

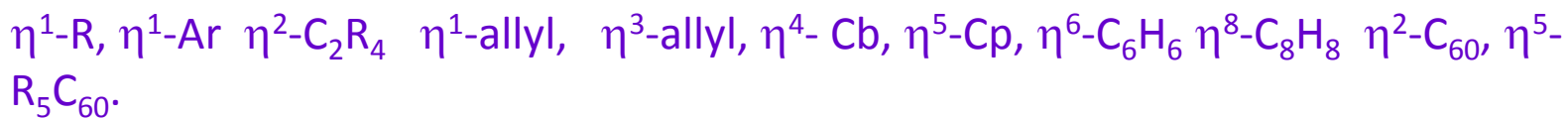
18 electron rule : How to count electrons

The rule states that *thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals 18.*

In general, the conditions favoring adherence to the 18 electron rule are, an **electron rich metal** (one that is in a low oxidation state) and ligands that are **good π -acceptors**

The **hapto symbol, η** , with a numerical superscript, provides a topological description by indicating the connectivity between the ligand and the central atom. For example, if all the five carbon atoms of a cyclopentadienyl moiety are equidistant from a metal atom, we term it as η^5 -cyclopentadienyl

Examples:



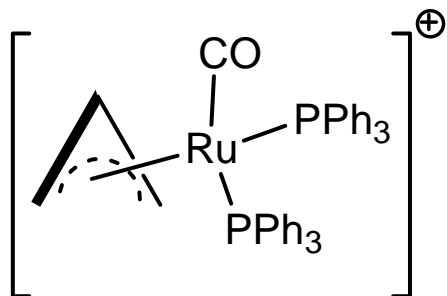
The symbol **μ** indicates bridging; normally we have μ_2 and rarely μ_3 bridging

Examples:

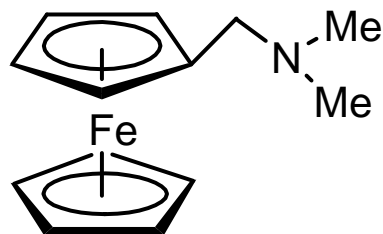


Methods of counting: Neutral atom method & Oxidation state method

Ligand	Neutral atom	Oxidation state		Ligand	Neutral atom	Oxidation state	
		Electron contribution	Formal charge			Electron contribution	Formal charge
Carbonyl (M-CO)	2	2	0	Halogen (M-X)	1	2	-1
Phosphine (M-PR ₃)	2	2	0	Alkyl (M-R)	1	2	-1
Amine (M-NR ₃)	2	2	0	Aryl (M-Ar)	1	2	-1
Amide (M-NR ₂)	1	2	-1	acyl (M-C(O)-R)	1	2	-1
Hydrogen (M-H)	1	2	-1	η^1 -cyclopentadienyl	1	2	-1
Alkene (sidewise) η^2 -	2	2	0	η^1 -allyl	1	2	-1
Alkyne (sidewise) η^2 -	2	2	0	η^3 -allyl	3	4	-1
η^2 -C ₆₀	2	2	0	η^5-cyclopentadienyl	5	6	-1
Nitrosyl bent	1	2	-1	η^6 -benzene	6	6	0
Nitrosyl linear	3	2	+1	η^7 -cycloheptatrienyl	7	6	+1
Carbene (M=CR ₂)	2	4	-2	Carbyne (M \equiv CR)	3	6	-3
Alkoxide (M-OR)	1	2	-1	Thiolate (M-SR)	1	2	-1
μ -CO (M-(CO)-M)	2	2	0	μ -H	1	2	-1
μ -alkyne	4	4	0	μ -X (M-X-M) X = halogen	3	4	-1
μ -alkyl	1	2	-1	μ -amido (M-(NR ₂)-M)	3	4	-1
μ -phosphido (M-(PR ₂)-M)	3	4	-1	μ -alkoxide (M-(OR)-M)	3	4	-1



	neutral atom method	oxidation state method
Ru	8	6 (Ru +2)
η^3 -allyl	3	4
2 PPh ₃	4	4
CO	2	2
charge	-1	not required
	16	16



Fe	8	6 (Fe +2)
2 η^5 -Cp	10	12
	18	18

Neutral atom method: Metal is taken as in zero oxidation state for counting purpose

