

Colors of transition metal complexes:

Intensity of Color

How intensity of color is expressed

$$A = \log_{10} \frac{I_o}{I} = \epsilon l c$$



The **molar absorption coefficient**, **molar extinction coefficient**, or **molar absorptivity** (ϵ), is a measurement of how strongly a chemical species absorbs light at a given wavelength. It is an intrinsic property of the species; the actual absorbance A , of a sample is dependent on the pathlength, ℓ , and the concentration, c , of the species via the **Beer–Lambert law**,

Selection rules:

Electronic transitions in a complex are governed by Selection rules

A selection rule is a quantum mechanical rule that describes the types of quantum mechanical **transitions that are permitted**.

They reflect the restrictions imposed on the state changes for an atom or molecule during an electronic transition.

Transitions **not** permitted by selection rules are said **forbidden**, which means that theoretically they must not occur (but in practice may occur with very low probabilities).

1. Laporte Selection Rule

Statement : Only allowed transitions are those occurring with a change in parity (flip in the sign of *one* spatial coordinate.) OR During an electronic transition the azimuthal quantum number can change only by ± 1 ($\Delta l = \pm 1$)

The Laporte selection rule reflects the fact that for light to interact with a molecule and be absorbed, there should be a change in dipole moment.



Otto Laporte
German American Physicist

Practical meaning of the Laporte rule

Allowed transitions are those which occur between **gerade** to **ungerade** or **ungerade** to **gerade** orbitals

Allowed

$g \longrightarrow u$ & $u \longrightarrow g$

Not allowed (FORBIDDEN)

$g \not\longrightarrow g$ & $u \not\longrightarrow u$

$t_{2g} \longrightarrow e_g$ is forbidden OR
According to Laporte selection rule
d \rightarrow d transitions are not allowed !

Gerade = symmetric w r t
centre of inversion
Ungerade = antisymmetric
w r t centre of inversion

This rule affects Octahedral and Square planar complexes as they have center of symmetry.

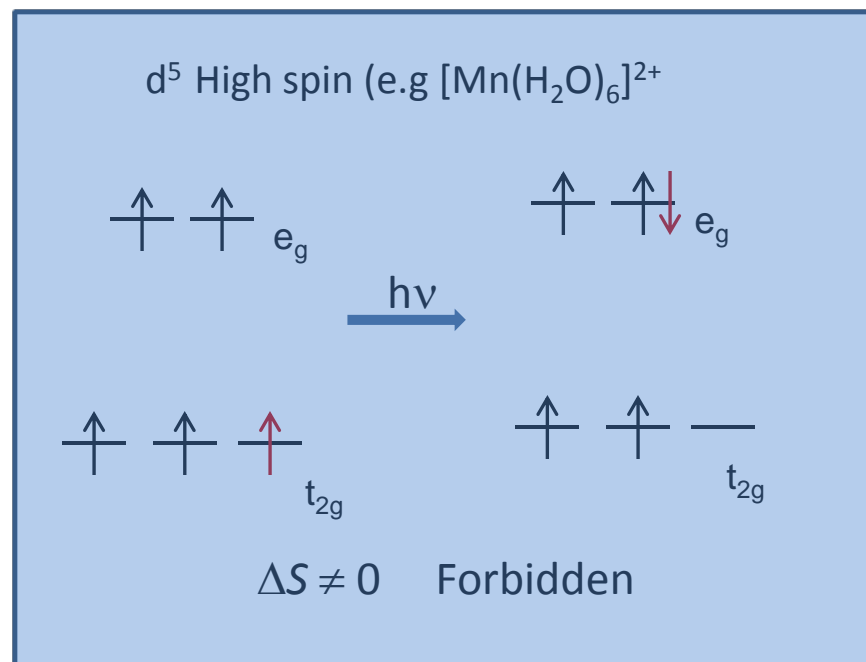
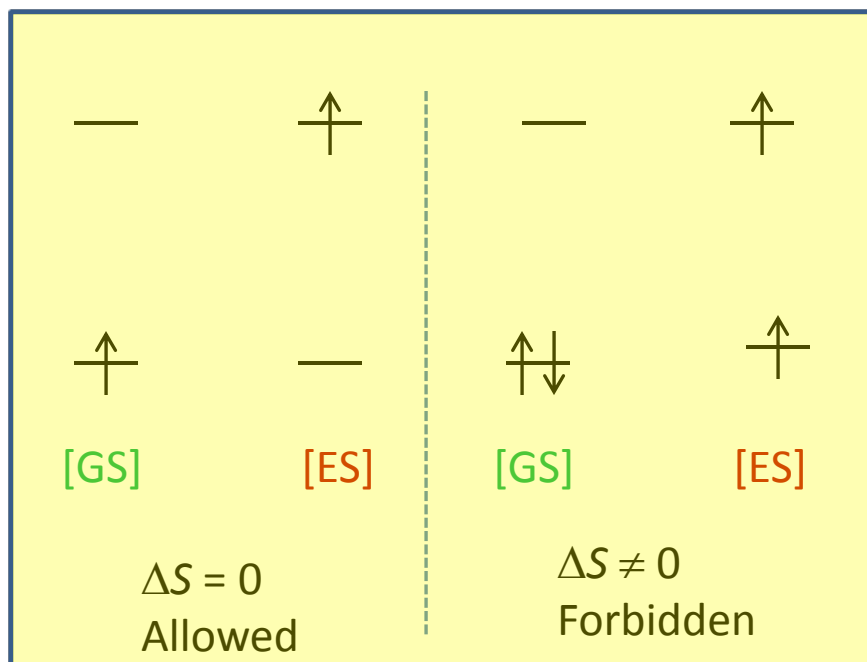
Tetrahedral complexes do not have center of symmetry: therefore this rule does not apply

2. Spin Selection Rule

Statement : This rule states that transitions that involve a change in spin multiplicity are forbidden. According to this rule, any transition for which $\Delta S = 0$ is allowed and $\Delta S \neq 0$ is forbidden

Practical significance of the Spin Selection rule

During an electronic transition, the electron should not change its spin

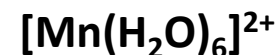
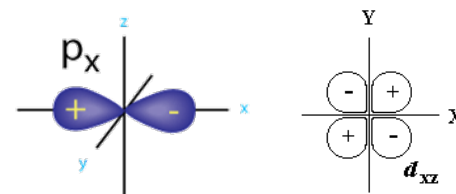
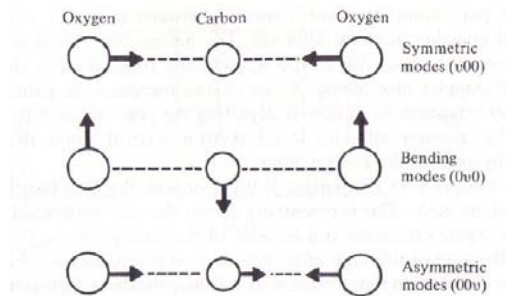


Why do we see 'forbidden' transitions at all?

