2 imines	4e-
μ-CH_3^-	1e-
μ-CH_2^{2-}	2e-
Sub-total:	*15e-*
Pd-Pd	1e-
TOTAL:	16e-

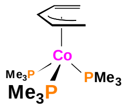
e-counting Problems:

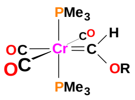


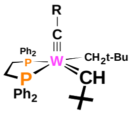
Re(+1) → d^6
η^6-benzene → 6
η^5-Cp^- → 6
18

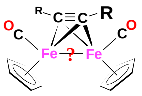


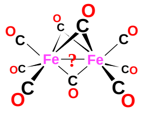


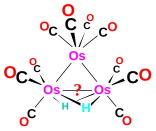


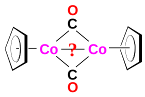


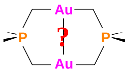


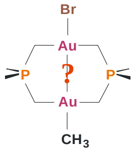


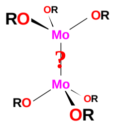


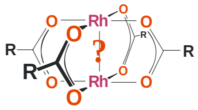












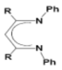
Problem. Sketch out a structure showing the geometry about the metal center as accurately as possible and clearly show the electron counting for the complexes below. Phosphine ligand abbreviations are defined in your notes (see the phosphine ligand section).

a) $[Cp_2Zr(\eta^3\text{-allyl})]^+$

b) $[Pd_2(\mu\text{-Cl})_2(bipy)_2]^{2+}$ (bipy = bipyridine)

c) $CpVCl(NMe_2)(PMe_3)$

d) $ScCl_2(\beta\text{-dikeiminato})(THF)$



e) $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ (C_{60} is neutral)

f) $[\textit{trans}\text{-}HOs(\equiv CR)Cl(N\equiv CCH_3)(PR_3)_2]^+$

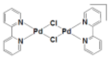
g) $[CpRu(CO)_2\{P(OR)_3\}]^+$

h) Pd(bipy)(Ph)(Me) (bipy = bipyridine)

a) $[Cp_2Zr(\eta^3\text{-allyl})]^+$

Zr(+4)	d^0
$2Cp^-$	12e-
$allyl^-$	4e-
Total:	16e-

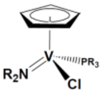
b) $[Pd_2(\mu\text{-Cl})_2(bipy)_2]^{2+}$ (bipy = bipyridine)



Pd(+2)	d^8
$2\mu\text{-Cl}^-$	4e-
bipy	4e-
Total:	16e-

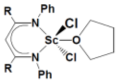
$Pd^{2+}(d^8)$ is usually happy at 16e- (although it can weakly coordinate one more ligand

c) $CpVCl(NMe_2)(PMe_3)$



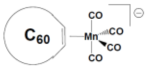
V(+3)	d^2
Cp^-	6e-
NR_2^-	4e-
Cl^-	2e-
PR_3	2e-
Total:	16e-

d) $ScCl_2(\beta\text{-dikeiminato})(THF)$



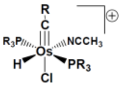
Sc(+3)	d^0
$\beta\text{-diimin-N}_2^-$	4e-
$2Cl^-$	4e-
THF	2e-
Total:	10e-

e) $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ (C_{60} is neutral)



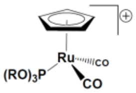
Mn(-1)	d^8
4CO	8e-
alkene	2e-
Total:	18e-

f) $[\textit{trans}\text{-}HOs(\equiv CR)Cl(N{\equiv}CCH_3)(PR_3)_2]^+$



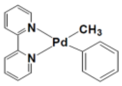
Os(+6)	d^2
CR^{3-}	6e-
H^-	2e-
Cl^-	2e-
$NCCH_3$	2e-
$2PR_3$	4e-
Total:	18e-

g) $[CpRu(CO)_2\{P(OR)_3\}]^+$



Ru(+2)	d^6
Cp^-	6e-
2CO	4e-
$P(OR)_3$	2e-
Total:	18e-

h) Pd(bipy)(Ph)(Me) (bipy = bipyridine)



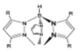
Pd(+2)	d^8
CH_3^-	2e-
Ph^-	2e-
bipy	4e-
Total:	16e-

i) $[Cp_2Ru_2(\mu\text{-Br})(CO)_4]^+$

j) $Ta_2(\mu\text{-CR})_2(CH_2SiMe_3)_4$

k) Cp_2ReCH_3

l) $TpNb(CO)(\eta^2\text{-N}{\equiv}CCH_3)(MeC{\equiv}CMe)$



m) $Cp_2Fe_2(\mu\text{-CO})_2(CO)_2$

n) $Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)$

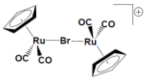
o) $Ir_4(CO)_{12}$ (tetrahedral Ir_4 core)

p) $CpW(NO)(CH_3)(\eta^3\text{-allyl})$

q) $Co_2(\mu\text{-HC}{\equiv}CH)(CO)_6$

r) $[Fe_2(\mu\text{-MeC}{\equiv}CMe)(\mu\text{-PR}_2)(CO)_6]^+$

i) $[Cp_2Ru_2(\mu\text{-}Br)(CO)_4]^+$

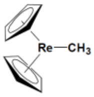


Ru(+2)	d^6
Cp^-	6e-
$\mu\text{-}Br^-$	2e-
2CO	4e-
Total:	18e-

j) $Ta_2(\mu\text{-}CR)_2(CH_2SiMe_3)_4$

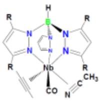
Ta(+5)	d^0
$2\text{-}\mu CR^{3-}$	6e-
$2CR_3^-$	4e-
Total:	10e-

k) Cp_2ReCH_3



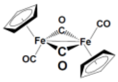
Re(+3)	d^4
$2Cp^-$	12e-
CR_3^-	2e-
Total:	18e-

l) $TpNb(CO)(\eta^2\text{-}N{=}CCH_3)(MeC{\equiv}CMe)$



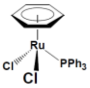
Nb(+1)	d^4
Tp^-	6e-
CO	2e-
R-C≡C-R	2e-
$\eta^2\text{-}NCCH_3$	2e-
Total:	16e-

m) $Cp_2Fe_2(\mu\text{-}CO)_2(CO)_2$



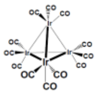
Fe(+1)	d^7
Cp^-	6e-
$2\text{-}\mu CO$	2e-
CO	2e-
Fe-Fe	1e-
Total:	18e-

n) $Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)$



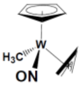
Ru(+2)	d^6
C_6H_6	6e-
$2Cl^-$	4e-
PR_3	2e-
Total:	18e-

o) $Ir_4(CO)_{12}$ (tetrahedral Ir_4 core)



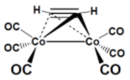
Ir(0)	d^9
3CO	6e-
3Ir-Ir	3e-
Total:	18e-

p) $CpW(NO)(CH_3)(\eta^3\text{-allyl})$



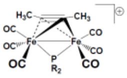
W(+2)	d^4
Cp^-	6e-
CH_3^-	2e-
$allyl^-$	4e-
NO^+	2e-
Total:	18e-

q) $Co_2(\mu\text{-}HC{\equiv}CH)(CO)_6$



Co(0)	d^9
μ-R-C≡C-R	2e-
3CO	6e-
Co-Co	1e-
Total:	18e-

r) $[Fe_2(\mu\text{-}MeC{\equiv}CMe)(\mu\text{-}PR_2)(CO)_6]^+$



Fe(+1)	d^7
μ-R-C≡C-R	2e-
$\mu\text{-}PR_2^-$	2e-
3CO	6e-
Fe-Fe	1e-
Total:	18e-

Problem. Propose an *18e- structure for the following metal/ligand combinations. Use at least one of each metal and ligand listed. Complexes should be neutral. Don't use more than 2 metal centers. Show your electron counting. Ligands are shown without charges, please indicate the proper ligand charge in your electron counting. Draw a reasonable structure showing the geometry about the metal center(s).*

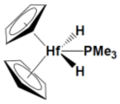
a) Hf, Cp, H, PMe_3

b) Nb, O, OMe, NR, $Me_2NCH_2CH_2NMe_2$

c) Mo, Cp, CH_3

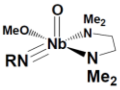
d) Re, Tp (tris(pyrazol)borate), allyl, NR_2

a) Hf, Cp, H, PMe_3



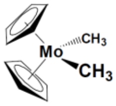
Hf(+4)	d^0
PR_3	2e-
$2Cp^-$	12e-
$2H^-$	4e-
Total:	18e-

b) Nb, O, OMe, NR, $Me_2NCH_2CH_2NMe_2$



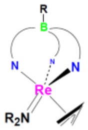
Nb(+5)	d^0
$2NR_3$	4e-
O^{2-}	4e-
NR^{2-}	6e-
OMe^-	4e-
Total:	18e-

c) Mo, Cp, CH_3



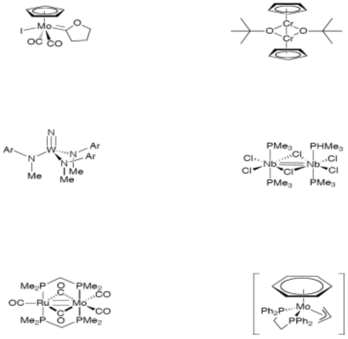
Mo(+4)	d^2
$2Cp^-$	12e-
$2CR_3^-$	4e-
Total:	18e-

d) Re, Tp (tris(pyrazol)borate), allyl, NR_2

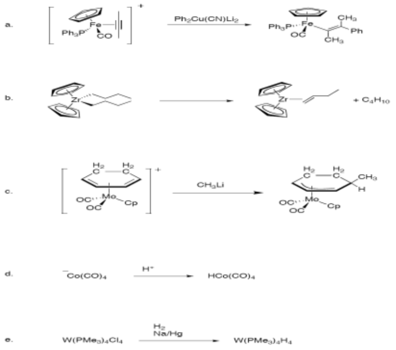


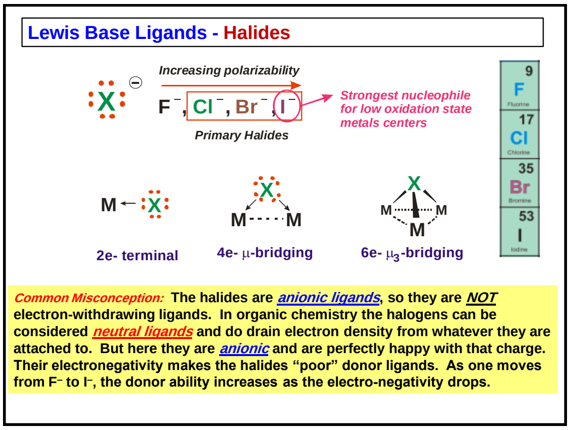
Re(+3)	d^4
Tp^-	6e-
NR_2^-	4e-
$allyl^-$	4e-
Total:	18e-

Problem. For each complex below, provide the oxidation state of the metal, the number of *d electrons,*and the total electron count for the complex. If there is more than one metal center, consider each separately.