Oxidation state method: We first arrive at the oxidation state of the metal by considering the number of anionic ligands present and overall charge of the complex

Suggestion: Focus on one counting method till you are confident

Easy way to remember ligand electron contribution for **neutral atom counting** method

	<i>Electron contribution</i>	
Neutral terminal :	CO, PR₃, NR₃	2 electrons
Anionic terminal :	X-, H-, R-, Ar-, R₂N-, R₂P-, RO-	1 electron
Hapto ligands	: η^2-C₂R₄ η^2-C₂R₂, η^4-C₂R₂, η^1-allyl, η^3-allyl, η^4-Cb, η^5-Cp, η^6-C₆H₆, η^7-C₇H₇, η^8-C₈H₈, η^2-C₆₀, η^5-R₅C₆₀	same as hapticity
bridging neutral	μ_2-CO, μ_3-CO	2 electrons
Bridging anionic	μ_2-CH₃, μ_2-H (no lone pairs)	1 electron
Bridging anionic (with 1 lone pair)	μ_2-Cl, μ_2^-OR, μ_2-PR₂, μ_2-NR₂	3 electrons
μ_3 -Cl (2 l.p)		5 electrons
Bridging alkyne		4 electrons
NO linear		3 electrons
NO bent (l. p on nitrogen)		1 electron
Carbene M=C		2 electron
Carbyne M \equiv C		3 electron

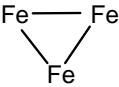
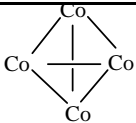
How to determine the total number of metal - metal bonds

Determine the total valence electrons (TVE) in the entire molecule (that is, the number of valence electrons of the metal plus the number of electrons from each ligand and the charge); say, it is A .

Subtract this number from $n \times 18$ where n is the number of metals in the complex, that is, $(n \times 18) - A$; say, it is B .

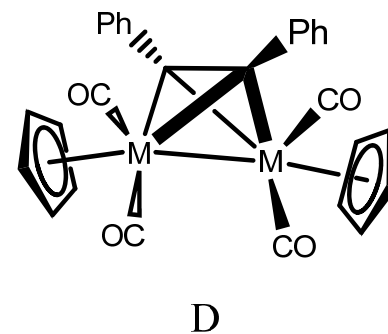
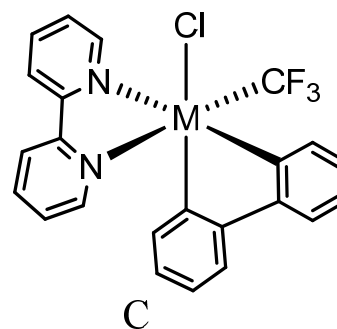
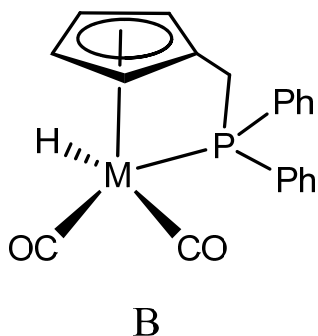
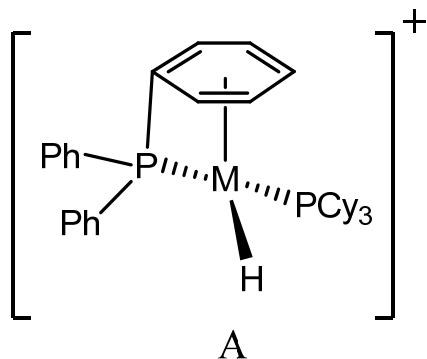
(a) B divided by 2 gives the total number of M–M bonds in the complex.

(b) A divided by n gives the number of electrons per metal. If the number of electrons is 18, it indicates that there is no M–M bond; if it is 17 electrons, it indicates that there is 1 M–M bond; if it is 16 electrons, it indicates that there are 2 M–M bonds and so on.

