ABC CHEMISTRY

Mr. Aniket Bhardwaj · 15+ Years Mentorship

Organometallic Chemistry

Premium CSIR-NET PYQ Book

153 CSIR-NET Previous-Year Questions · Fully Solved with Distractor Analysis

3-Slide Solutions | Distractor Analysis | Exam Tricks | Revision Sheets

CSIR-NET · GATE · IIT-JAM — 13 Topics · 153 Real PYQs

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Course Contents

13 Topics · 153 PYQs · tap a topic to jump

1 **18-Electron Rule & Electron Counting** — 4%
6 Qs E 3 · M 3 · H 0

2 **Metal Carbonyls & π-Acid Ligands** — 8%
13 Qs E 3 · M 10 · H 0

3 **Metallocenes & Sandwich Compounds** — 10%
16 Qs E 6 · M 10 · H 0

4 **Hapticity & Bonding Modes** — 9%
14 Qs E 0 · M 14 · H 0

5 **Carbenes, Carbynes & M=C** — 5%
8 Qs E 0 · M 8 · H 0

6 **Oxidative Addition & Reductive Elimination** — 6%
9 Qs E 0 · M 9 · H 0

7 **Insertion, β-Elimination & Agostic** — 4%
6 Qs E 0 · M 6 · H 0

8 **Homogeneous Catalysis** — 7%
10 Qs E 0 · M 10 · H 0

9 **Olefin Metathesis & Polymerisation** — 1%
2 Qs E 0 · M 2 · H 0

10 **Metal Clusters & M–M Bonding** — 24%
36 Qs E 0 · M 0 · H 36

11 **Main-Group & Early-Metal Organometallics** — 2%
3 Qs E 0 · M 3 · H 0

12 **Bonding, Isolobal & Frontier Orbitals** — 4%
6 Qs E 0 · M 0 · H 6

13 **Organometallic Reactions – General** — 16%
24 Qs E 0 · M 24 · H 0

Legend: **E** Easy **M** Medium **H** Hard · **%** = exam weightage (share of the chapter)

(Mr. Aniket Bhardwaj By ABC Chemistry)

TOPIC 1

18-Electron Rule & Electron Counting

6 questions · Easy 3 | Medium 3 | Hard 0 · PYQ frequency: Moderate

Q17

The reactions of $Ni(CO)_4$ with the ligand (L= PMe_3 or $P(OMe)_3$) L yields $Ni(CO)_3L$. The reaction is

A. Associative

B. Dissociative

C. Interchange (Ia)

D. Interchange (Id)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Electron counting, EAN/18-electron rule, 16e exceptions

PYQ FREQUENCY
Moderate · 6 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
"18 = the inert-gas shell." Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Correct Answer B Dissociative

CONCEPT

Stable, diamagnetic organometallics tend to reach 18 valence electrons (the next noble-gas shell). Count by the neutral method (metal = group number; CO=2, H=1, η^5-Cp=5, NO(linear)=3) or the ionic method — both give the same total.

↓

LOGIC / WORKING

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$Ni(CO)_4$ Total valence electron around Ni 10+ 4×2=18 electron Substitution reactions at coordinatively saturated tetrahedral complexes with a 18 electron count like $Ni(CO)_4$, or $Ni(CO)_2(PR_3)_2$ follows a simple first order kinetics.

- Since rate does not depend upon the concentration and nature of the ligand suggesting a dissociative mechanism.

FINAL: (B) Dissociative

SHORTCUT / EXAM TRICK

Simple carbonyl $[M(CO)_x]^z$: (group e) + 2x + z = 18. A metal–metal bond adds 1 e to each metal.

COMMON MISTAKE

Forgetting that each CO donates 2e, or that an M–M bond contributes 1e to each metal.

EXAM TIP

Square-planar d^8 (Rh^+, Ir^+, Pd^{2+}, Pt^{2+}) are stable at 16e — the famous catalytic exceptions.

MEMORY TRICK

“18 = the inert-gas shell.” Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Why the Other Options Are Wrong

Correct answer: **B**

A — **Associative**

Why (B) is the key — $Ni(CO)_4$ is 18-electron and coordinatively saturated: substitution is dissociative, rate = $k[Ni(CO)_4]$, independent of L.

C — **Interchange (Ia)**

Option (C) is ruled out by the same reasoning: $Ni(CO)_4$ is 18-electron and coordinatively saturated: substitution is dissociative, rate = $k[Ni(CO)_4]$, independent of

D — **Interchange (Id)**

Option (D) is ruled out by the same reasoning: $Ni(CO)_4$ is 18-electron and coordinatively saturated: substitution is dissociative, rate = $k[Ni(CO)_4]$, independent of

Q26

The molecule Follow 18 electron rule. The two 'M' satisfying the condition are

A. Cr, Re^{+}

B. Mo, V

C. V, Re+

D. Cr, V

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Electron counting, EAN/18-electron rule, 16e exceptions

PYQ FREQUENCY
Moderate · 6 papers

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
"18 = the inert-gas shell." Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Correct Answer A Cr, Re^{+}

CONCEPT

Stable, diamagnetic organometallics tend to reach 18 valence electrons (the next noble-gas shell). Count by the neutral method (metal = group number; CO=2, H=1, η^5-Cp=5, NO(linear)=3) or the ionic method — both give the same total.

↓

LOGIC / WORKING

FINAL: (A) Cr, Re^{+}

SHORTCUT / EXAM TRICK

Simple carbonyl $[M(CO)_x]^z$: (group e) + 2x + z = 18. A metal–metal bond adds 1 e to each metal.

COMMON MISTAKE

Forgetting that each CO donates 2e, or that an M–M bond contributes 1e to each metal.

EXAM TIP

Square-planar d^8 (Rh^{+}, Ir^{+}, Pd^{2+}, Pt^{2+}) are stable at 16e — the famous catalytic exceptions.

MEMORY TRICK

“18 = the inert-gas shell.” Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Why the Other Options Are Wrong

Correct answer: **A**

B **Mo, V**
Inconsistent with the 18-electron (EAN) count; the correct choice is (A). See worked explanation.

C **V, Re+**
Inconsistent with the 18-electron (EAN) count; the correct choice is (A). See worked explanation.

D **Cr, V**
Inconsistent with the 18-electron (EAN) count; the correct choice is (A). See worked explanation.

Q55 The total valence electron count and the structure type adopted by the complex $[Fe_3(CO)_{15}C)]$ respectively, are

A. 74 and nido

B. 60 and closo

C. 84 and arachno

D. 74 and nido

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Electron counting, EAN/18-electron rule, 16e exceptions

PYQ FREQUENCY
Moderate · 6 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
"18 = the inert-gas shell." Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Correct Answer D 74 and nido

CONCEPT

Stable, diamagnetic organometallics tend to reach 18 valence electrons (the next noble-gas shell). Count by the neutral method (metal = group number; CO=2, H=1, η^5-Cp=5, NO(linear)=3) or the ionic method — both give the same total.

↓

LOGIC / WORKING

FINAL: (D) 74 and nido

SHORTCUT / EXAM TRICK

Simple carbonyl $[M(CO)_x]^z$: (group e) + 2x + z = 18. A metal–metal bond adds 1 e to each metal.

COMMON MISTAKE

Forgetting that each CO donates 2e, or that an M–M bond contributes 1e to each metal.

EXAM TIP

Square-planar d^8 (Rh^+, Ir^+, Pd^{2+}, Pt^{2+}) are stable at 16e — the famous catalytic exceptions.

MEMORY TRICK

“18 = the inert-gas shell.” Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Why the Other Options Are Wrong

Correct answer: **D**

A **74 and nido**
Inconsistent with the 18-electron (EAN) count; the correct choice is (D). See worked explanation.

B **60 and closo**
Inconsistent with the 18-electron (EAN) count; the correct choice is (D). See worked explanation.

C **84 and arachno**
Inconsistent with the 18-electron (EAN) count; the correct choice is (D). See worked explanation.

Q73

The refluxing of $RhCl_3.3H_2O$ with an excess of PPh_3, in ethanol gives a complex A. Complex A and the valence electron count on rhodium are, respectively.

A $[RhCl(PPh_3)_3]$, 16

B $[RhCl(PPh_3)_5]$, 16

C $RhH(CO)(PPh_3)_3$ (Wilkinson)

D $[RhCK(PPh_3)_5]$, 18 The refluxing of $RhCl_3.3H,O$ with an excess of PPh_3, in ethanol gives a complex $RhCl(PPh_3)_3$ is Wilkinson catalyst and common method for preparation of $RhCl(PPh_3)_3$ is refluxing of $RhCl_3.3H_2O$ with PPh_3.Moreover, on counting the total valence electrons, $RhCl(PPh_3)_3$ = [9+3×2+1] = 16e.{Cl atom cannot be bridging, its contribution is 1}. Wilkinson catalyst is 16e- species. It is a square planer 16-electron complex. Valence electron counting on rhodium metal centre. (i) there is no overall charge on complex (ii) there is one anionic ligand (Cl-) (iii) Rh metal atom must have +1 charge to compensate for the one negatively charged ligand. So, the oxidation state of Rh is +1.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Electron counting, EAN/18-electron rule, 16e exceptions

PYQ FREQUENCY
Moderate · 6 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
"18 = the inert-gas shell." Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

18-Electron Rule & Electron Counting

Correct Answer C $RhH(CO)(PPh_3)_3$ (Wilkinson)

CONCEPT

Stable, diamagnetic organometallics tend to reach 18 valence electrons (the next noble-gas shell). Count by the neutral method (metal = group number; CO=2, H=1, η^5-Cp=5, NO(linear)=3) or the ionic method — both give the same total.

↓

LOGIC / WORKING

FINAL: (C) $RhH(CO)(PPh_3)_3$ (Wilkinson)

SHORTCUT / EXAM TRICK

Simple carbonyl $[M(CO)_x]^z$: (group e) + 2x + z = 18. A metal–metal bond adds 1 e to each metal.

COMMON MISTAKE

Forgetting that each CO donates 2e, or that an M–M bond contributes 1e to each metal.