Problem. For each of the following reactions, indicate whether the metal is oxidized, reduced, or retains the same oxidation state?





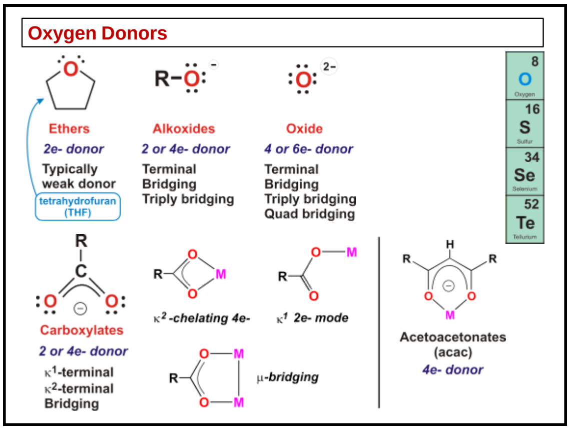
Lewis Base Ligands - Halides

2e- terminal

4e- μ-bridging

6e- μ_3-bridging

Common Misconception: **The halides are *anionic ligands*, so they are *NOT* electron-withdrawing ligands. In organic chemistry the halogens can be considered *neutral ligands* and do drain electron density from whatever they are attached to. But here they are *anionic* and are perfectly happy with that charge. Their electronegativity makes the halides "poor" donor ligands. As one moves from F^- to I^-, the donor ability increases as the electro-negativity drops.**



Oxygen Donors

Ethers
2e- donor
Typically weak donor
tetrahydrofuran (THF)

Alkoxides
2 or 4e- donor
Terminal
Bridging
Triply bridging

Oxide
4 or 6e- donor
Terminal
Bridging
Triply bridging
Quad bridging

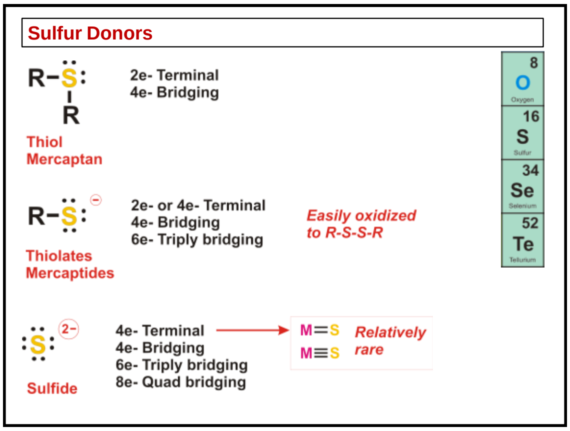
Carboxylates
2 or 4e- donor
κ1-terminal
κ2-terminal
Bridging

κ2-chelating 4e-

κ1 2e- mode

μ-bridging

Acetoacetonates (acac)
4e- donor



Sulfur Donors

Thiol
Mercaptan

2e- Terminal
4e- Bridging

Thiolates
Mercaptides

2e- or 4e- Terminal
4e- Bridging
6e- Triply bridging

Easily oxidized to R-S-S-R

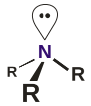
Sulfide

4e- Terminal
4e- Bridging
6e- Triply bridging
8e- Quad bridging

M=S
M≡S

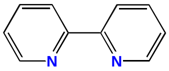
Relatively rare

Nitrogen Donors

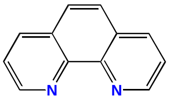


In general, alkylated amines are not particularly good ligands. This is mainly due to the relatively short N-C bond distances and the stereoelectronic problems generated from this.

Chelating amines have fewer steric problems and are better ligands for transition metal centers. Perhaps the most famous neutral nitrogen donor ligand is bipyridine or bipyridyl, almost universally abbreviated bipy.

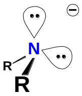


Bipy = Bipyridine



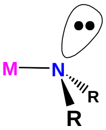
Phen = phenanthroline

Inorganic Amides

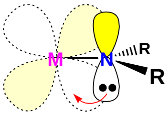


Strong Base & Nucleophile
Terminal (2 or 4e-) donor
4e- Bridging donor

The lone pairs in an amide are about 2eV higher in energy than in OR^-. This makes an amide a considerably stronger donor.

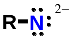


2e- donor
pyramidal geometry



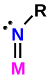
4e- donor
trigonal planar

Alkyl-Imido (nitrene) Ligand



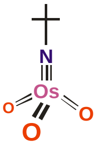
Imido (nitrene)

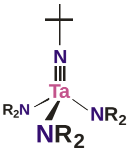
4e- or 6e- Terminal
4e- Bridging
6e- Triply bridging

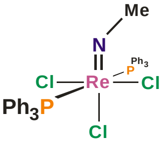


Bent
(nucleophillic nitrogen)

Linear
(electrophillic nitrogen)



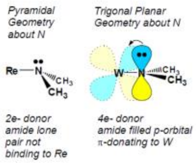




As one moves to the right-hand side of the periodic table, one tends to get less M-L multiple bonding

Problem: Consider the complexes Re(NMe$_2$)(CO)$_3$(dmpe) and W(NMe$_2$)Br(dmpe)$_2$. In the Re complex the NMe$_2^-$ ligand is **not acting as a π-donating ligand, while in the W complex it is acting as a strong π-** donating ligand. Discuss how the NMe$_2^-$ ligand is acting as a π-donating ligand for the W complex and why it is **not acting as such for the Re complex, even though the Re atom is probably more electron deficient due** to the three π-backbonding CO ligands. When the NMe$_2^-$ ligand acts as a 4e- σ- and π-donating ligand, its geometry is different from when it acts as a simple σ-donating 2e- donor. What is this difference in geometry?

The Re complex counts up to 18e- with the amide ligand acting as a simple 2e- donor. If it was a 4e- π-donating ligand, one would get a 20e- count, which would be bad. Thus, there is no reason for it to want to donate more than 2e-. The W complex, on the other hand, has a 16e- count with the amide acting as a simple 2e- donor. Thus, there is an empty metal orbital available that can interact with the filled lone pair on the amide, allowing it to act as a π-donating 4e- donor ligand.



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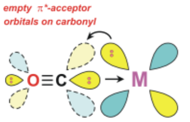
2. Carbonyls, Phosphines & Hydrides

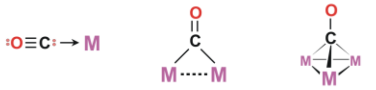
Carbonyl Ligands - C≡O



powerful π-acceptor ligand!

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

Standard Bonding Modes:



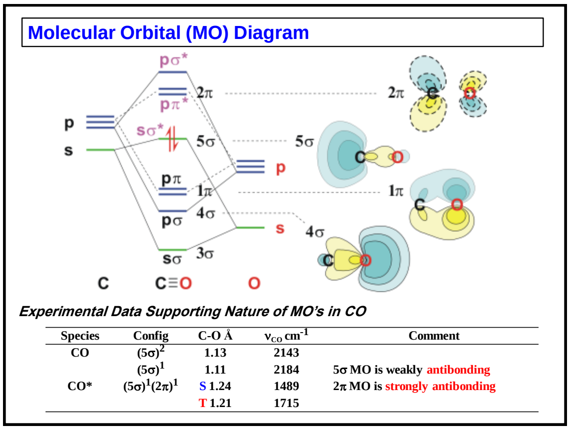
terminal mode
2e$^-$ neutral donor

μ_2- ***bridging mode***
2e$^-$ neutral donor

μ_3- ***bridging mode***
3e$^-$ neutral donor

Examples of *neutral*, binary metal carbonyls:

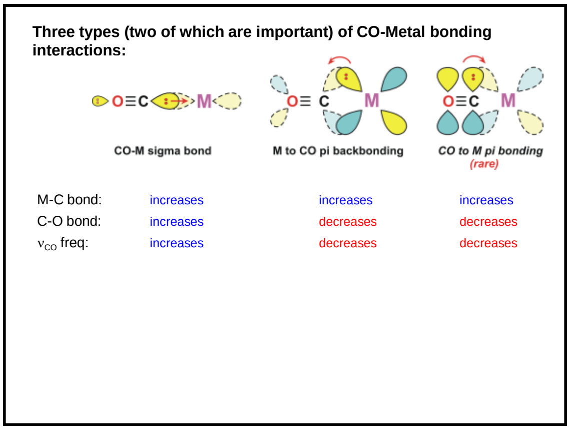
4	5	6	7	8	9	10	11
Ti	V(CO)$_6$	Cr(CO)$_6$	Mn$_2$(CO)$_{10}$	Fe(CO)$_5$ Fe$_2$(CO)$_9$ *Fe$_3$(CO)$_{12}$*	Co$_2$(CO)$_8$ Co$_4$(CO)$_{12}$	Ni(CO)$_4$	Cu
Zr	Nb	Mo(CO)$_6$	Tc$_2$(CO)$_{10}$	Ru(CO)$_5$ Ru$_3$(CO)$_{12}$	Rh$_4$(CO)$_{12}$ Rh$_6$(CO)$_{16}$	Pd	Ag
Hf	Ta	W(CO)$_6$	Re$_2$(CO)$_{10}$	Os(CO)$_5$ Os$_3$(CO)$_{12}$	Ir$_4$(CO)$_{12}$	Pt	Au



Molecular Orbital (MO) Diagram

Experimental Data Supporting Nature of MO's in CO

Species	Config	C-O Å	ν_{CO} cm^{-1}	Comment
CO	$(5\sigma)^2$	1.13	2143	
	$(5\sigma)^1$	1.11	2184	5σ MO is weakly antibonding
CO*	$(5\sigma)^1(2\pi)^1$	S 1.24	1489	2π MO is strongly antibonding
		T 1.21	1715	



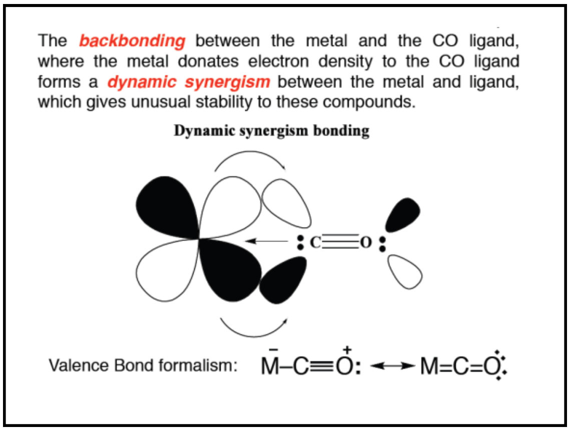
Three types (two of which are important) of CO-Metal bonding interactions:

CO-M sigma bond

M to CO pi backbonding

CO to M pi bonding (rare)

	CO-M sigma bond	M to CO pi backbonding	CO to M pi bonding (rare)
M-C bond:	increases	increases	increases
C-O bond:	increases	decreases	decreases
ν_{CO} freq:	increases	decreases	decreases



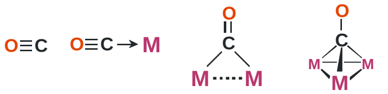
The ***backbonding*** between the metal and the CO ligand, where the metal donates electron density to the CO ligand forms a ***dynamic synergism*** between the metal and ligand, which gives unusual stability to these compounds.

