

M.Sc. 3rd SEMESTER
Multiple Choice Questions

CSIR/NET-QUESTIONS

In the base-catalysed substitution of Cl^- by $[\text{OH}]^-$ in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ under strongly basic conditions, the first step in the mechanism is:

- conversion of an ammine to amido ligand
- substitution of Cl^- by $[\text{OH}]^-$
- dissociation of Cl^- to give a 5-coordinate intermediate
- association of $[\text{OH}]^-$ to give a 7-coordinate intermediate

Which ordering *correctly* describes the tendency of a ligand to direct ligand substitution in a square planar complex to a position opposite to itself?

- $[\text{CN}]^- > [\text{NO}_2]^- > \text{Br}^- > \text{NH}_3$
- $[\text{CN}]^- > \text{Br}^- > \text{NH}_3 > [\text{NO}_2]^-$
- $[\text{NO}_2]^- > [\text{CN}]^- > \text{NH}_3 > \text{Br}^-$
- $\text{Br}^- > [\text{CN}]^- > \text{NH}_3 > [\text{NO}_2]^-$

Anation is:

- the substitution of an uncharged ligand by an anionic ligand
- the substitution of an uncharged ligand by another uncharged ligand
- the substitution of an anionic ligand by another anionic ligand
- the substitution of an anionic ligand by an uncharged ligand

Three of the following ions are kinetically inert, one is labile. Which ion is labile?

- Rh^{3+}
- Ti^{3+}
- Ru^{2+}
- Cr^{3+}

Which ordering *correctly* shows the variation in rates of water exchange in high-spin aqua complexes $[M(OH_2)_6]^{n+}$?

- $Co^{2+} > Cr^{2+}$
- $V^{2+} > Co^{2+}$
- $Cr^{3+} > Fe^{3+}$
- $Cr^{2+} > Cr^{3+}$

The usual form of the experimental rate law for substitution in square planar Pt(II) complexes contains two terms:

$$\text{Rate} = k_1[\text{PtL}_3\text{X}] + k_2[\text{PtL}_3\text{X}][\text{Y}]$$

where PtL_3X is the starting complex and Y is the entering group. The reason for the two-term law is that:

- there are competitive associative and dissociative pathways
- there are two competing dissociative pathways
- the solvent enters in the rate-determining step, and then two competing fast steps follow
- the solvent competes with Y in the rate-determining step

Which statement about the *trans*-effect and the *trans*-influence is correct?

- The *trans*-influence is a ground-state effect, whereas the *trans*-effect has a kinetic origin
- The *trans*-effect is a ground-state effect, whereas the *trans*-influence has a kinetic origin
- Both the *trans*-effect and *trans*-influence are ground-state effects
- Rates of substitution are affected by the *trans*-effect but have nothing to do with the *trans*-influence of ligands

The reactions of $[\text{PtCl}_4]^{2-}$ with NH_3 (reaction I) and of $[\text{PtCl}_4]^{2-}$ with $[\text{NO}_2]^-$ followed by NH_3 (reaction II) are ways of preparing:

- I: *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$; II: *trans*- $[\text{PtCl}_2(\text{NH}_3)(\text{NO}_2)]^-$
- I: *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$; II: *trans*- $[\text{PtCl}_2(\text{NH}_3)(\text{NO}_2)]^-$
- I: *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$; II: *cis*- $[\text{PtCl}_2(\text{NH}_3)(\text{NO}_2)]^-$
- I: *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$; II: *cis*- $[\text{PtCl}_2(\text{NH}_3)(\text{NO}_2)]^-$

Which statement is *correct*?

- A dissociative mechanism is a 2-step mechanism with the leaving group departing in the second step
- An associative mechanism is a 2-step mechanism; the intermediate has a lower coordination number than the starting complex
- In a dissociative interchange mechanism, bond breaking dominates over bond formation
- In an associative interchange mechanism, the entering group associates with the substrate after the leaving group has departed

Which ion is *kinetically inert*?

- Cr²⁺
- Co³⁺
- Co²⁺
- Fe³⁺

1. A reaction sequence in which an intermediate of reduced coordination number is formed by the departure of the leaving group is called:

- A. an associative mechanism
- B. a dissociative mechanism
- C. an interchange mechanism

2. The rate-determining step in octahedral complex substitution is believed to be:

- A. an associative step
- B. a dissociative step
- C. an interchange step

3. Find the correct statement:

- A. Octahedral substitution reactions that go through a square-pyramidal intermediate result in the retention of the original geometry. A trigonal-bipyramidal intermediate may lead to isomerization.
- B. Octahedral substitution reactions that go through a square-pyramidal intermediate do not retain the original geometry. A trigonal-bipyramidal intermediate may lead to isomerization.
- C. Octahedral substitution reactions that go through a trigonal-bipyramidal intermediate result in the retention of the original geometry. A square-pyramidal intermediate may lead to isomerization.

4. Inner-sphere and outer-sphere redox mechanisms are different in that:

- A.** The inner-sphere mechanism involves simple electron transfers, while the outer-sphere mechanism involves atom transfers. The inner-sphere mechanism forms a bridged transition state involving the reactants' coordination spheres, while the outer-sphere one does not.
- B.** The inner-sphere mechanism involves atom transfers, while the outer-sphere mechanism involves simple electron transfers. The outer-sphere mechanism forms a bridged transition state involving the reactants' coordination spheres, while the inner-sphere one does not.
- C.** The inner-sphere mechanism involves atom transfers, while the outer-sphere mechanism involves simple electron transfers. The inner-sphere mechanism forms a bridged transition state involving the reactants' coordination spheres, while the outer-sphere one does not.

