DIRECTORATE OF DISTANCE & CONTINUING EDUCATIONS MANONMANIAM SUNDARANAR UNIVERSITY TIRUNELVELI – 627012

OPEN AND DISTANCE LEARING(ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRMMES FROM THE ACADEMIC YEAR 2023 – 2024)

M.Sc. CHEMSITY COURSE MATERIALS

COORDINATION CHEMISTRY II

SCHM41

By

S. NAGARAJAN

Assistant Professor

Department of Chemistry

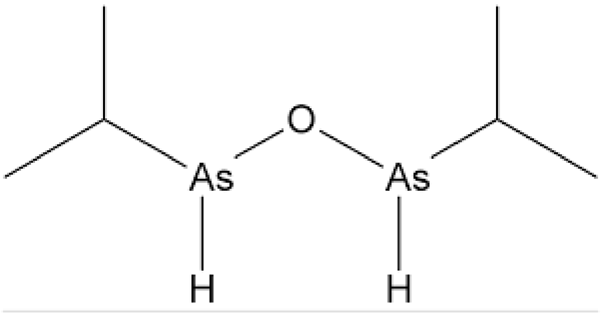
Manonmaniam Sundaranar University

Tirunelveli 627012

UNIT – I

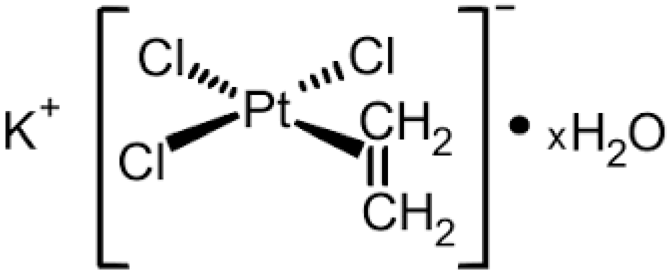
ORGANOMETALLIC COMPOUND

- An organometallic compound is the one that possesses a metal-carbon bond.
- In (1760) a French Chemist, Louis Claude Cadet of Paris military pharmacy, prepared first organometallic compound (even though arsenic is not a true metal), when he was working on invisible inks based on cobalt salt solutions containing arsenic, $[(CH_3)_2As]_2O$ (Cacodyl oxide), often called Cadet's fuming liquid.

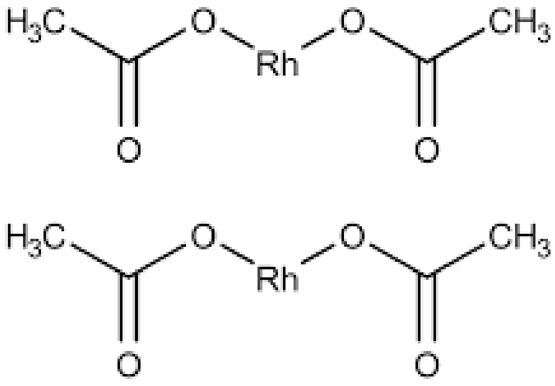


- The first olefin complex synthesized in (1827) by William Christopher Zeise (Danish

Organic chemist), who obtained yellow needle-like crystals



- "Organometallic compounds are those in which a metal atom (including non- metals such as B, Si, P, As, Se etc. which are less electronegative than carbon) is bonded directly to at least one carbon atom of a hydrocarbon radical or molecule".
- The compounds like acetates and alkoxides are not covered under this definition because in these compounds metal is not directly attached to carbon.



THE 18-ELECTRON RULE

The 18-electron rule arises from the idea that a transition metal complex becomes stable when it achieves an electron configuration similar to that of a noble gas. For most transition metals, this means filling the valence shells: 5 d-orbitals (10 electrons), 3 p-orbitals (6 electrons), and 1 s-orbital (2 electrons), leading to a total of 18 electrons.

Examples:

- Metal carbonyls like $[Fe(CO)_5]$ and $[Ni(CO)_4]$.
- Sandwich compounds such as ferrocene ($[Fe(\eta^5\text{-}C_5H_5)_2]$).
- Complexes where π-acceptor ligands (like CO) stabilize the metal center.

COUNTING ELECTRONS IN COMPLEXES

- The 18-electron rule has remarkable utility for predicting the stabilities and structures of organometallic compounds.
- The 18-electron rule not only predicts the stability of metal complexes, but in some cases, it also predicts the presence of metal-metal bonding and bridging ligands or terminal ligands.

