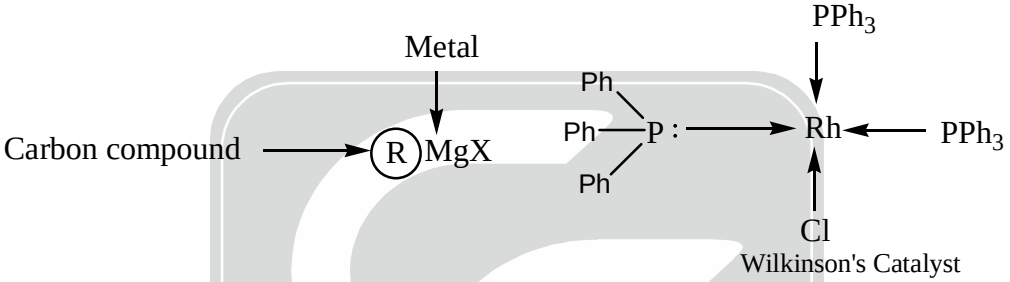
Chapter 1

Introduction to Organometallic Compounds

Introduction :

Edward Frankland was father of organometallic chemistry for a complex to be organometallic compound, there should be atleast one metal-carbon bond. For example, RMgX



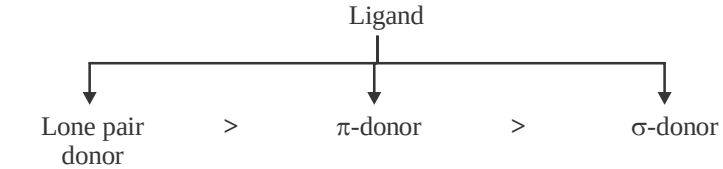
Wilkinson's catalyst is used for hydrogenation of alkene and alkyne.

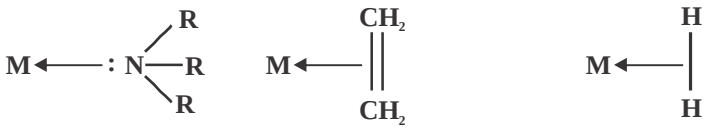
During the catalytic cyclic, a stage comes where the metal Rh is attached with carbon. Therefore, it is said to be an organometallic compound.

NaCN : It has metal-carbon bond but dispite of this, NaCN is not organometallic compound.
So, the above given definition of organometallic compound is not rigid, it is flexible.

Bonding in organometallic complexes:

Ligands are of three types:

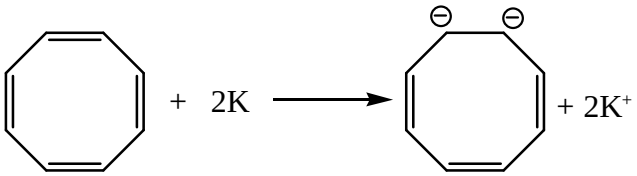


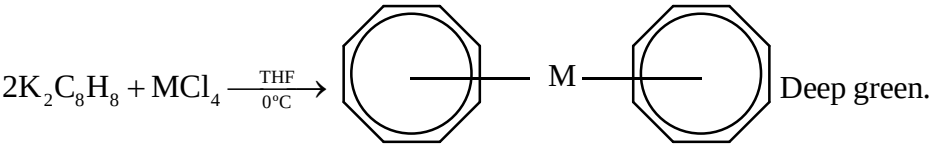


Bonding may be ionic, coordinate and it may be covalent. The covalent bonding are of the two types
(i) Localized (ii) delocalised

Classification of an organometallic compounds:

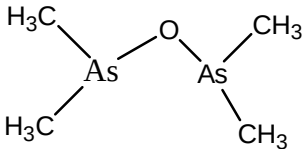
On the basis of metal present in organometallic compounds
(1) If metal is main group element then it is said to be main group compound.
e.g. t-BuLi, RMgX, Me_2Hg, TEL, n-BuLi, $Al(CH_3)_3$.
(2) **Transition metal organometallic compound:** If the metal is from transition metals.
e.g. $Rh(PPh_3)_3Cl$, $Pd(PPh_3)_4$, R_2CuLi, $Fe(CO)_5$.
(3) Lanthanide/Actinide organometallic compound : If metal is from f-block metals.