Dynamic synergism bonding

Valence Bond formalism: $\overset{-}{M}-C\equiv\overset{+}{\dot{O}}: \longleftrightarrow M=C=\ddot{O}:$

Carbonyl Infrared (IR) Stretching Frequencies

- 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 π-backbonded to the CO.
- The **number** (and intensity) of the carbonyl bands observed depends on the number of CO ligands present and the symmetry of the metal complex. There are also secondary effects such as Fermi resonance and overtone interactions that can complicate carbonyl IR spectra.



	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)

C–O stretching frequencies, ν(C-O)

Put more electron density on metal
– by charge
– by ligands which cannot π-accept

Remaining CO's have to take up the charge (e^--density) on the metal
See effects on ν(C-O).

$Ni(CO)_4$ $[Co(CO)_4]^-$ $Fe(CO)_4^{2-}$
2057 cm^{-1} 1886 cm^{-1} 1786 cm^{-1}
———> ———> more –ve charge

$Mn(dien)(CO)_3^+$ ~ 2020, 1900 cm^{-1}
$Cr(dien)(CO)_3$ ~1900, 1760 cm^{-1} (dien not π-acceptor)

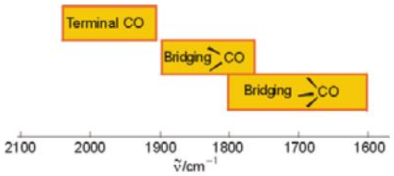
2. As the metal center becomes increasingly electron rich the stretching frequency drops

The influence of coordination and charge on CO stretching frequency

Compound	Frequency (cm^{-1})
$CO_{(g)}$	2143
$[Mn(CO)_6]^+$	2090
$[Cr(CO)_6]$	2000
$[V(CO)_6]^-$	1860
$[Ti(CO)_6]^{2-}$	1750

Summary

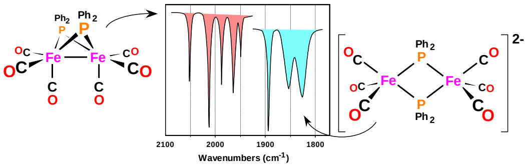
1. As the CO bridges more metal centers its stretching frequency drops – same for all p ligands
– More back donation

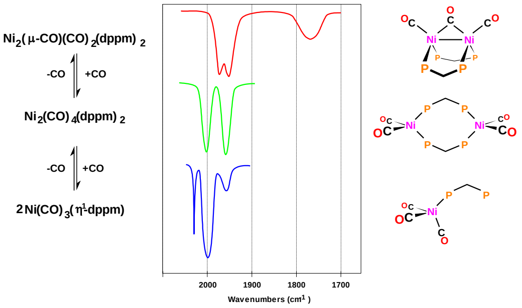


Electronic Effects on ν_{CO}

As the electron density on a metal center increases, more π-back-bonding 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





$Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$

-CO ⇅ +CO

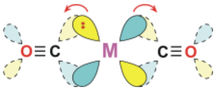
$Ni_2(CO)_4(dppm)_2$

-CO ⇅ +CO

$2\,Ni(CO)_3(\eta^1\text{-}dppm)$

Ligand Electronic Effects on ν_{CO}

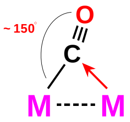
Complex	ν_{CO} cm^{-1}
$Mo(CO)_3(PF_3)_3$	2090, 2055
$Mo(CO)_3(PCl_3)_3$	2040, 1991
$Mo(CO)_3[P(OMe)_3]_3$	1977, 1888
$Mo(CO)_3(PPh_3)_3$	1934, 1835
$Mo(CO)_3(NCCH_3)_3$	1915, 1783
$Mo(CO)_3(\text{triamine})_3$	1898, 1758
$Mo(CO)_3(\text{pyridine})_3$	1888, 1746



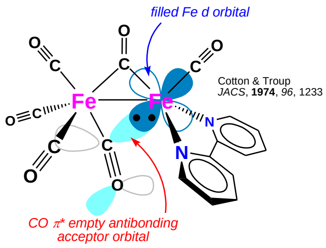
Based on CO IR stretching frequencies, the following ligands can be ranked from **best** π-acceptor to **worst**:

NO^+ > CO > PF_3 > RN≡C > PCl_3 > $P(OR)_3$ > PR_3 > RC≡N > NH_3

Semi-Bridging Carbonyls



Unsymmetrical bridging form. π* system accepts electron density from second metal center. Distortions away from a linear M-CO (180°) or a symmetrically bridging CO (120°). Typical M-CO angle around 150° (but with considerable variations).

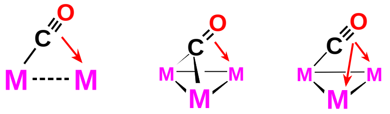


filled Fe d orbital

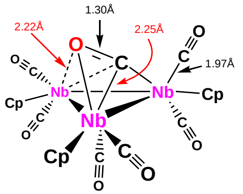
Cotton & Troup
JACS, **1974**, *96*, 1233

CO π empty antibonding acceptor orbital*

σ/π Bridging CO’s

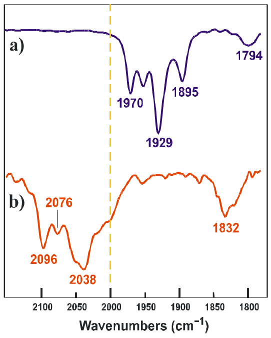


CO acting as π-donor or π-acceptor?



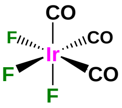
Herrman & coworkers
JACS, **1981**, *103, 1692*

Problem: **Which of the following metal carbonyl IR spectra represents the compound with the least amount of electron density on the metal center? Briefly discuss the reasoning for your choice. Which compound will lose CO the easiest?**

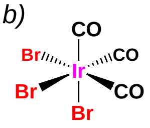


Problem: **Which of the following metal carbonyl compounds will have the highest νCO stretching frequency in the IR? Why? Will this be the most electron-rich or deficient compound?**

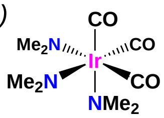
a)



b)



c)

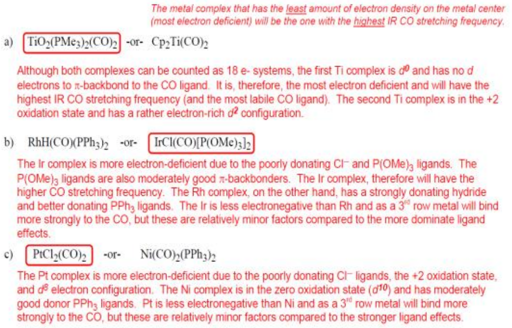


Problem. For each of the following pairs of metal complexes, circle the one that will have the ***highest CO stretching frequency. Briefly and clearly discuss your reasoning for each case.***

a) $TiO_2(PMe_3)_2(CO)_2$ -or- $Cp_2Ti(CO)_2$

b) $RhH(CO)(PPh_3)_2$ -or- $IrCl(CO)[P(OMe)_3]_2$

c) $PtCl_2(CO)_2$ -or- $Ni(CO)_2(PPh_3)_2$



The metal complex that has the least amount of electron density on the metal center (most electron deficient) will be the one with the highest IR CO stretching frequency.

a) $\boxed{TiO_2(PMe_3)_2(CO)_2}$ -or- $Cp_2Ti(CO)_2$

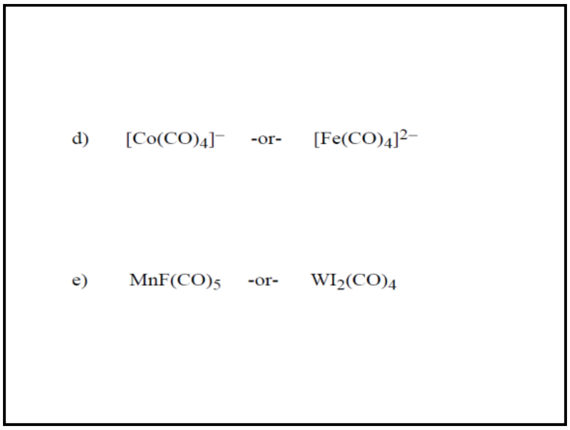
Although both complexes can be counted as 18 e- systems, the first Ti complex is d^0 and has no *d* electrons to π-backbond to the CO ligand. It is, therefore, the most electron deficient and will have the highest IR CO stretching frequency (and the most labile CO ligand). The second Ti complex is in the +2 oxidation state and has a rather electron-rich d^2 configuration.

b) $RhH(CO)(PPh_3)_2$ -or- $\boxed{IrCl(CO)[P(OMe)_3]_2}$

The Ir complex is more electron-deficient due to the poorly donating Cl^- and $P(OMe)_3$ ligands. The $P(OMe)_3$ ligands are also moderately good π-backbonders. The Ir complex, therefore will have the higher CO stretching frequency. The Rh complex, on the other hand, has a strongly donating hydride and better donating PPh_3 ligands. The Ir is less electronegative than Rh and as a 3rd row metal will bind more strongly to the CO, but these are relatively minor factors compared to the more dominate ligand effects.