16-Electron Rule

- **Definition**: Certain organometallic compounds are stable with 16 valence electrons instead of 18. This is especially common for complexes involving square planar geometry.

- **Key Examples**:
  - Many d^8 square planar complexes like $[PtCl_2(PPh_3)_2]$.
  - Complexes of transition metals like palladium and platinum.

Common Examples

- **$[PtCl_2(PPh_3)_2]$**: Platinum in this square planar complex is in the +2 oxidation state, contributing 8 d-electrons. Each PPh_3 (triphenylphosphine) donates 2 electrons, and each Cl^- contributes 2 electrons, leading to $8+2\times2+2\times2=16$
- **$[RhCl(CO)(PPh_3)_2]$**: Similar electron counting applies here.

There are two popular procedures for electron counting:

i. Neutral atom method or covalent method

ii. Oxidation state method or ionic method

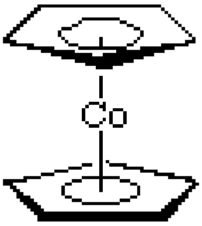
The steps for counting the electrons present in the valence shell of central metal in a metal carbonyl:

i. The electrons present in the valence shell of the central metal atom are counted and then electrons are added to it or subtracted from it depending upon the nature of charge (negative or positive) present on it.

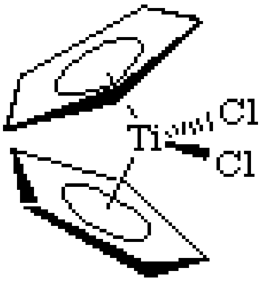
ii. Each terminal carbonyl group contributes 2e to the valence shell of the central metal.

iii. The bridging carbonyl group (M - CO - M) contributes 1e to the valence shell of each metal atom.

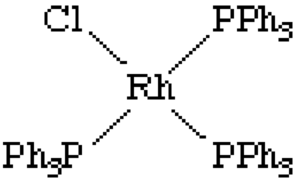
iv. The metal-metal (M-M) bond contributes le to the valence shell of each metal atom.



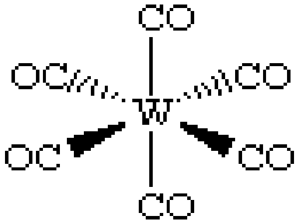
ionic		covalent	
Co^{II}	7 e$^-$	Co	9 e$^-$
2 Cp$^-$	12 e$^-$	2 Cp$^{\bullet}$	10 e$^-$
Total	19 e$^-$	**Total**	19 e$^-$



Ti^{IV}	0 e$^-$	Ti	4 e$^-$
2 Cl$^-$	4 e$^-$	2 Cl$^{\bullet}$	2 e$^-$
2 Cp$^-$	12 e$^-$	2 Cp$^{\bullet}$	10 e$^-$
Total	16 e$^-$	**Total**	16 e$^-$

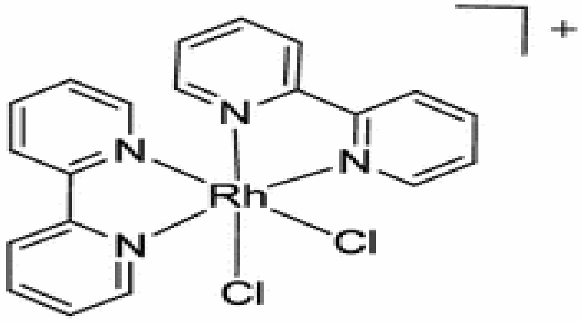


Rh^{I}	8 e$^-$	Rh	9 e$^-$
Cl$^-$	2 e$^-$	Cl$^{\bullet}$	1 e$^-$
3 PPh$_3$	6 e$^-$	3 PPh$_3$	6 e$^-$
Total	16 e$^-$	**Total**	16 e$^-$



W^0	6 e$^-$	W	6 e$^-$
6 CO	12 e$^-$	6 CO	12 e$^-$
Total	18 e$^-$	**Total**	18 e$^-$

Example 1: $[RhCl_2(bpy)_2]^+$



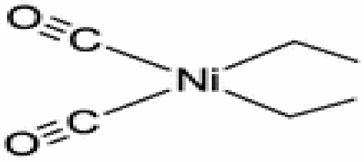
Ionic model:

Rh(III)	d^6	6 e^-
bpy	4 e^- x 2	8 e^-
Cl^-	2 e^- x 2	4 e^-
		18 e^-

Covalent model:

Rh(0)	d^9	9 e^-
bpy	4 e^- x 2	8 e^-
Cl·	1 e^- x 2	2 e^-
		19 e^-
(*overall +1 charge*)		– 1 e^-
		18 e^-

Example 2: $[Ni(Et)_2(CO)_2]$

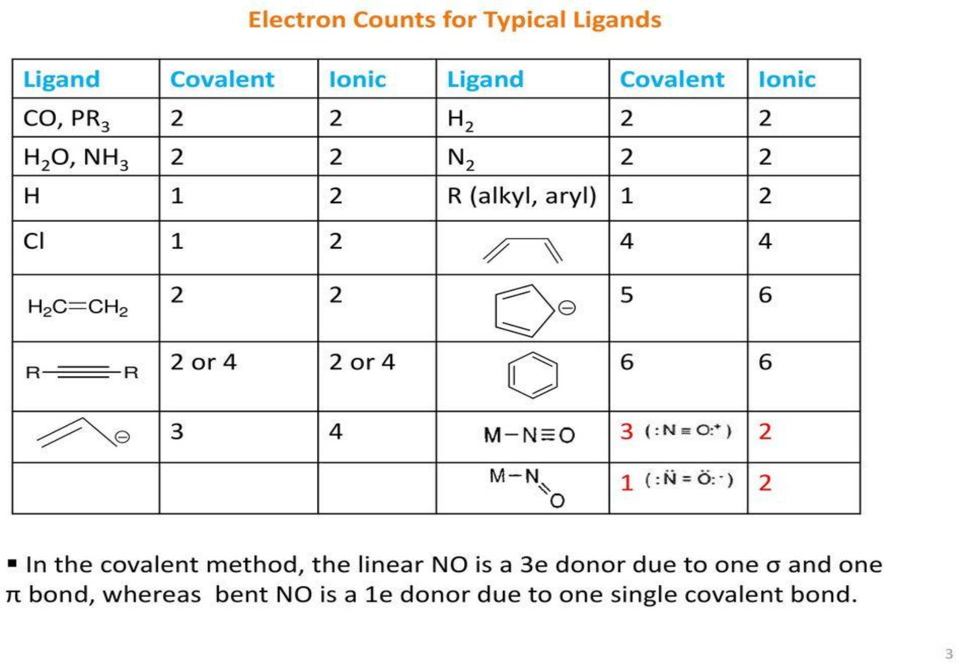


Ionic model:

Ni(II)	d^8	8 e^-
CO	2 e^- x 2	4 e^-
Et^-	2 e^- x 2	4 e^-
		16 e^-

Covalent model:

Ni(0)	d^{10}	10 e^-
CO	2 e^- x 2	4 e^-
Et·	1 e^- x 2	2 e^-
		16 e^-



Electron Counts for Typical Ligands

Ligand	Covalent	Ionic	Ligand	Covalent	Ionic
CO, PR_3	2	2	H_2	2	2
H_2O, NH_3	2	2	N_2	2	2
H	1	2	R (alkyl, aryl)	1	2
Cl	1	2		4	4
$H_2C{=}CH_2$	2	2		5	6
$R-C\equiv C-R$	2 or 4	2 or 4		6	6
	3	4	$M-N\equiv O$	3 ($:N\equiv O:^+$)	2
			M−N=O	1 ($:\ddot{N}=\ddot{O}:^-$)	2

- In the covalent method, the linear NO is a 3e donor due to one σ and one π bond, whereas bent NO is a 1e donor due to one single covalent bond.

Bonding in Metal-Olefin Complexes

Metal-olefin complexes are coordination compounds where a transition metal is bonded to an alkene (olefin) through its π electrons. A classic example is Zeise's salt: $K[PtCl_3(C_2H_4)]\cdot H_2O$.

Nature of Bonding

The bonding between the metal and the olefin involves two key interactions described by the Dewar–Chatt–Duncanson model:

1. **σ-Donation**
   The π electrons of the olefin double bond donate electron density into a vacant d-orbital (usually dσ) of the metal, forming a σ bond between the olefin and the metal center.