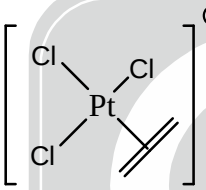


where, M can also be replaced by Pa, Nd.

• First main group organometallic compounds was Cacodyl oxide $\left[(CH_3)_2\,As\right]_2\,O$



• First T.S. metal organometallic compound was Zeise's Salt

Square planar  or $K\left[PtCl_3(C_2H_4)\right]$

Formula for calculation of O.S. in organometallic compound:

C = M + L (where, O.S. = oxidation state)

Where, C = charge on co-ordination sphere

M = O.S. of metal

L = formal charge on ligand.

e.g. Oxidation state of zeise's salt

$\underset{\text{Trichloro ethylene platinate (II) ion}}{\left[PtCl_3(C_2H_4)\right]^-}$ $\quad -1 = x - 3 \quad \boxed{x = +2}$

Effective Atomic Number (EAN) rule:

Sidgwick proposed this rule. The sum of the electrons on the metal plus electrons donated by ligands is called EAN. When EAN is equal to 36(Kr), 54(Xe), 86(Rn) then it is said that EAN Rule is obeyed and the compound is found to be stable. In this concept metal is consider to be **Lewis Acid** and ligand is consider to be **Lewis Base.**

(1) $Ni(CO)_4$
EAN = 28+8 = 36

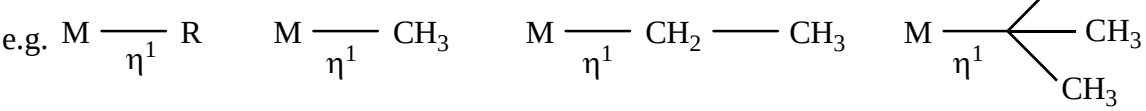
(2) $Cr(CO)_6$
EAN= 24 + 12 = 36

(3) $(C_5H_5)_2\,Fe$
EAN = 10 + 26 = 36

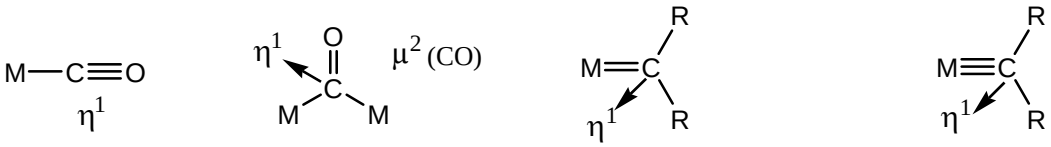
Hapticity :

It is the property of ligand. It is represented by η. The number of donor atom of a ligand is directly attached with the metal is said to be the hapticity.

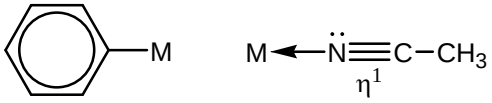
$\eta^n \rightarrow$ Number of donar atom attached with metal.

e.g. 

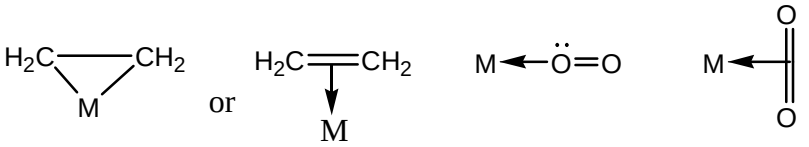
A ligand which joins two /more metals is said to be bridged. It is represented by μ^n this indicates the number of metals bridges, where *n* is number of metal bridged.



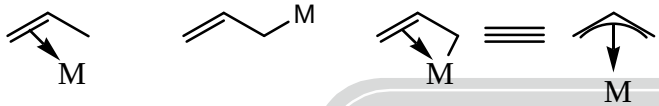
Only one donor atom of ligand attached, so hapticity is one



η^1-phenyl



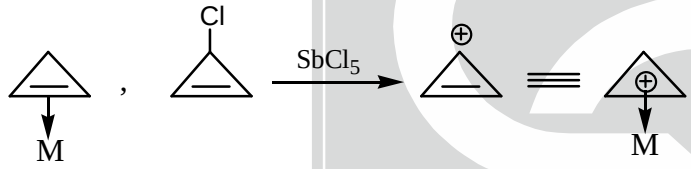
η^2 η^2 η^1 (O_2) $\eta^2(O_2)$



η^2 η^1 -allyl η^3– allyl η^3– allyl

A ligand which can show more than one hapticity is called fluxonial.

e.g. allyl shows η^1 & η^3



η^2–C_3H_4 η^3–C_3H_3

Cyclopentadienyl:

η^1–Cp η^3–Cp η^5–Cp

18 electron rule :

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.

