

# Important Questions on Organometallic Compounds



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1. Which of the following follows the 18 electron rule?
 

A. $\text{CpMn}(\text{CO})_2\text{CPh}_3$	B. $\text{Fe}(\text{CO})_4$
C. $\text{Cr}(\text{CO})_2(\text{NCMe})_2$	D. $\text{IrCl}_3(\text{PPh}_3)_2(\text{AsPh}_2)^-$
  
2. The structure of  $\text{Rh}_6(\text{CO})_{16}$  is:
 

A. Closo	B. Nido
C. Arachno	D. Hypo
  
3. Correct order of M-C bond order:
 

A. $\text{Cr}(\text{CO})_4 < [\text{Ti}(\text{CO})_4]^{-2} < [\text{Mn}(\text{CO})_4]^+ < [\text{V}(\text{CO})_4]^-$
B. $[\text{Mn}(\text{CO})_4]^+ < [\text{V}(\text{CO})_4]^- < \text{Cr}(\text{CO})_4 < [\text{Ti}(\text{CO})_4]^{-2}$
C. $[\text{Mn}(\text{CO})_4]^+ < \text{Cr}(\text{CO})_4 < [\text{V}(\text{CO})_4]^- < [\text{Ti}(\text{CO})_4]^{-2}$
D. $[\text{Cr}(\text{CO})_4] < [\text{Mn}(\text{CO})_4]^+ < [\text{V}(\text{CO})_4]^- < [\text{Ti}(\text{CO})_4]^{-2}$
  
4. In the oxidative addition of  $\text{H}_2$  to  $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{X}]$ , X can be Cl, Br, I, the rate order of rate with different X is:
 

A. $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}] < [\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{I}] < [\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Br}]$
B. $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{I}] < [\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}] < [\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Br}]$
C. $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{I}] < [\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Br}] < [\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$
D. $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}] < [\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Br}] < [\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{I}]$
  
5.  $[\text{Fe}(\eta^5\text{cp})(\text{CO})_2(\text{C}_2\text{H}_5)]$  cannot undergo beta hydride elimination because
 

A. It does not have beta hydrogen.	B. It cannot form a coplanar transition state.
C. It violates bredt's rule.	D. It is a stable $18 e^-$ complex.
  
6. Determine the Metal-Metal bond present in  $(\eta^4\text{-C}_4\text{H}_4)_2\text{Fe}_2(\text{CO})_3$ .
 

A. 1	B. 2	C. 4	D. 3
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7. Determine the structure and type of centre respectively of compound  $[\text{Fe}_4(\text{CO})_{12}\text{C}]^{2-}$ .
 

A. Octahedral, Arachno	B. Triangular Bipyramidal, Nido
C. butterfly, Arachno	D. Square Bipyramidal, Closo
  
8. On reducing  $\text{Fe}_3(\text{CO})_{12}$  with an excess of sodium, a carbonylated ion is formed. The ion is isoelectronic with:
 

A. $[\text{Mn}(\text{CO})_5]^-$	B. $[\text{Ni}(\text{CO})_4]$
C. $[\text{Mn}(\text{CO})_5]^+$	D. $[\text{V}(\text{CO})_6]^-$
  
9. Which of the following sets is isolobal to BH?
 

A. $\text{Fe}(\text{CO})_4, \text{CH}_2, \text{CpCo}$	B. $\text{Fe}(\text{CO})_3, \text{C}, \text{CpCo}$
C. $\text{Fe}(\text{CO})_3, \text{CH}_2, \text{CpCo}$	D. $\text{Fe}(\text{CO})_3, \text{CH}_2, \text{CpMn}$
  
10. Determine the unknown quantity in  $[\text{CpW}(\text{CO})_x]_2$ . It is given that this complex contains a W-W single bond.
 

A. 6	B. 3	C. 4	D. 5
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### Answer Key

1. D	2. A	3. C	4. D	5. D	6. D	7. C
8. B	9. B	10. B				

### Solutions

#### Solution 1.

In CpMn(CO)<sub>3</sub>CPh<sub>3</sub>, contribution of CPh<sub>3</sub> is 1 because it has 1 extra electron to donate.

Total valence electron count of CpMn(CO)<sub>3</sub>CPh<sub>3</sub> = 5+7+(3×2)+1 = 19 e<sup>-</sup>

In Fe(CO)<sub>4</sub>, Total valence electron count of Fe(CO)<sub>4</sub> = 8+ (4×2) = 16 e<sup>-</sup>

In Cr(CO)<sub>2</sub>(NCMe)<sub>2</sub>, contribution of (NCMe)<sub>2</sub> is 2 because after forming 3 bonds with CMe, N has 1 lone pair left, so, total valence electron count of Cr(CO)<sub>2</sub>(NCMe)<sub>2</sub> : 6 +(2×2)+(2×2) = 14 e<sup>-</sup>

In IrCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(AsPh<sub>2</sub>)], contribution of AsPh<sub>2</sub> is 1 because As belongs to the N family and they have a tendency to form 3 bonds. Here, As will form only 2 bonds, so 1 electron is left for bonding.

Total valence electron count of IrCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(AsPh<sub>2</sub>)] = 9+(1×3) +(2×2)+1+1 = 18e<sup>-</sup>

#### Solution 2.

In [Rh<sub>6</sub>(CO)<sub>16</sub>], no. of metals >4 so, it is a high nuclearity metal carbonyl cluster in which 12 electrons are always present outside the Polyhedra.