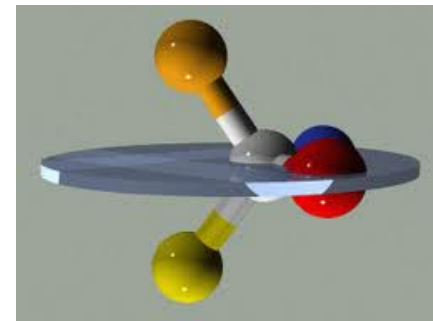
Relaxation of the selection rules

There are three mechanisms that allow 'forbidden' electronic transitions to become somewhat 'allowed' resulting in some intensity of the color expected.

- 1) **Vibronic Coupling:** During some unsymmetrical vibrations of a molecule there can be a temporary/transient loss of the centre of symmetry. Loss of center of symmetry helps to overcome the **Laporte selection rule**. Also time required for an electronic transition to occur (lifetime 10^{-18} sec) is much less than the time required for a vibration to occur (lifetime 10^{-13} sec)
- 2) **Mixing of states:** The states in a complex are never pure, and so some of the symmetry properties (g or u) of neighboring states become mixed into those of the states involved in a 'forbidden' transition. **For example mixing of d (gerade) and p (ungerade) orbitals results in partial breakdown of the Laporte rule**
- 3) **Spin orbit coupling:** Partial lifting of the **spin selection rule** is possible when there is coupling of the spin and orbital angular momentum, known as the spin-orbit coupling (common in heavier transition metals)



The spectra of complexes of tetrahedral metal ions:



As we have seen, a tetrahedron has no center of symmetry, and so orbitals in such symmetry cannot be *gerade*. Hence the d-levels in a tetrahedral complex are e and t_2 , with no 'g' for *gerade*.

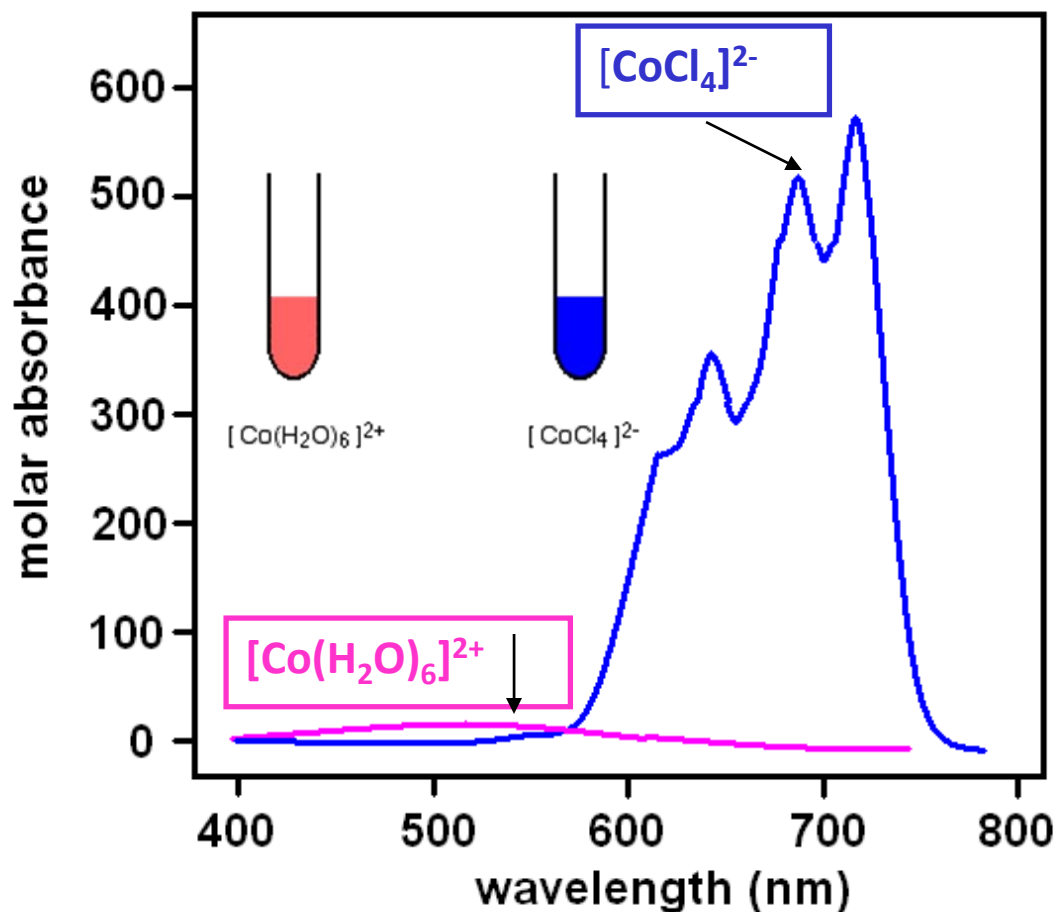
This largely overcomes the Laporte selection rules, so that tetrahedral complexes tend to be more intense in color. Thus, we see that dissolving CoCl_2 in water produces a pale pink solution of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, but on adding HCl tetrahedral $[\text{CoCl}_4]^{2-}$ forms, which has a very intense blue color.