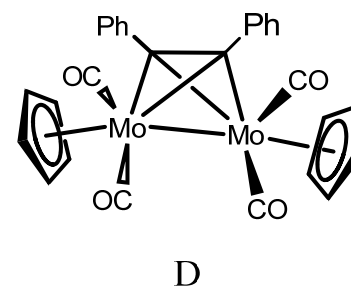
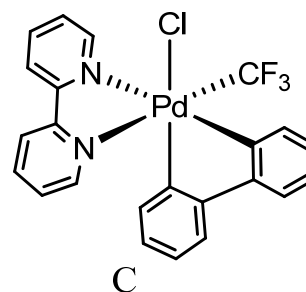
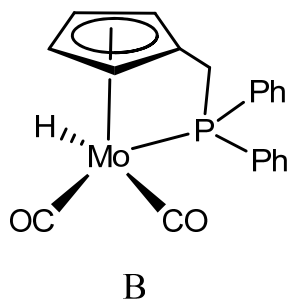
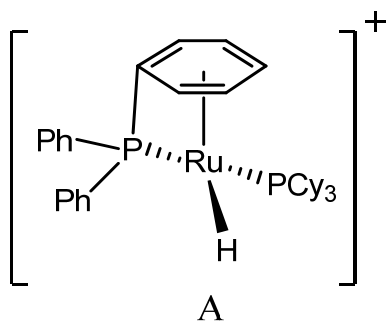
Molecule	TVE (A)	$(18 \times n) - A$ (B)	Total M–M bonds (B/2)	Bonds per metal	Basic geometry of metal atoms
$\text{Fe}_3(\text{CO})_{12}$	48	$54 - 48 = 6$	$6/2 = 3$	$48/3 = 16$; 2	
$\text{Co}_4(\text{CO})_{12}$	60	$72 - 60 = 12$	$12/2 = 6$	$60/4 = 15$; 3	
$[\eta^5\text{-CpMo}(\text{CO})_2]_2$	30	$36 - 30 = 6$	$6/2 = 3$	$30/2 = 15$; 3	$\text{Mo} \equiv \text{Mo}$
$(\eta^4\text{-C}_4\text{H}_4)_2\text{Fe}_2(\text{CO})_3$	30	$36 - 30 = 6$	$6/2 = 3$	$30/2 = 15$; 3	$\text{Fe} \equiv \text{Fe}$
$\text{Fe}_2(\text{CO})_9$	34	$36 - 34 = 2$	$2/2 = 1$	$34/2 = 16$; 1	$\text{Fe}-\text{Fe}$

Problem solving

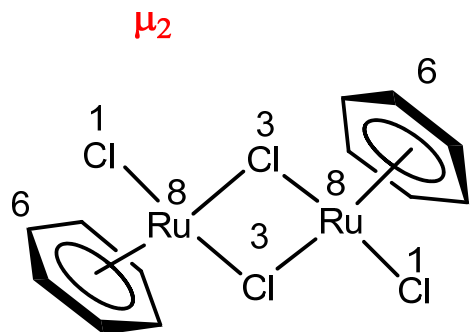
The following organometallic compounds are stable and has a second row transition metal at its centre. Find out the metal and its oxidation state



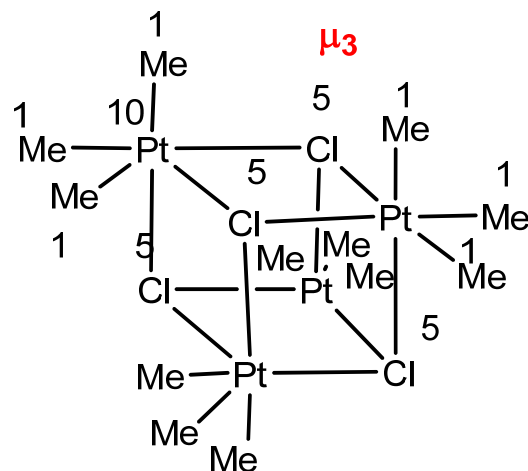
yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41
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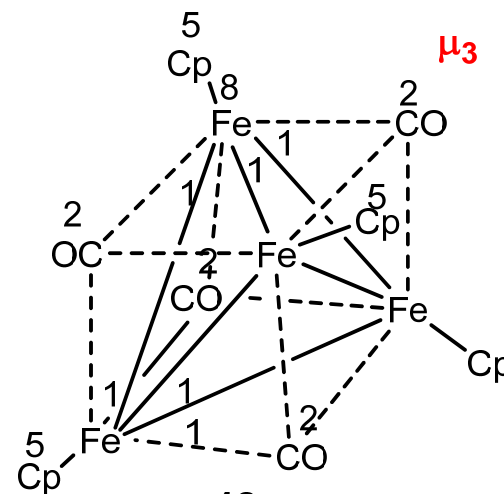
A few worked out examples