Total electron count (TEC) of [Rh<sub>6</sub>(CO)<sub>16</sub>] = (6×9) +(16×2) =86

So, polyhedral electron pair = (TEC- 12×N)/2

= [86-(12×6)]/2 = 7

No. of electron pair = 6+1

Its structure is like [B<sub>6</sub>H<sub>6</sub>]<sup>-2</sup>.

So, the structure is closo.

#### Solution 3.

Due to backbonding, there will be more e<sup>-</sup> density present in carbonyl antibonding orbital due to which bond strength of C-O bond decreases while the bond strength of M-C bond increases. More the electron density on the central metal atom, more will be the backbonding. Hence, the order of M-C bond order is:

[Mn(CO)<sub>4</sub>]<sup>+</sup> < Cr(CO)<sub>4</sub> < [V(CO)<sub>4</sub>]<sup>-</sup> < [Ti(CO)<sub>4</sub>]<sup>-2</sup>

#### Solution 4.

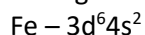
In oxidative addition of any ligand, the increase in oxidation state by +2 takes place and along with this, increase in coordination no. of +2 takes place due to addition of two ligands. Oxidative addition occurs much more readily in case of electron rich metal. In all the given complexes, only the halide ligand differs. On changing X to Cl, Br, I, electron donation increases, metal becomes more electron rich, hence, rate of oxidative addition increases.

#### Solution 5.

[Fe(η<sup>5</sup>cp)(CO)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)] cannot undergo beta hydride elimination because it is a stable 18 electron complex due to which it directly cannot undergoes beta hydride elimination. It has beta hydrogen. It can also form coplanar transition state. Here, bredt's rule is not applicable because this is applicable to cyclic bridged complexes.

### Solution 6.

The ligands are arranged in such a way that each metal atom follows the 18 electron rule.



Total valence electron (TVE) count of  $(n^4\text{-C}_4\text{H}_4)\text{Fe}_2(\text{CO})_3$

$$= (4 \times 2) + (8 \times 2) + (2 \times 3)$$

$$= 30$$

$$\text{Metal-Metal Bond} = 18 \times n - \text{TVE} / 2$$

$$= (18 \times 2) - 30 / 2$$

$$= 3$$

### Solution 7.

Determination of structure for HNCC: -

Step I → Calculate TVE (Total Valence e- count.)

Step II → Add the value of the valence electron of interstitial atoms.

Step III → Calculate Skeletal electron Pair (S) as:

$$S = (\text{TVE} - n \times 12) / 2$$

n = Number of metals in the given cluster.

Step IV → The structure is arranged according to the Wade rule, If skeletal electron pair is,

S = n - 1: Super closo

S = n: Hyper closo

S = n + 1: Closo

S = n + 2: Nido

S = n + 3: Arachno

S = n + 4: Hypo

Calculating T.V.E as:

C = 4 e<sup>-</sup> Contribution because it is encapsulated atom

Os = 3d<sup>6</sup>4s<sup>2</sup> = 8 e<sup>-</sup> contribution

$$= 4 + (8 \times 4) + (12 \times 2) + 2$$

$$= 62 \text{ e}^- \text{ :- Geometry will be butterfly}$$

$$\text{Skeletal Electron pair} = (\text{TVE} - 12 \times N) / 2$$

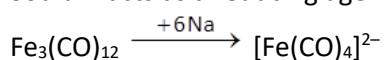
$$= (62 - 48) / 2$$

$$= 8$$

S = n + 3 hence, it is an example of arachno.

### Solution 8.

Sodium acts as a reducing agent. It will break the M-M bond and form carbonylated ion.



$[\text{Fe}(\text{CO})_4]^{2-}$  contains Fe<sup>2-</sup> ion having electronic configuration of 3d<sup>8</sup>4s<sup>2</sup>. This electronic configuration is isoelectronic with Ni(O)

Ni electronic conf. = 3d<sup>8</sup>4s<sup>2</sup>

Hence, the ion is isoelectronic with  $[\text{Ni}(\text{CO})_4]$ .

### Solution 9.

Valence electrons of BH = 3 + 1 = 4

It has deficiency of 4 to fulfil the octet rule i.e it has 4 holes.

$$\text{In Fe}(\text{CO})_4: \text{TEC} = 8 + (2 \times 4) = 16$$

It has a deficiency of 2 electrons to fulfil the 18-electron rule, so it has 2 holes.

CH<sub>2</sub> valence electrons: 4 + 2 = 6, there is a deficiency of 2 electrons to fulfil the octet.

$$\text{In Fe}(\text{CO})_3: \text{TEC} = 8 + (2 \times 3) = 14$$

**Solution 10.**

Given that it has 1 W-W bond, the 1 fragment contains 17 electrons.

TVE is  $17e^- \times 2 = 34e^-$

$[\text{CpW}(\text{CO})_x]_2$

Now, electrons contributed by each ligand is:

Cp =  $5e^-$

CO =  $2e^-$

W =  $6e^-$

$\text{CpW}(\text{CO})_x = 17e^-$

$5 + 6 + 2x = 17e^-$

$2x = 6$

$x = 3$



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