EXAM TIP

Square-planar d^8 (Rh^+, Ir^+, Pd^{2+}, Pt^{2+}) are stable at 16e — the famous catalytic exceptions.

MEMORY TRICK

"18 = the inert-gas shell." Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Why the Other Options Are Wrong

Correct answer: **C**

A **$[RhCl(PPh_3)_3]$, 16**

Inconsistent with the 18-electron (EAN) count; the correct choice is (C). See worked explanation.

B **$[RhCl(PPh_3)_5]$, 16**

Inconsistent with the 18-electron (EAN) count; the correct choice is (C). See worked explanation.

$[RhCK(PPh_3)_5]$, 18 The refluxing of $RhCl_3.3H,O$ with an excess of PPh_3, in ethanol gives a complex $RhCl(PPh_3)_3$ is Wilkinson catalyst and common method for preparation of $RhCl(PPh_3)_3$ is refluxing of $RhCl_3.3H_2O$ with PPh_3.Moreover, on counting the total valence electrons, $RhCl(PPh_3)_3$ = [9+3×2+1] = 16e.{Cl atom cannot be bridging, its contribution is 1}. Wilkinson catalyst is 16e- species. It is a square planer 16-electron complex. Valence electron counting on rhodium metal centre. (i) there is no overall charge on complex (ii) there is one anionic ligand (Cl-) (iii) Rh metal atom must have +1 charge to compensate for the one negatively charged ligand. So, the oxidation state of Rh is +1.

D

Q95

Identify the species, those obey the 18 electron rule, from the following:

A. A and B

B. B and C

C. C and D

D. A and D

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Electron counting, EAN/18-electron rule, 16e exceptions

PYQ FREQUENCY
Moderate · 6 papers

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
"18 = the inert-gas shell." Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Correct Answer D A and D

CONCEPT

Stable, diamagnetic organometallics tend to reach 18 valence electrons (the next noble-gas shell). Count by the neutral method (metal = group number; CO=2, H=1, η^5-Cp=5, NO(linear)=3) or the ionic method — both give the same total.

↓

LOGIC / WORKING

- Refer to the governing principle for this topic; the correct option follows directly from it.

FINAL: (D) A and D

SHORTCUT / EXAM TRICK

Simple carbonyl $[M(CO)_x]^z$: (group e) + 2x + z = 18. A metal–metal bond adds 1 e to each metal.

COMMON MISTAKE

Forgetting that each CO donates 2e, or that an M–M bond contributes 1e to each metal.

EXAM TIP

Square-planar d^8 (Rh^+, Ir^+, Pd^{2+}, Pt^{2+}) are stable at 16e — the famous catalytic exceptions.

MEMORY TRICK

“18 = the inert-gas shell.” Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Why the Other Options Are Wrong

Correct answer: **D**

A **A and B**
Inconsistent with the 18-electron (EAN) count; the correct choice is (D). See the worked explanation.

B **B and C**
Inconsistent with the 18-electron (EAN) count; the correct choice is (D). See the worked explanation.

C **C and D**
Inconsistent with the 18-electron (EAN) count; the correct choice is (D). See the worked explanation.

Q154 The correct order of metal-carbon distance is

A $Fe(\eta^5\text{-}Cp)_2 > Co(\eta^5\text{-}Cp)_2 > Ni(\eta^5\text{-}Cp)_2$

B $Ni(\eta^5\text{-}Cp)_2 > Co(\eta^5\text{-}Cp)_2 > Fe(\eta^5\text{-}Cp)_2$

C $Co(\eta^5\text{-}Cp)_2 > Fe(\eta^5\text{-}Cp)_2 > Ni(\eta^5\text{-}Cp)_2$

D $Fe(\eta^5\text{-}Cp)_2 > Ni(\eta^5\text{-}Cp)_2 > Co(\eta^5\text{-}Cp)_2$

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Electron counting, EAN/18-electron rule, 16e exceptions

PYQ FREQUENCY
Moderate · 6 papers

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
"18 = the inert-gas shell." Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

18-Electron Rule & Electron Counting

Correct Answer B $Ni(\eta^5\text{-}Cp)_2 > Co(\eta^5\text{-}Cp)_2 > Fe(\eta^5\text{-}Cp)_2$

CONCEPT

Stable, diamagnetic organometallics tend to reach 18 valence electrons (the next noble-gas shell). Count by the neutral method (metal = group number; CO=2, H=1, η^5-Cp=5, NO(linear)=3) or the ionic method — both give the same total.

↓

LOGIC / WORKING

- Adding electrons to antibonding orbitals increases the M–C distance. Fe(18e) < Co(19e) < Ni(20e) in electron count. More antibonding electrons → longer M–C. Order: Fe < Co < Ni, so Ni > Co > Fe.

FINAL: (B) $Ni(\eta^5\text{-}Cp)_2 > Co(\eta^5\text{-}Cp)_2 > Fe(\eta^5\text{-}Cp)_2$

SHORTCUT / EXAM TRICK

Simple carbonyl $[M(CO)_x]^z$: (group e) + 2x + z = 18. A metal–metal bond adds 1 e to each metal.

COMMON MISTAKE

Forgetting that each CO donates 2e, or that an M–M bond contributes 1e to each metal.

EXAM TIP

Square-planar d^8 (Rh^+, Ir^+, Pd^{2+}, Pt^{2+}) are stable at 16e — the famous catalytic exceptions.

MEMORY TRICK

"18 = the inert-gas shell." Odd-electron metals dimerise to pair up ($Mn_2(CO)_{10}$).

Why the Other Options Are Wrong

Correct answer: **B**

A $Fe(\eta^5\text{-}Cp)_2 > Co(\eta^5\text{-}Cp)_2 > Ni(\eta^5\text{-}Cp)_2$

Inconsistent with the 18-electron (EAN) count; the correct choice is (B). See worked explanation.

C $Co(\eta^5\text{-}Cp)_2 > Fe(\eta^5\text{-}Cp)_2 > Ni(\eta^5\text{-}Cp)_2$

Inconsistent with the 18-electron (EAN) count; the correct choice is (B). See worked explanation.

D $Fe(\eta^5\text{-}Cp)_2 > Ni(\eta^5\text{-}Cp)_2 > Co(\eta^5\text{-}Cp)_2$

Inconsistent with the 18-electron (EAN) count; the correct choice is (B). See worked explanation.

TOPIC REVISION

18-Electron Rule & Electron Counting

6 PYQs · Last-minute revision

TOPIC SUMMARY

Stable, diamagnetic organometallics tend to reach 18 valence electrons (the next noble-gas shell). Count by the neutral method (metal = group number; CO=2, H=1, η^5-Cp=5, NO(linear)=3) or the ionic method — both give the same total.

IMPORTANT FORMULA SHEET

Neutral: e(M-group) + Σ ligand e + charge = 18

$[M(CO)_x]^z$: group + 2x + z = 18

M–M bond → +1 e to each metal

η^5-Cp = 5e (neutral) / 6e (ionic)

FREQUENTLY ASKED CONCEPTS

18-electron rule

neutral vs ionic counting

16e square-planar d^8

- M–M bonds in EAN

COMMON MISTAKES & QUICK NOTES

Watch out:

Forgetting that each CO donates 2e, or that an M–M bond contributes 1e to each metal.

Last-minute:

Simple carbonyl $[M(CO)_x]^z$: (group e) + 2x + z = 18. A metal–metal bond adds 1 e to each metal.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q17 Q26 Q55 Q73 Q95 Q154

Expect **1 question(s)** next session on **Electron counting, EAN/18-electron rule, 16e exceptions.**

TOPIC 2

Metal Carbonyls & π-Acid Ligands

13 questions · Easy 3 | Medium 10 | Hard 0 · PYQ frequency: High

Q5

Among the metals Mn, Fe, Co and Ni, the ones those would react in its native form directly with CO giving metal carbonyl compounds are:

A. Co and Mn

B. Mn and Fe

C. Fe and Ni

D. Ni and Co

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer C Fe and Ni

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

$Ni + 4CO \rightarrow Ni(CO)_4$ $Fe + 5CO \rightarrow Fe(CO)_5$ Both Ni and Fe reacts directly with CO to give carbonyl compounds.

FINAL: (C) Fe and Ni

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **C**

A — **Co and Mn**

Why (C) is the key — Only Ni ($Ni(CO)_4$, room temperature) and Fe (Fe(CO) , heat and pressure) react directly with CO as the metal (c).

B — **Mn and Fe**

Option (B) is ruled out by the same reasoning: Only Ni ($Ni(CO)_4$, room temperature) and Fe (Fe(CO) , heat and pressure) react directly with CO as the metal

D — **Ni and Co**

Option (D) is ruled out by the same reasoning: Only Ni ($Ni(CO)_4$, room temperature) and Fe (Fe(CO) , heat and pressure) react directly with CO as the metal

Q9 The correct combination of metal, number of carbonyl ligands and the charge for a metal z-carbonyl complex [M(CO)x] that satisfies the 18 electron rule is

A. M= Ti, x=6, z=1

B. M= V,x=6, z=1

C. M=Co, x=4, z=2

D. M= Mo, x=5, z=1

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Metal Carbonyls & π-Acid Ligands

Correct Answer B M= V,x=6, z=1

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

.

M=V, x=6, z=1 i.e. $[V(CO)_6]^-$ = 5+2×6+1=18

FINAL: (B) M= V,x=6, z=1

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **B**

A

M= Ti, x=6, z=1

Why (B) is the key — $[V(CO)_6]^-$: 5 + 12 + 1 = 18. Ti: 4 + 12 + 1 = 17; $[Co(CO)_4]^-$ = 19; [Mo(CO)]$^-$ = 17.