- 18 electron rule is only applicable for transition metal organometallic compound.
- The main group organometallic compound follows octet rule.
- Square planar complex follows 16 electron rule.
- The complex which follow 16 and 18 electron rule are stable.
- Complex which follow 17 electron rule and 19 electron rule are paramagnetic
- Organometallic compound which follows this configuration $\rightarrow ns^2np^6(n-1)d^{10}$ than complex is stable.

$$2+6+10=18\,e^-$$

For complex, total number of electron = the number of valence electron donated by the metal + number of electron donated by the ligand $\pm$ charge.

There are two methods for calculation of 18 electron

(1) Oxidation state method (2) Neutral atom method

e.g. **(i) Ferrocene**

Oxidation State Method :

O.S. of Fe

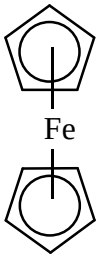
O = M – 2

M = +2

Fe = 6 × 1 = 6

Cp = 6×2 = 12

18 e⁻



Neutral atom method :

Cp = 5×2 = 10

Fe = 8×1 = 8

18 e⁻

Ferrocene follows 18 electron rule.

(ii) $Mn(CO)_5CH_3$.

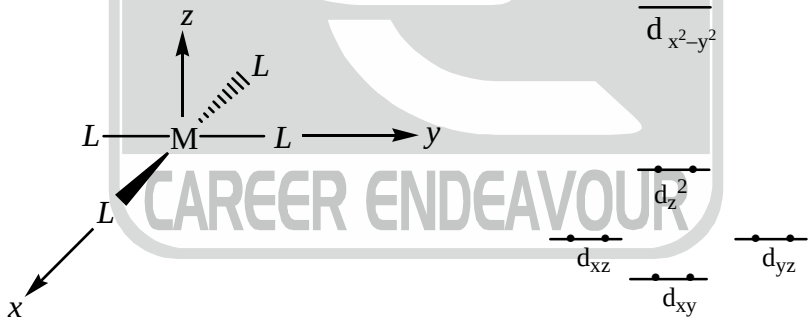
Neutral atomic method := 7 + 10 + 1 = 18 electron

O.S. Method = 6 + 2 + 10 = 18 electron

0 = M – 1, M = +1

Note : Why 16 electron is stable?

Metals with d^8 electrons : The d^8 metals have a tendency to form square planar 16-electron complexes. This tendency is weak for group 8 (Fe, Ru and Os in zero oxidation state) and strong for group 9, 10 and 11 (Rh(I), Pd(II), Pt(II), Au(III). A square planar complexes TVE = 16. This is due to the fact that the $d_{x^2-y^2}$ orbital cannot be occupied in the square-planar geometry, because it has a high energy. Thus, the complexes are stable with the 16-electron count.



Note:

- Complex which follows 17 electron rule is strong oxidizing agent.
- Complex which follows 19 electron rule is strong reducing agent.

e.g. Which of the following complex is strong oxidizing agent and strong reducing agaent?

(a) $Fe(CO)_5$ $(18\ e^-)$ (b) $\left[V(CO)_6\right]^{2-}$ $(19\ e^-)$

(c) $\left[Co(CO)_4\right]^-$ $(18\ e^-)$ (d) $\left[Mn(CO)_5\right]$ $(17\ e^-)$

Soln. (d) is strong oxidizing agent because follows 17 electron rule.
(b) is strong reducing agent because follows 19 electron rule.

Table: Common ligands and their electron contributions.