5. In which of the following cases one should consider the base hydrolysis as a predominant mechanism?

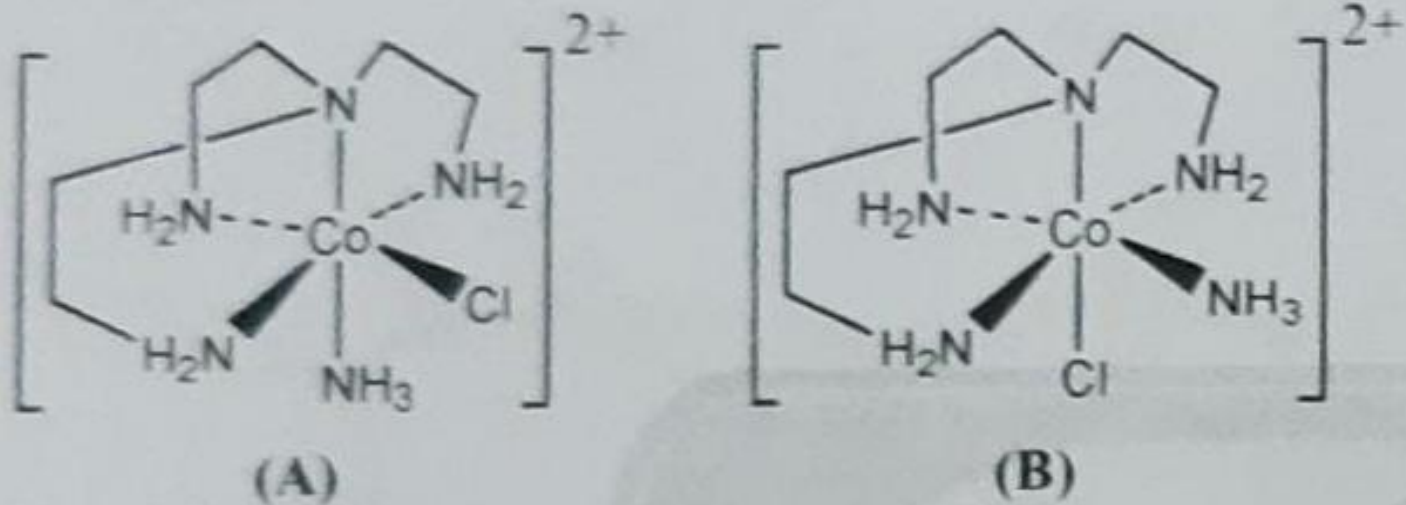
- A.** Any time the solution contains high concentration of OH⁻ ions.
- B.** In the cases when hydroxyl groups (OH⁻) are coordinated on the metal and the concentration of H₃O⁺ ions is high in the solution.
- C.** In the cases when the acidic hydrogens are present on the ligands (for example coordinated NH₃) and OH⁻ ions are present in the solution.

6. Find the correct statement:

A. Steric crowding disfavours associative mechanisms.

B. Since the octahedral complexes follow dissociative mechanism, the nature of the leaving group never influences the substitution rate.

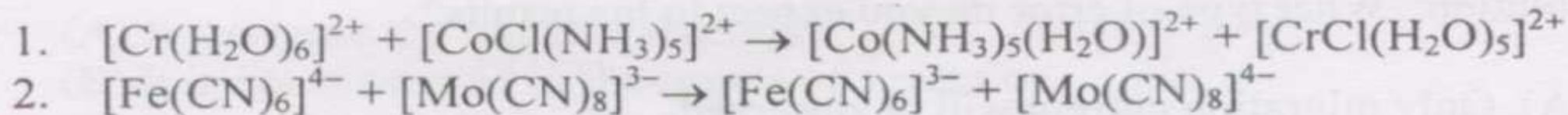
C. The Eigen–Wilkins mechanism explains the substitution reactions in the square-planar complexes.



The isomers **A** and **B** undergo base hydrolysis by forming a trigonal bipyramidal intermediate. The correct statement is

- (a) **A** reacts faster than **B** and both results in a mixture of products
- (b) **B** reacts faster than **A** and both results in a mixture of products
- (c) **A** reacts faster than **B** and **B** results in a mixture of products
- (d) **B** reacts faster than **A** and **A** results in a mixture of products.

Q.31 Consider the reactions



Which one of the following is the correct statement?

- (i) Both involve an inner sphere mechanism
- (ii) Both involve an outer sphere mechanism
- (iii) Reaction 1 follows inner sphere and reaction 2 follows outer sphere mechanism
- (iv) Reaction 1 follows outer sphere and reaction 2 follows inner sphere mechanism

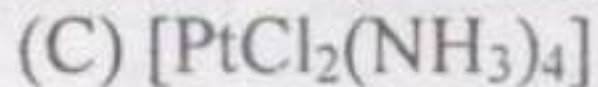
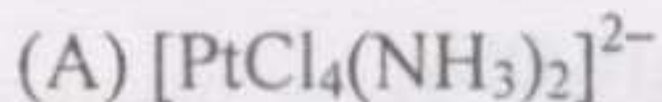
(A) i

(B) ii

(C) iv

(D) iii

Q.36 The reaction of $[\text{PtCl}_4]^{2-}$ with NH_3 gives rise to



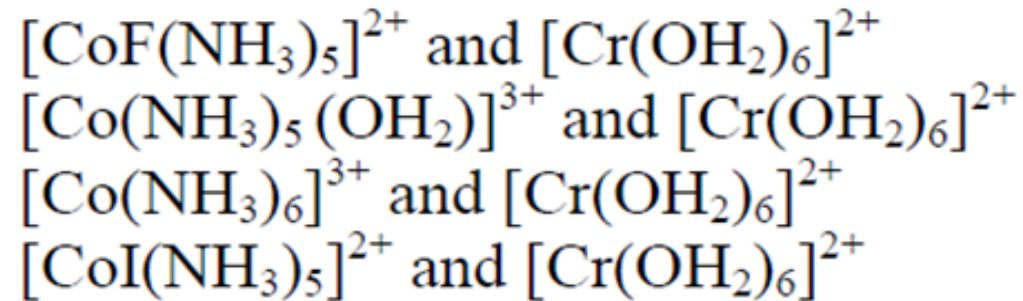
Some further generalizations are as follows:

- 1 All complexes of *s*-block ions except the smallest (Be^{2+} and Mg^{2+}) are very labile.
- 2 Complexes of the M(III) ions of the *f*-block are all very labile.
- 3 Complexes of the d^{10} ions (Zn^{2+} , Cd^{2+} , and Hg^{2+}) are normally very labile.
- 4 Across the 3*d* series, complexes of *d*-block M(II) ions are generally moderately labile, with distorted Cu(II) complexes among the most labile.
- 5 Complexes of M(III) ions are distinctly less labile than M(II) ions.
- 6 *d*-Metal complexes with d^3 and low-spin d^6 configurations (for example Cr(III), Fe(II), and Co(III)) are generally nonlabile as they have large LFSEs. Chelate complexes with the same configuration, such as $[\text{Fe}(\text{phen})_3]^{2+}$, are particularly inert.
- 7 Nonlability is common among the complexes of the 4*d* and 5*d* series, which reflects the high LFSE and strength of the metal–ligand bonding.

Q.24 An intermediate formed during the hydroformylation of olefins using $\text{Co}_2(\text{CO})_8$ as catalyst is

- (A) $\text{HCo}(\text{CO})_6$ (B) $\text{H}_4\text{Co}(\text{CO})_3$ (C) $\text{H}_2\text{Co}(\text{CO})_4$ (D) $\text{HCo}(\text{CO})_4$

Consider the following pairs of complexes



The electron transfer rate will be fastest in the pair

- (A) $[\text{CoF}(\text{NH}_3)_5]^{2+}$ and $[\text{Cr}(\text{OH}_2)_6]^{2+}$ (B) $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ and $[\text{Cr}(\text{OH}_2)_6]^{2+}$
 (C) $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{OH}_2)_6]^{2+}$ (D) $[\text{CoI}(\text{NH}_3)_5]^{2+}$ and $[\text{Cr}(\text{OH}_2)_6]^{2+}$

31. As a ligand Cl^- is

1. only a σ -donor
2. only a π -donor
3. both a σ -donor and a π -donor
4. a σ -donor and a π -acceptor

For the Wacker process, pick the correct statement (s) from the following:

- (A) Pd(II) is reduced to Pd(0) by Cu(I)
- (B) Pd(0) is oxidized to Pd(II) by Cu(II)
- (C) Cu(II) promotes the reductive elimination

correct answer is

1. A and C

2. B and C

3. A and B

4. B Only

Choose the correct set of statements for *cis*-platin.