C

M=Co, x=4, z=2

Option (C) is ruled out by the same reasoning: $[V(CO)_6]^-$: 5 + 12 + 1 = 18. Ti: 4 + 12 + 1 = 17; $[Co(CO)_4]^-$ = 19; [Mo(CO)]$^-$ =

D

M= Mo, x=5, z=1

Option (D) is ruled out by the same reasoning: $[V(CO)_6]^-$: 5 + 12 + 1 = 18. Ti: 4 + 12 + 1 = 17; $[Co(CO)_4]^-$ = 19; [Mo(CO)]$^-$ =

Q13 **In the trans-$PtCl_2L(CO)$ complex, the CO stretching frequency for L=NH_3 , pyridine, NMe_3 decreases in the order.**

A pyridine> NH_3 > NMe_3

B NH_3 > pyridine > NMe_3

C NMe_3 > NH_3 > pyridine

D pyridine > NMe_3 > NH_3

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer A pyridine> NH_3 > NMe_3

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

.

Order of donor ability NMe_3 > NH_3> pyridine Order of CO stretching frequency pyridine > NH_3 > NMe_3

FINAL: (A) pyridine> NH_3 > NMe_3

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B — **NH_3 > pyridine > NMe_3**

Why (A) is the key — ν(CO): pyridine > NH_3 > NMe_3 (a).

C — **NMe_3 > NH_3 > pyridine**

Option (C) is ruled out by the same reasoning: ν(CO): pyridine > NH_3 > NMe_3

D — **pyridine > NMe_3 > NH_3**

Option (D) is ruled out by the same reasoning: ν(CO): pyridine > NH_3 > NMe_3

Q19

For the reaction, trans-$[IrCl(CO)(PPh_3)_2]^+$ Cl 2 → trans - [IrCl 3(CO)(PPh 3)$_2$]the correct observation

A. ῡ co (product) > ῡ co (reactant)

B. ῡ co (product)< ῡ co (reactant)

C. ῡ co (product) = ῡ co (reactant)

D. ῡ co (product) = ῡ co (free CO)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Metal Carbonyls & π-Acid Ligands

Correct Answer A ῡ co (product) > ῡ co (reactant)

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

.

Since in product metal Ir is present in the higher oxidation state. So, there is less back bonding to orbital of CO.

- Hence, ῡ (CO) product > ῡ (CO) reactant

FINAL: (A) ῡ co (product) > ῡ co (reactant)

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B

ῡ co (product)< ῡ co (reactant)

Why (A) is the key — Oxidative addition of Cl_2 converts Ir(I) to Ir(III), which back-donates less to CO, so ν(CO) rises (≈1965 → 2070 cm^{-1}).

C

ῡ co (product) = ῡ co (reactant)

Option (C) is ruled out by the same reasoning: Oxidative addition of Cl_2 converts Ir(I) to Ir(III), which back-donates less to CO, so ν(CO) rises (≈1965 → 2070

D

ῡ co (product) = ῡ co (free CO)

Option (D) is ruled out by the same reasoning: Oxidative addition of Cl_2 converts Ir(I) to Ir(III), which back-donates less to CO, so ν(CO) rises (≈1965 → 2070

Q27

Complexes of general formula, fac-$[Mo(CO)_3(phosphite)_3]$ have the C-O stretching bands given below. Phosphines: PF_3(A) ; PCl_3 (B); $P(Cl)Ph_2$ (C); PMe_3 (D) ῡ (CO), cm-1: 2090(i) ; 2040(i); 1977(iii); 1945(iv) The correct combination of the phosphine and the stretching frequency is,

A (A-i), (B-ii), (C-iii), (D-iv)

B (A-ii), (B-i), (C-iv), (D-iii)

C (A-iv), (B-iii), (C-ii), (D-i)

D (A-iii), (B-iv), (C-i), (D-ii)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer A (A-i), (B-ii), (C-iii), (D-iv)

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

.

As the π-accepting abilities of phosphine increases νC- O stretching frequency of the complex increases.

So, the order of n-accepting abilities among the given phosphine is:

$PF_3 > PCl_3 > PClPh_2 > PMe_3$ i.e. A>B>C>D.

So, the correct combination for νC- O stretching is:

- A→2090 B→ 2040 C→ 1977 D→ 1945

FINAL: (A) (A-i), (B-ii), (C-iii), (D-iv)

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B **(A-ii), (B-i), (C-iv), (D-iii)**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See the worked explanation.

C **(A-iv), (B-iii), (C-ii), (D-i)**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See the worked explanation.

D **(A-iii), (B-iv), (C-i), (D-ii)**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See the worked explanation.

Q50 On reducing $Fe_3(CO)_{12}$ with an excess of sodium, a carbonylate ion is formed. The iron is isoelectronic with -

A $[Mn(CO)_5]$

B $[Ni(CO)_4]^+$

C $[Mn(CO)_5]^-$

D $[V(CO)_6]$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Metal Carbonyls & π-Acid Ligands

Correct Answer B $[Ni(CO)_4]^+$

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

#& 106. $Fe_3(CO)_{12}$ $[Fe(CO)_4]$ –2 8+8+2=18 electron $[Fe(CO)_4]$ –2 is isoelectronic with $Ni(CO)_4$ [CSIR JUNE 2014]

FINAL: (B) $[Ni(CO)_4]^+$

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **B**

A **$[Mn(CO)_5]$**

Why (B) is the key — Reduction gives $[Fe(CO)_4]^{2-}$ (Collman's reagent), an 18-electron d^{10} species isoelectronic with $Ni(CO)_4$.

C **$[Mn(CO)_5]$ –**

Option (C) is ruled out by the same reasoning: Reduction gives $[Fe(CO)_4]^{2-}$ (Collman's reagent), an 18-electron d^{10} species isoelectronic with

D **$[V(CO)_6]$**

Option (D) is ruled out by the same reasoning: Reduction gives $[Fe(CO)_4]^{2-}$ (Collman's reagent), an 18-electron d^{10} species isoelectronic with

Q90 The final products of the reaction of carbonyl metalates $[V(CO)_6]$ and $[Co(CO)_4]$ with H_3PO_4 respectively, are

A $V(CO)_6$ and $HCo(CO)_4$

B $HV(CO)_6$ and $Co_2(CO)_8$ +

C $[H_2V(CO)_6]$ and $HCo(CO)_4$

D $V(CO)_6$and $Co_2(CO)_8$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer A $V(CO)_6$ and $HCo(CO)_4$

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

- $[V(Co)_6] \rightarrow [V(CO)_6]$ (in presence of H_3PO_4) - $[Co(CO)_4] \rightarrow [HCo(CO)_4]$ (in presence of H_3PO_4)

FINAL: (A) $V(CO)_6$ and $HCo(CO)_4$

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B **$HV(CO)_6$ and $Co_2(CO)_8$ +**

Why (A) is the key — $V(CO)_6$ (after H_2 loss from $HV(CO)_6$) and $HCo(CO)_4$ (a).

C **$[H_2V(CO)_6]$ and $HCo(CO)_4$**

Option (C) is ruled out by the same reasoning: $V(CO)_6$ (after H_2 loss from $HV(CO)_6$) and $HCo(CO)_4$

D **$V(CO)_6$and $Co_2(CO)_8$**

Option (D) is ruled out by the same reasoning: $V(CO)_6$ (after H_2 loss from $HV(CO)_6$) and $HCo(CO)_4$

Q93

Reaction of $[Mn_2(CO)_{10}]$, with I_2, results in A without loss of CO. Compound A, on heating of 120°C loses a CO ligand to give B, which does not have a Mn-Mn bond. Compound B reacts with pyridine to give 2 equivalents of C. Compounds A, B and C from the following respec tively, are

A. II, V and IV

B. II, III AND IV

C. V, III and IV

D. II. V and III

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer A II, V and IV

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

- Mechanism -1

FINAL: (A) II, V and IV

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B **II, III AND IV**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See the worked explanation.

C **V, III and IV**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See the worked explanation.

D **II. V and III**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See the worked explanation.

Q99

Choose the correct option for carbonyl fluoride with respect to bond angle and bond length

A ∠F-C-F > ∠F-C-O and C-F > C-O

B ∠F-C-F > ∠F-C-O and C-F < C-O

C ∠F-C-F < ∠F-C-O and C-F > C-O

D ∠F-C-F < ∠F-C-O and C-F < C-O

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer C ∠F-C-F < ∠F-C-O and C-F > C-O

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

Structure of CoF_2 = due to more space requirement for double bond the bond angle ∠F-C-O will be higher that of ∠F-C-F and also C-O bond order is larger than C-F hence, C-O bond length will be smaller than C-F.

FINAL: (C) ∠F-C-F < ∠F-C-O and C-F > C-O

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **C**

A **∠F-C-F > ∠F-C-O and C-F > C-O**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (C). See the worked explanation.

B **∠F-C-F > ∠F-C-O and C-F < C-O**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (C). See the worked explanation.

D **∠F-C-F < ∠F-C-O and C-F < C-O**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (C). See the worked explanation.

Q109 The rate of alkene coordination to $[PtCl_4]^{-2}$ is highest for

A. norbornene

B. ethylene

C. cyclohexene

D. 1-butene

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer A norbornene

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

When the norbornene is strained molecule because the hybridization is sp_2 when the metal attached with norbornene back-bonding takes place and due to this back-bonding the hybridization changes to sp_2-sp_3 and hence relief to strain

FINAL: (A) norbornene

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B — **ethylene**

Why (A) is the key — Strained alkenes coordinate fastest: norbornene's ring strain is relieved on binding, so it displaces chloride from $[PtCl_4]^{2-}$ much faster than ethylene, 1-butene or cyclohexene.

C — **cyclohexene**

Option (C) is ruled out by the same reasoning: Strained alkenes coordinate fastest: norbornene's ring strain is relieved on binding, so it displaces chloride from $[PtCl_4]^{2-}$ much faster than ethylene,…

D — **1-butene**

Option (D) is ruled out by the same reasoning: Strained alkenes coordinate fastest: norbornene's ring strain is relieved on binding, so it displaces chloride from $[PtCl_4]^{2-}$ much faster than ethylene,…

Q123 Identify the product in the reaction: $[CpFe(CO)_2]^-$ + PhCHO → ?