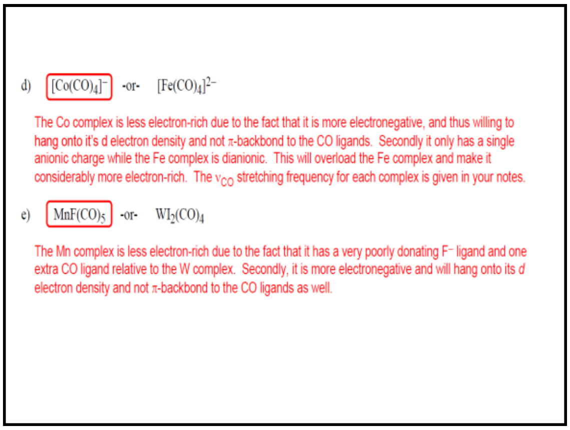
c) $\boxed{PtCl_2(CO)_2}$ -or- $Ni(CO)_2(PPh_3)_2$

The Pt complex is more electron-deficient due to the poorly donating Cl^- ligands, the +2 oxidation state, and d^8 electron configuration. The Ni complex is in the zero oxidation state (d^{10}) and has moderately good donor PPh_3 ligands. Pt is less electronegative than Ni and as a 3rd row metal will bind more strongly to the CO, but these are relatively minor factors compared to the stronger ligand effects.



d) $[Co(CO)_4]^-$ -or- $[Fe(CO)_4]^{2-}$

e) $MnF(CO)_5$ -or- $WI_2(CO)_4$



d) $\boxed{[Co(CO)_4]^-}$ -or- $[Fe(CO)_4]^{2-}$

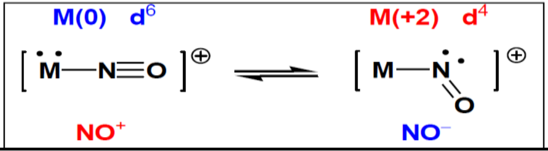
The Co complex is less electron-rich due to the fact that it is more electronegative, and thus willing to hang onto it's d electron density and not π-backbond to the CO ligands. Secondly it only has a single anionic charge while the Fe complex is dianionic. This will overload the Fe complex and make it considerably more electron-rich. The ν_{CO} stretching frequency for each complex is given in your notes.

e) $\boxed{MnF(CO)_5}$ -or- $WI_2(CO)_4$

The Mn complex is less electron-rich due to the fact that it has a very poorly donating F^- ligand and one extra CO ligand relative to the W complex. Secondly, it is more electronegative and will hang onto its *d* electron density and not π-backbond to the CO ligands as well.

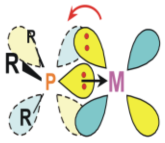
Problem: The nitrosyl ligand usually coordinates as a cationic ligand, NO^+. It can, however, occasionally act as an anionic NO^- ligand. When it is behaving as an anionic ligand it adopts a bent coordination geometry. Discuss (using Lewis dot-like figures) the distribution of electrons in both kinds of M-NO complexes and how these affect the structures (linear vs. bent). Assume in both cases that you are dealing with a $[M\text{-}NO]^+$ unit (positive charge on the overall complex) where the metal has 2 or more d electrons. Clearly show the relative oxidation states of the metal and the relative d electron count for each bonding case (linear vs. bent). It is mentioned that in some ways NO^- is the extreme case of NO^+ acting as a hyper π backbonding ligand. Explain what is meant by that statement.

NO^+ is isoelectronic with CO, that is, it has the same bonding and electronic structure. The difference is that the more electronegative nitrogen atom combined with the net positive charge work together to make NO^+ the strongest π -backbonding ligand known. In fact, it can backbond enough to formally oxidize the metal center by two electrons to transform the NO^+ ligand into a NO^- ligand. This is shown below in the transfer of a pair of electrons from the metal to the NO^+ ligand to produce the bent NO^- ligand. The lone pair that used to be on the metal center is now on the nitrogen of the NO^- ligand. This is what I was referring to as hyper-π- backbonding. When the NO^+ ligand turns into a NO^- ligand it has formally oxidized



Phosphine Ligands – PR_3

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



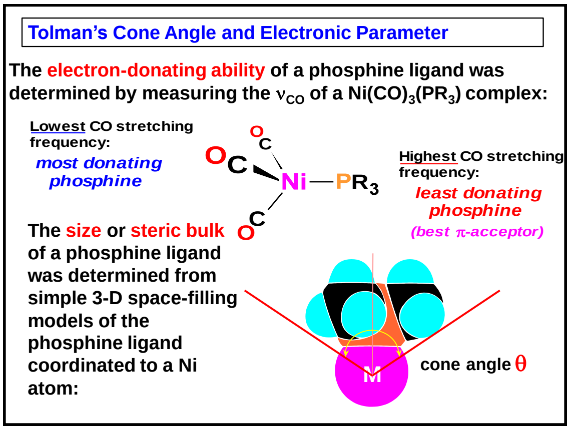
neutral 2e⁻ donor

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



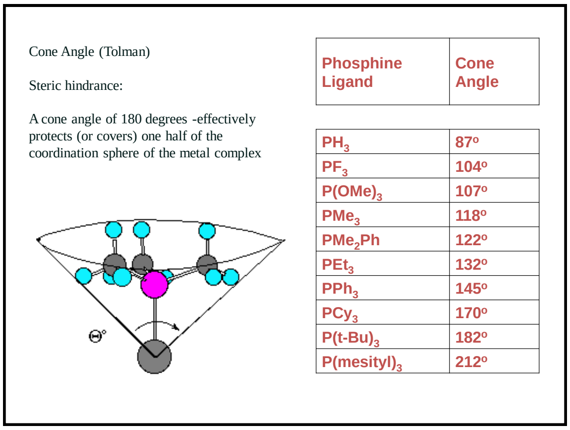
Tolman's Cone Angle and Electronic Parameter

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:

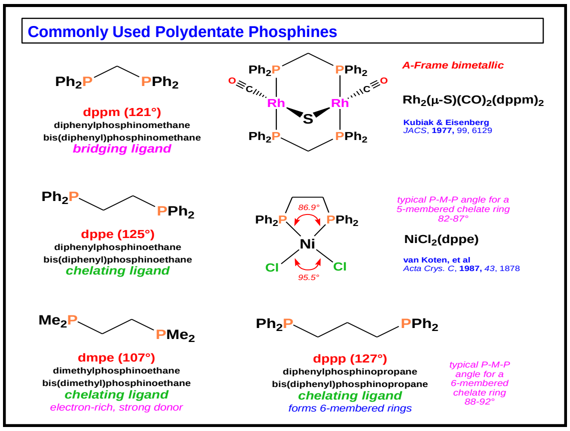


Cone Angle (Tolman)

Steric hindrance:

A cone angle of 180 degrees -effectively protects (or covers) one half of the coordination sphere of the metal complex

Phosphine Ligand	Cone Angle
PH_3	87º
PF_3	104º
$P(OMe)_3$	107º
PMe_3	118º
PMe_2Ph	122º
PEt_3	132º
PPh_3	145º
PCy_3	170º
$P(t\text{-}Bu)_3$	182º
$P(mesityl)_3$	212º



Commonly Used Polydentate Phosphines

dppm (121°)
diphenylphosphinomethane
bis(diphenyl)phosphinomethane
bridging ligand

A-Frame bimetallic

$Rh_2(\mu\text{-}S)(CO)_2(dppm)_2$

Kubiak & Eisenberg
JACS, **1977,** 99, 6129

dppe (125°)
diphenylphosphinoethane
bis(diphenyl)phosphinoethane
chelating ligand

typical P-M-P angle for a 5-membered chelate ring 82-87°

$NiCl_2(dppe)$

van Koten, et al
Acta Crys. C, **1987,** *43*, 1878

dmpe (107°)
dimethylphosphinoethane
bis(dimethyl)phosphinoethane
chelating ligand
electron-rich, strong donor

dppp (127°)
diphenylphosphinopropane
bis(diphenyl)phosphinopropane
chelating ligand
forms 6-membered rings

typical P-M-P angle for a 6-membered chelate ring 88-92°

Some Structural Information

Phosphines have only been characterized as simple 2 e$^-$ donating, terminal-only ligands. No true μ-bridging monophosphines are known (although bridging ***phosphides***, PR_2^-, are very common).

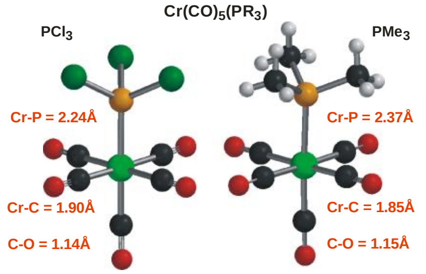
Phosphines generally tend to orient *trans* to one another in order to minimize steric interactions (especially true for bulky PR_3). Chelating bisphosphine ligands are used to enforce *cisoidal* coordination geometries when needed.

Some typical first row M-PR_3 average bond distances:

Ti-P	2.6 Å
V-P	2.5 Å
Cr-P	2.4 Å
Ni-P	2.1 Å

M-P bonds are the strongest for alkylated phosphine ligands bonding to a neutral or monocationic middle to later transition metal center that is electron-deficient. High oxidation state early transition metals are too "hard" to have very effective bonding to most phosphines, although more and more early transition metal phosphine complexes are being characterized and found to be reasonably stable.

Bond Length vs. Bond Strength steric effect



Conclusions

For most systems a shorter bond *usually indicates a* stronger bond when comparing similar atoms and bonds. For metal-ligand complexes there can be exceptions to this when the ligands in question have fairly different donor/acceptor properties.In $Cr(CO)_5(PCl_3)$ the shorter bond distance relative to $Cr(CO)_5(PMe_3)$ arises due to the combination of a contracted lower energy P orbitals and moderate to significant π -backbonding. The DFT calculations indicate that the PMe_3 complex has stronger M-P bonding despite the significantly longer Cr-P distance (2.37Å vs. 2.24Å)

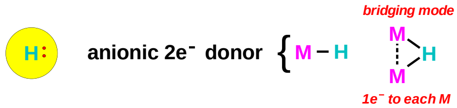
Consider the following equilibrium:
$CoBr_2(CO)L_2 \longrightarrow CoBr_2L_2 + CO$
The equilibrium constants for the reaction with various L ligands are given in the table below. Explain the trends in K_d.

L	K_d	ν_{CO} (cm^{-1})	cone angle
PEt_3	1	1985	132°
PPr_3	1.1	1980	135°
PEt_2Ph	2.5	1990	135°
$PEtPh_2$	24	1990	140°
PPh_3	750	1995	145°

Generally, the more electron-donating the phosphine the lower the ν_{CO} stretching frequency. This means stronger π-backbonding to the CO and stronger M-CO bonding. Thus, a lower K_d dissociation value. Steric effects, however, can over-ride the electronic effects. PPr_3, for example, is a stronger donor than PEt_3, but the K_d value actually increases slightly. This is due to the larger cone angle of the PPr_3 ligand. This causes more steric crowding around the metal favoring CO dissociation.

In going from PPr_3 to PEt_2Ph, the cone angle is the same, but the PEt_2Ph ligand is not as strong a donor, so we see an increase in the ν_{CO} stretching frequency (weaker M-CO bonding) and more dissociation. The increased steric size of the $PEtPh_2$ ligand causes a ten-fold increase in the dissociation, even though the ν_{CO} stays about the same. PPh_3 is the biggest ligand and poorest donor so we see the largest increase in the CO dissociation.