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

SOLVED PROBLEMS

1. The compound which obeys 18-electron rule is: **[GATE 2000]**

(a) $Mn(CO)_3$ (b) $Fe(CO)_4$ (c) $V(CO)_6$ (d) $Cr(CO)_6$

Soln. $[Cr(CO)_6]$

TVE = 6 + 6×2 = 6 + 12 = 18

Correct option is (d)

2. The complex which obeys the 18 electron rule is **[GATE 2002]**

(a) $Fe(CO)_4$ (b) $Ni(CO)_3(PPh_3)$ (c) $Cr(CO)_5$ (d) $Cr(C_5H_5)_2$

Soln. $Ni(CO)_3(PPh_3)$

TVE = 10 + 3×2 + 2 = 18

Correct option is (b)

3. The bonding of cyclopentadienyl in $Ti(Cp)_4$ is such that **[GATE 2002]**

(a) all Cp rings are pentahapto

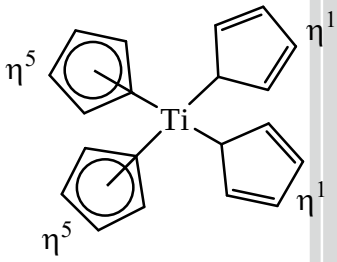
(b) one Cp ring is pentahapto and the other three rings are monohapto

(c) two Cp rings are monohapto and the other two rings are pentahapto

(d) All Cp rings are monohapto

Soln. Structure of $Ti(Cp)_4 \rightarrow d^o \Rightarrow$ follow 16 electron rule.

TVE = 4 + 2×1 + 2×5 = 16



Correct option is (c)

4. Among the complexes (i) $[(C_6H_6)_2Cr]$, (ii) $[HMn(CO)_5]$, (iii) $[(CH_3CO)Rh(CO)I_3]^-$ and (iv) $[CpFe(CO)_2(CH_3)]$, the 18-electron rule is not followed in **[GATE 2003]**

(a) iii only (b) ii and iii (c) i and iv (d) ii only.

Soln. (i) $[(C_6H_6)_2Cr]$, TVE = 6 + 6×2 = 18

(ii) $[HMn(CO)_5]$, TVE = 7 + 2×5 + 1 = 18

(iii) $[(CH_3CO)Rh(CO)I_3]^-$, TVE = 9 + 1 + 1 + 2 + 3×1 = 16

(iv) $[CpFe(CO)_2(CH_3)]$, TVE = 8 + 5 + 2×2+1= 18

Correct option is (a)

5. The neutral complex which follows the 18-electron rule is **[GATE 2005]**

(a) $(\eta^5 - C_5H_5)Fe(CO)_2$ (b) $(\eta^5 - C_5H_5)Mo(CO)_3$

(c) $(\eta^5 - C_5H_5)_2CO$ (d) $(\eta^5 - C_5H_5)Re(\eta^6 - C_6H_6)$

Soln. $(\eta^5 - C_5H_5)Re(\eta^6 - C_6H_6)$

TVE = 5 + 7 + 6 = 18

Correct option is (d)