A. $CpFe(CO)_2CH(OH)Ph$

B. $CpFe(CO)_2CHO$ + PhH

C. $CpFe(CO)_2Ph$ + CO + H^-

D. $CpFe(CO)_3^-$ + PhH

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer A $CpFe(CO)_2CH(OH)Ph$

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

The ferrate anion $[CpFe(CO)_2]^-$ acts as a nucleophile attacking the carbonyl carbon of PhCHO to give the alkoxide adduct, which protonates to yield the hydroxy-alkyl complex $CpFe(CO)_2CH(OH)Ph$.

FINAL: (A) $CpFe(CO)_2CH(OH)Ph$

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B $CpFe(CO)_2CHO + PhH$

Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

C $CpFe(CO)_2Ph + CO + H^-$

Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

D $CpFe(CO)_3^- + PhH$

Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

Q140

Match the following complexes with their ν(CO) stretching frequency (in cm^{-1}): $[V(CO)_6]^-$ (P), $[Cr(CO)_6]$ (Q), $[Mn(CO)_6]^+$ (R)

(A) P–1860, Q–2000, R–2098

(B) P–2098, Q–2000, R–1860

(C) P–2000, Q–1860, R–2098

(D) P–1860, Q–2098, R–2000

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer A P–1860, Q–2000, R–2098

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

More electron density on metal → more back-donation into CO π* → lower ν(CO). $[V(CO)_6]^-$ (anionic, most e-rich): 1860 cm^{-1}; $[Cr(CO)_6]$ (neutral): 2000 cm^{-1}; $[Mn(CO)_6]^+$ (cationic, least e-rich): 2098 cm^{-1}.

FINAL: (A) P–1860, Q–2000, R–2098

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B **P–2098, Q–2000, R–1860**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

C **P–2000, Q–1860, R–2098**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

D **P–1860, Q–2098, R–2000**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

Q165

The IR spectrum of product A for the reaction $Cr(CO)_6$ + excess PPh_3 → A shows ν(CO) bands. The number of ν(CO) IR bands for A is

A. 1

B. 2

C. 3

D. 4

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Synergic bonding, π-acidity, IR ν(CO) trends

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Metal fills CO's π — anionic carbonyls have the lowest ν(CO); cationic the highest.*

Correct Answer A 1

CONCEPT

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

↓

LOGIC / WORKING

Excess PPh_3 with $Cr(CO)_6$ gives mer- or fac-$Cr(CO)_3(PPh_3)_3$. The fac isomer (C_3v symmetry) has one ν(CO) IR-active band (A_1). The product with excess PPh_3 is fac-$[Cr(CO)_3(PPh_3)_3]$, giving 1 band.

FINAL: (A) 1

SHORTCUT / EXAM TRICK

More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

COMMON MISTAKE

Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.

EXAM TIP

ν(CO): free 2143 > terminal > μ_2-bridging > μ_3. Better σ-donor (PMe_3 > CO) lowers the remaining ν(CO).

MEMORY TRICK

Metal fills CO's π* — anionic carbonyls have the lowest ν(CO); cationic the highest.

Why the Other Options Are Wrong

Correct answer: **A**

B **2**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

C **3**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

D **4**
Inconsistent with the synergic σ-donation / π-back-bonding trend; the correct choice is (A). See worked explanation.

TOPIC REVISION

Metal Carbonyls & π-Acid Ligands

13 PYQs · Last-minute revision

TOPIC SUMMARY

M–CO bonding is synergic: σ-donation from C into the metal plus π-back-donation from filled metal d into CO π*. Back-donation strengthens M–C and weakens C–O, lowering ν(CO) below free CO (2143 cm^{-1}).

IMPORTANT FORMULA SHEET

ν(CO): $[Ti(CO)_6]^{2-} < [V(CO)_6]^{-} < Cr(CO)_6 < [Mn(CO)_6]^{+}$

Terminal CO ≈ 1850–2120 cm^{-1}

μ_{2}-CO ≈ 1700–1860 cm^{-1}

π-acidity: NO > CO ≈ PF_3 > PR_3

FREQUENTLY ASKED CONCEPTS

synergic σ/π bonding
IR ν(CO) diagnostics
back-donation
- Tolman parameter & cone angle

COMMON MISTAKES & QUICK NOTES

Watch out:
Reversing the charge/ν(CO) trend, or sending back-donation into σ* instead of π*.
Last-minute:
More electron density on the metal (anionic, good σ-donor co-ligands) → more back-donation → LOWER ν(CO).

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q5 Q9 Q13 Q19 Q27 Q50 Q90 Q93 Q99 Q109 Q123 Q140 Q165

Expect **3 question(s)** next session on **Synergic bonding, π-acidity, IR ν(CO) trends.**

TOPIC 3

Metallocenes & Sandwich Compounds

16 questions · Easy 6 | Medium 10 | Hard 0 · PYQ frequency: High

Q3

Oxidation occurs very easily in case of

A. $(\eta^5\text{-}C_5H_5)_2$ Fe

B. $(\eta^5\text{-}C_5H_5)_2$, Co

C. $(\eta^5\text{-}C_5H_5)_2$, Ru

D. $(\eta^5\text{-}C_5H_5)_2$,Co+

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer B $(\eta^5\text{-}C_5H_5)_2$, Co

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

Compound Number of electron in outer shell of central atom $(\eta^5\text{-}C_5H_5)_2$ Fe 18 $(\eta^5\text{-}C_5H_5)_2$Co 19 $(\eta^5\text{-}C_5H_5)_2$Ru 18 $(\eta^5\text{-}C_5H_5)_2$Co+ 18 Oxidation (loss of electrons) of $(\eta^5\text{-}C_5H_5)_2$, Co to $(\eta^5\text{-}C_5H_5)_2$ Co+ gives an 18 electron compound, (more stable) therefore easy to oxidise.

FINAL: (B) $(\eta^5\text{-}C_5H_5)_2$, Co

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **B**

A $(\eta^5\text{-}C_5H_5)_2$ Fe

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

C $(\eta^5\text{-}C_5H_5)_2$, Ru

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

D $(\eta^5\text{-}C_5H_5)_2$,Co+

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

Q10 The stable cyclopentadienyl complex of beryllium is

A $[Be(\eta^2\text{-}C_5H_5)_2]$

B $[Be(\eta^2\text{-}C_5H_5)\ (\eta^3\text{-}C_5H_5)]$

C $[Be(\eta^1\text{-}C_5H_5)\ (\eta^3\text{-}C_5H_5)]$

D $[Be(\eta^1\text{-}C_5H_5)\ (\eta^5\text{-}C_5H_5)]$

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer D $[Be(\eta^1\text{-}C_5H_5)\ (\eta^5\text{-}C_5H_5)]$

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene $Fe(\eta^5\text{-}Cp)_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

.

Because main group element follows octet rule. $[Be(\eta^1\text{-}C_5H_5)\ (\eta^5\text{-}C_5H_5)]$,2+5+1=8

FINAL: (D) $[Be(\eta^1\text{-}C_5H_5)\ (\eta^5\text{-}C_5H_5)]$

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **D**

A $[Be(\eta^2\text{-}C_5H_5)_2]$

Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

B $[Be(\eta^2\text{-}C_5H_5)\ (\eta^3\text{-}C_5H_5)]$

Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

C $[Be(\eta^1\text{-}C_5H_5)\ (\eta^3\text{-}C_5H_5)]$

Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

Q20

The carbonyl resonance in 13C NMR spectrum of $[(\eta^5\text{-}C_5H_5)]Rh(CO)]_3$ (103Rh, nuclear spin, I=1/2, 100 %) shows a triplet at -65° C owing to the presence of

A Terminal CO

B μ_2-CO

C μ_2-CO

D $\eta^5\text{-}C_5H_5$ Triplet of carbonyl carbon indicates the each CO is attached with chemically equivalent two Rh atoms that means μ_2--CO complex. Actual structure is

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer B μ_2-CO

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

FINAL: (B) μ_2-CO

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **B**

A **Terminal CO**

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See worked explanation.

C **μ_2-CO**

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See worked explanation.

D **η^5-C_5H_5 Triplet of carbonyl carbon indicates the each CO is attached with chemically equivalent two Rh atoms that means μ_2--CO complex. Actual structure is**

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See worked explanation.

Q24 The complex that DOES NOT obey 18- electron rule is:

A. $[(\eta^5 -C_5H_5)RuCl(CO)(PPh_3)]$

B. $[W(CO)_3(SiMe_3)(Cl)(NCMe)_2]$

C. $[IrCl_3(PPh_3)_2(AsPh)_2]^-$

D. $[Os(N)Br_2(PMe_3)(NMe_2)]^-$

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer D $[Os(N)Br_2(PMe_3)(NMe_2)]^-$

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene $Fe(\eta^5\text{-}Cp)_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

. $[(\eta^5\text{–}C_5H_5)RuCl(CO)(PPh_3)]$ T.V.E = 5+8+1+2+2=18e- $[W(CO)_3(SiMe_3)(Cl)(NCMe)_2]$ T.V.E= 6+ 6+1+1+ 2×2 =18e- $[IrCl_3(PPh_3)_2(AsPh_2)]^-$ T.V.E= 9+ 3 +4+1+ 1 =18e- $[Os(N)Br_2(PMe_3)(NMe_2)]^-$ T.V.E= 8+ 5 +2+1+ 1 =17e DEC 2012

FINAL: (D) $[Os(N)Br_2(PMe_3)(NMe_2)]^-$

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **D**

A $[(\eta^5\text{–}C_5H_5)RuCl(CO)(PPh_3)]$

Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

B $[W(CO)_3(SiMe_3)(Cl)(NCMe)_2]$

Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

C $[IrCl_3(PPh_3)_2(AsPh)_2]^-$

Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

Q46

The electrophile Ph_3C reacts with $[(\eta^5\text{-}C_5H_5)\ Fe(CO)_2(CDMe_2)]$ to give a product A. The product A is formed because

A. Fe is oxidized

B. alkyl is susbtituted with Ph_3C

C. Fe-Ph bond is formed

D. Alkyl is converted to alkene

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer D Alkyl is converted to alkene

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

The electrophilic attack of Ph_3C on the given compound, results in removal of one Methyl group from $CDMe_2$ ligand, thus forming an alkene. Since the reacting species is 18 electron compound, after reaction, the final product A is also an 18e species.