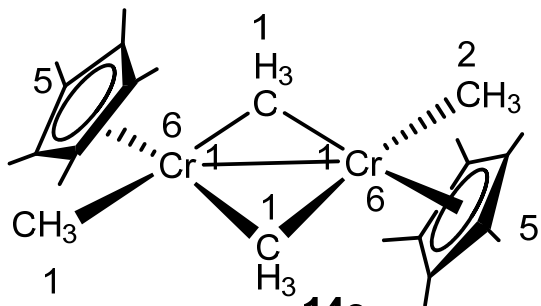
18e



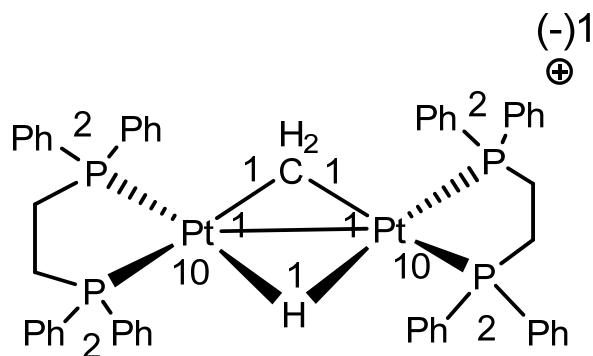
18e



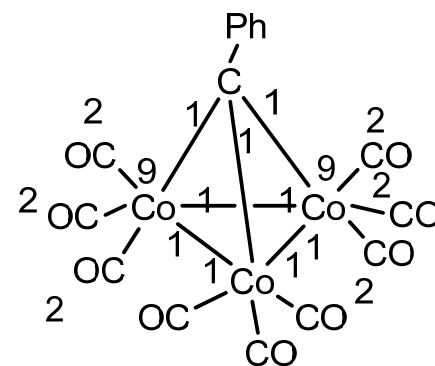
18e



14e



16e



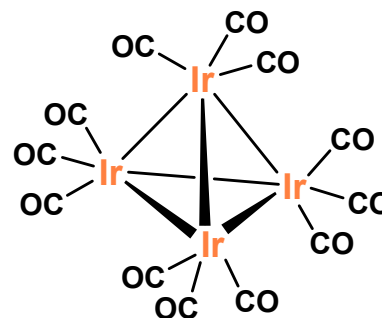
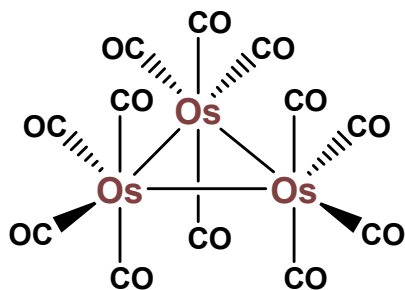
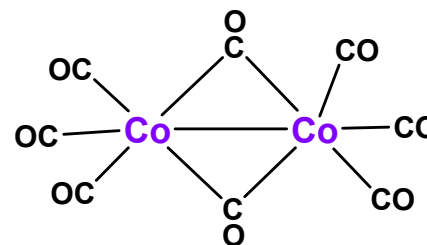
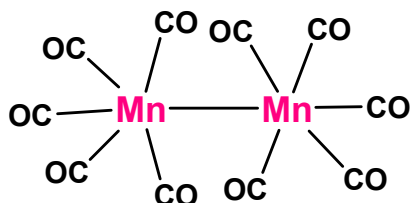
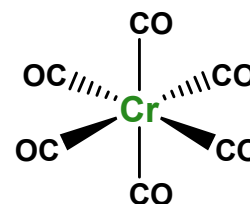
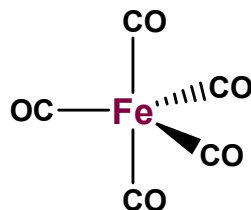
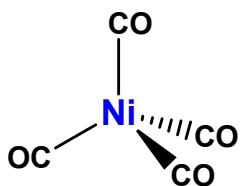
18e

Understanding metal –metal bond electron count become easier if you compare and see how octet is attained by each Cl atom of Cl_2