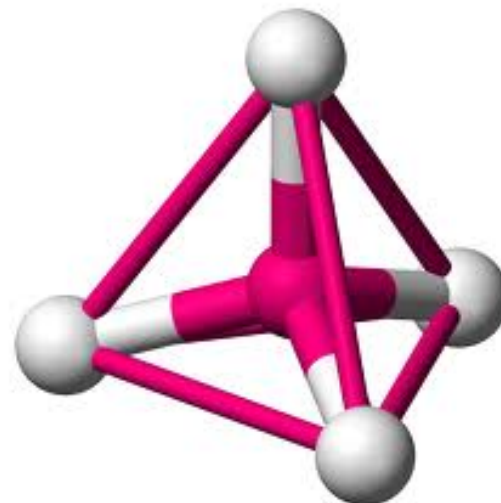
Cobalt blue was known in China before 1400 BC when it was used for pottery glazes, but it was always a rare pigment because cobalt minerals were scarce. Today, cobalt is still used to colour porcelain, pottery, glass, tiles and enamel jewellery. Its rich blue colour is also known as Sèvres blue and Thénard blue



The spectra of octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and tetrahedral $[\text{CoCl}_4]^{2-}$ ions:

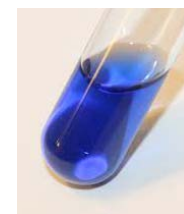


Intense d-d bands in the blue tetrahedral complex $[\text{CoCl}_4]^{2-}$, as compared with the much weaker band in the pink octahedral complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. This difference arises because the T_d complex has no center of symmetry, helping to overcome the $g \rightarrow g$ Laporte selection rule.



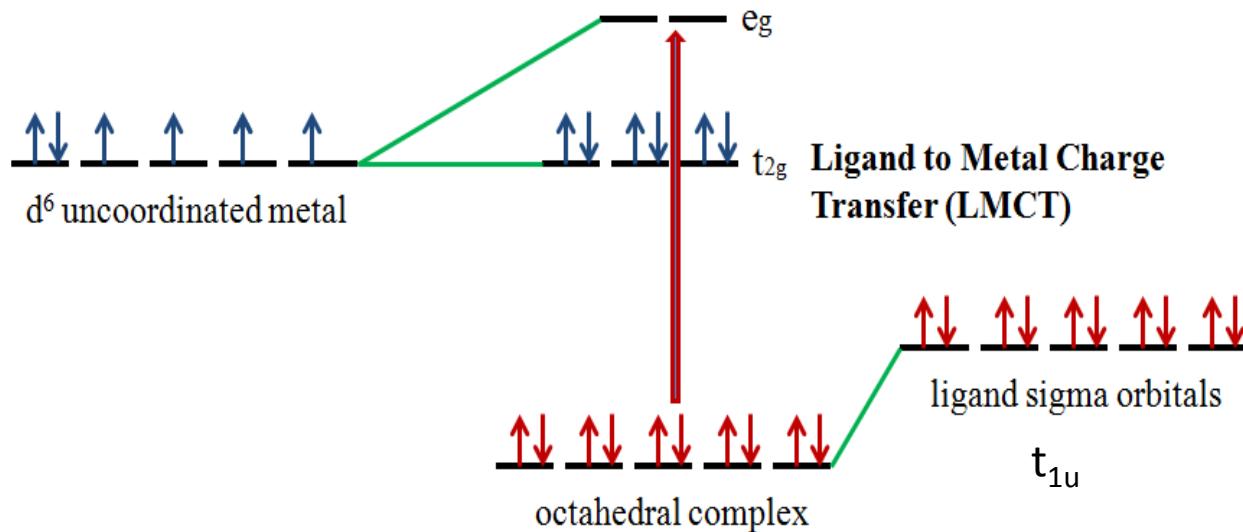
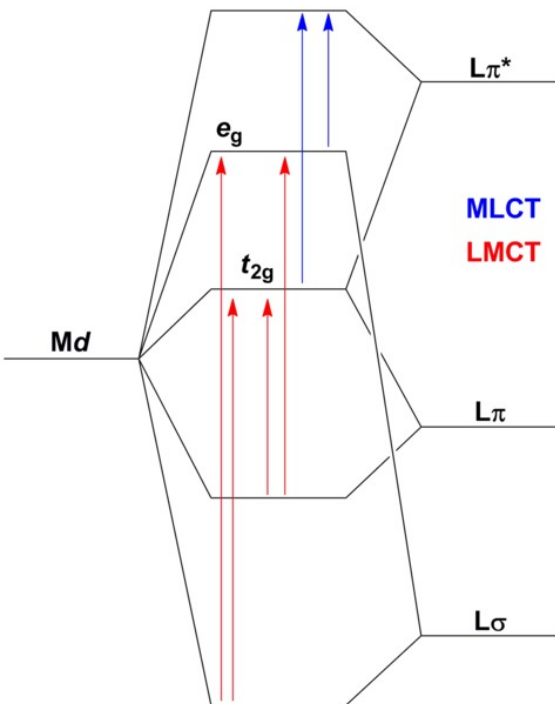
Classification of intensities of electronic transitions

Transition type	Example	Typical values of ϵ /m ² mol ⁻¹
Spin forbidden, Laporte forbidden (partly allowed by spin-orbit coupling)	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	0.1
Spin allowed (octahedral complex), Laporte forbidden (partly allowed by vibronic coupling and d-p mixing)	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	1 - 10
Spin allowed (tetrahedral complex), Laporte allowed (but still retain some original character)	$[\text{CoCl}_4]^{2-}$	50 - 150
Spin allowed, Laporte allowed e.g. charge transfer bands	KMnO_4	1000 - 10 ⁶



Molecular orbital picture required to explain charge transfer spectra

Includes both σ and π (*back bonding*) bonding



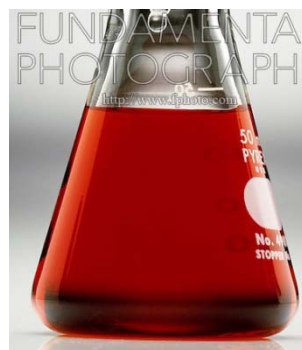
KMnO4



Prussian Blue



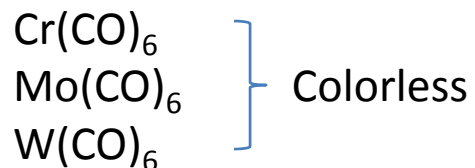
Ferric Thiocyanate



Pot. Dichromate



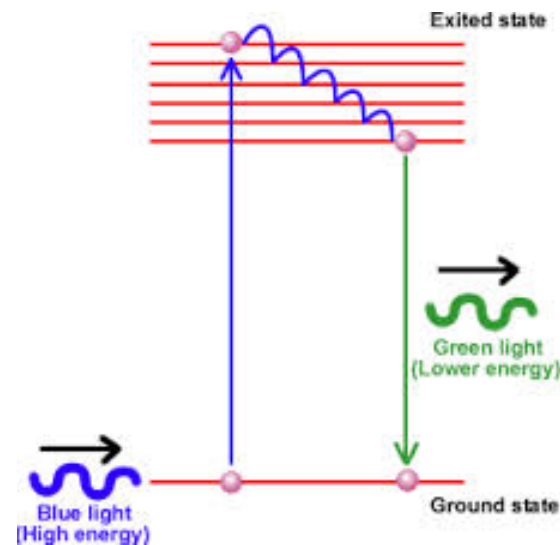
What happens if the absorption of electromagnetic radiation for an octahedral complex falls in the ultra violet range?