Hydride Ligands – H^-



bridging mode

anionic $2e^-$ donor

$1e^-$ to each M

Hydride nomenclature comes from the NMR behavior:

M-H ~ –5 to –25 ppm *for $d^1 \longrightarrow d^9$ metals!!*

upfield shift indicates "hydridic" chemical nature

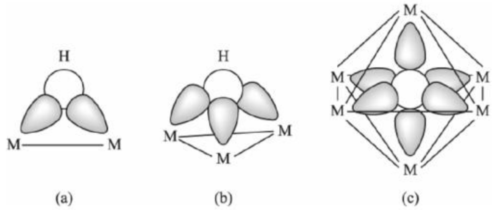
$HCo(CO)_4$ ^1H NMR = –10.7 ppm

BUT: $HCo(CO)_4 \longrightarrow H^+ + [Co(CO)_4]^-$ *strong acid in H_2O, MeOH similar to HCl !!*

d^0 $Cp^*_2ZrH_2$ δ = + 7.5 ppm

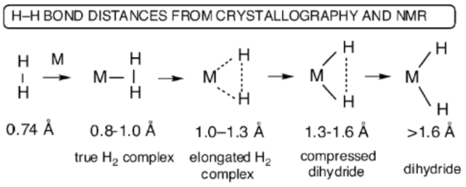
d^{10} $[HCu\{P(p\text{-tolyl})_3\}]_6$ δ = + 3.5 ppm

IR Spectra:
M-H 2200 - 1600 cm^{-1} } can be very weak or absent
$M_2(\mu\text{-H})$ 1600 - 800 cm^{-1} } broader (weak or absent)



Overlap of the H 1*s* orbital with (a) two or (b) three appropriate metal hybrid orbitals to form μ-H and μ_3-H bridges. Interstitial hydride ligands (c) are also possible, forming a 7c-2e bond.

Metal-Dihydrogen (H_2) Complexes –> Hydrides

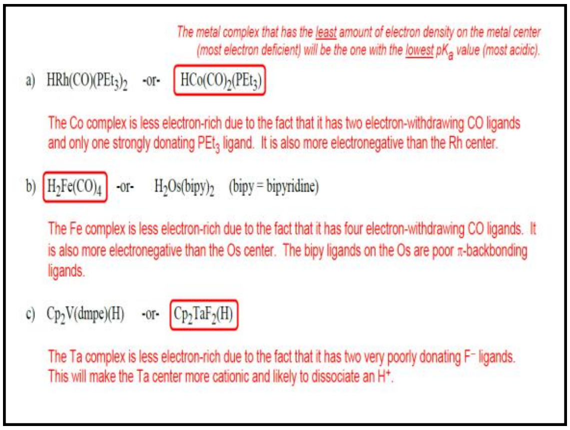


Problem: For each of the following pairs of metal hydride complexes, circle the one that should have the ***lowest pKa value. Briefly and clearly discuss your reasoning for each case.***

a) $HRh(CO)(PEt_3)_2$ -or- $HCo(CO)_2(PEt_3)$

b) $H_2Fe(CO)_4$ -or- $H_2Os(bipy)_2$ (bipy = bipyridine)

c) $Cp_2V(dmpe)(H)$ -or- $Cp_2TaF_2(H)$



The metal complex that has the <u>least</u> amount of electron density on the metal center (most electron deficient) will be the one with the <u>lowest</u> pK_a value (most acidic).

a) $HRh(CO)(PEt_3)_2$ -or- $\boxed{HCo(CO)_2(PEt_3)}$

The Co complex is less electron-rich due to the fact that it has two electron-withdrawing CO ligands and only one strongly donating PEt_3 ligand. It is also more electronegative than the Rh center.

b) $\boxed{H_2Fe(CO)_4}$ -or- $H_2Os(bipy)_2$ (bipy = bipyridine)

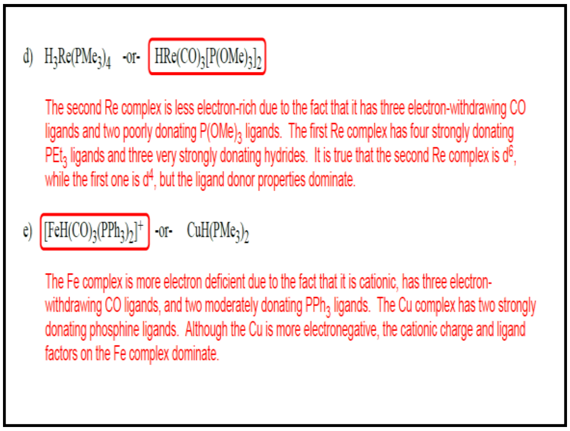
The Fe complex is less electron-rich due to the fact that it has four electron-withdrawing CO ligands. It is also more electronegative than the Os center. The bipy ligands on the Os are poor π-backbonding ligands.

c) $Cp_2V(dmpe)(H)$ -or- $\boxed{Cp_2TaF_2(H)}$

The Ta complex is less electron-rich due to the fact that it has two very poorly donating F^- ligands. This will make the Ta center more cationic and likely to dissociate an H^+.

d) $H_3Re(PMe_3)_4$ -or- $HRe(CO)_3[P(OMe)_3]_2$

e) $[FeH(CO)_3(PPh_3)_2]^+$ -or- $CuH(PMe_3)_2$



d) $H_3Re(PMe_3)_4$ -or- $\boxed{HRe(CO)_3[P(OMe)_3]_2}$

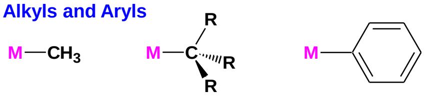
The second Re complex is less electron-rich due to the fact that it has three electron-withdrawing CO ligands and two poorly donating $P(OMe)_3$ ligands. The first Re complex has four strongly donating PEt_3 ligands and three very strongly donating hydrides. It is true that the second Re complex is d^6, while the first one is d^4, but the ligand donor properties dominate.

e) $\boxed{[FeH(CO)_3(PPh_3)_2]^+}$ -or- $CuH(PMe_3)_2$

The Fe complex is more electron deficient due to the fact that it is cationic, has three electron-withdrawing CO ligands, and two moderately donating PPh_3 ligands. The Cu complex has two strongly donating phosphine ligands. Although the Cu is more electronegative, the cationic charge and ligand factors on the Fe complex dominate.

3. σ bound carbon ligands: alkyls and aryls

Alkyls and Aryls



Anionic 2 e- donors

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

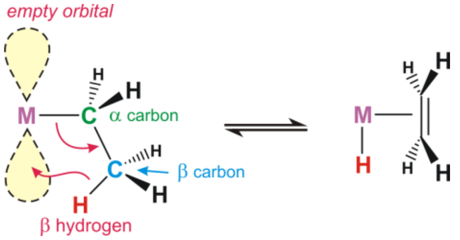
Increasing the carbon substitution (replacing hydrogens with hydrocarbon groups such as methyl, ethyl, isopropyl) usually increases the donor strength, but steric factors can come into play and weaken the metal-alkyl bond (e.g., t-butyl groups are often too sterically hindered to bind well).

Alkyls and Aryls

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.

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.

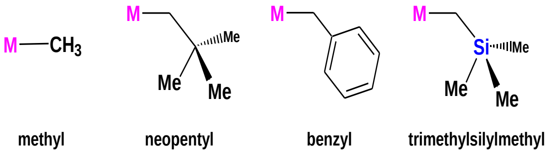
β-Hydride Elimination



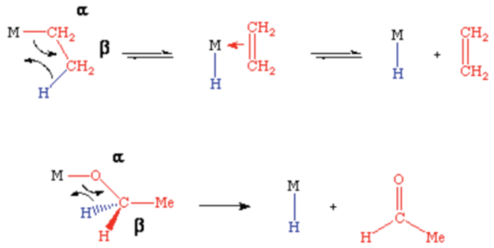
Note that in order to have a β-hydride elimination you MUST have a empty orbital on the metal cisoidal (next) to the alkyl ligand. You also must have β-hydrogens present on the alkyl.

β-Hydride Elimination

In order to prepare stable M-alkyl complexes one generally needs to stay away from alkyls with β-hydrogens (or avoid metals with empty coordination sites). Some common ligands used to avoid β-hydride elimination reactions are shown below.



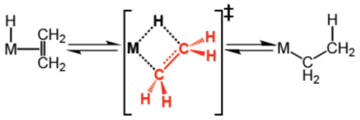
Metal-Alkyl Complexes and β-Hydride Eliminations



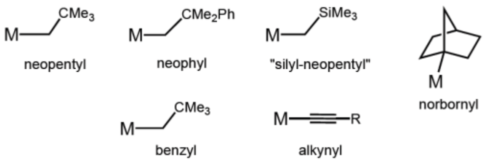
Hydride transfers to M, resulting olefin may or may not stay coordinated
Requirements – (i) Vacant site. (ii) complex usually has less than 18e⁻, Otherwise a 20 electron complex results immediately

Beta-hydride Elimination

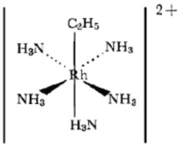
Mechanism ——> Four-center transition state inferred



Stable M-alkyls – No beta-hydride elimination



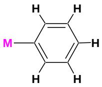
Rh(III)
d^6
low-spin



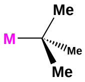
Ex: Stabilize M-alkyl-to β-hydride elimination: have a stable complex where ligands do not come off to create vacant site, that which is needed

Problems:

a) Why doesn't a 16e- M-phenyl do a β-hydride elimination?



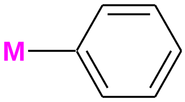
b) Would a 16 e- M-(*t*-butyl) complex be stable or not? Why?



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.

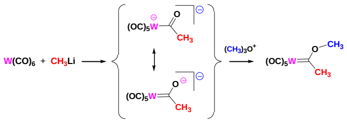
Aryls do have the potential for both π-donation and π-backbonding through the filled aryl π-orbitals and empty π* antibonding orbitals.



4. σ/π-bonded carbon ligands: carbenes, carbynes

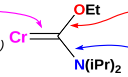
Fischer Carbenes

In 1964 Fischer's group prepared the first transition metal carbon double bond, which he called a carbene, after the very reactive neutral organic CR_2 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)*

Transition Metal Carbene Complexes – 2

M-carbon double bonds —> Metal-carbene complexes – 2 types

R = H, alkyl, aryl etc.

R = alkyl, aryl etc.
E = O, S, N

Fischer carbene complexes (right)

low oxidation state M; heteroatoms at carbene carbon atom

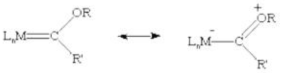
E.O. Fischer (1st Carbene complex (1964, then Nobel Prize with Wilkinson, for metallocenes)

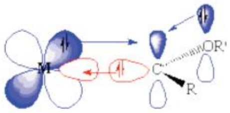
Schrock carbene complexes:

higher oxidation state; C or H substituents at carbene C-atom

"alkylidene complex" Richard Schrock MIT, 2005 Nobel Prize for olefin metathesis (shared with Robert Grubbs (Cal Tech) and Y. Chauvin (France).