Exceptions to the 18 electron rule

- Square planar organometallic complexes of the late transition metals (16e).
- Some organometallic complexes of the early transition metals (e.g. Cp_2TiCl_2 , WMe_6 , Me_2NbCl_3 , CpWOCl_3) [A possible reason for the same is that some of the orbitals of these complexes are too high in energy for effective utilization in bonding or the ligands are mostly σ donors.]
- Some high valent d^0 complexes have a lower electron count than 18.
- Sterically demanding bulky ligands force complexes to have less than 18 electrons.
- The 18 electron rule fails when bonding of organometallic clusters of moderate to big sizes (6 Metal atoms and above) are considered.
- The rule is not applicable to organometallic compounds of main group metals as well as to those of lanthanide and actinide metals.

Metal carbonyls



Coordination number around the metal normally remains six or lesser.
 species such as $\text{Mn}(\text{CO})_5$, $\text{Co}(\text{CO})_4$ dimerize to gain 18 electrons

17 electron

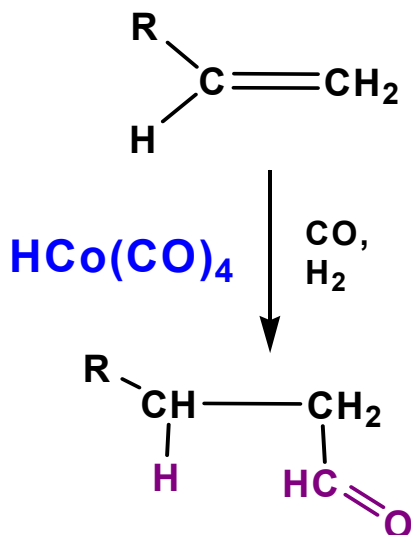
$\text{V}(\text{CO})_6$ does not dimerize.

Why study metal carbonyls ?

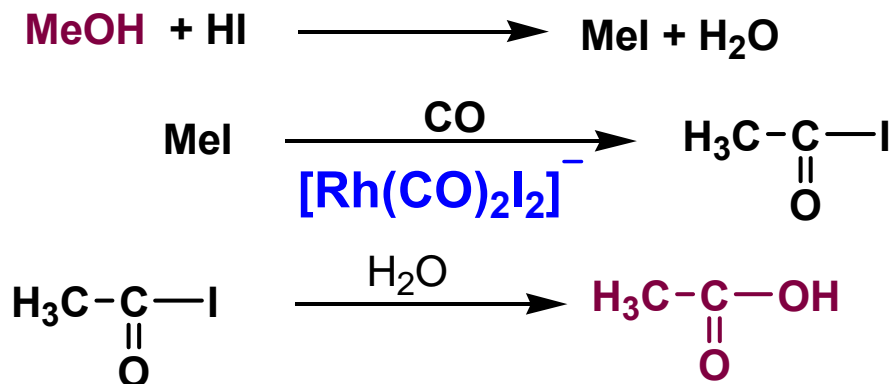
Simplest of organometallic compounds where M-C σ bonding is well understood. CO is one of the strongest π acceptor ligands. Back bonding (π bonding) and variation in electronic properties of CO can be monitored very efficiently by **Infrared spectroscopy**