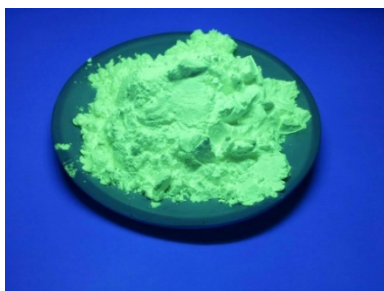
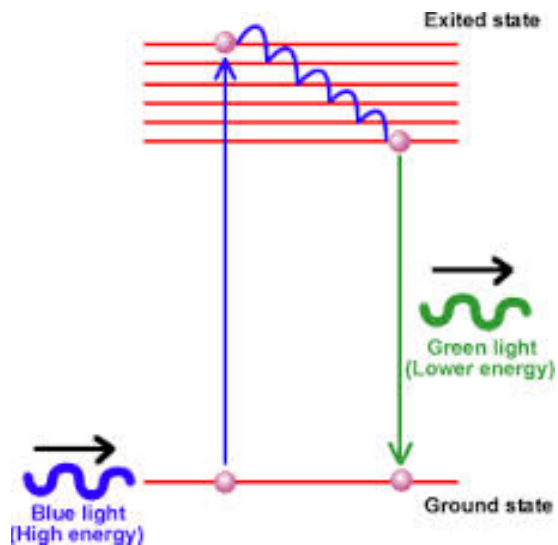
However some complexes also show a phenomenon known as **Fluorescence**

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. In most cases the **emitted light has a longer wavelength** and a lower energy than the absorbed radiation.

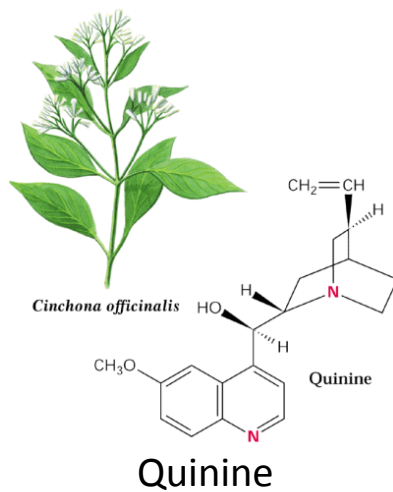
So if such complexes are irradiated with UV light, the excited electron will lose some energy and then fall back to ground state emitting (fluorescent) light in the visible range



Emission spectra, Black light, UV-A radiation and fluorescence



Zn_2SiO_4



Advantages and Disadvantages of Crystal Field Theory

Advantages over Valence Bond theory

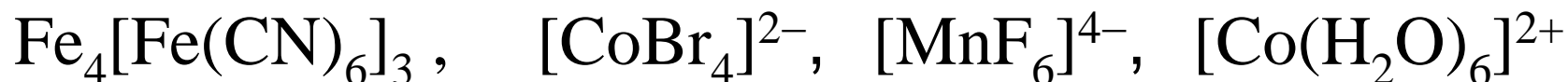
1. *Explains colors of complexes*
2. *Explains magnetic properties of complexes (without knowing hybridization) and temperature dependence of magnetic moments.*
3. *Classifies ligands as weak and strong*
4. *Explains anomalies in physical properties of metal complexes*
5. *Explains distortion in shape observed for some metal complexes*

Disadvantages or drawbacks

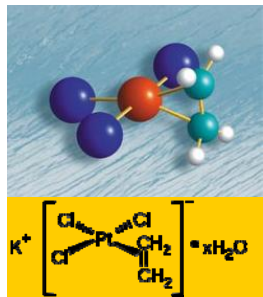
1. *Evidences for the presence of covalent bonding (orbital overlap) in metal complexes have been disregarded.
e.g Does not explain why CO although neutral is a very strong ligand*
2. *Cannot predict shape of complexes (since not based on hybridization)*
3. *Charge Transfer spectra not explained by CFT alone*

Problem Solving

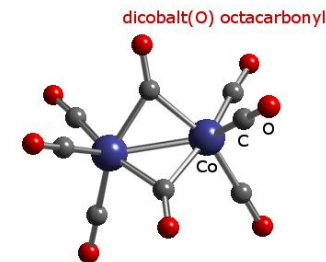
Arrange the given metal complexes in the increasing order of intensity of color (ϵ) shown by them. Justify your order by writing below each the status of the selection rules for these complexes (no partial marks)



Least intense			Most intense
Spin Forbidden Laporte Forbidden	Spin Allowed Laporte Forbidden	Spin Allowed Laporte Allowed (Tetrahedral)	Spin Allowed Laporte Allowed Charge – Transfer transition