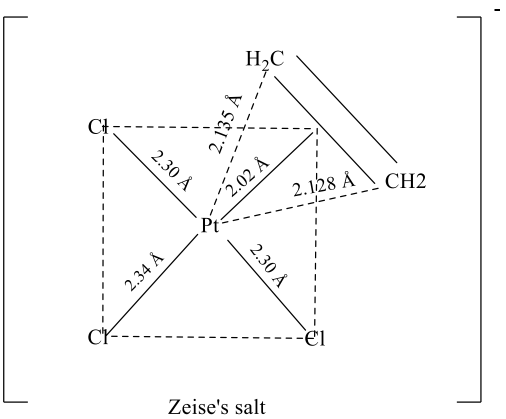
2. **π-Back Donation**
   Simultaneously, a filled d-orbital (usually dπ) of the metal donates electron density back into the empty π* (antibonding) orbital of the olefin. This π-back bonding strengthens the metal-olefin interaction and weakens the C=C bond in the olefin.

Consequences of Bonding

- C=C bond length increases due to electron density transfer into the π* orbital.
- IR stretching frequency (νC=C) decreases.
- Olefin becomes susceptible to nucleophilic attack at the β-position.

Example: Zeise’s Salt

$K[PtCl_3(C_2H_4)]\cdot H_2O$ is a classic example. Ethylene coordinates to Pt (II) through both σ-donation and π-back donation. C=C bond length increases from 1.34 Å in free ethylene to 1.37 Å in the complex. Pt–C bond lengths are typically around 2.13 Å.



Zeise's salt

Structure:

The structure of anion of the Zeis’s salt – Neuron diffraction technique.

- Its geometry is square planar.
- Name - Trichloro(η^2 ethylene) platinate (II)

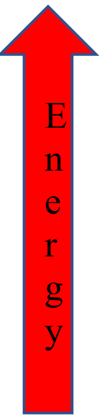
Structural features:

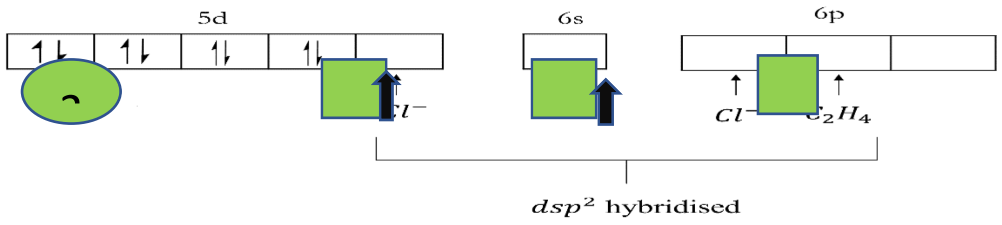
1. Pt^{+2} ion is present at the centre of a square-plane.
2. Three corners of the square-plane are occupied by Cl^-, ions.
3. $\mathrm{C}_2\mathrm{H}_4$ occupies the fourth coordination site of the square-planar complex.
   $\mathrm{C} = \mathrm{C}$ bond $\perp$ to the PtCl_3 plane.
4. The Pt-Cl distance trance to the ethylene is longer than the other Pt-Cl distance.
5. Length of coordinated alkene C-C bond 1.375 Å > Free ethylene molecule $\mathrm{C} = \mathrm{C}$ bond length 1.337 Å.
6. The originally planar ethylene becomes non-planar on bonding itself to Pt.
7. Two carbon atoms are almost equivalent distance from the Pt ion.