A range of metal carbonyls are used as **catalysts in Chemical Industry**

Hydroformylation Alkene to Aldehyde



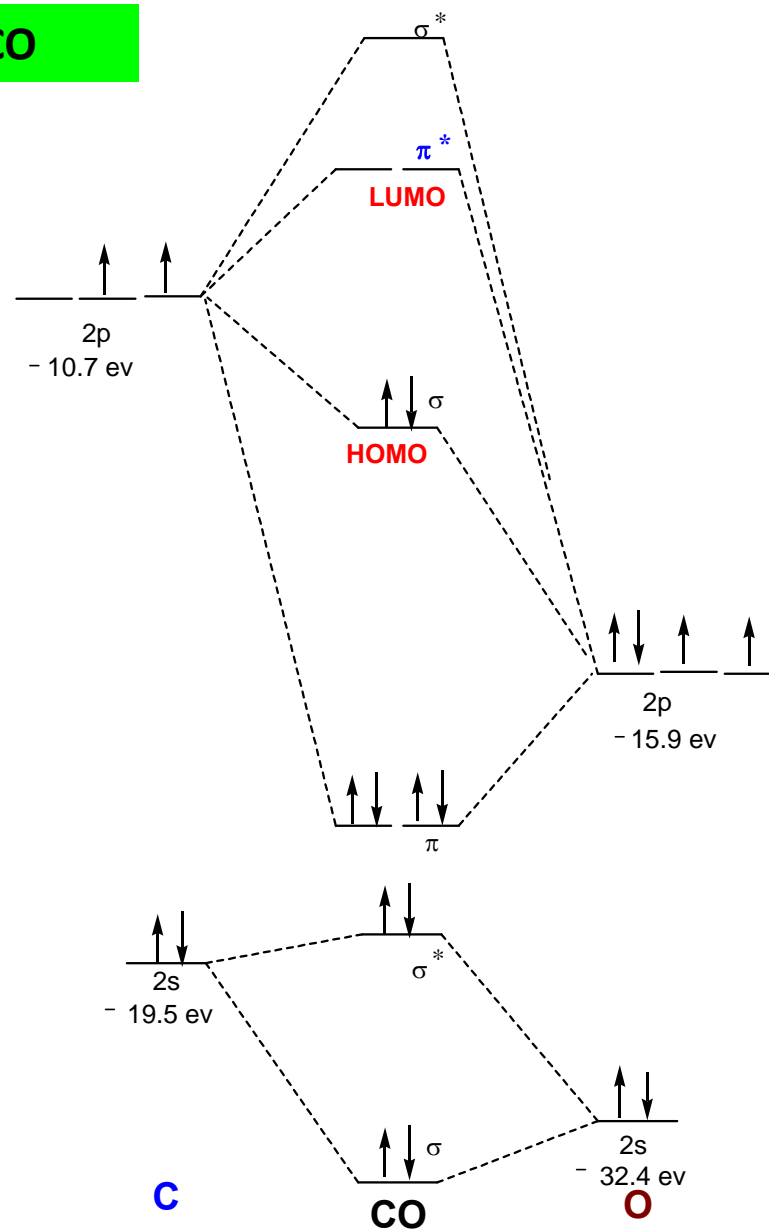
Methanol to Acetic acid Process

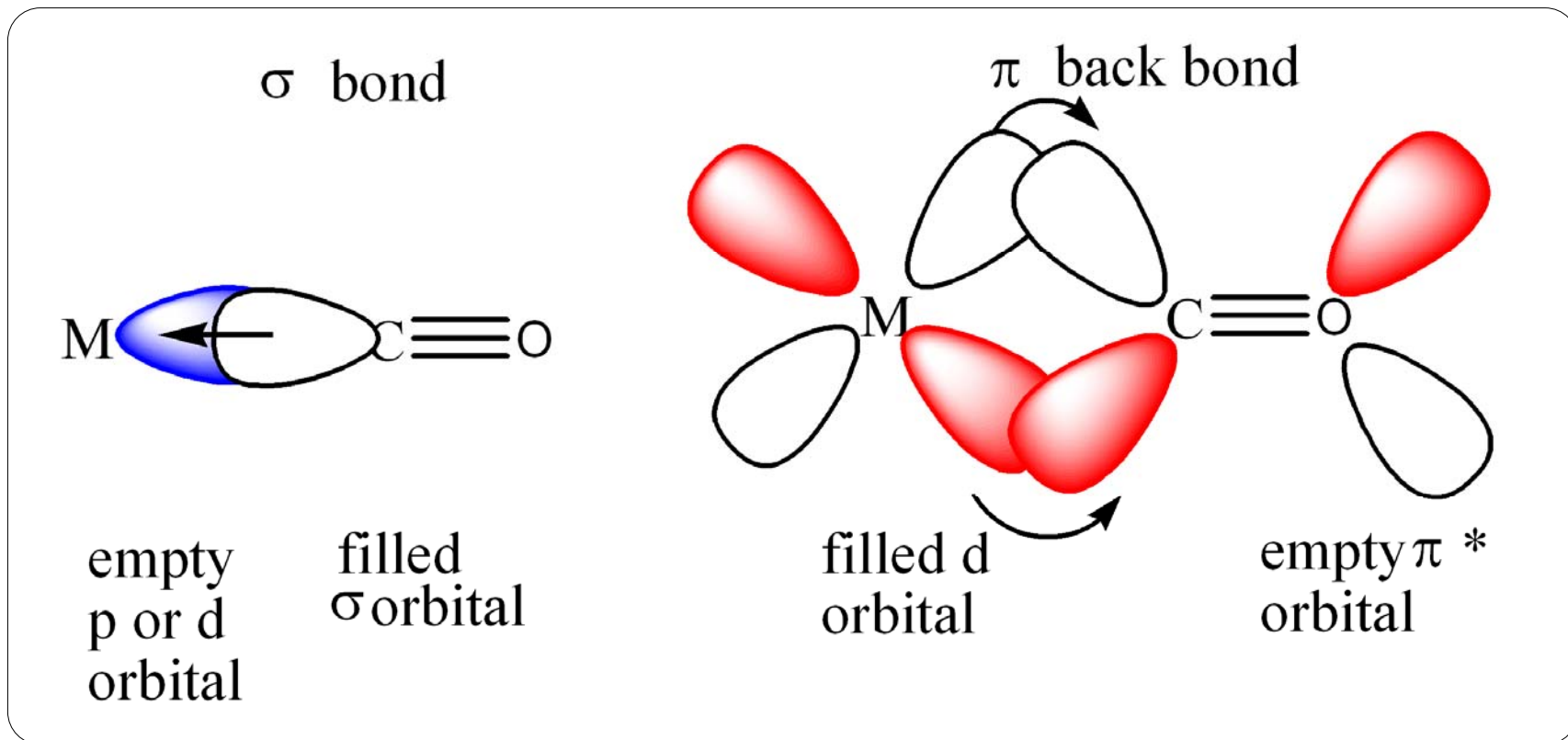


Molecular Orbital diagram of CO

Why does CO bind a metal through its less electronegative carbon atom than its more electronegative oxygen? What makes it a good π acceptor?

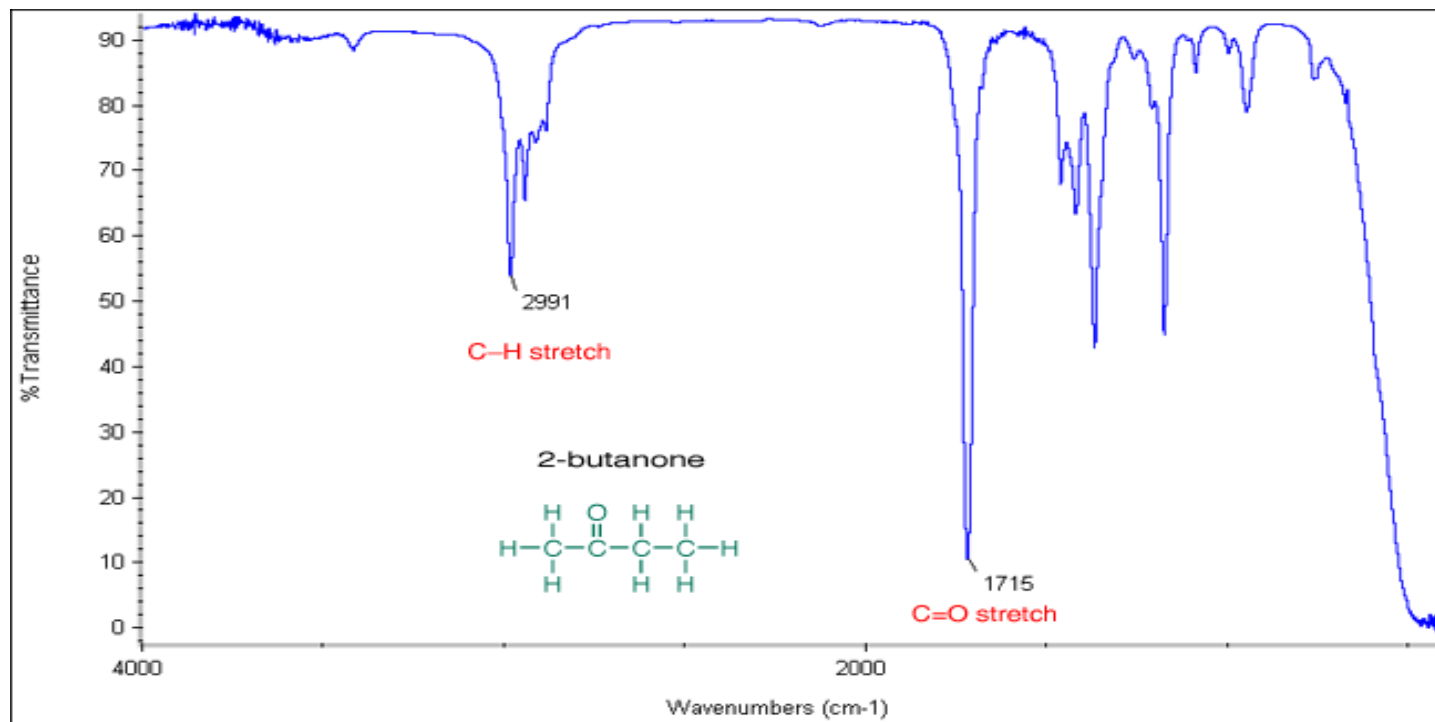
The highest occupied molecular orbital (**HOMO**) of CO is weakly antibonding (compared with the O atomic orbitals) and is an MO which is carbon based. Secondly, the π^* antibonding orbital which is the lowest unoccupied molecular orbital (**LUMO**) is also of comparatively lower energy which makes it possible to interact with metal t_{2g} orbitals for π bonding. There exists a strong back bonding of metal electrons to the π^* antibonding orbitals of CO