Organometallic Chemistry

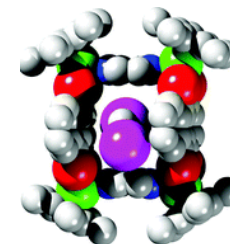
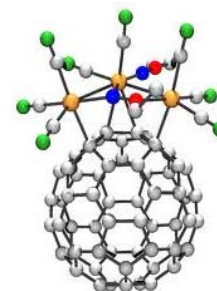
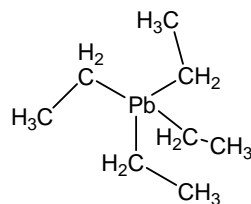
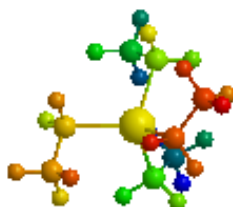
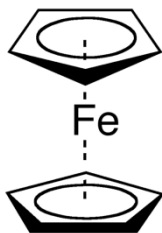
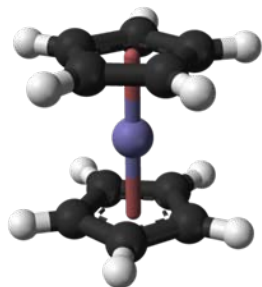
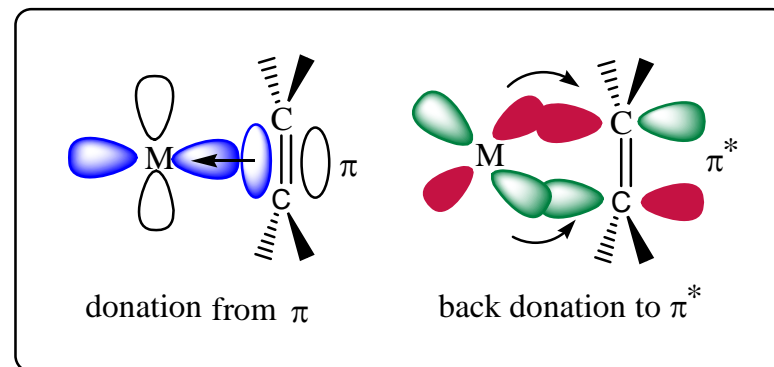
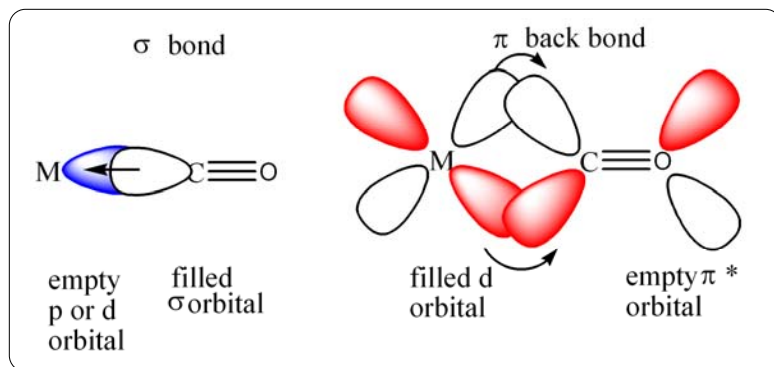


An area which bridges organic and inorganic chemistry

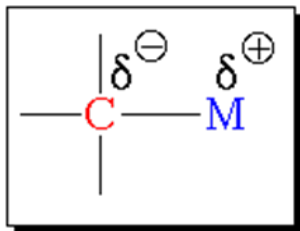
A branch of coordination chemistry where the complex has one or more metal-carbon bonds

The metal-ligand interactions are mostly π acid type

M-C bond can be a σ type or π type bond



What all compounds are considered as **organometallic**?



C always more electronegative compared to M

The leading journals of the field define an "organometallic" compound as one in which there is a **bonding interaction (ionic or covalent, localized or delocalized) between one or more carbon atoms of an organic group or molecule and a main group, transition, lanthanide, or actinide metal atom (or atoms).**

Following longstanding tradition, organic derivatives of the metalloids such as **boron, silicon, germanium, arsenic, and tellurium** also are included in this definition.

It is also understood that the element to which carbon is bound is **more electropositive than carbon** in organometallic chemistry.

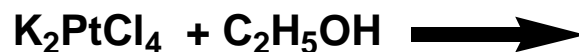
*Traditional chemists do not agree for classifying **metal cyanide complexes** as organometallic*

Zeise's Salt- The first transition metal organometallic compound



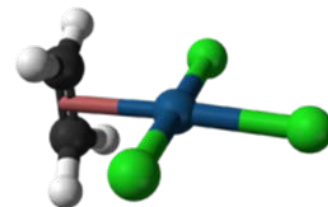
W C Zeise, Danish
pharmacist, 1789- 1847

Also father of the
chemistry of
mercaptans R-SH



Discovery 1827

*Structure ~ 150 years
later*



'The breakthrough, the isolation of a pure, crystalline compound came when Zeise added potassium chloride to a concentrated PtCl₄ /ethyl alcohol reaction solution and evaporated the resulting solution. Beautiful lemon yellow crystals, often one half inch or more in length were isolated. On longer exposure to air and light, they gradually became covered with a black crust. They contained water of hydration, which was lost when they were kept over concentrated sulfuric acid in vacuo or when heated to around 100°C. Chemists in those days often reported how the compounds that they had prepared tasted. Zeise described the taste of this potassium salt as metallic, astringent and long lasting.'

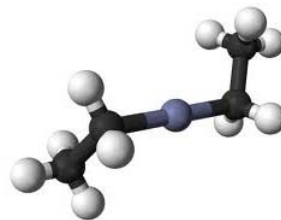
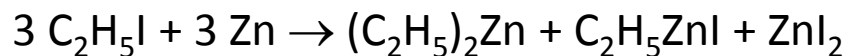
Dietmar Seyferth, Organometallics, 2001, 20, 2



Edward Frankland
1825-1899

*Frankland coined the
term
"Organometallic"*

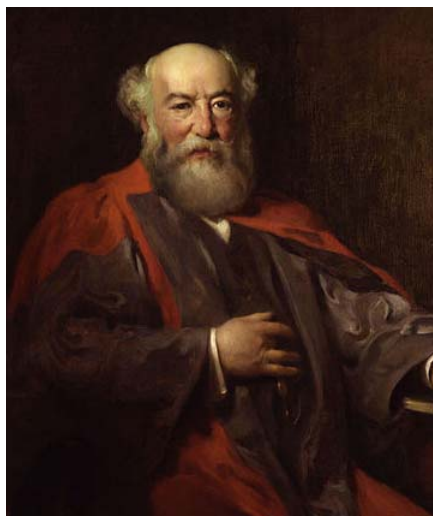
First σ bonded Organometallic Compound- Diethyl zinc



Student of Robert Bunsen (Bunsen burner fame!). Prepared diethyl zinc while trying to make ethyl radicals.