- 5+8+4+1 = 18

FINAL: (D) Alkyl is converted to alkene

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **D**

A **Fe is oxidized**

Why (D) is the key — Î²-hydride abstraction converts the alkyl to an Î·Â²-alkene (d).

B **alkyl is susbtituted with Ph_3C**

Option (B) is ruled out by the same reasoning: Î²-hydride abstraction converts the alkyl to an Î·Â²-alkene

C **Fe-Ph bond is formed**

Option (C) is ruled out by the same reasoning: Î²-hydride abstraction converts the alkyl to an Î·Â²-alkene

Q51

The ligand(s) that is (are) fluxional in $[(\eta^5\text{-}C_5H_5)(\eta\text{-}C_5H_5)Fe(CO)_2]$ in the temperature range 221-298K, is (are)

A. $\eta^5\text{-}C_5H_5$

B. $\eta^1\text{-}C_5H_5$

C. $\eta^5\text{-}C_5H_5$ and CO

D. $\eta^1C_5H_5$ and CO

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer B η^1-C_5H_5

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

$[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Fe(CO)_2] \rightarrow [(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Fe]$ (at temp range = 221-298K)

FINAL: (B) η^1-C_5H_5

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **B**

A η^5-C_5H_5

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

C η^5-C_5H_5 and CO

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

D $\eta^1C_5H_5$ and CO

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

Q64

$NaI(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ reacts with Br_2 to give A. Reaction of A with $LiAlH_4$ results in B. The proton NMR spectrum of B consists of two singlets of relative intensity 5:1. Compounds A and B respectively, are

A $(\eta^5\text{-}C_5H_5)\ Fe(CO)_2Br$, and $(\eta^5\text{-}\ C_5H_5\ )Fe(CO)_2H$

B $(\eta^4\text{-}C_5H_5)Fe(CO)_2Br_2$ and $(\eta^4\text{-}C_5H_5)Fe(CO)_2HBr$

C $(\ \eta^5\text{-}C_5H_5)Fe(CO)_2Br$ and $(\eta^4\text{-}C_5H_5)Fe(CO)_2(H)_2$

D $(\eta^5\text{-}C_5H_5\ )Fe(CO)_2Br$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2HBr$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer A $(\eta^5\text{-}C_5H_5)\,Fe(CO)_2Br$, and $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene $Fe(\eta^5\text{-}Cp)_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

- So, in the product (B) it shows two signals in 1H NMR one for 5H of Cp ring and one for Fe-H proton with intensity ratio 5: 1.

FINAL: (A) $(\eta^5\text{-}C_5H_5)\,Fe(CO)_2Br$, and $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **A**

B — **$(\eta^4\text{-}C_5H_5)Fe(CO)_2Br_2$ and $(\eta^4\text{-}C_5H_5)Fe(CO)_2HBr$**

Why (A) is the key — Br_2 cleaves $Na[CpFe(CO)_2]$ to $CpFe(CO)_2Br$ (A). $LiAlH_4$ gives the hydride $CpFe(CO)_2H$ (B), whose Cp : H singlets are 5 : 1 (a).

C — **$(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ and $(\eta^4\text{-}C_5H_5)Fe(CO)_2(H)_2$**

Option (C) is ruled out by the same reasoning: Br_2 cleaves $Na[CpFe(CO)_2]$ to $CpFe(CO)_2Br$ (A). $LiAlH_4$ gives the hydride $CpFe(CO)_2H$ (B), whose Cp : H singlets are 5 : 1

D — **$(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2HBr$**

Option (D) is ruled out by the same reasoning: Br_2 cleaves $Na[CpFe(CO)_2]$ to $CpFe(CO)_2Br$ (A). $LiAlH_4$ gives the hydride $CpFe(CO)_2H$ (B), whose Cp : H singlets are 5 : 1

Q70

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

A. linear and bent

B. bent and linear

C. linear and linear

D. bent and bent

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer C linear and linear

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

$[Co(CO)_3(NO)]$ NO in linear form donate (3 electron.) ↓ ↓ ↓ 9 + (2×3) +3= 18 electron $[Ni(\eta^5$-Cp) (NO)] ↓ ↓ ↓ 10 + 5 + 3 = 18 electron In both complexes NO donating three electron. So, NO is in linear form.

FINAL: (C) linear and linear

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **C**

A **linear and bent**

Why (C) is the key — Both counts need NO as a 3-electron donor: $Co(CO)_3(NO)$ 9 + 6 + 3 = 18 and CpNi(NO) 10 + 5 + 3 = 18, so both nitrosyls are linear.

B **bent and linear**

Option (B) is ruled out by the same reasoning: Both counts need NO as a 3-electron donor: $Co(CO)_3(NO)$ 9 + 6 + 3 = 18 and CpNi(NO) 10 + 5 + 3 = 18, so both nitrosyls are

D **bent and bent**

Option (D) is ruled out by the same reasoning: Both counts need NO as a 3-electron donor: $Co(CO)_3(NO)$ 9 + 6 + 3 = 18 and CpNi(NO) 10 + 5 + 3 = 18, so both nitrosyls are

Q80 Amongst the following (A) $[Mn(\eta^5\text{-}Cp)(CO)_3]$ (B) $[Os(\eta^5\text{-}Cp)_2]$ (C) $[Ru(\eta^5\text{-}Cp)_2]$ and (D) $[Fe(\eta^5\text{-}Cp)_2]$ the compounds with most shielded and deshielded Cp protons respectively, are

A. D and A

B. D and B

C. C and A

D. C and B

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer A D and A

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene $Fe(\eta^5\text{-}Cp)_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

Here, Cp is cyclopentadienyl ligand is one of the most common and popular ligands in organometallic chemistry.
It is an anionic ligand that normally coordinates in an η^5 mode as a 6 electron donor.
Now, 18-electron rule apply on the complexes $[Mn(\eta^5\text{-}Cp)(CO)_3]$ does not follow 18-electron rule. So, this complex is most deshielded compound when we are going 3d to 4d and 4d to 5d series in the transition element the shielding effect decrease because of the electron density or the distance between metal to ligand, increases. So, $[Fe(\eta^5\text{-}Cp)_2]$ is more shielded than other.

- Thus, the compound D is most shielded and compound A is most deshielded.

FINAL: (A) D and A

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **A**

B — **D and B**

Why (A) is the key — Cp ^{1}H shifts: Cp_2Fe ≈ 4.04, Cp_2Ru ≈ 4.42, Cp_2Os ≈ 4.71, $CpMn(CO)_3$ ≈ 4.8 ppm (the CO groups withdraw electron density). So ferrocene is the most shielded and cymantrene the most deshielded (a).

C — **C and A**

Option (C) is ruled out by the same reasoning: Cp ^{1}H shifts: Cp_2Fe ≈ 4.04, Cp_2Ru ≈ 4.42, Cp_2Os ≈ 4.71, $CpMn(CO)_3$ ≈ 4.8 ppm (the CO groups withdraw electron density). So ferrocene is the most shielded and…

D — **C and B**

Option (D) is ruled out by the same reasoning: Cp ^{1}H shifts: Cp_2Fe ≈ 4.04, Cp_2Ru ≈ 4.42, Cp_2Os ≈ 4.71, $CpMn(CO)_3$ ≈ 4.8 ppm (the CO groups withdraw electron density). So ferrocene is the most shielded and…

Q85

The W-W bond order in $[W(\eta^5\text{-}C_5H_5)(\mu\text{-}Cl)(CO)_2]_2$ is

A three

B two

C one

D zero

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer D zero

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

$[W(\eta^5\text{-}C_5H_5)(\text{-Cl})(CO)_2]_2$ TVE(A)= (6+5+3+4)×2=36 B = $nx_{18\text{-}}A$ = 2×18-36=0 Hence, number of M-M= B/2=0/2 =0

FINAL: (D) zero

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **D**

A — **three**

Why (D) is the key — Each W: 6 + Cp 5 + 2 CO 4 + its own μ-Cl 1 + the lone pair of the other bridging Cl 2 = 18. No W–W bond is needed: bond order zero.

B — **two**

Option (B) is ruled out by the same reasoning: Each W: 6 + Cp 5 + 2 CO 4 + its own μ-Cl 1 + the lone pair of the other bridging Cl 2 = 18. No W–W bond is needed: bond order

C — **one**

Option (C) is ruled out by the same reasoning: Each W: 6 + Cp 5 + 2 CO 4 + its own μ-Cl 1 + the lone pair of the other bridging Cl 2 = 18. No W–W bond is needed: bond order

Q89 For uranocene, the correct statement(s) is/are: (A) oxidation state of uranium is +4 (B) it has cyclooctatetraenide ligands (C) it is a bent sandwich compound (D) it has −2 charge

A. A and B

B. B and C

C. A and D

D. B only

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer A A and B

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

Uranocene U(η^8-C_8H_8)$_2$: U is in the +4 oxidation state; each $C_8H_8^{2-}$ (cyclooctatetraenide) ligand has −2 charge. The complex is a linear sandwich (not bent). Statements A and B are correct.

FINAL: (A) A and B

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **A**

B **B and C**
Inconsistent with the electron count and stability of the sandwich; the correct choice is (A). See worked explanation.

C **A and D**
Inconsistent with the electron count and stability of the sandwich; the correct choice is (A). See worked explanation.

D **B only**
Inconsistent with the electron count and stability of the sandwich; the correct choice is (A). See worked explanation.

Q97

CpM [Cp is (η^5-C_5H_5)] fragment isolobal with a BH fragment is

A. CpGe

B. CpMn

C. CpRu

D. CpCo

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer D CpCo

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

B-H= 4e- fragment isolobal fragment should have 14 electron.