Transition Metal Carbene Complexes – 3

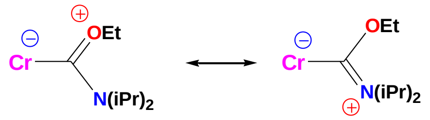




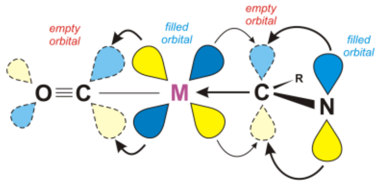
MO/AO perspective: one lone pair is donated from the singlet carbene to an empty d-orbital on the metal (red), and a lone pair is back-donated from a filled metal orbital into a vacant p_z orbital on carbon (blue). There is competition for this vacant orbital by the lone pair(s) on the heteroatom, consistent with our second resonance structure.

Overall, bonding resembles that of carbon monoxide. Therefore, carbene ligands are usually thought of as neutral species, unlike dianionic Schrock alkylidenes (which usually lack electrons for back-donation).

However, electron counting is just a formalism!



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!!***).



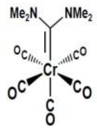
competition for π-backbonding from the metal and the lone pair orbital(s) on the functional group(s) to the carbene empty orbital (N and S the best, then O, Ph, and other π-donating or lone pair containing groups)

	Weak M=C	**Strong M=C**
Metal	Electron-deficient (electron withdrawing ligands like CO, NO, 1st row metal, electronegative metal)	Electron-rich (electron donating ligands, 3rd row metal)
Carbene groups	Good donating functional groups that can π-bond to the carbene (like NR2, SR, OR, Ph); *more than one donating group really weakens the M-C bond!!*	Simple sigma donors like H or CH3 that can't π-donate to the Carbene carbon atom.

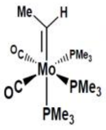
Most Fischer Carbenes favor the **weak bonding situation**, where the metal has a *d⁶* configuration (counting the carbene as neutral ligand), CO ligands, and the carbene has π-donating groups. The *d⁶* configuration naturally favors the middle to late transition metals. The strong carbene bonding situation is actually considerably more reactive, much like the reactivity of a C=C double bond vs. a C-C single bond.

Problem: Circle the correct ordering of the following group of Fisher carbenes from the strongest M=CR$_2$ bond to weakest. Explain your reasoning.

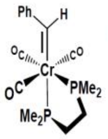
a)



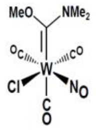
b)



c)



d)



a > b > c > d

b > c > d > a

d > c > b > a

c > a > d > b

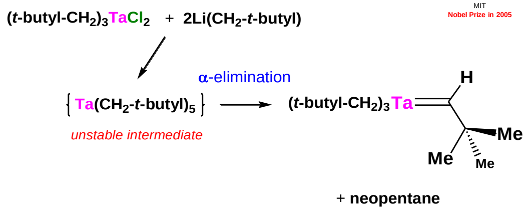
a>b>c>d [✓ b>c>d>a] d>c>b>a c>a>d>b

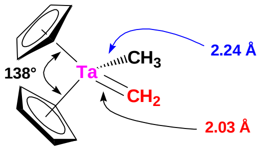
b) has the strongest carbene bond because it has the poorest π-donating groups on the carbene carbon atom – this will allow the empty p-orbital on the carbene to be fully available to π-backbond to the filled d-orbitals on the metal. The Mo center is also the most electron-rich due to the strong donating alkylated phosphine ligands and the lower electronegativity of the Mo center. The Cr center in c) also has strong donating phosphine ligands, but the Cr is a little more electronegative than the Mo and can hang onto its electrons better and not π-backbond as much. The Mo center also has the second-row stronger M-L bonding effect to help it. The Cr complex c) also has a phenyl group on the carbene carbon that can π-donate to the empty p-orbital and weaken the ability of the carbene to π-backbond to the metal center. d) has the next weakest carbene-M bonding due to the strong π-donating OMe and NMe_2 groups on the carbene filling up that empty p-orbital and the very strong π-backbonding of the NO^+ ligand that drains electron-density off the W atom. a) has the very weakest M-carbene bond due to the two strong π-donating NMe_2 groups on the carbene and the lack of any good donor groups on the metal.

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:

Richard Schrock
MIT
Nobel Prize in 2005

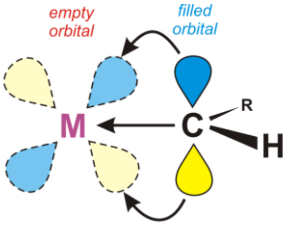




The Ta=CH_2 bond is distinctly shorter than the Ta-CH_3 single bond!

Fischer Carbenes	Schrock Alkylidenes
Nucleophillic attacks at carbon atom of carbene (carbon is electron deficient)	Electrophillic attacks at carbon atom of alkylidene (carbon is electron-rich)
Electrophillic attacks on metal center (metal is more electron-rich, often d^6 18 e- system)	Nucleophillic attacks on metal center (metal is electron-deficient, usually d^2 or d^0 16 or 14 e- count)
Carbene is *stabilized* by heteroatom groups that can π-bond to it. Likes NR_2, SR, OR, or Ph groups.	Alkylidene is *destabilized* by heteroatom groups that can π-bond to it. Strongly prefers H or simple alkyl groups.
Later transition metals favored, especially with d6 counts (carbene as neutral 2e- donor ligand)	Early transition metals favored, especially with do centers (alkylidene as dianionic 4e- donor)

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)

So How Should I Electron Count??

The various methods of electron-counting carbenes and alkylidenes are:

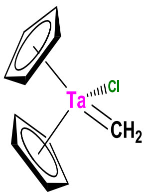
1) both as neutral 2 e- donor ligands (but still draw a M=C double bond)
2) both as dianionic 4 e- donor ligands
3) Fischer carbenes as neutral 2 e- donor ligands. Typically group 6 or higher metals with a d^6 or d^8 electron count (sometimes d^4).
4) Schrock alkylidenes as dianionic 4 e- donor ligands. Typically group 4 or 5 metals with d^0 electron counts. Also later transition metals in high oxidation states (d^0, d^2, or d^4).

Of course, in order to do method 3 or 4, you have to realize whether you have a Fischer or Schrock system.

As far as the overall electron-count is concerned, it DOESN'T matter which electron-counting method you use, since both give you the same overall electron-count!!

It can be important to tell them apart since Schrock alkylidenes almost always have stronger (but often still very reactive) M=C bonds compared to Fischer carbenes. So on a question asking you to order a series of carbene and/or alkylidene complexes, it is generally important to figure out which is which.

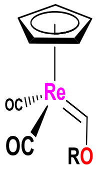
Problem: Identify the following complexes as a Fischer carbene or Schrock alkylidene.



neutral carbene

Ta(+3)	d^2
2 Cp$^-$	12 e-
Cl$^-$	2 e-
CH$_2$	2 e-
	18 e-

d^2 early TM using neutral carbene indicates a Schrock alkylidene complex

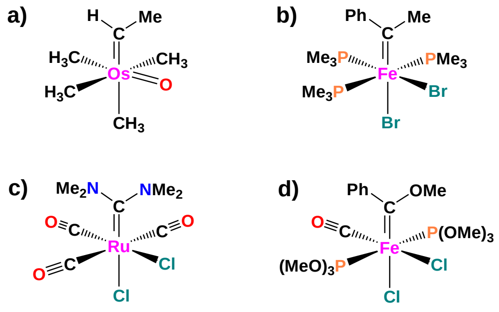


neutral carbene

Re(+1)	d^6
Cp$^-$	6 e-
2CO	4 e-
C(OR)H	2 e-
	18 e-

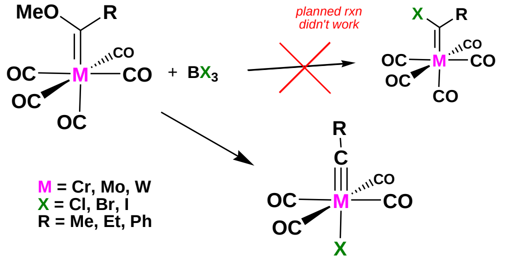
d^6 mid-TM using neutral carbene indicates a Fisher carbene complex

Problem: Order the following M=C complexes from the one with the highest M=CR_2 rotational barrier to the lowest. What factors affect the M=C rotational barrier? Identify each complex as either a Fisher carbene or a Schrock alkylidene.



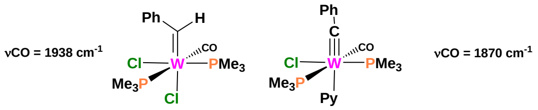
Carbynes/Alkylidynes

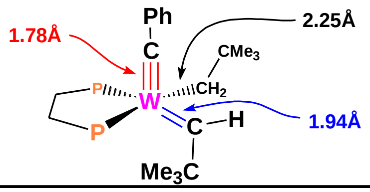
E. O. Fischer accidentally prepared the first M≡C-R triple bonded compound in 1973:

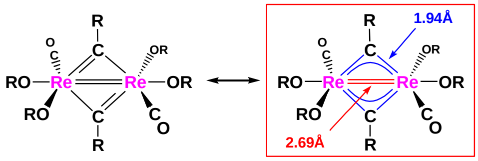


M = Cr, Mo, W
X = Cl, Br, I
R = Me, Et, Ph

Thus, one can simply treat **carbynes** and **alkylidynes** as trianionic (-3) 6e- donating ligands. They are very strong donors as might be expected from the relatively low electronegativity of carbon and the -3 formal charge.







Schrock, JOMC, 1996

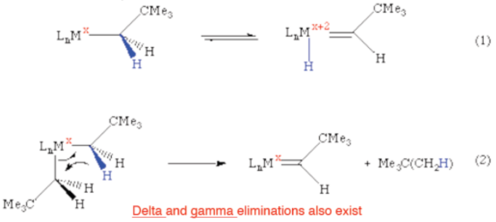
Problem: **Which of the following ligands will coordinate the strongest to the empty coordination site on the metal complexes shown below.**

CO, PMe_3, $P(OMe)_3$, CH_3^-, F^-, CF_3^-

- **a) $[Mn(CO)_5]^+$**
- **b) $ReBr(PMe_3)_4$**
- **c) $[Ni(CH_3)(CO)_2]^+$**

α-hydride elimination

Alpha-hydride elimination is the transfer of a hydride (hydrogen atom) from the alpha-position on a ligand to the metal center. The process can be thought of as a type of oxidative addition reaction as the metal center is oxidized by two electrons (Eq 1). As the reaction involves a formal oxidation of the metal, alpha-elimination can not occur in a d^0 or d^1 metal complex. In these cases, a variant called alpha-abstraction can occur. Alpha-abstraction does not result in a change of oxidation state and the alpha-hydrogen is transferred directly to an adjacent ligand instead of the metal center (Eq 2):



Delta and gamma eliminations also exist

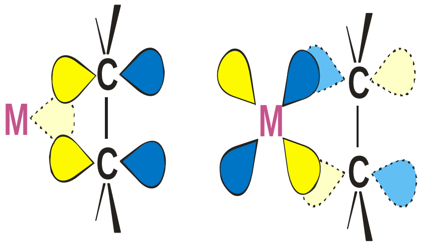
5. π-bonded carbon ligands: alkene, alkynes, allyl, cyclobutadiene, arenes, cyclopentadienyl

Alkenes/Alkynes

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.