6. Find oxidation state of the following compounds? **[TIFR 2012]**

(a) $PdCl_2$ (b) $Pd(PPh_3)_4$

(c) $Pd(OAc)_2$ (d) Pd(Br)Ph

Soln. (a) $PdCl_2$

$x–2 = 0, x = 2$

Oxidation state = +2

(b) $Pd(PPh_3)_4$

$x+0 = 0, x = 0$

Oxidation state = 0

(c) $Pd(OAc)_2$

$x+2(–1) =0, x = 2$

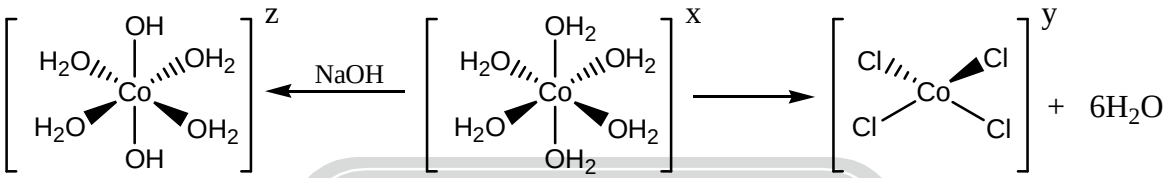
Oxidation state = + 2

(d) Pd(Br)Ph

$x+(–1) + (–1) = 0 \Rightarrow x – 2 = 0, x = 2$

Oxidation state = +2

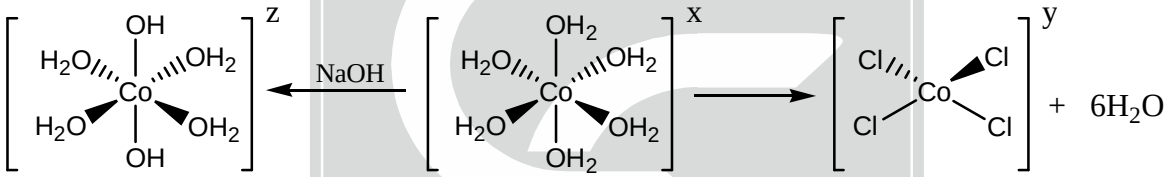
7. For Co in oxidation state II, predict the overall charges of the coordination complexes shown in the reactions below: **[TIFR 2015]**



(a) z = +2; x = –2; y = +2 (b) z = 0; x = +2; y = –2

(c) z = 0; x = +2; y = +2 (d) z = –2; x = +2; y = –2

Soln.



M + L = C

(+) 2 + 2(–1) + 4(0) = Z

Z = 0

M + L = C

(+) 2 + 6(0) = X

X = +2

M + L = C

(+) 2 + 4(–1) = Y

Y = –2

Correct answer is (b)

8. On the basis of 18 electron rule, find out the value of n.

(i) $TcBr(CO)_n$ (ii) $Na_2[Fe(CO)_n]$

(iii) $[Mn(CO)_n]^-$ (iv) $[IrCl_2(CS)_n(PPh_3)_2(H)]$

(v) $[Rh(CO)_3]^n$

Soln. (i) $TcBr(CO)_n$

$7 + 1 + 2n = 18$

$n = 5$

(ii) $Na_2[Fe(CO)_n]$

$8 + 2 + 2n = 18, 2n = 8$

$n = 4$

(iii) $[Mn(CO)_n]^-$

$7 + 2n + 1 = 18$

$2n = 10 = 5$

(iv) $[IrCl_2(CS)_n(PPh_3)_2(H)]$

$9 + 2 + 4 + 1 + 2n = 18, \ 2n = 18 – 16$

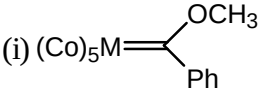
$n = 1$

(v) $[Rh(CO)_3]^n$

$6 + 9 + n = 18$

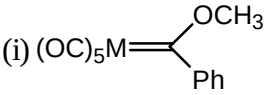
$n = 18 - 15, n = 3$

9. On the basis of 18 electron rule find out the value of M, where M is first row (3d series element) and then find out the element

(i) 

(ii) $\left[\left(\eta^4\text{-}C_4H_4\right)\left(\eta^5\text{-}C_5H_5\right)M\right]^+$

(iii) $\left[\left(\eta^3\text{-allyl}\right)\left(\eta^5\text{-Cp}\right)M(CO)\right]^-$

Soln. (i) 

$M \rightarrow$ 1 st row (3d)
$10 + M + 2 = 18$
$M = 6$
So, M = Cr.

(iii) $\left[\left(\eta^3\text{-allyl}\right)\left(\eta^5\text{-Cp}\right)M(CO)\right]^-$

$3 + 5 + M + 2 + 1 = 18$
$M = 18 - 11$
$M = 7$
So, M = Mn

(ii) $\left[\left(\eta^4\text{-}C_4H_4\right)\left(\eta^5\text{-}C_5H_5\right)M\right]^+$

$4 + 5 - 1 + M = 18$
$M = 10$
So, M = Ni

UNSOLVED PROBLEMS

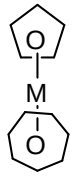
1. What change could be necessary for the following complex to obey 18 electrons rule.