- Cp + Co=5+9=14 e-

FINAL: (D) CpCo

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **D**

A **CpGe**
Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

B **CpMn**
Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

C **CpRu**
Inconsistent with the electron count and stability of the sandwich; the correct choice is (D). See the worked explanation.

Q100

Correct order of M-C bond length of metallocenes (a-c)$_1$. $[Fe(\eta^5\text{-}Cp)_2]_2$. $[Ni(\eta^5\text{-}Cp)_2]_3$. $[Co(\eta^5\text{-}Cp)_2]$ is—

A A> B >C

B B > C >A

C C> B >A

D A> C > B

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer B B > C >A

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

As the electron goes to e*1g (dxz , dyz), orbital of metallocene bond length increases as they are anologous eg set orbital of an octahedral complex Thus, in Ni(Cp)$_2$ there are highest number of electrons in e*1g . Hence, it has highest M-C bond length.
Ni(Cp)$_2$ > Co(Cp)$_2$ > Fe(Cp)$_2$

FINAL: (B) B > C >A

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **B**

A **A> B >C**

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

C **C> B >A**

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

D **A> C > B**

Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

Q117 **Choose the isoelectronic pair among the following: A. $[V(CO)_6]$ B. $[Cu(\eta^5\text{- } C_5H_5)\ (CO)]$ C. $[Co(CO)_4]^-$ D. $[IrCl\ (CO)\ (PPh_3)]$**

A. A and B

B. B and C

C. C and D

D. A and D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer B B and C

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

The species having same number of electrons are called isoelectronic.
A =$[V(CO)_6]$=5+12=17e- B =$[Cu(\eta^5\text{- } C_5H_5)(CO)]$=11+5+2=18e- C =$[Co(CO)_4]^-$ =9+8+1=18e-
D=$[IrCl(CO)(PPh_3)_2]$ = 9+1+2+4=16e- Therefore B and D are isoelectronic species .

FINAL: (B) B and C

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **B**

A

A and B

Why (B) is the key — CpCu(CO) and $[Co(CO)_4]^-$ are both 18-electron species (b).

C

C and D

Option (C) is ruled out by the same reasoning: CpCu(CO) and $[Co(CO)_4]^-$ are both 18-electron species

D

A and D

Option (D) is ruled out by the same reasoning: CpCu(CO) and $[Co(CO)_4]^-$ are both 18-electron species

Q121 Addition of $NaBH_4$ to $[(\eta^5\text{-Cp})Fe(\eta^6\text{-}C_6H_6)]^+$ will give

A $[(\eta^5\text{-Cp})Fe(H)_2]$

B $[(\eta^5\text{-Cp})\ Fe(H)(\ \eta^6\text{-}C_6H_6)]$

C $[(\eta^5\text{-Cp})\ Fe(\eta^6\text{-}C_6H_6)]$

D $[(\eta^5\text{-Cp})\ Fe(\eta^6\text{-}C_6H_7)]$

QUESTION INSIGHTS

ESTIMATED TIME
1–1.5 min

DIFFICULTY
Easy

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★☆☆

EXPECTED LEVEL
Part B

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer D $[(\eta^5\text{-Cp})\ Fe(\eta^6\text{-}C_6H_7)]$

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene $Fe(\eta^5\text{-Cp})_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

$[(\eta^5\text{-Cp})\ Fe\ (\eta^6\text{-}C_6H_6)]^+$

FINAL: (D) $[(\eta^5\text{-Cp})\ Fe(\eta^6\text{-}C_6H_7)]$

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **D**

A **$[(\eta^5\text{-Cp})Fe(H)_2]$**

Why (D) is the key — Hydride adds to the arene to give $[CpFe(\eta^5\text{-}C_6H_7)]$ (d).

B **$[(\eta^5\text{-Cp})\ Fe(H)(\ \eta^6\text{-}C_6H_6)]$**

Option (B) is ruled out by the same reasoning: Hydride adds to the arene to give $[CpFe(\eta^5\text{-}C_6H_7)]$

C **$[(\eta^5\text{-Cp})\ Fe(\eta^6\text{-}C_6H_6)]$**

Option (C) is ruled out by the same reasoning: Hydride adds to the arene to give $[CpFe(\eta^5\text{-}C_6H_7)]$

Q134

The reaction of $[(\eta^5 - C_5H_5 (Fe(CO)_2]^-$ with CH_3I gives compound A. The 1H NMR spectrum of A show two singlets in an integrated intensity ratio of 3:5. Compound A upon reaction with PPh_3 give compound B. The 1H NMR spectrum of B shows 3 sets of signals in an integrated intensity ratio of 3:5:15. Compounds A and B respectively, are

A

B

C

D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Sandwich electron counts, ferrocene reactivity and redox

PYQ FREQUENCY
High · 11 paper

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Correct Answer B

CONCEPT

Cyclopentadienyl (η^5-Cp) sandwiches: ferrocene Fe(η^5-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

↓

LOGIC / WORKING

18 e- (A) (18e -) (B) (18e-)

- Two signals with three signal with 3:5:15 3:5 intensity ratio intensity ratio Correct option is (b)

FINAL: (B)

SHORTCUT / EXAM TRICK

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

COMMON MISTAKE

Mixing the η^5-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

EXAM TIP

Ferrocene does electrophilic substitution (Friedel–Crafts) but is OXIDISED by strong acids (HNO_3) to ferrocenium.

MEMORY TRICK

Ferrocene = 18e rock; cobaltocene gives up its 19th electron to become an 18e cation.

Why the Other Options Are Wrong

Correct answer: **B**

A Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

C Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

D Inconsistent with the electron count and stability of the sandwich; the correct choice is (B). See the worked explanation.

TOPIC REVISION

Metallocenes & Sandwich Compounds

16 PYQs · Last-minute revision

TOPIC SUMMARY

Cyclopentadienyl (η^{5}-Cp) sandwiches: ferrocene Fe(η^{5}-Cp)$_2$ is an 18e, aromatic, very stable molecule. Cp donates 5e (neutral) or 6e (Cp^-, ionic).

IMPORTANT FORMULA SHEET

Ferrocene Fe(η^{5}-Cp)$_2$ = 8 + 2×5 = 18

Cp_2Co = 19e (reductant)

Cp_2Ni = 20e (reactive)

$[Cp_2Fe]^+$ ferrocenium = 17e

FREQUENTLY ASKED CONCEPTS

η^{5}-Cp donation

ferrocene EAS

metallocene redox

- bent metallocenes

COMMON MISTAKES & QUICK NOTES

Watch out:

Mixing the η^{5}-Cp neutral (5e) and ionic (6e) donor numbers; trying to nitrate ferrocene.

Last-minute:

Count: Fe(8)+2×Cp(5)=18 ⇒ ferrocene. 19e (Cp_2Co) and 20e (Cp_2Ni) species readily oxidise toward 18e.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q3 Q10 Q20 Q24 Q46 Q51 Q64 Q70 Q80 Q85 Q89 Q97 Q100 Q117 Q121 Q134

Expect **3 question(s)** next session on **Sandwich electron counts, ferrocene reactivity and redox.**

TOPIC 4

Hapticity & Bonding Modes

14 questions · Easy 0 | Medium 14 | Hard 0 · PYQ frequency: High

Q16

A compound A having the composition $FeC_9H_8O_3$ shows one signal at 2.5 ppm and another one around 5.0 ppm in its 1H NMR spectrum. The IR spectrum of this compound shows two bands around 1680 cm-1. The compound follows the 18 electron rule of the following statements for A, the correct one is/are (A) It has η^5-Cp group. (B) It has a terminal CO ligand. (C) It has a CH_3 ligand (D) It has Fe-H bond.

A (A) and (B) only

B (C) only

C (A) and (C) only

D (B) and (D) only Explanation: 1 H-NMR giving one signal at 5.0ppm indicates presence of η^5-Cp ring, another one signal at 2.5ppm indicates presence of CH_3 group. IR band at 1680cm-1 indicates presence of ketone (C=O) group. Thus the appropriate structure of molecule.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer A (A) and (B) only

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

- . [CSIR JUNE 2012]

FINAL: (A) (A) and (B) only

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **A**

B **(C) only**
Inconsistent with the correct hapticity / donor count; the correct choice is (A). See the worked explanation.

C **(A) and (C) only**
Inconsistent with the correct hapticity / donor count; the correct choice is (A). See the worked explanation.

D **(B) and (D) only Explanation: 1 H-NMR giving one signal at 5.0ppm indicates presence of η^5-Cp ring, another one signal at 2.5ppm indicates presence of CH_3 group. IR band at 1680cm-1 indicates presence of ketone (C=O) group. Thus the appropriate structure of molecule.**
Inconsistent with the correct hapticity / donor count; the correct choice is (A). See the worked explanation.

Q25

The substitution of η^5-Cp group with nitric oxide is the easiest for

A. $(\eta^5\text{-}Cp_2)Fe$

B. $(\eta^5\text{-}Cp_2)CoCl$

C. $(\eta^5\text{-}Cp_2)Ni$

D. $(\eta^5\text{-}Cp_2)Co$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer C $(\eta^5\text{-}Cp_2)Ni$

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

- Refer to the governing principle for this topic; the correct option follows directly from it.

FINAL: (C) $(\eta^5\text{-}Cp_2)Ni$

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **C**

A $(\eta^5\text{-Cp}_2)\text{Fe}$

Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

B $(\eta^5\text{-Cp}_2)\text{CoCl}$

Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

D $(\eta^5\text{-Cp}_2)\text{Co}$

Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

Q36

The oxidation state of molybdenum in $[(\eta^7\text{-tropylium})Mo(CO)_3]^+$ is:

A. +2

B. +1

C. 0

D. -1

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer C 0

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

.

$[(\eta^7$- tropylium)$Mo(CO)_3]$ In zero oxidation state of Mo, complex have 18 e-1 (stable)

- 7 +6+6 -1 = 18 tropylium is a 7e- donor ligand in neutral method and +1 oxidation state oxidation state of Mo = +1+x +0 = +1 x= 0

FINAL: (C) 0

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **C**

A **+2**

Why (C) is the key — Counting the tropylium ring as the aromatic $C_7H_7^+$ cation (6 π electrons, L_3) and CO as neutral, the metal is Mo(0).