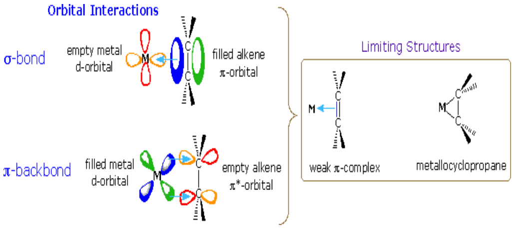
Alkenes/Alkynes

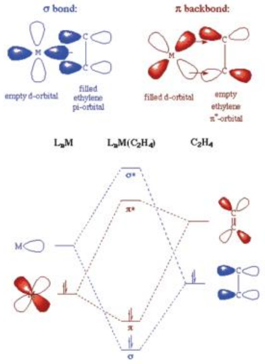


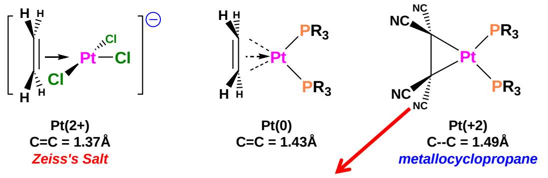
Dewar-Chatt-Duncanson bonding model (1953)

σ-donation via the filled alkene π-system

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





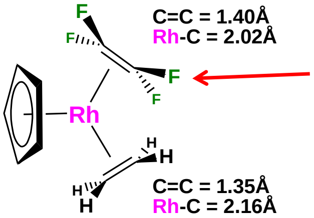


Pt(2+)
C=C = 1.37Å
Zeiss's Salt

Pt(0)
C=C = 1.43Å

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

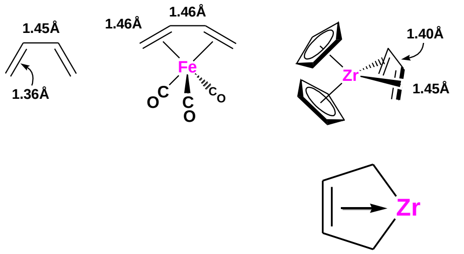
If the metal is electron-rich enough and/or if there are electron-withdrawing groups on the alkene, one can actually get a formal oxidation of the metal via the transfer of 2e- to the alkene to form a dianionic metallocyclopropane ligand that is now coordinated via two anionic alkyl σ-bonds (thus the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



C=C = 1.40Å
Rh-C = 2.02Å

C=C = 1.35Å
Rh-C = 2.16Å

The electron-withdrawing fluorine groups on the $F_2C=CF_2$ alkene makes it a better π-acceptor ligand. This *weakens* the C=C bond, but ***strengthens*** the alkene-metal bond.



Zr is in a very low oxidation state (**+2**, but really wants to be **+4**) and is, therefore, extremely electron-rich. So electron-rich that it transfers two electrons to the butadiene via the π-backdonation and generates a metallo-cyclopentene resonance structure

Electronic Effects

Ethylene Complex	**νC=C (cm^{-1})**
Free Ethylene	**1623**
$[Ag(H_2C{=}CH_2)_2]^+$	**1584**
$Fe(CO)_4(H_2C{=}CH_2)$	**1551**
$[Re(CO)_4(H_2C{=}CH_2)_2]^+$	**1539**
$[CpFe(CO)_2(H_2C{=}CH_2)]^+$	**1527**
$Pd_2Cl_4(H_2C{=}CH_2)_2$	**1525**
$[PtCl_3(H_2C{=}CH_2)]^-$	**1516**
$CpMn(CO)_2(H_2C{=}CH_2)$	**1508**
$Pt_2Cl_4(H_2C{=}CH_2)_2$	**1506**
$CpRh(H_2C{=}CH_2)_2$	**1493**

The ***thermodynamic stability*** of metal-alkene complexes is strongly affected by the nature of the alkene (and metal):

1) Electron-withdrawing groups on the alkene generally increase the strength of the metal-alkene bonding, while electron-donating groups generally decrease the stability. Exception (backdonation)
2) In cases where *cis-trans* isomerism is possible, the more stable complex is almost always formed by the *cis*-alkene (steric factors).

3) Metal complexes of ring-strained cycloalkenes (e.g., cyclopropene) display higher than expected stability. The ring strain raises the energy of the cycloalkene ring system making it a better donor to the metal center **(better orbital energy matching).**
4) Chelating dienes show the expected stabilization from the chelate effect. The most common examples are norbornadiene and cyclooctadiene as shown.

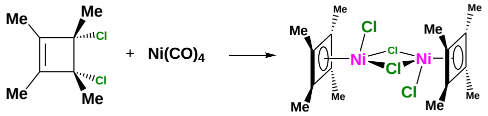
norbornadiene complex

cyclooctadiene complex

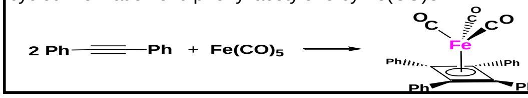
5) **Third-row metals** form the strongest bonds and most stable complexes (as with most ligands).

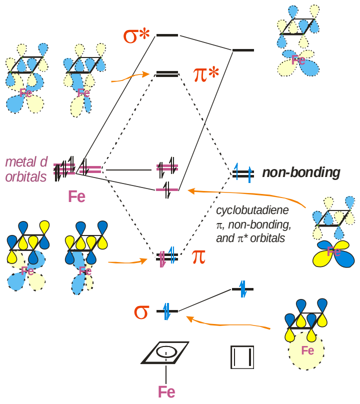
Cyclobutadiene

A triumph of the early days of organometallic chemistry was the successful synthesis of $(\eta^4\text{-}C_4H_4)_2Ni_2(\mu\text{-}Cl)_2Cl_2$, a stable metal-coordinated cyclobutadiene molecule, by Criegee in 1959. This was actually predicted theoretically by Longuet-Higgins and Orgel in 1956 using an early form of molecular orbital theory.



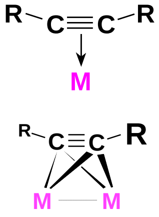
A simpler route was discovered shortly after involving the cyclodimerization of diphenyl acetylene by Fe(CO)5:





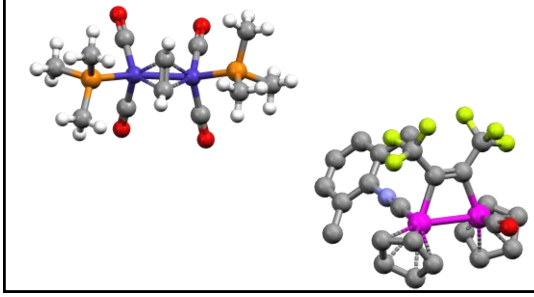
Alkynes

Alkynes are essentially like alkenes, only with another perpendicular pair of π-electrons. Thus they can act as neutral 2 or 4 e- donors, depending on the needs of the metal center. They are also much better bridging ligands because of this second set of π-electrons.



Note how the bridging alkyne is drawn. This indicates a perpendicular bridging mode and that both carbons are interacting equally with both metals (the alkyne is donating 2e- to each metal). It dos NOT indicate that each carbon has 6 bonds to it !!

When alkynes bridge, they almost always do so perpendicular to the M-M axis, the parallel bridging mode is known, but is quite rare:

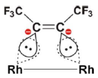


Consider $Cp_2Rh_2[\mu\text{-}(CF_3CCCF_3)](CO)(CNR)$. The Rh-Rh bond distance is 2.67 Å strongly indicating the presence of a covalent bond between the two rhodium atoms.

(a) show the electron-counting for this complex including Rh oxidation state, ligand charges, # of e- donated, etc. Only one Rh center needs to be counted since both the CO and C≡NR ligands are neutral 2e- donors making the complex electronically symmetrical from an electron counting viewpoint.

The electron-withdrawing groups on the alkyne allow it to oxidize each Rh center by 1e- to put each into the +2 oxidation state (d^7) and convert the alkyne into a dianionic bridging *alkene ligand. This is analogous to the alkene example on the* first page of the alkene chapter where the electron withdrawing cyano groups allow it to formally oxidize the Pt center and make a σ-coodinated metallocyclopropane complex.

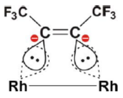
Rh(+2)	d7
Cp-	6e-
$[CF_3C{=}CCF_3]^{2-}$	2e-
CO (or CNR)	2e-
Rh-Rh	1e-
	18e-



(b) Why does the alkyne ligand orient parallel to the Rh-Rh bond? From an organic hybridization and bonding viewpoint how should the "alkyne" be considered? Draw a simple orbital picture showing how the filled "alkyne" orbitals are overlapping with the empty Rh orbitals (use the diagram below as a starting point, ignore all other ligands).

The 2e- reduction of the alkyne changes the carbon hybridization from *sp to sp^2 (double bond like). Each carbon* center now has a *sp^2 hybrid orbital in the plane of the double bond with a lone-pair to bond to each Rh center. By* using these stronger σ-donating orbitals the "alkyne" ligand now must orient parallel to the Rh-Rh bond axis.

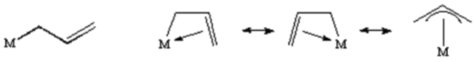
Remember that ligands with π-systems and σ-lone pairs generally prefer bonding to the metal via the σ-lone pairs.



Broblem: Aside from CO, what other ligands mentioned in the lectures can act like π-backbonding (or π-acceptor) ligands and would have easily monitored IR stretching frequencies (in the 2800-1600 cm^{-1} region) that might prove useful as "sensors" for measuring the amount of electron density (or lack there of) on a transition metal center? [*Hint: there are 3 or 4* reasonable choices] Discuss which of these would be the best choice for this and why.

We are looking for ligands that have X=Y or X≡Y (X, Y = C, N, O) with double or triple bonding between the two atoms. Only these will have characteristic IR stretching frequencies in the range indicated. The best, of course, is N≡O$^+$, followed by C≡N-R (isocyanide), R-C≡C-R (alkynes), and $R_2C{=}CR_2$ (alkenes). Nitriles (N≡C-R) are another possibility, but it was mentioned in the notes and lecture that these are not particularly good π-acceptors. Anionic ligands like C≡N$^-$, C≡C-R$^-$, and CH=CR$_2^-$ are not good π-acceptors due to their anionic charges.