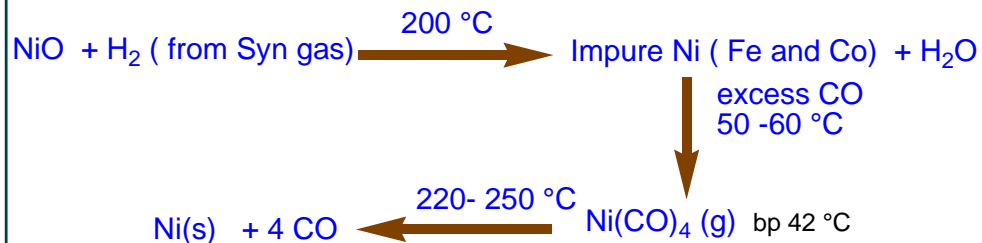


As the early 1850s English chemist Edward Frankland described flasks exploding, throwing bright green flames across his lab, as he heroically distilled dialkylzinc compounds under an atmosphere of **hydrogen**.



Metal carbonyls

The Mond process of Nickel purification

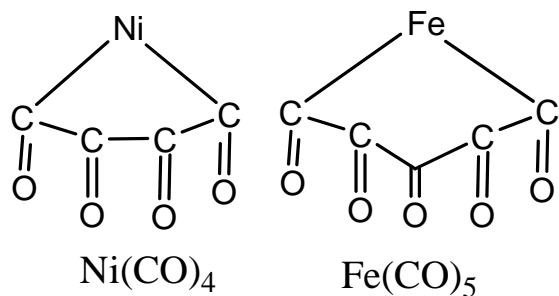


1890

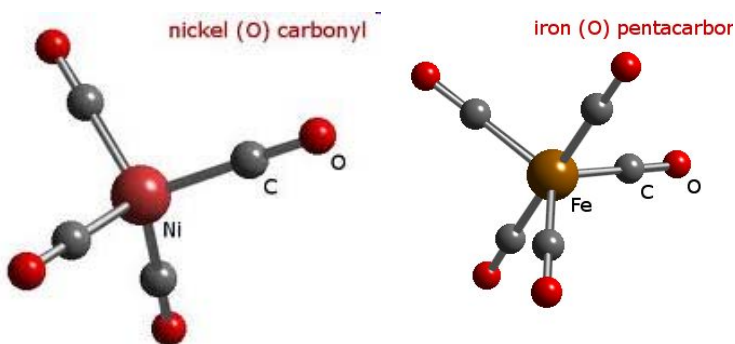
1891

1910

'Mond nickel company' was making over 3000 tons of nickel in 1910 with a purity level of 99.9%



1890-1930 textbooks

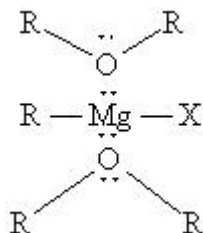


Mo(CO)₆

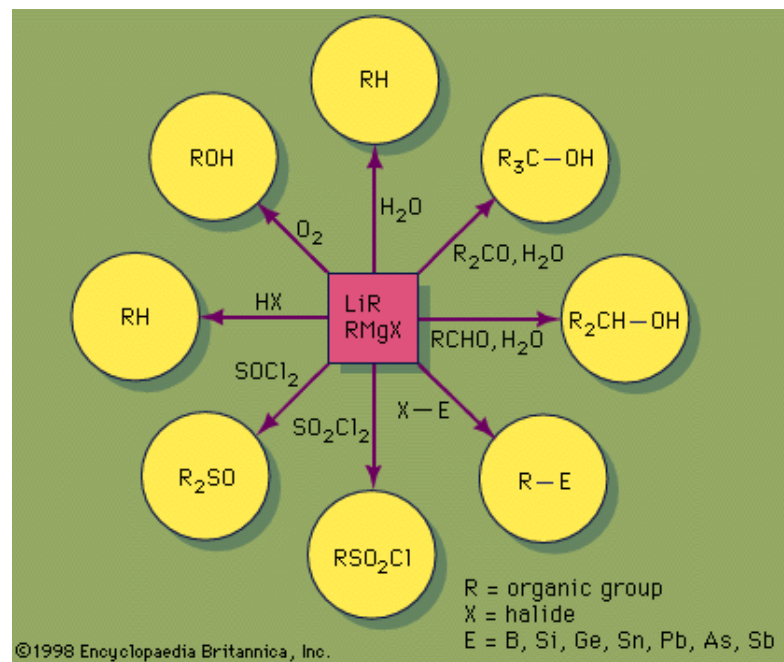
The Grignard Reagent



**François Auguste
Victor Grignard 1871-
1935**



He was the student of Philippe Barbier (Barbier reaction [Zn]) He discovered the Grignard reaction [Mg]) in 1900. He became a professor at the University of Nancy in 1910 and was awarded the Nobel Prize in Chemistry in 1912.

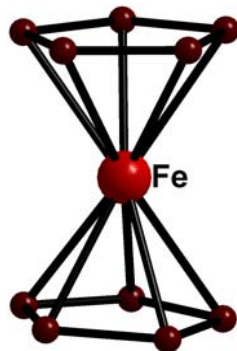
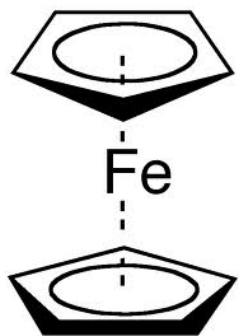




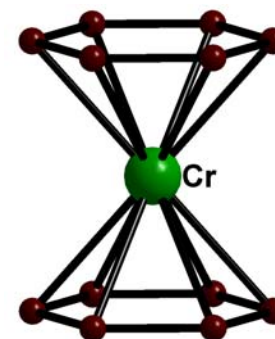
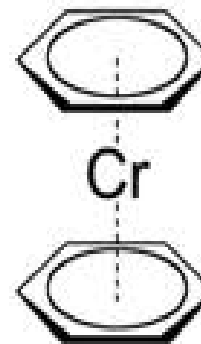
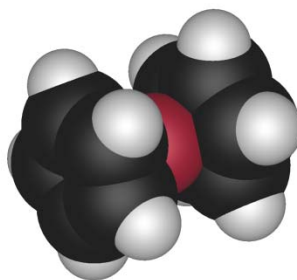
Hapto ligands and Sandwich compounds