- (A) It can be prepared from $K_2[PtCl_4]$.
- (B) It can be prepared from $[Pt(NH_3)_4Cl_2]$.
- (C) In its preparation, the observed trans effect for Cl^- is greater than that of NH_3 .
- (D) In blood it stays in equilibrium with *cis*- $[Pt(NH_3)_2Cl(H_2O)]^+$.
- (E) In DNA strand, it binds to two adjacent cytosine bases.

The correct set is

1. A, C and D

2. A, C, D and E

3. B, C and D

4. B, C, D and E

The water exchange rates for the complex ions follow the order

- (A) $[\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 (B) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} > [\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{V}(\text{H}_2\text{O})_6]^{2+}$
 (C) $[\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+} > [\text{V}(\text{H}_2\text{O})_6]^{2+}$
 (D) $[\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{V}(\text{H}_2\text{O})_6]^{2+} > [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

The correct statement with respect to the bonding of the ligands, Me_3N and Me_3P with the metal ions Be^{2+} and Pd^{2+} is,

- (A) the ligands bind equally strong with both the metal ions as they are dicationic
 (B) the ligands bind equally strong with both the metal ions as both the ligands are pyramidal
 (C) the binding is stronger for Me_3N with Be^{2+} and Me_3P with Pd^{2+}
 (D) the binding is stronger for Me_3N with Pd^{2+} and Me_3P with Be^{2+}

Reductive elimination step in hydrogenation of alkenes by Wilkinson catalyst results in (neglecting solvent in coordination sphere of Rh)

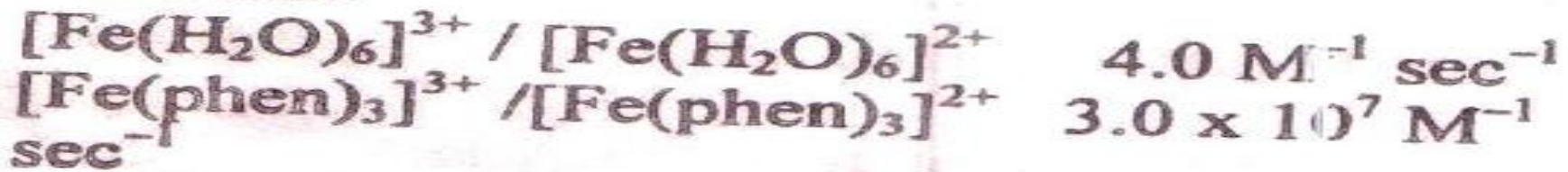
1. T-shaped $[\text{Rh}(\text{PPh}_3)_2\text{Cl}]$
2. Trigonal-planar $[\text{Rh}(\text{PPh}_3)_2\text{Cl}]^{2+}$
3. T-shaped $[\text{Rh}(\text{H})(\text{PPh}_3)\text{Cl}]^+$
4. Trigonal-planar $[\text{Rh}(\text{H})(\text{PPh}_3)_2]$

Base hydrolysis of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ is an overall second order reaction, whereas that of $[\text{Co}(\text{CN})_6]^{3-}$ is of first order. The rates depend in both cases solely on the concentrations of the cobalt complex. This may be due to

- A. presence of ionizable proton in $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ but not in $[\text{Co}(\text{CN})_6]^{3-}$
 - B. $\text{S}_{\text{N}}^1\text{CB}$ mechanism in the case of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ only
 - C. $\text{S}_{\text{N}}^1\text{CB}$ mechanism in the case of $[\text{Co}(\text{CN})_6]^{3-}$ only
 - D. $\text{S}_{\text{N}}^1\text{CB}$ mechanism in both the complexes
- Correct explanation(s) is/are

- | | |
|------------|------------|
| 1. A and B | 2. A and C |
| 3. B only | 4. A and D |

72. Consider the second order rate constants for the following outer-sphere electron transfer reactions:



(phen = 1,10-phenanthroline)

The enhanced rate constant for the second reaction is due to the fact that

1. The 'phen' is a π -acceptor ligand that allows mixing of electron donor and acceptor orbitals that enhances the rate of electron transfer.
2. The 'phen' is a π -donor ligand that enhances the rate of electron transfer.
3. The 'phen' forms charge transfer complex with iron and facilitates the electron transfer.
4. The 'phen' forms kinetically labile complex with iron and facilitates the electron transfer.

Q.42 When one CO group is replaced by PPh₃ in [Cr(CO)₆], which one of the following statements is **TRUE**?

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- (A) The Cr-C bond length increases and CO bond length decreases
- (B) The Cr-C bond length decreases and CO bond length decreases
- (C) The Cr-C bond length decreases and CO bond length increases
- (D) The Cr-C bond length increases and CO bond length increases

Q.43 Identify X in the reaction, $[\text{Pt}(\text{NH}_3)_4]^{2+} + 2 \text{HCl} \rightarrow \text{X}$

- (A) *cis*-[PtCl₂(NH₃)₂]
- (B) *trans*-[PtCl₂(NH₃)₂]
- (C) [PtCl(NH₃)₃]⁺
- (D) [PtCl₃(NH₃)]⁻

(87) Aqueous Cr²⁺ effects one electron reduction of [Co(NH₃)₅Cl]²⁺ giving compound Y. compound Y undergoes rapid hydrolysis. Y is,

- (1.) [Co(NH₃)₅]²⁺
- (2.) [Co(NH₃)₅(OH)]⁺
- (3.) [Co(NH₃)₄(OH)₂]
- (4.) [Cr(H₂O)₅Cl]²⁺

(89) The correct statement about the substitution reaction of $[\text{Co}(\text{CN})_5(\text{Cl})]^{3-}$ with OH^- to give $[\text{Co}(\text{CN})_5(\text{OH})]^{3-}$ is,

- (1.) it obeys first order kinetics
- (2.) its rate is proportional to the concentration of both the reactants
- (3.) it follows the $\text{S}_{\text{N}}^1\text{CB}$ mechanism
- (4.) its rate is dependent only on the concentration of $[\text{OH}]^-$

29. The binding modes of NO in 18 electron compounds $[\text{Co}(\text{CO})_3(\text{NO})]$ and $[\text{Ni}(\eta^5\text{-Cp})(\text{NO})]$, respectively, are

1. Linear and bent
2. Bent and linear
3. Linear and linear.
4. Bent and bent.

38. Intense band generally observed for a carbonyl group in the IR spectrum is due to

1. The force constant of CO bond is large
2. The force constant of CO bond is small
3. There is no change in dipole moment for CO bond stretching
4. The dipole moment change due to CO bond stretching is large