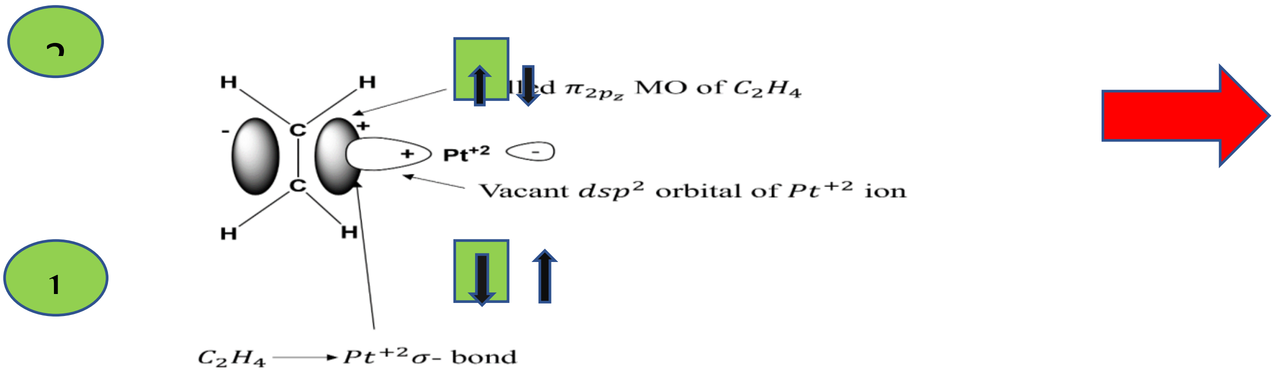
Ground state

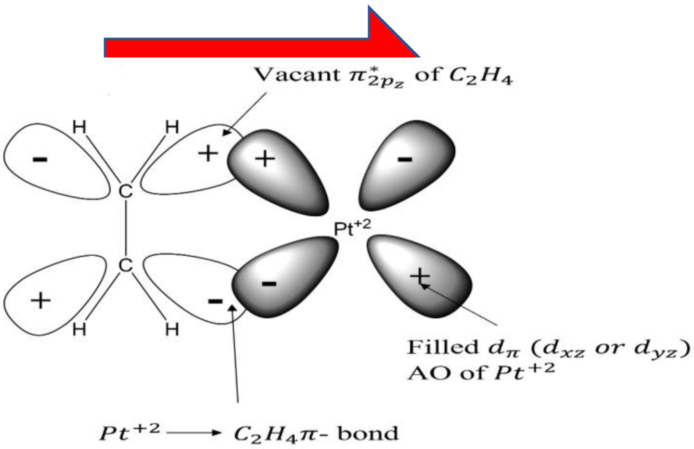
Bonding:

- The Pt^{+2} ion of the anion of Zeise salt is dsp^2 hybridised.
- Pt^{+2} ion has four vacant dsp^2 hybrid orbitals.
- Pt - $5d^9 6s^1$, Pt^{+2} - $5d^8 6s^0$



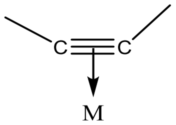


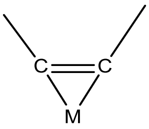


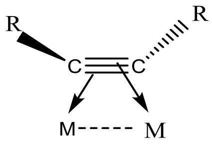


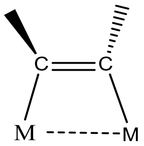
Bonding in Metal-Acetylene Complexes

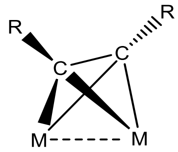
Alkynes are quite similar to alkenes in their coordination behaviour but have another perpendicular pair of n-electrons. Consequently, they can act as neutral 2 or 4e donors. Because of the second set of n-electrons, their bridging ability is also much better Possible modes of bonding of alkynes to metals.



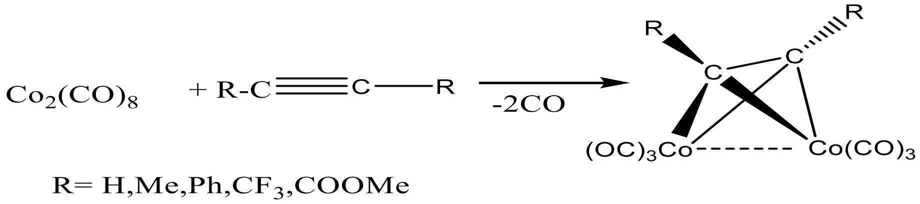








The following synthetic methods show how different types of bonding of metal to alkynes can occur



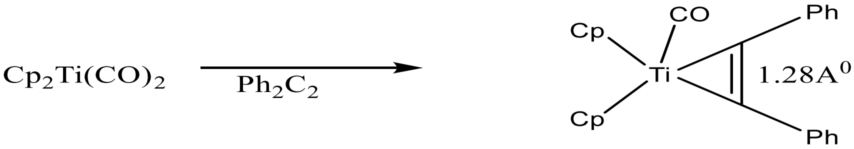
C≡C

H≡H $1974 Cm^{-1}$

Me≡Me $2055 Cm^{-1}$

C—C of complex $1403 Cm^{-1}$ (R-H)

$1633 Cm^{-1}$ (R ═ Me)



Metal-acetylene complexes are organometallic complexes that contain a metal center bonded to an acetylene molecule (C_2H_2). The metal-acetylene bonding in such complexes is a combination of σ and π interactions.

$$\text{H-C} \equiv C - H$$

Types of Bonding in Metal-Acetylene Complexes

- σ-Bonding: The σ-bonding involves donation of electron density from the acetylene ligand to the metal center through the σ-orbitals of the acetylene. This bonding mode is typically observed in complexes where the metal center is in a low oxidation state.