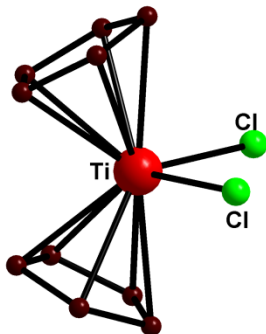
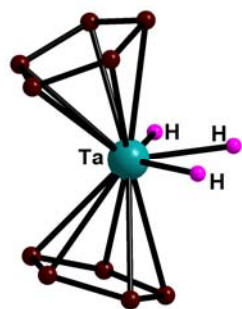
The **hapto** symbol, η , with a numerical superscript, provides a topological description by indicating the number of carbon atoms at a bonding distance to the metal



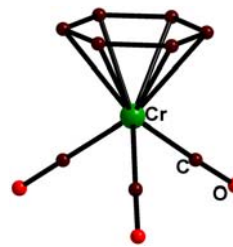
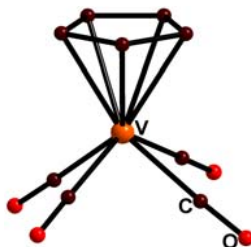
Sandwich



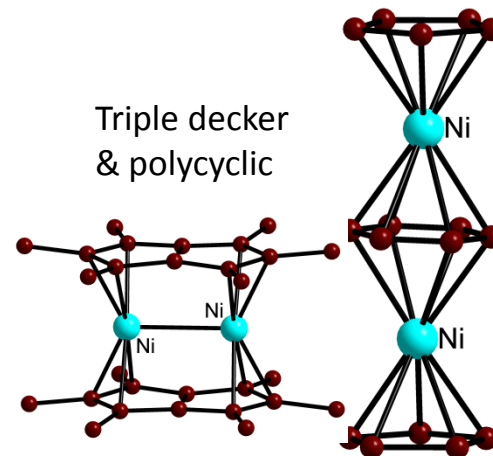
Bent Sandwich



Half Sandwich



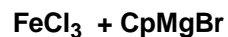
Triple decker
& polycyclic



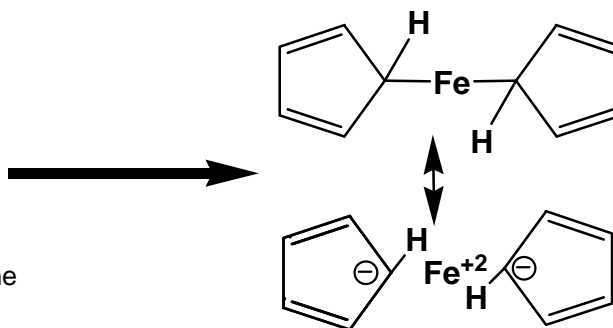
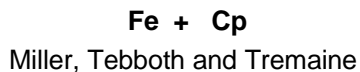
Ferrocene: Pathbreaking discovery of a sandwich compound



Pauson

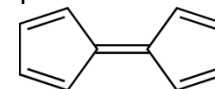


Kealy and Pauson

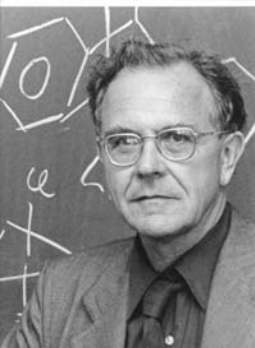


Kealy

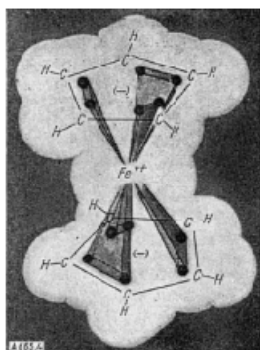
expected fulvalene



A new type of organo-iron compound, Nature 1951
Dicyclopentadienyl iron, J. Chem. Soc., 1952



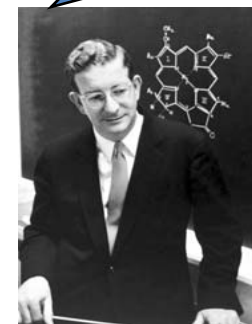
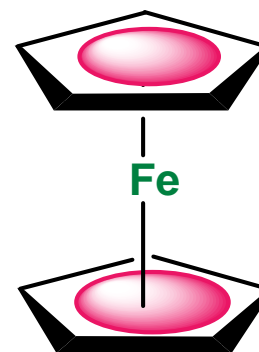
G. Wilkinson



1973 Nobel Prize
 'sandwich compounds'



E. O. Fischer



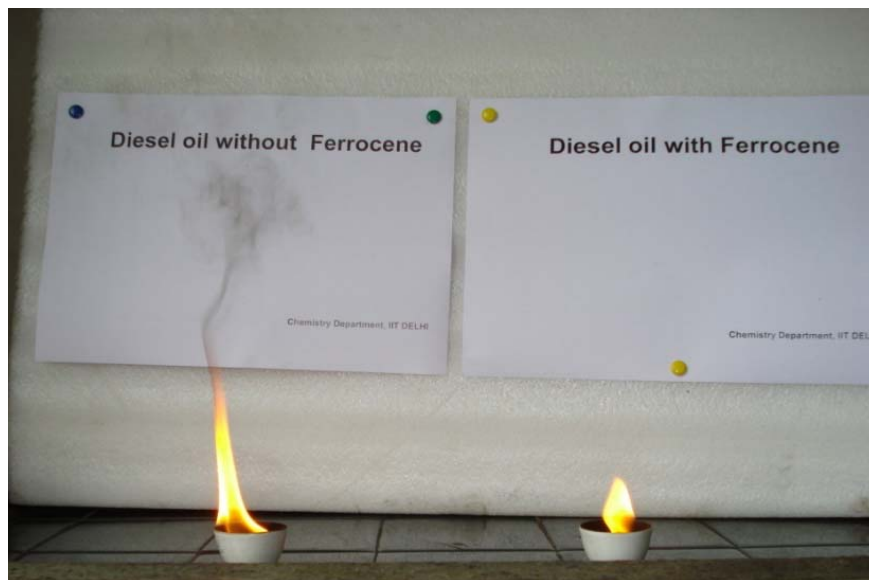
R. B. Woodward
 1965 Nobel Prize
 'art of organic synthesis'

Wilkinson, Rosenblum, Whitney, Woodward, J. Am. Chem. Soc., 1952

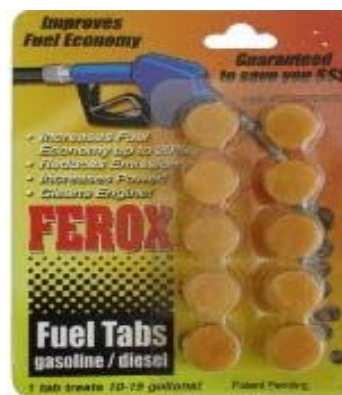
Ferrocene: Fuel additive, smoke suppressant and chiral catalyst precursor



Ferrocene powder



Ferrocene crystals



Ferox Gas & Diesel Fuel Additive is a catalyst that is an eco-friendly fuel additive and horsepower booster. It allegedly increases mileage from between 10 and 20% while also significantly reducing harmful emissions.