36. The reaction $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-} + \text{X}^- \rightarrow [\text{Co}(\text{CN})_5\text{X}]^{2-} + \text{H}_2\text{O}$ follows a/an:
1. Interchange dissociative (I_d) mechanism
 2. Dissociative (D) mechanism
 3. Associative (A) mechanism
 4. Interchange Associative (I_a) mechanism

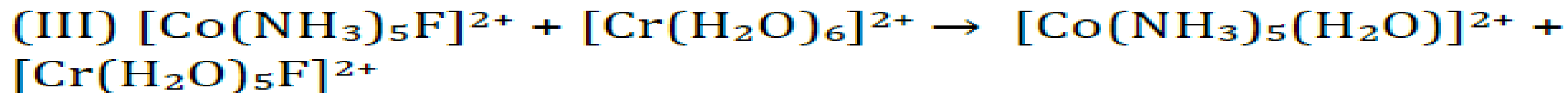
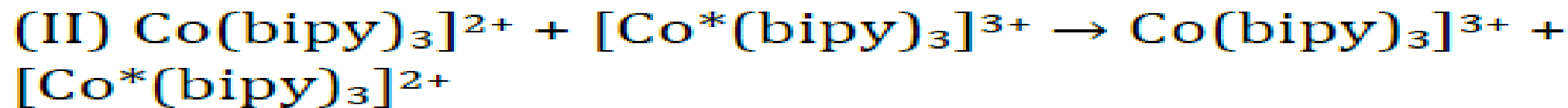
42. The refluxing of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with an excess of PPh_3 in ethanol gives a complex A. Complex A and the valence electron count on rhodium are, respectively,

- | | |
|---|---|
| 1. $[\text{RhCl}(\text{PPh}_3)_3]$, 16 | 2. $[\text{RhCl}(\text{PPh}_3)_5]$, 16 |
| 3. $[\text{RhCl}(\text{PPh}_3)_3]$, 18 | 4. $[\text{RhCl}(\text{PPh}_3)_5]$, 18 |

82. With respect to σ and π bonding in $\text{Pt}-\text{C}\equiv\text{N}$ in the structure given below, which of the following represent the correct bonding

1. $\text{M}(\sigma) \rightarrow \text{L}(\sigma)$ and $\text{M}(\pi) \rightarrow \text{L}(\pi^*)$
2. $\text{L}(\sigma) \rightarrow \text{M}(\pi)$ and $\text{L}(\pi) \rightarrow \text{M}(\pi)$
3. $\text{L}(\pi) \rightarrow \text{M}(\pi)$ and $\text{L}(\sigma) \rightarrow \text{M}(\pi)$
4. $\text{L}(\pi) \rightarrow \text{M}(\sigma)$ and $\text{M}(\pi) \rightarrow \text{L}(\pi^*)$

76. Consider the statements A-D regarding equations III:



(A) Marcus equation is applicable to I and ii.

(B) Marcus equation is applicable to II only.

(C) Equations I and II involve inner sphere electron transfer.

(D) Equations I and III involve inner sphere electron transfer.

The correct statements are:

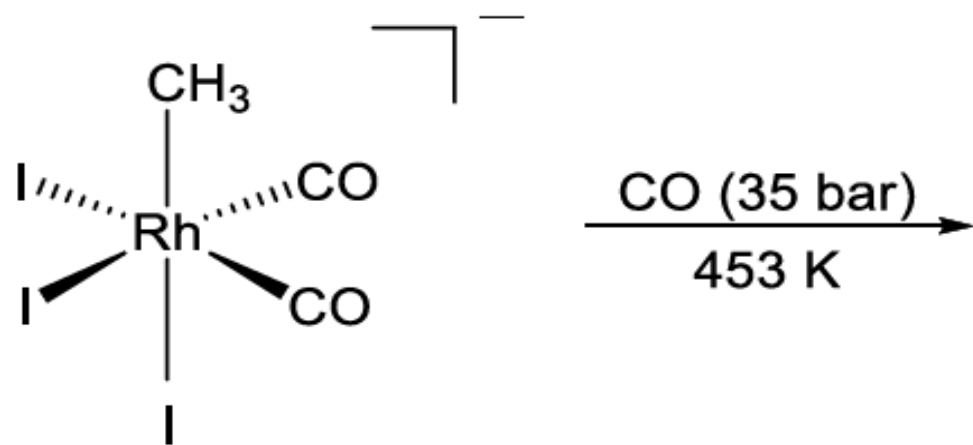
1. A and B

3. B and D

2. B and C

4. C and D

Q.33 The elimination product of the following reaction is



(A) I_2

(B) CH_3I

(C) CH_3COI

(D) I_3^-

Q.38 Second-order rate constant for the reaction between $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ ($n = 3$ for $\text{X} = \text{NH}_3$ and H_2O ; $n = 2$ for $\text{X} = \text{Cl}^-$) and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ at room temperature varies with the X as

(A) $\text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^-$

(B) $\text{Cl}^- > \text{H}_2\text{O} > \text{NH}_3$

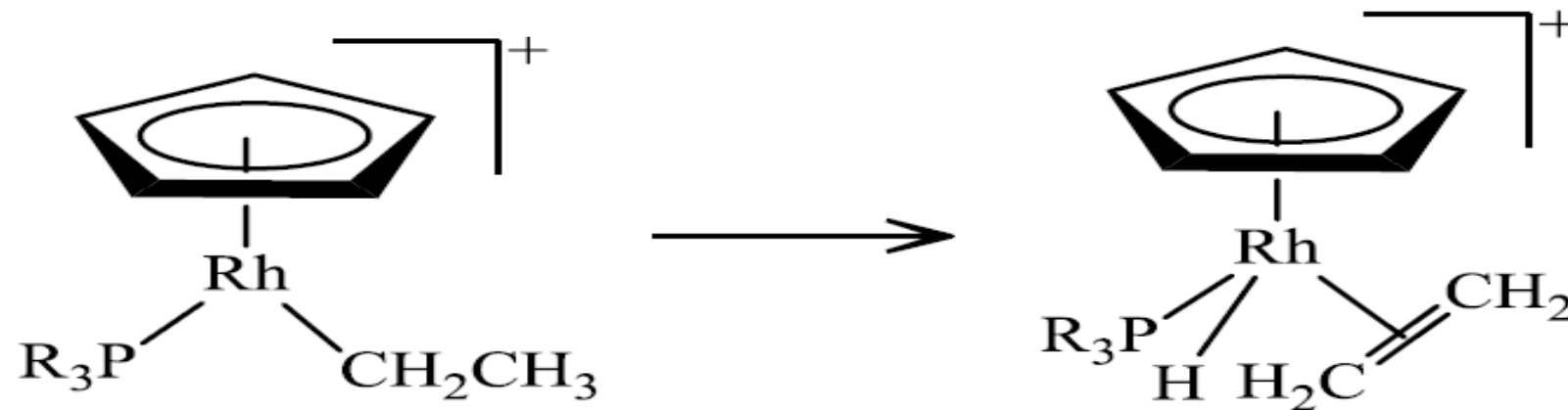
(C) $\text{NH}_3 > \text{Cl}^- > \text{H}_2\text{O}$