Allyl Ligand Organometallic Complexes



η^1-form

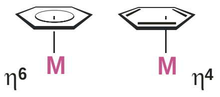
unidentate 2-e^- anionic ligand
rarely observed form
$[CH_2{=}CHCH_2Co(CN)_5]^{3-}$
$[CH_2{=}CHCH_2Mn(CO)_5]$
C–C stretch ~ 1620 cm^{-1}

η^3-form

alkyl + neutral alkene (2-e^-)—> bidentate
most common structure
behaves as delocalized π-system
3 (4) electrons now valence electrons

Arenes

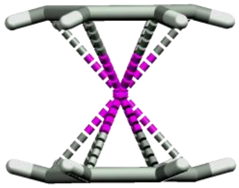
Arenes (benzene being the simplest member of this family) typically coordinate in an η6 fashion and as such are **neutral 6 e- donors**, although they can adopt lower coordination modes (η^4 and η^2).



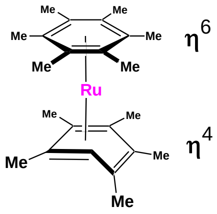
π-Backbonding

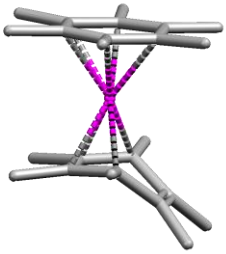
π-backdonation plays a relatively important role in arene bonding and chemistry. Arenes tend to favor metals in low oxidation states and often generate surprisingly stable complexes. $Cr(C_6H_6)_2$, for example, is kinetically inert to most substitution reactions, no doubt due to its 18 e- configuration, but also due to the mix of π-bonding and backbonding.

Remember that CO and NO^+ are far, far stronger π-backbonding ligands.

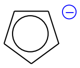


A dramatic example of the "power" of the 18e- electronic configuration is seen for $[Ru(C_6Me_6)_2]^{2+}$. This can be reduced to neutral $Ru(C_6Me_6)_2$, but electron-counting with two η^6-C_6Me_6 ligands gives you a 20e- complex.



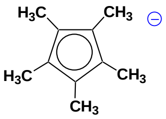


Cyclopentadienyl ligands – Cp's



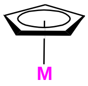
6e- strong donor

Cp

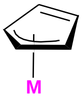


6e- stronger donor bulky ligand

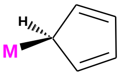
Cp*



η^5

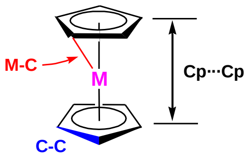


η^3



η^1

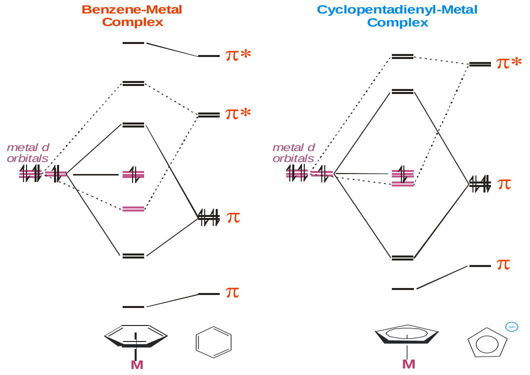
Structural Features



M	M-C	Cp…Cp	C-C
Fe	2.04	3.29	1.42
[Fe]$^+$	2.07	3.40	1.40
Ru	2.19	3.64	1.43
Os	2.19	3.61	1.45
Co	2.10	3.44	1.41
[Co]$^+$	2.03	3.24	1.42
Ni	2.18	3.63	1.41

The changes in the neutral Fe, Co, Ni metallocenes are a direct result of going from 18e- (Fe) to 19e- (Co) to 20e- (Ni) counts. The extra electrons for the Co and Ni complexes are going into M-Cp antibonding orbitals, which are delocalized and progressively weaken the M-Cp bonding, leading to the increase in bond distances. This in spite of the fact that the metal's covalent radius is *decreasing* as one goes from Fe to Ni.

MO Comparison of Cp^- vs. Arene Ligands

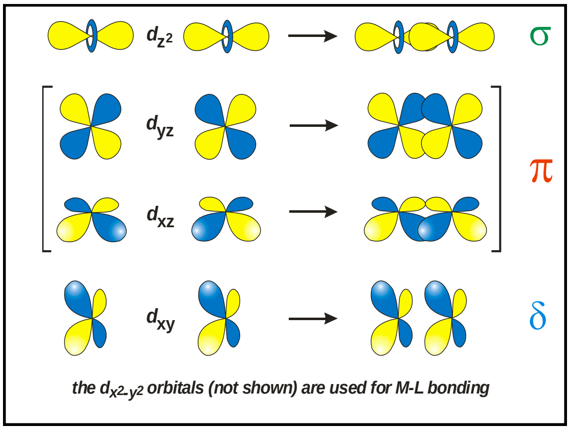


6- Metal-Metal Bonding

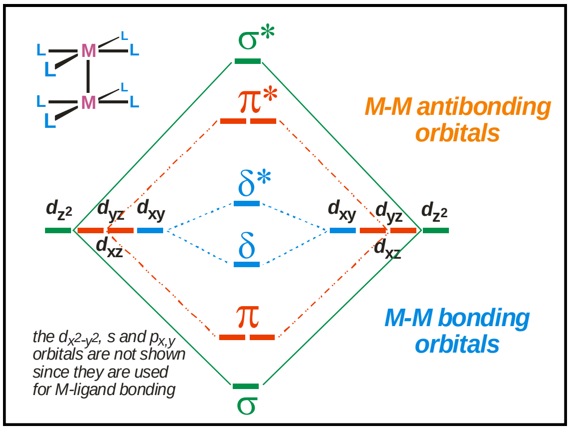
Covalent: **Electron precise bonds. M-M bond counts as one e- from each metal center. Most common type of M-M bonding.**

Dative: **Where one metal uses a filled *d* orbital "lone pair" to coordinate to an empty orbital on a second, more unsaturated metal. Most dative bonding situations can also be electron-counted as covalent bonds.**

Symmetry: **Weak metal-metal interactions caused by molecular orbital symmetry interactions of filled & empty M-M bonding and/or antibonding orbitals. Typically seen for d8 metals. Not at all common.**



the $d_{x^2-y^2}$ orbitals (not shown) are used for M-L bonding



M-M antibonding orbitals

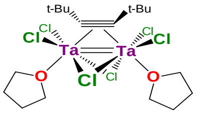
M-M bonding orbitals

the $d_{x^2-y^2}$, s and $p_{x,y}$ orbitals are not shown since they are used for M-ligand bonding

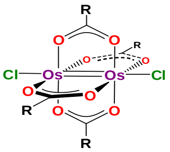
Electron Count	Resulting M-M Bond
d^1 - d^1	Single bond
d^2 - d^2	Double bond
d^3 - d^3	Triple bond
d^4 - d^4	Quadruple bond *optimum*
d^5 - d^5	Triple bond
d^6 - d^6	Double bond *(M-L bonding usually dominates)*
d^7 - d^7	Single bond
d^8 - d^8	No bond *(symmetry interaction)*

Some Covalent Multiple Bonded Examples:

Double Bonds



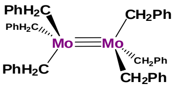
Ta=Ta = 2.68 Å



Os=Os = 2.30 Å

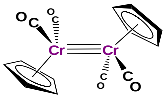
Triple Bonds

Chisholm d^3-d^3 Triple Bonds



Mo-Mo = 2.17 Å

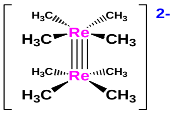
d^5-d^5 Triple Bond

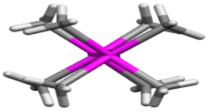


Cr-Cr = 2.27 Å

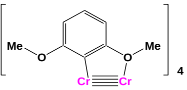
Quadruple Bonds (Cotton)

d^4-d^4 electronic configurations often lead to the formation of quadruple M-M bonds. Prof. F. Albert Cotton at Texas A&M was famous for his discovery and extensive studies of M-M quadruple bonds (and other M-M bonded systems).

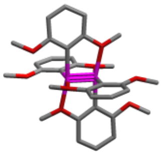




Re-Re = 2.18 Å



Cr-Cr = 1.85 Å



F. Albert Cotton
Texas A&M University

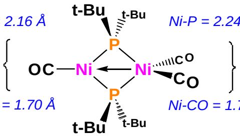
Dative M-M Bonds (unsymmetrical M-M bonded complexes)

Ni-P = 2.16 Å

Ni-P = 2.24 Å

planar coordination like Ni(+2)

tetrahedral coordination like Ni(0)



Ni-CO = 1.70 Å

Ni-CO = 1.78 Å

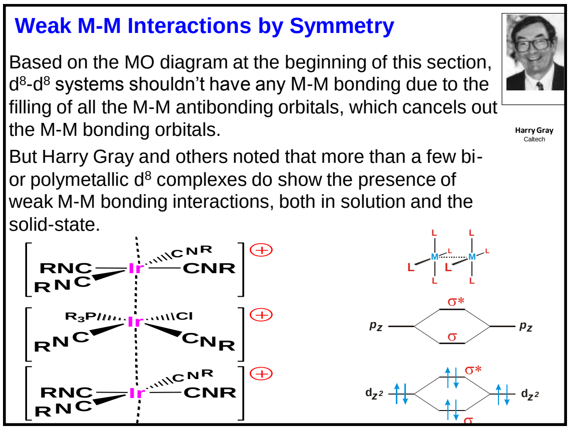
Ni-Ni = 2.41 Å

Covalent M-M Bonding

Left Ni		**Right Ni**	
Ni(+1)	d9	Ni(+1)	d9
$[\mu\text{-PR}_2]^-$	2e-	$[\mu\text{-PR}_2]^-$	2e-
$\mu\text{-PR}_2$	2e-	$\mu\text{-PR}_2$	2e-
CO	2e-	2CO	4e-
M-M	1e-	M-M	1e-
Total	**16e-**	**Total**	**18e-**

Dative

Left Ni		**Right Ni**	
Ni(+2)	d8	Ni(0)	d10
$2[\mu\text{-PR}_2]^-$	4e-	$2\mu\text{-PR}_2$	4e-
CO	2e-	2CO	4e-
Ni←Ni(0)	2e-		
Total	**16e-**	**Total**	**18e-**



Weak M-M Interactions by Symmetry

Based on the MO diagram at the beginning of this section, d^8-d^8 systems shouldn't have any M-M bonding due to the filling of all the M-M antibonding orbitals, which cancels out the M-M bonding orbitals.

But Harry Gray and others noted that more than a few bi- or polymetallic d^8 complexes do show the presence of weak M-M bonding interactions, both in solution and the solid-state.

Harry Gray
Caltech