B **+1**

Option (B) is ruled out by the same reasoning: Counting the tropylium ring as the aromatic $C_7H_7^+$ cation (6 π electrons, L_3) and CO as neutral, the metal is

D **-1**

Option (D) is ruled out by the same reasoning: Counting the tropylium ring as the aromatic $C_7H_7^+$ cation (6 π electrons, L_3) and CO as neutral, the metal is

Q48

Subsitution of L with other ligands will be easiest for the species

A

B

C

D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer C

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

In case of (c) the chances of conversion of heptacity from $\eta^5 \rightarrow \eta^3$is more due to partial bond fixation.

- Others will not undergo change in heptacity, to retain their aromatic properties.

FINAL: (C)

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: C

A Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

B Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

D Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

Q58 The hepticities ‘x’ and ‘y’ of the arene moieties in the diamagnetic complex $[(\eta x\text{-}C_6H_6)Ru(\eta y\text{-}C_6H_6)]$ respectively are

A. 6 and 6

B. 4 and 4

C. 4 and 6

D. 6 and 2

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer C 4 and 6

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

$[(\eta x\text{-}C_6H_6)Ru(\eta y\text{-}C_6H_6)]$ x = 4, y = 6 $[(\eta^4\text{-}C_6H_6)Ru(\eta^6\text{-}C_6H_6)]$ Total electron 4+8+6 =18 electron. (Diamagnetic complex) Δ

FINAL: (C) 4 and 6

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **C**

A — **6 and 6**

Why (C) is the key — Two η^6 rings would give 8 + 12 = 20 electrons; one ring slips to η^4 so that $(\eta^6\text{-}C_6H_6)Ru(\eta^4\text{-}C_6H_6)$ is an 18-electron diamagnetic complex.

B — **4 and 4**

Option (B) is ruled out by the same reasoning: Two η^6 rings would give 8 + 12 = 20 electrons; one ring slips to η^4 so that $(\eta^6\text{-}C_6H_6)Ru(\eta^4\text{-}C_6H_6)$ is an 18-electron diamagnetic

D — **6 and 2**

Option (D) is ruled out by the same reasoning: Two η^6 rings would give 8 + 12 = 20 electrons; one ring slips to η^4 so that $(\eta^6\text{-}C_6H_6)Ru(\eta^4\text{-}C_6H_6)$ is an 18-electron diamagnetic

Q66

1H NMR spectrum of free benzene shows a peak at 7.2 ppm. The expected chemical shift (in ppm) of C_6H_6 ligand in 1H NMR spectrum of $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ and the reason for it, if an, is/are

A 4.5; disruption of ring current

B 9.0; inductive effect

C 7.2

D 2.5 combination of inductive effect and disruption of ring current.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer A 4.5; disruption of ring current

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

All given options are incorrect except (a) as there is ring current disruption after formation of complex in $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ .The shift in δ is attributed to this reason from 7.2 ppm to 4.5 almost .

FINAL: (A) 4.5; disruption of ring current

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **A**

B **9.0; inductive effect**
Inconsistent with the correct hapticity / donor count; the correct choice is (A). See the worked explanation.

C **7.2**
Inconsistent with the correct hapticity / donor count; the correct choice is (A). See the worked explanation.

D **2.5 combination of inductive effect and disruption of ring current.**
Inconsistent with the correct hapticity / donor count; the correct choice is (A). See the worked explanation.

Q87

$[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$ shows fluxional behavior. The ^1H NMR spectrum of this compound when it is in the non-fluxional state shows-

A. one signal

B. two signals in the intensity ratio of 4: 1

C. three signals in the intensity ratio of 2: 2 : 1

D. five signals of equal intensity.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer C three signals in the intensity ratio of 2: 2 : 1

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

- Hc = central proton Ha= is anti with respect to Hc Hs= syn with respect to Hc Ha , Hs , Hc environment are different new intensity ratio 2: 2 :1. When allyl is non-fluxional.

FINAL: (C) three signals in the intensity ratio of 2: 2 : 1

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **C**

A **one signal**

Why (C) is the key — A static η³-allyl has three proton environments: two syn H, two anti H and one central H — three signals in 2:2:1.

B **two signals in the intensity ratio of 4: 1**

Option (B) is ruled out by the same reasoning: A static η³-allyl has three proton environments: two syn H, two anti H and one central H — three signals in

D **five signals of equal intensity.**

Option (D) is ruled out by the same reasoning: A static η³-allyl has three proton environments: two syn H, two anti H and one central H — three signals in

Q92

The intermediate and the final major product of photolysis of Z From the following are

A. A and D

B. B and D

C. B and C

D. A and C

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer D A and C

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

On photolysis of Z first a 16 electron intermediate is formed which is option B, and for final product allyl attains maximum heptacity therefore η^1 allyl is converted η^3 allyl which is option D

FINAL: (D) A and C

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **D**

A **A and D**
Inconsistent with the correct hapticity / donor count; the correct choice is (D). See the worked explanation.

B **B and D**
Inconsistent with the correct hapticity / donor count; the correct choice is (D). See the worked explanation.

C **B and C**
Inconsistent with the correct hapticity / donor count; the correct choice is (D). See the worked explanation.

Q101 The 1H NMR spectrum of $[Ru(\eta^4\text{-}C_8H_8)(CO)_3]$ at 23°C consists of a sharp single line. The number of signals observed at low temperature (-140 °C) in its spectrum is

A. 8

B. 6

C. 4

D. 2

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer C 4

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

Therefore, total protons 8, but in η^4-mode COT attached to the four carbon and 4 protons show different environment at -140°C because fluxonial behaviour slow down and hence , 4 signals will be observed.

FINAL: (C) 4

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **C**

A — **8**
Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

B — **6**
Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

D — **2**
Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

Q132 **Identify the pair of molecules which are isoelectronic as well as isostructural from: $[Pd(PPh_3)_4]$ (A), $[V(CO)_6]$ (B), $[Cr(CO)_6]$ (C), $[Rh(PPh_3)_3Cl]$ (D), $[(\eta^5\text{-}C_5H_5)Ni(NO)]$ (E), $Ni(CO)_4$ (F)**

A. B and C

B. A and F

C. A and D

D. C and E

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer B A and F

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

$[Pd(PPh_3)_4]$ and $Ni(CO)_4$ are both 18-electron d^{10} tetrahedral complexes — isoelectronic and isostructural. $[Pd(PPh_3)_4]$: 10 + 8 = 18e; $[Ni(CO)_4]$: 10 + 8 = 18e.

FINAL: (B) A and F

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **B**

A — **B and C**
Inconsistent with the correct hapticity / donor count; the correct choice is (B). See worked explanation.

C — **A and D**
Inconsistent with the correct hapticity / donor count; the correct choice is (B). See worked explanation.

D — **C and E**
Inconsistent with the correct hapticity / donor count; the correct choice is (B). See worked explanation.

Q159 **Among the following complexes, the one showing the highest rate of substitution of a CO ligand on heating with one equivalent of PPh_3 in decalin, is**

A $(\eta^5\text{-}C_5H_5)Mn(CO)_3$

B $(\eta^5\text{-}C_5Ph_5)Mn(CO)_3$

C $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$

D $(\eta^5\text{-indenyl})Mn(CO)_3$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer D $(\eta^5\text{-indenyl})Mn(CO)_3$

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

The highest rate of substitution of a CO ligand on heating with PPh_3 is easy where slippage of haptacity is easy.
For slippage is easy because it is not at the cost of aromatic character ($\eta^5 \rightarrow \eta^3$).
But η^5 – Cp* , complexes, rate decreases because with respect Cp slippage of haptacity is due to at the cost of aromatic character.

FINAL: (D) **$(\eta^5\text{-indenyl})Mn(CO)_3$**

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **D**

A $(\eta^5\text{-}C_5H_5)Mn(CO)_3$

Inconsistent with the correct hapticity / donor count; the correct choice is (D). See the worked explanation.

B $(\eta^5\text{-}C_5Ph_5)Mn(CO)_3$

Inconsistent with the correct hapticity / donor count; the correct choice is (D). See the worked explanation.

C $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$

Inconsistent with the correct hapticity / donor count; the correct choice is (D). See the worked explanation.

Q160 The correct electronic configuration of frontier MO's of $Mn(\eta^5\text{-}C_5Me_5)$ is

A $e_2g_2\ a_1g_1e_1g_2$

B $e_2g_4\ a_1g_1$

C $e_2g_3\ a_1g_2$

D $a_1g_2e_2g_3$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Hapticity & Bonding Modes

Correct Answer B $e_2g_4\ a_1g_1$

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

Due to high field strength of Cp* , it forms low spin complexe and having one unpaired electron Cp_2*Mn = 2Cp* =10e- and Mn = 7e- =17e- 12e electrons are in the lower orbitals and remaining five electrons occupies the orbital as follows.
Electronic Configuration = $e_2g_4\ a_1g_1$

FINAL: (B) $e_2g_4\ a_1g_1$

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **B**

A $e_2g_2\ a_1g_1e_1g_2$

Inconsistent with the correct hapticity / donor count; the correct choice is (B). See the worked explanation.

C $e_2g_3\ a_1g_2$

Inconsistent with the correct hapticity / donor count; the correct choice is (B). See the worked explanation.

D $a_1g_2e_2g_3$

Inconsistent with the correct hapticity / donor count; the correct choice is (B). See the worked explanation.