(D) $\text{H}_2\text{O} > \text{NH}_3 > \text{Cl}^-$

78. The compound that undergoes oxidative addition reaction in presence of H_2 is

1. $[Mn(CO)_5]^-$
2. $[(\eta^5-C_5H_5)Mo(CO)_3]^-$
3. $[IrCl(CO)(PPh_3)_2]$
4. $[(\eta^5-C_5H_5)_2ReH]$

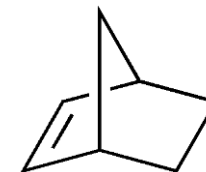
22. The following transformation is an example of



- (1) oxidative addition
- (2) insertion
- (3) β -hydride elimination
- (4) reductive elimination

27. The rate of alkene coordination to $[\text{PtCl}_4]^{2-}$ is highest for

1. norbornene
2. ethylene
3. cyclohexene
4. 1-butene



74. Consider the following statements, **I** and **II**:

I: $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ catalytically converts CH_3I and CO to CH_3COI

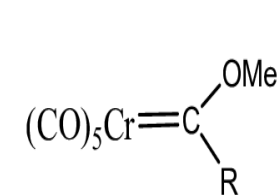
II: $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ is diamagnetic in nature

the correct from the following is

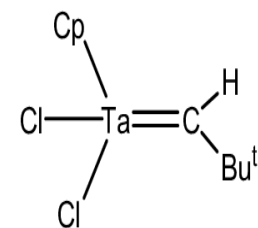
1. **I** and **II** are correct and **II** is an explanation of **I**
2. **I** and **II** are correct and **II** is not an explanation of **I**
3. **I** is correct and **II** is incorrect
4. **I** and **II** are incorrect

83. For OH^- catalysed $\text{S}_{\text{N}}1$ conjugate base mechanism of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, the species obtained in the first step of the reaction is/are

1. $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+} + \text{Cl}^-$
2. $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+ + \text{H}_2\text{O}$
3. $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)]^{2+} + \text{Cl}^-$
4. $[\text{Co}(\text{NH}_3)_5\text{Cl}(\text{OH})]^+$ only



A Fisher Carbene



A Schrock Carbene

92. The correct statement for a Fischer carbene complex is

1. the carbene carbon is electrophilic in nature
2. metal exists in high oxidation state
3. metal fragment and carbene are in the triplet states
4. CO ligands destabilize the complex

(29) The oxidizing power of $[\text{CrO}_4]^{2-}$, $[\text{MnO}_4]^{2-}$, and $[\text{FeO}_4]^{2-}$ follows the order

- (1.) $[\text{CrO}_4]^{2-} < [\text{MnO}_4]^{2-} < [\text{FeO}_4]^{2-}$
- (2.) $[\text{FeO}_4]^{2-} < [\text{MnO}_4]^{2-} < [\text{CrO}_4]^{2-}$
- (3.) $[\text{MnO}_4]^{2-} < [\text{FeO}_4]^{2-} < [\text{CrO}_4]^{2-}$
- (4.) $[\text{CrO}_4]^{2-} < [\text{FeO}_4]^{2-} < [\text{MnO}_4]^{2-}$

(28) Among the following, species expected to show fluxional behavior are

- (A) $[\text{NiCl}_4]^{2-}$ (tetrahedral),
 - (B) IF_7 (pentagonal bipyramidal),
 - (C) $[\text{CoF}_6]^{3-}$ (octahedral),
 - (D) $\text{Fe}(\text{CO})_5$ (trigonal, bipyramidal)
- (1.) B and C
 - (2.) B and D
 - (3.) C and D
 - (4.) A and D

Question

Which of the following is NOT suitable as catalyst for Hydrofomylation? (Dec)

Choices

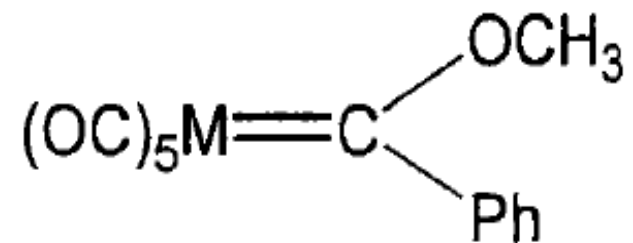
CHOICE (4)	
a.	$H_2 Rh (PPh_3) Cl$
b.	$H Rh(CO)PPh_3$
c.	$H CO(CO)_4$
d.	$H CO (CO)_3 P Bu_3$

Among the following correct statement is: (Dec)

Choices

CHOICE (4)	
a.	CH_2 is isolobal to $Mn (CO)_4$
b.	CH is isolobal to $CO(CO)_3$
c.	CH_2 is isolobal to $Ni(CO)_2$
d.	CH is isolobal to $Fe(CO)_4$

34. The molecule



obeys 18 e rule. The two 'M' satisfying the condition are

1. Cr, Re^+

2. Mo, V

3. V, Re^+

4. Cr, V

Number of metal-metal bond in $\text{Ir}_4(\text{CO})_{12}$

Choices

CHOICE (4)	
a.	4
b.	6
c.	10
d.	12

Rate of oxidative addition for compounds having same number of electron will vary as:

Dr. S.K

Choices

CHOICE (4)

a.	Irrelevant answer
b.	Ni (II) < CO (I) < Fe (0)
c.	Pd (II) < Rh (I) < Ru (0)
d.	Fe (0) < CO (I) < Ni (II)

In hydroformation reaction, reaction intermediate $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}(\text{CO})_4$ (Dec)

Choices

CHOICE (4)

a.	Reacts with H_2
b.	Forms an acyl intermediate $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCO}(\text{CO})_3$
c.	Eliminates propane.
d.	Forms an adduct with an olefin reactant

The number of metal-metal bonds in $W_2(OPh)_6$

Choices

CHOICE (4)	
a.	3
b.	4
c.	1
d.	2

$[(CO)_5Mn(Me)] + CO \longrightarrow [(CO)_5Mn\{C(O)Me\}]$ is an example for: (June)

Choices

CHOICE (4)	
a.	Oxidative addition
b.	Migratory insertion.
c.	Nucleophilic substitution
d.	Electrophilic substitution

Olefin hydrogenation using Wilkinson's catalyst initiates with- (MHRD sample p

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Choices

CHOICE (4)	
a.	A phosphine addition to $Rh(PPh_3)_2Cl$
b.	Olefin addition to $Rh(PPh_3)_3Cl$
c.	A phosphine dissociation from $Rh(PPh_3)_3Cl$
d.	Olefin addition to $Rh(PPh_3)_2Cl$

The organic species isolable to $[Fe(CO)_2(PPh_3)]^-$ is (June)

Choices

CHOICE (4)	
a.	CH
b.	CH_2^-
c.	CH_3
d.	CH_2^+

The rate-determining step in the catalytic synthesis of acetic acid by Monsanto process is (December)