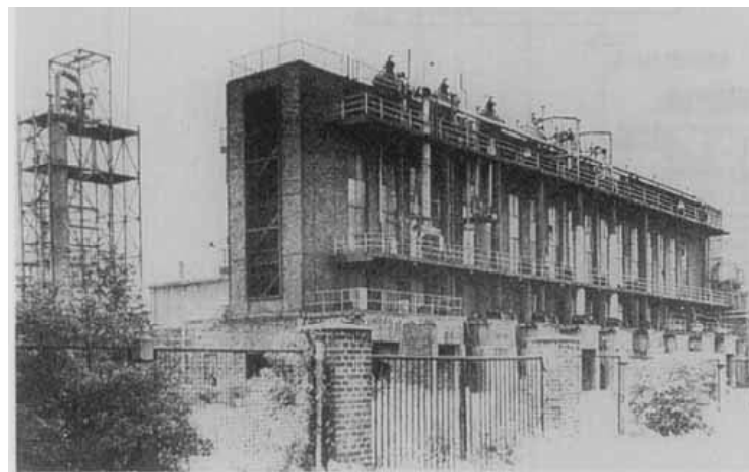
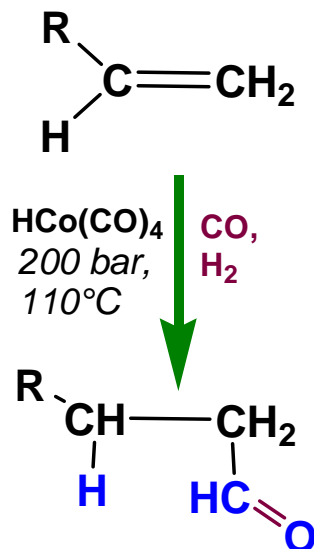
First organometallics in homogeneous catalysis-

The Hydroformylation (1938)

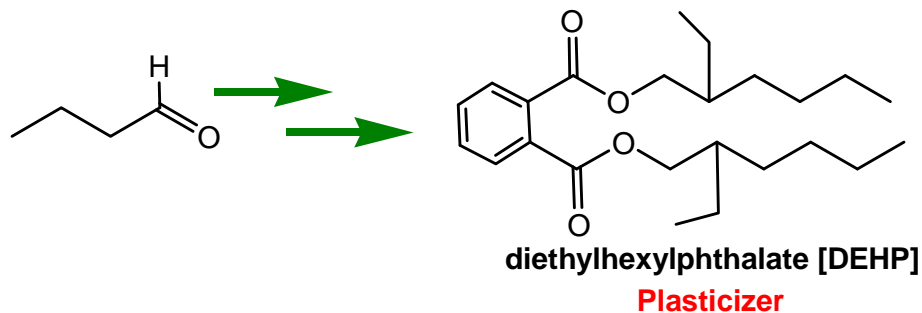


Otto Roelen

Pioneer in Industrial
homogeneous catalysis
(1897-1993)



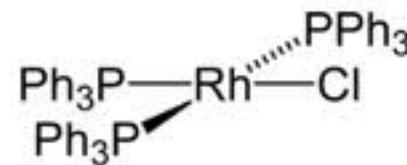
First Industrial plant- hydroformylation



detergents

Organometallic catalysts in industrial synthesis : Three Nobel Prizes 2000, 2005 and 2010

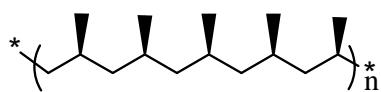
Hydrogenation



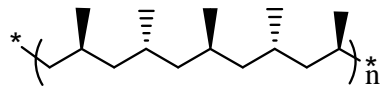
Methanol to acetic acid process



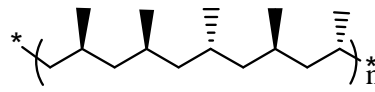
Olefin polymerization and oligomerization



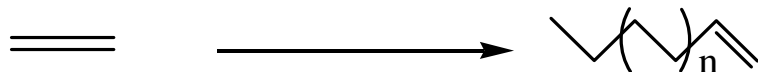
Isotactic polypropylene



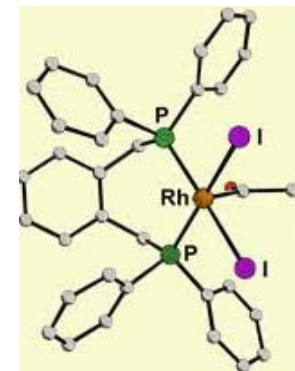
Syndiotactic polypropylene



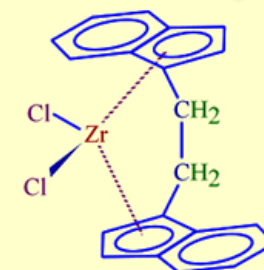
Atactic polypropylene



C ₄ -C ₈	40%
C ₁₀ -C ₁₈	40 %
C ₂₀ & >	20 %



A Metallocene Catalyst



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 favouring 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:

η^1 -R, η^1 -Ar η^2 -C₂R₄ η^1 -allyl, η^3 -allyl, η^4 -Cb, η^5 -Cp, η^6 -C₆H₆ η^8 -C₈H₈ η^2 -C₆₀, η^5 -R₅C₆₀.

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

Examples:

μ_2 -CO, μ_3 -CO, μ_2 -CH₃, μ_2 -H, μ_2 -Cl, , μ_3 -Cl, μ_2 -OR, μ_2 -PR₂, μ_2 -NR₂

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≡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