- π-Bonding: The π-bonding involves the donation of electron density from the metal center to the acetylene ligand through the π-orbitals of the acetylene. This bonding mode is generally observed in the complexes where the metal center is in its high oxidation state.

Bonding Modes in Metal-Acetylene Complexes

- η^2-Bonding: The acetylene ligand is bound to the metal center through two carbon atoms in this bonding mode, involving a σ-bond.
- η^4-Bonding: In this bonding mode, the acetylene ligand is bonded to the metal center through all four atoms (two carbon and two hydrogen atoms) and a mix of σ- and π-bonds is created.

Formation and Bonding

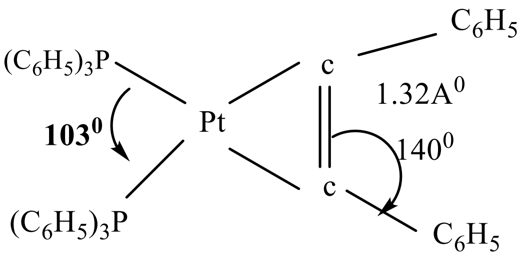
- Acetylene, with its triple bond, can coordinate to a metal center through its π-electrons, just like alkenes (with double bonds) coordinate to metal centers.
- The interaction between the metal and the acetylene ligand can be both sigma (σ) and pi (π) in nature, whereby a metal-alkyne complex is created.
- Alkynes tend to bind more strongly to a transition metal than alkenes
- The metal-acetylene complexes, the triple-bonded acetylene ligand is sp-hybridized, such that each carbon forms two sigma and two pi bonds, with the metal coordinating via these bonds
- Acetylene (C_2H_2) is a linear molecule containing a carbon-carbon triple bond, and both carbons are sp-hybridized.

SP Hybridization:

- In sp hybridization, one s and one p orbital hybridize to form two sp hybrid orbitals, which are at 180° to each other. Py and Pz molecular axis perpendicular.

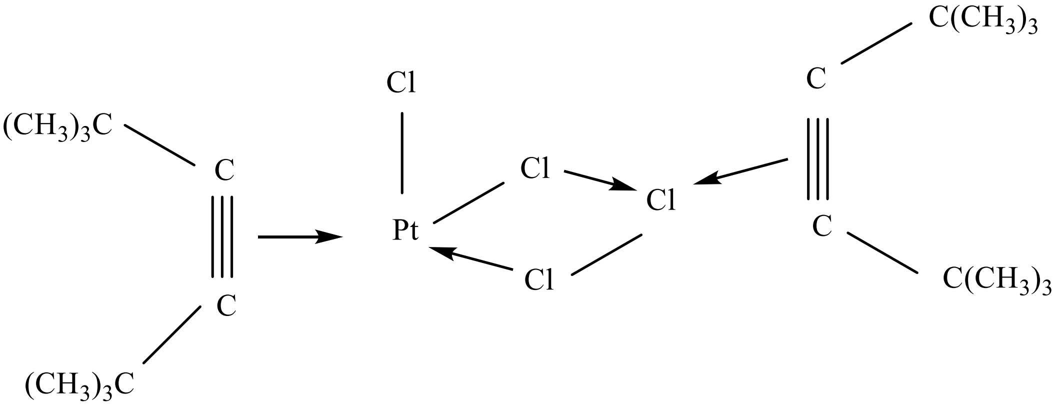
METAL-ACETYLENE COMPLEXES

- The metal-acetylene complexes are similar to the metal-olefin complexes in their formation and formulae. The alkynes also have *Π* system that could be involved in bonding similar to that in metal-alkene complexes. however, the bonding in then is more complicated than that in olefin complexes, because there are more types of bonding possible with triple bonds. An example for an acetylene complex is the pt-diphenylacetylene [pt($C_6H_5C \equiv CC_6H_5$) (PPH_3).