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Choices

CHOICE (4)

a.	coordination of CO to $[RhI_3CO(COCH_3)]^-$
b.	loss of CH_3COI from $[RhI_3(CO)_2(COCH_3)]^-$
c.	Oxidative addition of CH_3I to $[RhI_2(CO)_2]^-$
d.	Migration of CH_3 group to CO of $[RhI_3(CO)_2(CH_3)]^-$

90. In hydrofomylation reaction using $[Rh(PPh_3)_3(CO)(H)]$ as the catalyst, addition of excess PPh_3 would

1. increase the rate of reaction
2. decrease the rate of reaction
3. not influence the rate of reaction
4. stop the reaction

2. For the redox reaction, the equilibrium constant $K = 2.0 \times 10^8$



Self exchange rates for oxidant & reductant are

$5.0 \text{ M}^{-1}\text{s}^{-1}$ & $4.0 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$. The approximate rate constant for the above redox rxn is

- A) 3.16×10^6 B) 2.0×10^6 C) 2.32×10^6 D) 3.16×10^4

Answer:

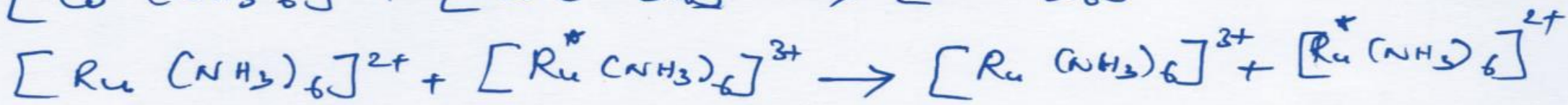
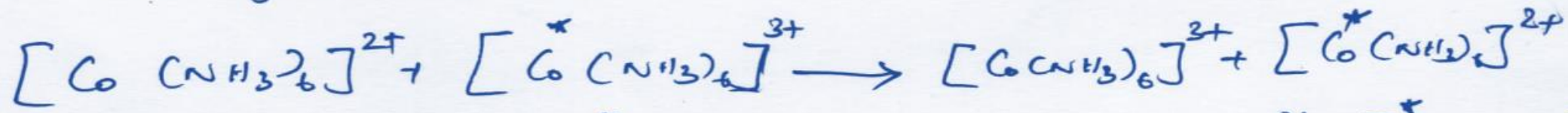
$$k_{12} = (k_{11} \cdot k_{22} \cdot K_{12} \cdot f_{12})^{1/2}$$

$$k_{12} = (5 \times 4 \times 10^3 \times 2 \times 10^8 \times 1)^{1/2}$$

$$k_{12} = (40 \times 10^{11})^{1/2} = (4 \times 10^{12})^{1/2}$$

$$k_{12} = 2 \times 10^6$$

2) For the following outer sphere electron transfer reactions,



the rate constants are $10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ and $8.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ respectively.

This difference in the rate constants is due to

- a change from high spin to low spin in Co^* and high spin to low spin in Ru.
- A change from low spin to high spin in Co^* and high spin to low spin in Ru^*
- a change from high spin to low spin in Co^* and low spin to high spin in Ru^*
- a change from low spin to high spin in Co^* and the low spin states remains unchanged in Ru.

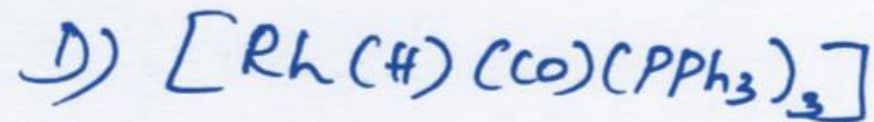
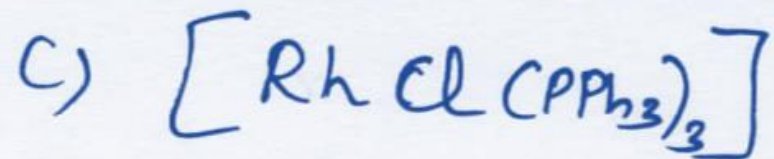
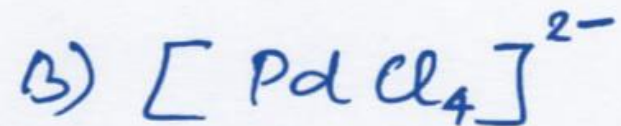
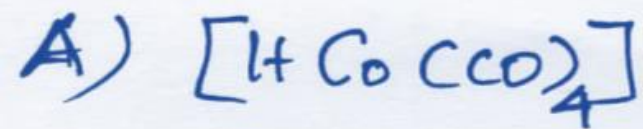
1) The complexes $[\text{Co}(\text{CN})_6]^{4-}$ (x), $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ (y) and $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (z) are respectively.

- A) x and z are labile; y is inert
 B) x is labile y and z are inert
 C) x and y are inert; z is labile
 D) x is inert; y and z are labile

2) Among the complexes $[\text{AlF}_6]^{3-}$, $[\text{PF}_6]^-$, $[\text{SiF}_6]^{2-}$ & $[\text{SF}_6]$ which is having ^{highest} ~~slow~~ ligand exchange rate?

A) $[\text{AlF}_6]^{3-}$ B) $[\text{PF}_6]^-$ C) $[\text{SiF}_6]^{2-}$ D) $[\text{SF}_6]$

1. The catalyst used in the conversion of ethylene to acetaldehyde using Wacker's process is



2. Wilkinson's Catalyst

A) is coordinatively saturated

B) does not obey the 18-electron rule

C) is used for oxidation of alcohol

D) ~~is~~ is an Iridium complex used in the preparation of important pharmaceutical products

1. Consider statements with respect to base hydrolysis of
 of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ to $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+}$ Dec. 2017

A. One of the ammine ligands acts as bronsted acid

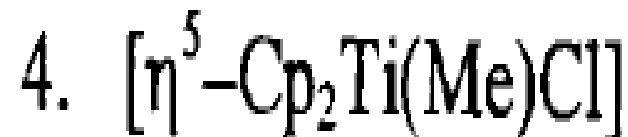
B. Entering group is water

C. hepta coordinated ~~sp³~~ Co^{3+} species is an intermediate

Correct statements are

1) A & B 2) A & C 3) B & C ~~4) C only~~

89. Which one of the following will NOT undergo oxidative addition by methyl iodide?



#1. Designate the following complexes X, Y and Z as inert or labile

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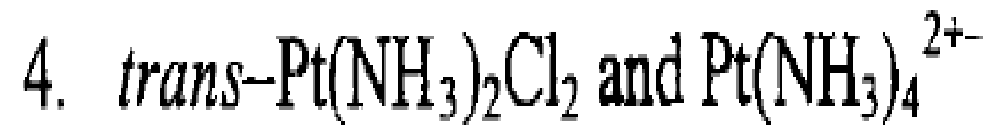
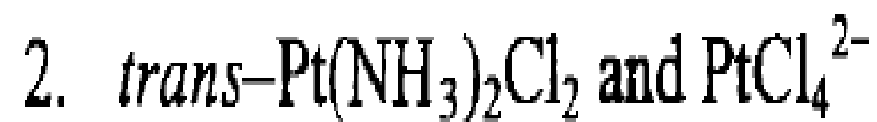
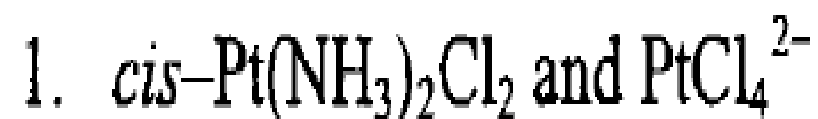
X = Pentachlorooxochromate(V)