(a) $[Co(CO)_3]^z$ (b) $[Ni(CO)_3(NO)]^z$

(c) $[(\eta^5 - Cp)Fe\ (CO)_2(PhC_2H)^z$

Ans. (a) $z = 3$ (b) $z = +1$ (c) $z = +1$

2. On the basis of 18 electrons rule, identify the first row transition metal for each of the following complexes.

(a)  (b)  (c) $[(CF_3)M(CO)_5]$

Ans. (a) M = Cr (b) M = Ni (c) M = Mn

3. Organometallic compound $[Mo(Cp)_2(CO)_2]$ follow 18 electrons rule the heptacity of two *cp* group are

(a) η^5, η^5 (b) η^3, η^5 (c) η^3, η^3 (d) none of these

Ans. (b)

4. The complex that does not obey 18 electrons rule

(a) $[Ru(N)(Br_2)(PMe_3)(NMe_2)]^-$ (b) $[CpCr(NO)_2Me]$

(c) $[CpTi(CO)_4]^-$ (d) $[Co(CO)_2(CS)(PPh_3)(Br)]$

Ans. (a)

5. What is the heptacity of cycloheptatrienyl ligand in a complex $[(C_7H_7)Mo(CO)_3]$

(a) 2 (b) 5 (c) 6 (d) 7

Ans. (c)

PRACTICE SET

1. Match each of the compounds in **List-I** with appropriate oxidation state from **List-II** and the coordination number from **List-III**. **[GATE 1995]**

List-I	List-II	List-III
(1) Zeise's salt	0	3
(2) $Ni(CO)_4$	1	4
(3) $[Co(NH_3)_5Cl]Cl_2$	2	5
	3	6

	List-I	List-II	List-III
(a)	(1, 2, 3)	(2, 0, 1)	(3, 4, 6)
(b)	(1, 2, 3)	(2, 3, 1)	(3, 4, 5)
(c)	(1, 2, 3)	(3, 0, 1)	(5, 4, 6)
(d)	(1, 2, 3)	(2, 0, 3)	(3, 4, 5)

2. Which case of the following is most easily reduced? **[GATE 1996]**
(a) $V(CO)_6$ (b) $Cr(CO)_6$ (c) $Fe(CO)_5$ (d) $Ni(CO)_4$

3. The organometallic compound $W(C_5H_5)_2(CO)_2$ follows the 18-electron rule. The hapticities of the two cyclopentadienyl groups are **[GATE 1996]**
(a) 5 and 5 (b) 3 and 5 (c) 3 and 3 (d) 1 and 5

4. Which one of the following molecules does not obey the 18-electron rule? **[GATE 1997]**
(a) $\left[Mn(CO)_6\right]^+$ (b) $Fe(CO)_5$ (c) $\left[Cr(CO)_5\right]^{2-}$ (d) $\left[Mn(CO)_4Cl_2\right]^{2-}$

5. Among the following, the unstable carbonyl species is **[GATE 1998]**
(a) $Mn(CO)_5Cl$ (b) $[Mn(CO)_5]^-$ (c) $[Mn(CO)_5]^+$ (d) $Mn(CO)_5$

6. Which of the following does not obey 18 electron rule? **[GATE 1999]**
(a) $Cr(CO)_6$ (b) $Fe(CO)_5$ (c) $V(CO)_6$ (d) $Mn_2(CO)_{10}$

7. Which of the following obey 18 electron rule? **[GATE 2000]**
(a) $Mn(CO)_3$ (b) $Fe(CO)_4$ (c) $V(CO)_6$ (d) $Cr(CO)_6$

8. Which of the following complex do not obey 18 electron rule.
(a) $\left[CpRu(Cl)(CO)(PPh_3)\right]$ (b) $\left[W(CO)_3(SiMe_3)(Cl)(NCMe)_2\right]$
(c) $\left[IrCl_3(PPh_3)_2(AsPh_2)\right]^-$ (d) $\left[As(N)Br_2(PMe_3)(NMe_2)\right]^-$

9. Which of the following Beryllium complex is stable?
(a) $\left[Be(\eta^5Cp)_2\right]$ (b) $\left[Be(\eta^2Cp)(\eta^1Cp)\right]$
(c) $\left[Be(\eta^1Cp)(\eta^3Cp)\right]$ (d) $\left[Be(\eta^1Cp)(\eta^5Cp)\right]$

Note: Main group elements follow octet rule, Valence electron of Be = 2, So, to complete octet, Needs 6 electrons.

ANSWER KEY					
Questions	1	2	3	4	5
Option	(a)	(a)	(b)	(d)	(d)
Questions	6	7	8	9	
Option	(c)	(d)	(d)	(d)	