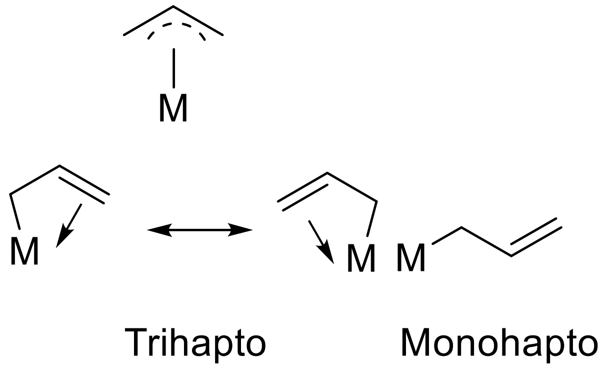
structure of bis (triphenylphosphine) diphenylacetyleneplatinum(0)

- The olefin unit lies almost in the plane of $Pt(PPH_3)_2$. The structure approximately square planar.
- Another example of alkyne complex is [$\{PtCl_2$ (t-BuC Ct –Bu)$\}_2$] it is bialkyne, binuclear complex.



METAL ALLYL COMPLEX

- The complex compounds in which the allyl group (CH_2-CH=CH_2) is attached to a metal are called metal allyl complex.
- The allyl ligand is often referred to as an actor ligand rather than a spectator ligand.
- The allyl ligand binds to metals in two ways i.e., in a η^1(monohapto) form and aη^3(trihapto)form.
- In its monohapto (η^1) form, it acts as a 1e^-donor X type of a ligand.
- In trihapto (η^3) form, it acts as a 3e^-donor LX type of a ligand.



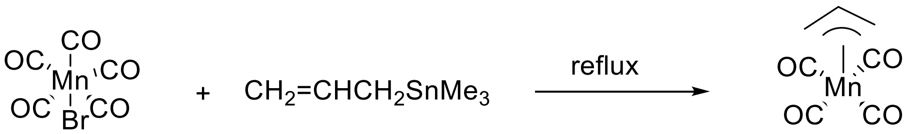
SYNTHESIS:

The metal allyl complexes are synthesized by the following methods.

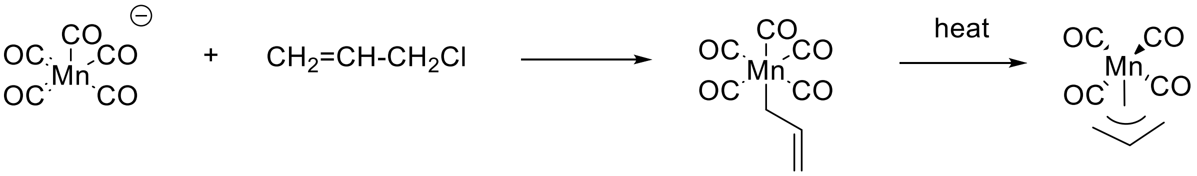
- From an alkene complex,

$$\mathrm{Mo(dpe)_2(\eta^2{-}propene)} \rightleftharpoons \mathrm{Mo(dpe)_2(\eta^3{-}allyl)H}$$

- By a nucleophilic attack of an allyl compound on metal complex,



- By an electrophilic attack of an allyl compound on metal complex,



STRUCTURE AND BONDING:

- The molecular orbitals namely Ψ_1, Ψ_2 and Ψ_3 of the allyl ligand interact with the metal in a metal-allyl complex.
- The energy of these molecular orbitals increase with the increase in the number of nodes.
- Of the three, the Ψ_1 and Ψ_2 orbitals usually engage in ligand to metal σ−donation, with Ψ_1 involving in a dative L−type bonding and Ψ_2 participating in a covalent X−type bonding with the metal d orbitals. Ψ_3 forms pi bond through backdonation of electrons.
- There are two peculiarities of the structures of η^3-allyl complexes. First, the plane of the allyl is canted at an angle θ with respect to the coordination polyhedron around the metal and θ is usually 5°-10°.
- The reason is that the interaction between Ψ_2 and the dxy orbital on the metal is improved if the allyl group moves in this way.

- The structures also show that the terminal CH_2 groups of the allyl are twisted about the C-C vector so as to rotate the anti-hydrogens H_a, away from the metal, and the syn hydrogens H_s, toward the metal as shown by the arrows.

- This allows the p orbital on these carbons to point more directly toward the metal, thus further improving the overlap.

- In the trihapto form, the C-C-C distances and bond angles may be 1.35 to 1.40 Angstroms with a C-C-C angle of 120^o. The degree of interaction also varies depending on the metal's electron configuration and oxidation state.

- The two C-C bonds are usually the same length, but there are some exceptions, particularly when strongly pi-bonding ligands are trans to the allyl ligand.