Y = Hexaiodomanganate(IV)

Z = Hexacyanoferrate(III)

- (1) X and Y are inert; Z is labile
- (2) X and Z are labile; Y is inert
- (3) X is inert; Y and Z are labile
- (4) X is labile; Y and Z are inert

87. The platinum complex of NH_3 and Cl^- ligands is an anti-tumour agent. The correct isomeric formula of the complex and its precursor are:



92. The rate of exchange of OH_2 present in the coordination sphere by $^{18}\text{OH}_2$ of, (i) $[\text{Cu}(\text{OH}_2)_6]^{2+}$; (ii) $[\text{Mn}(\text{OH}_2)_6]^{2+}$; (iii) $[\text{Fe}(\text{OH}_2)_6]^{2+}$; (iv) $[\text{Ni}(\text{OH}_2)_6]^{2+}$, follows an order

1. (i) > (ii) > (iii) > (iv)

2. (i) > (iv) > (iii) > (ii)

3. (ii) > (iii) > (iv) > (i)

4. (iii) > (i) > (iv) > (ii)

72. Complexes of general formula, *fac*- $[\text{Mo}(\text{CO})_3(\text{phosphine})_3]$ have the C-O stretching bands as given below.

Phosphines: PF_3 (A); PCl_3 (B); $\text{P}(\text{Cl})\text{Ph}_2$ (C); PMe_3 (D)

$\nu(\text{CO}), \text{cm}^{-1}$: 2090 (i); 2040 (ii); 1977 (iii); 1945 (iv)

The correct combination of the phosphine and the stretching frequency is,

1. (A – i) (B – ii) (C – iii) (D – iv)

2. (A – ii) (B – i) (C – iv) (D – iii)

3. (A – iv) (B – iii) (C – ii) (D – i)

4. (A – iii) (B – iv) (C – i) (D – ii)

79. In the cluster $[\text{Co}_3(\text{CH})(\text{CO})_9]$ obeying 18e rule, the number of metal-metal bonds and the bridging ligands respectively, are

1. 3 and 1 CH 2. 0 and 3 CO 3. 3 and 1 CO 4. 6 and 1 CH

24. An organometallic fragment that is isolobal to CH_3^+ is

1. $[\text{Fe}(\text{CO})_5]$ 2. $[\text{Mn}(\text{CO})_5]$
3. $[\text{Cr}(\text{CO})_5]$ 4. $[\text{Ni}(\text{CO})_3]^+$

46. The mechanism of the reaction between $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{bpy})_3]^{3+}$ ($\text{bpy} = 2, 2'$ -bipyridine) is [GATE 2010]
- (a) outer-sphere electron-transfer (b) inner-sphere electron-transfer
(c) self-exchange reaction (d) ligand-exchange followed by electron transfer.

31. The relative rates of water exchange for the hydrated complexes of (a) Ni^{2+} , (b) V^{2+} and (c) Cr^{3+} ions follow the trend

1. $(a) > (b) > (c)$

2. $(a) < (b) < (c)$

3. $(a) > (b) < (c)$

4. $(a) < (b) > (c)$

23. Choose the isoelectronic pair among the following:

(A) $[\text{V}(\text{CO})_6]$, (B) $[\text{Cu}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]$, (C) $[\text{Co}(\text{CO})_4]^-$, (D) $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$

1. A and B

2. B and C

3. C and D

4. A and D

The correct statement for the CO and N₂ ligands in the complexes *trans*- [IrCl(CO)(PPh₃)₂] and *trans*-[IrCl(N₂)(PPh₃)₂] is:

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1. N₂ is both better σ-donor and better π-acceptor ligand than CO
2. CO is a better π-acceptor, but poor σ-donor ligand than N₂
3. CO is a better σ-donor, but poor π-acceptor ligand than N₂
4. CO is both better σ-donor and better π-acceptor ligand than N₂

For the given reaction



the correct statement with respect to the rate of electron transfer process is

o-phen = *o*-phenanthroline; *Co is labeled atom

ptions :

02437981.

fast electron transfer; L = NH₃; n = 6

02437982.

slow electron transfer; L = *o*-phen; n = 3

02437983.

very slow electron transfer; L = NH₃; n = 6

very slow electron transfer; L = *o*-phen; n = 3

Among the following combinations of metal carbonyl clusters and their skeletal structures, identify the correct ones.

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A. $\text{Co}_6(\text{CO})_{14}^{4-}$ → capped trigonal bipyramid

B. $\text{Ni}_6(\text{CO})_{12}^{2-}$ → trigonal antiprism

C. $\text{Rh}_6\text{C}(\text{CO})_{15}^{2-}$ → trigonal prism

D. $\text{Os}_6(\text{CO})_{18}$ → octahedron

Choose the **correct** answer from the options given below:

1. A, C and D only
2. B and C only
3. B and D only
4. C and D only

For octahedral geometry the triad with **no** net gain in CFSE, when the ligand field changes from weak to strong, is

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1. Fe^{2+} , Co^{3+} , Mn^{3+}
2. Ni^{2+} , Pt^{2+} , Cr^{3+}
3. Mn^{2+} , Fe^{3+} , Ni^{3+}
4. Co^{2+} , Os^{3+} , Rh^{3+}

In solution, Vaska's complex is known to bind O_2 reversibly. In the product, oxidation state of the metal ion center coordination geometry and mode of binding of O_2 , respectively are

1. +3, octahedron and side-on
2. +3, square pyramid and end-on
3. +1, octahedron and side-on
4. +1, trigonal bipyramid and end-on

Isolobal pairs from the fragments (A-D) is /are

A. {BH}

B. {Fe(CO)₃}

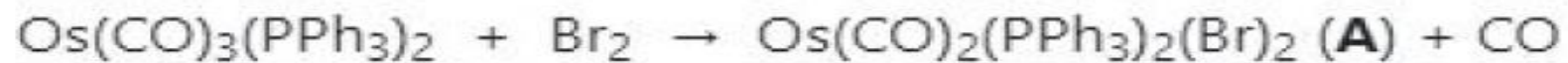
C. {P}

D. {Co(CO)₃}

Choose the **correct** answer from the options given below:

1. A and D; B and C
2. A and B; C and D
3. A and B only
4. A and C; B and D

Consider the following reactions.