Counting the electrons helps to predict stability of metal carbonyls. But **it will not tell you whether a CO is bridging or terminal**

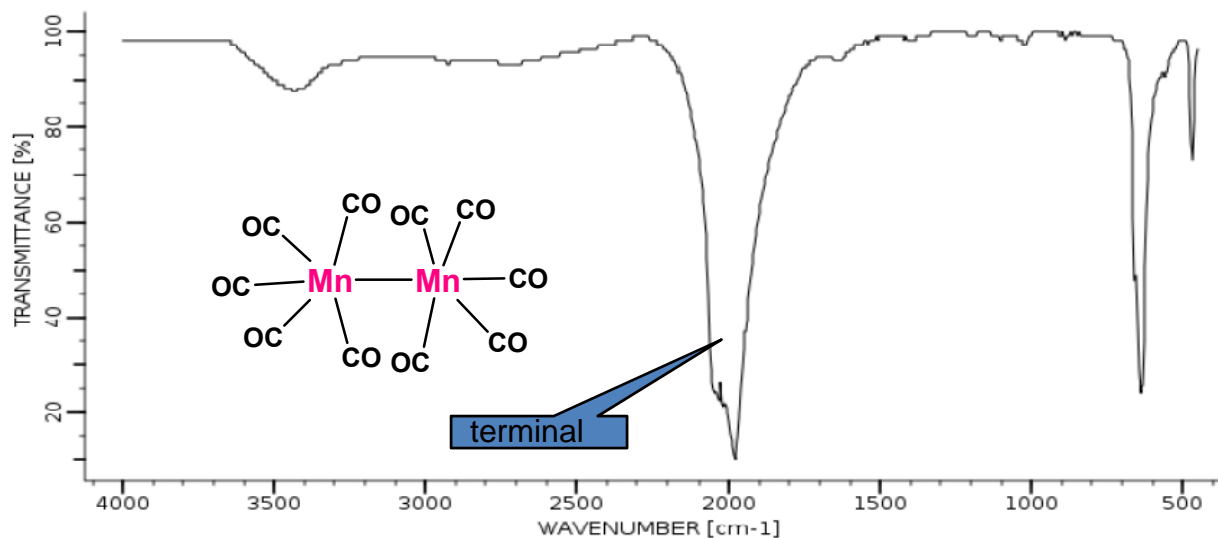
Infrared Spectroscopy- A spectro-analytical tool in chemistry



Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a compound positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Functional groups are identified based on vibrational modes of the groups such a stretching, bending etc. Different vibrational modes absorb characteristic frequencies of IR radiation. An infrared spectrophotometer is an instrument that passes infrared light through a molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis. Absorption of radiation lowers the percentage transmittance value.



Infrared Spectroscopy- Spectra of Metal Carbonyls



The range in which the band appears decides bridging or terminal .

The number of bands is only related to the symmetry of the molecule