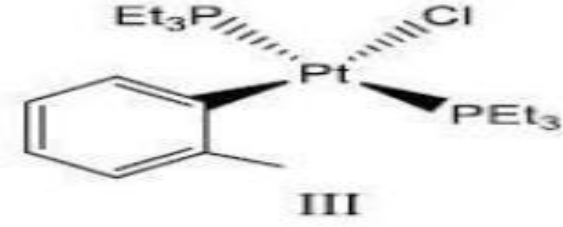
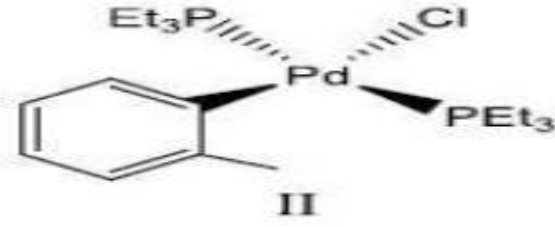
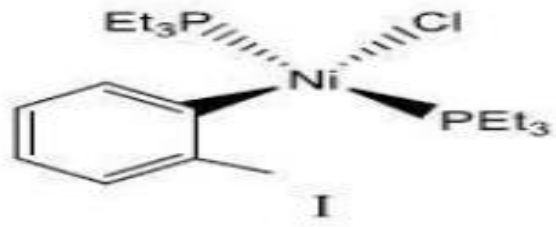


The correct stereochemical dispositions of the Br ligands in **A** and the CO ligands in **B**, respectively, are

1. *trans* and *fac*
2. *trans* and *mer*
3. *cis* and *fac*
4. *cis* and *mer*

The order of rate of substitution of chloride by pyridine (in ethanol) in the following complexes

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is

Options :

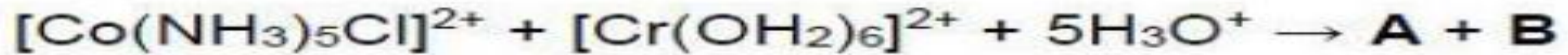
8024371029. $\text{I} > \text{II} > \text{III}$

8024371030. $\text{I} \approx \text{II} \approx \text{III}$

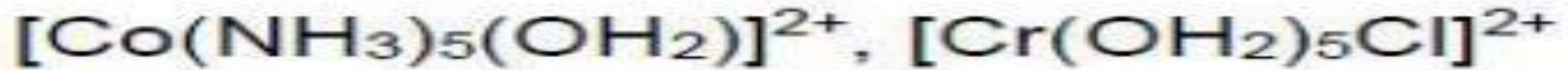
8024371031. $\text{I} > \text{II} \approx \text{III}$

8024371032. $\text{I} < \text{II} \approx \text{III}$

The products **A** and **B** for the given reaction



are, respectively



Question

Reduction of $\{Ru(NH_3)_5(\textit{isonicotinamide})\}^{3+}$ with $Cr(H_2O)_6^{2+}$ occurs by inner sphere mechanism and rate of the reaction is determined by dissociation of the successor complex. It is due to the (June)

Choices

CHOICE (4)	RESPONSE
a. Inert Ru bridged to inert Cr.	<input type="checkbox"/>
b. Labile Ru bridged to inert Cr.	<input type="checkbox"/>
c. Labile Ru bridged to labile Cr.	<input type="checkbox"/>
d. Inert Ru bridged to labile Cr.	<input type="checkbox"/>

Identify order of increasing π - acidity of following ligands: C_2F_4 , NEt_3 , CO , C_2H_4 . (June CSIR)

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Choices

CHOICE (4)	
a.	$CO < C_2F_4 < C_2H_4 < NEt_3$
b.	$C_2F_4 < C_2H_4 < NEt_3 < CO$
c.	$C_2H_4 < NEt_3 < CO < C_2F_4$
d.	$NEt_3 < C_2H_4 < C_2F_4 > CO$

Green Coloured $Ni(PPh_2Et)_2Br_2$ has magnetic moment $3.20 B.M.$ The geometry and number of isomers possible for complex are (Dec)

Choices

CHOICE (4)	
a.	Square planar, 2
b.	Tetrahedral, 2
c.	Tetrahedral, 1
d.	Square planar, 1

An octahedral metal ion M^{2+} has magnetic moment of $4.0 B.M.$. correct combination of metal ion and $d - e^-$ configuration is given by _____ (Dec)

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Choices

CHOICE (4)		RESPONSE
a.	$Co^{2+}, t_{2g}^5 eg^2$	<input type="checkbox"/>
b.	$Fe^{2+}, t_{2g}^4 eg^2$	<input type="checkbox"/>
c.	$Mn^{2+}, t_{2g}^3 eg^1$	<input type="checkbox"/>
d.	Cr^{2+}, t_{2g}^4, eg^2	<input type="checkbox"/>

A true statement about base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ is (Dec)

Choices

CHOICE (4)	
a.	R. D. S involves dissociation of chloride ion $[Co(NH_3)_4NH_2Cl]^+$
b.	It is a first order reaction.
c.	Rate is independent of concentration of base
d.	R. D. S involves abstraction of proton from $[Co(NH_3)_5Cl]^{2+}$

Which of the following pair will generally result in co-ordination complexes, when ligand is Cl^- or OH^-

1. *Be (II)* , *Ba (II)*
2. *Ba (II)* , *Co (II)*
3. *Co (II)* , *Zn (II)*
4. *Be (II)* , *Zn (II)* (June)

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Choices

CHOICE (4)	
a.	3 and 4
b.	1 and 4
c.	1 and 2
d.	2 and 3

$NiBr_2$ reacts with $(Et)(Ph)_2Ph$ at $-78^\circ C$ in CS_2 to give red compounds 'A', which turns green at R. T. to 'B' of same formula. Magnetic moment of 'A' and 'B' are 0 and 3.2 BM, respectively. Geometries of A and B are (June CSIR)

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Choices

CHOICE (4)		RESPONSE
a.	Square planar and Tetrahedral	<input type="checkbox"/>
b.	Square planar and Octahedral	<input type="checkbox"/>
c.	Tetrahedral and square planar	<input type="checkbox"/>
d.	Tetrahedral and Octahedral	<input type="checkbox"/>

Co-ordination number and geometry of cerium in $[Ce(NO_3)_6]^{2-}$ are

Choices

CHOICE (4)	
a.	8 and cubic
b.	6 and octahedron
c.	12 and icosahedral
d.	6 and trigonal prism

$[Co(H_2O)_6]^{2+}$ has light pink colour and $[CoCl_4]^{2-}$ has deep blue colour due to (Dec CSIR)

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Choices

CHOICE (4)

a.	d-d transition in first and MLCT transition in second
b.	d-d transition in both
c.	LMCT transitions in both
d.	MLCT transition in first and d-d transition in second

The geometry/shape of the Fe_4 core of the cluster $[Fe_4C(CO)_{12}]^{2-}$ is

Options :

Tetrahedron

Square pyramid

Butterfly

Trigonal bipyramid