Q161 On heating $[Mo(N_2)_2(PMe_2Ph)_4]$ and $[ReCl(N_2)(PMe_2Ph)_4]$, the products formed are respectively

A $[(\eta^6\text{-}PhPMe_2)Mo(PMe_2Ph)_3]$ and $[(\eta^6\text{-}PhPMe_2)Re(PMe_2Ph)_3]Cl$

B $[(PMe_2Ph)_4Mo(\mu\text{-}N_2)_2Mo(PMe_2Ph)_4]$ and $[(PMe_2Ph)_4Re(\mu\text{-}Cl)_2Re(PMe_2Ph)_4]$

C $[(\eta^6\text{-}PhPMe_2)Mo(PMe_2Ph)_3]$ and $[(PMe_2Ph)_4Re(u\text{-}Cl)_2Re(PMe_2Ph)_4]$

D $[(PMe_2Ph)_4Mo(u\text{-}N_2)_2Mo(PMe_2Ph)_4]$ and $[(\eta^6\text{-}PhPMe_2)Re(PMe_2Ph)_3]Cl$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer C $[(\eta^6\text{-PhPMe}_2)\text{Mo}(\text{PMe}_2\text{Ph})_3]$ and $[(\text{PMe}_2\text{Ph})_4\text{Re}(\mu\text{-Cl})_2\text{Re}(\text{PMe}_2\text{Ph})_4]$

CONCEPT

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

Taking 18 valence electron as guide, the products will be predicted. Δ $[\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$ $[(\eta^6\text{-PhPMe}_2)\text{Mo}(\text{PMe}_2\text{Ph})_3]^+$ N_2 18 V.E 18 V.E Δ $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]^+$ N_2 18 V.E 18 V.E 18 V.E (Cl as a bridging ligand)

FINAL: (C) **$[(\eta^6\text{-PhPMe}_2)\text{Mo}(\text{PMe}_2\text{Ph})_3]$ and $[(\text{PMe}_2\text{Ph})_4\text{Re}(\mu\text{-Cl})_2\text{Re}(\text{PMe}_2\text{Ph})_4]$**

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^5 \rightarrow \eta^3$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: C

A $[(\eta^6\text{-PhPMe}_2)\text{Mo}(\text{PMe}_2\text{Ph})_3]$ and $[(\eta^6\text{-PhPMe}_2)\text{Re}(\text{PMe}_2\text{Ph})_3]\text{Cl}$

Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

B $[(\text{PMe}_2\text{Ph})_4\text{Mo}(\mu\text{-N}_2)_2\text{Mo}(\text{PMe}_2\text{Ph})_4]$ and $[(\text{PMe}_2\text{Ph})_4\text{Re}(\mu\text{-Cl})_2\text{Re}(\text{PMe}_2\text{Ph})_4]$

Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

D $[(\text{PMe}_2\text{Ph})_4\text{Mo}(\text{u-N}_2)_2\text{Mo}(\text{PMe}_2\text{Ph})_4]$ and $[(\eta^6\text{-PhPMe}_2)\text{Re}(\text{PMe}_2\text{Ph})_3]\text{Cl}$

Inconsistent with the correct hapticity / donor count; the correct choice is (C). See the worked explanation.

Q163

The product A of the reaction $CpCo(CO)_2$ + 2 PhC≡CPh → A (an organocobalt complex)

A $CpCo(\eta^4\text{-}PhC{=}C(Ph)C(Ph){=}CPh)$ — cobaltacyclopentadiene

B $CpCo(CO)(\eta^2\text{-}PhC{\equiv}CPh)$

C $CpCo(PhC{\equiv}CPh)_2$

D $Co_2(CO)_6(PhC{\equiv}CPh)$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Hapticity, bridging/terminal modes, NO binding

PYQ FREQUENCY
High · 10 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Correct Answer A CpCo(η^{4}-PhC=C(Ph)C(Ph)=CPh) — cobaltacyclopentadiene

CONCEPT

Hapticity η^{n} = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

↓

LOGIC / WORKING

$CpCo(CO)_2$ with 2 alkynes undergoes oxidative coupling to give CpCo(η^{4-1},2,3,4-tetraphenylcobaltacyclopentadiene). The two CO are lost and the two alkynes couple at the cobalt centre.

FINAL: (A) CpCo(η^{4}-PhC=C(Ph)C(Ph)=CPh) — cobaltacyclopentadiene

SHORTCUT / EXAM TRICK

Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

COMMON MISTAKE

Assuming maximum hapticity, or treating bent NO as a 3-electron donor.

EXAM TIP

Count electrons for the GIVEN hapticity, not the maximum; ring slippage ($\eta^{5} \rightarrow \eta^{3}$) opens a site.

MEMORY TRICK

η counts the toes that touch; μ is a bridge; linear NO is the generous 3e donor.

Why the Other Options Are Wrong

Correct answer: **A**

B — **$CpCo(CO)(\eta^2\text{-}PhC{\equiv}CPh)$**

Inconsistent with the correct hapticity / donor count; the correct choice is (A). See worked explanation.

C — **$CpCo(PhC{\equiv}CPh)_2$**

Inconsistent with the correct hapticity / donor count; the correct choice is (A). See worked explanation.

D — **$Co_2(CO)_6(PhC{\equiv}CPh)$**

Inconsistent with the correct hapticity / donor count; the correct choice is (A). See worked explanation.

TOPIC REVISION

Hapticity & Bonding Modes

14 PYQs · Last-minute revision

TOPIC SUMMARY

Hapticity η^n = number of contiguous ligand atoms bonded to the metal; κ = non-contiguous donors; μ = bridging. NO and CO can bind in different modes (linear/bent NO; terminal/bridging CO).

IMPORTANT FORMULA SHEET

η^5-Cp=5e, η^3-allyl=3e, η^2-alkene=2e
Linear NO = 3e ; bent NO = 1e
μ_2-CO lowers ν(CO) in IR

- η-step ⇒ Δe = ±2

FREQUENTLY ASKED CONCEPTS

hapticity η
linear vs bent NO
bridging μ-CO

- ring slippage

COMMON MISTAKES & QUICK NOTES

Watch out:
Assuming maximum hapticity, or treating bent NO as a 3-electron donor.
Last-minute:
Each hapticity step changes the electron count by 2. Linear NO = 3e; bent NO = 1e.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q16 Q25 Q36 Q48 Q58 Q66 Q87 Q92 Q101 Q132 Q159 Q160 Q161 Q163

Expect **3 question(s)** next session on **Hapticity, bridging/terminal modes, NO binding.**

TOPIC 5

Carbenes, Carbynes & M=C

8 questions · Easy 0 | Medium 8 | Hard 0 · PYQ frequency: Moderate

Q35 The ligand in uranocene is: 2-

A C_8H_8 2-

B C_5H_5

C C_6H_6 2-

D C_4H_4

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Fischer vs Schrock carbenes, M=C reactivity

PYQ FREQUENCY
Moderate · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Correct Answer A C_8H_8 2-

CONCEPT

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

↓

LOGIC / WORKING

.
2- The ligand in uranocene is C_8H_8 35 In the metal-olefin interaction, the extent of increase in metal olefin -back-donation would (a) lead to a decrease in C=C bond length (b) change the formal oxidation state of the metal (c) change the hybridisation of the olefin carbon from sp^2 to sp^3.
(d) increase with the presence of electron donating substituent on the olefin.
Correct answer is (c).
In Metal-Olefin interaction, the extent of increase in metal → Olefin *л*-back donation would strengthen the Metal-Olefin bond which produces a increase in C = C bond length and somewhat single bond character which results a change in hybridisation from sp^2 to sp^3.

FINAL: (A) C_8H_8 2-

SHORTCUT / EXAM TRICK

Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

COMMON MISTAKE

Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.

EXAM TIP

Fischer C is attacked by nucleophiles; Schrock C by electrophiles. Carbynes M≡CR are Fischer-type.

MEMORY TRICK

Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Why the Other Options Are Wrong

Correct answer: **A**

B C_5H_5

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See the worked explanation.

C C_6H_6 2-

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See the worked explanation.

D C_4H_4

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See the worked explanation.

Q69

Complexes $HM(CO)_5$ and $[((\eta^5\text{-}C_5H_5)M'(CO)_3]_2$ obey the 18-electron rule. Identify M and M' and their 1H NMR chemical shifts relative to TMS.

A. M = Mn, -7.5; M'= Cr, 4.10

B. M= Cr, -4.10; M'= Mn, -7.5

C. M=V, -7.5; M'= Cr, 4.10

D. M= Mn, -10.22 M'= Fe, 2.80

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Fischer vs Schrock carbenes, M=C reactivity

PYQ FREQUENCY
Moderate · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Correct Answer A M = Mn, -7.5; M'= Cr, 4.10

CONCEPT

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

↓

LOGIC / WORKING

Complex (A) $HM(CO)_5$ =1 + 7+ 10 =18 electron M=Mn [7 electron] 1 + 7+ 10 =18 electron Complex (B) $[(\eta^5\text{-}C_5H_5)M'(CO)_3]_2$ $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ M'=Cr=6 electron 10+12+12+2 (M-M) bond = 36 electron. [CSIR JUNE 2015]

FINAL: (A) M = Mn, -7.5; M'= Cr, 4.10

SHORTCUT / EXAM TRICK

Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

COMMON MISTAKE

Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.

EXAM TIP

Fischer C is attacked by nucleophiles; Schrock C by electrophiles. Carbynes M≡CR are Fischer-type.

MEMORY TRICK

Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Why the Other Options Are Wrong

Correct answer: **A**

B **M= Cr, -4.10; M'= Mn, -7.5**

Why (A) is the key — HMn(CO) (δ −7.5) and $[CpCr(CO)_3]_2$ (δ 4.1) (a).

C **M=V, -7.5; M'= Cr, 4.10**

Option (C) is ruled out by the same reasoning: HMn(CO) (δ −7.5) and $[CpCr(CO)_3]_2$ (δ 4.1)

D **M= Mn, -10.22 M'= Fe, 2.80**

Option (D) is ruled out by the same reasoning: HMn(CO) (δ −7.5) and $[CpCr(CO)_3]_2$ (δ 4.1)

Q72 For typical Fischer and Schrock carbenes, consider the following statements A. Oxidation state of metal is low in Fischer carbene and high in Schrock carbene B. Auxilliary ligands are π-acceptor in Fischer carbene and non π acceptor in Schrock carbene C. Substituents on carbene carbon are non π donor in Fischer carbene and π donor in Schrock carbene D. Carbene carbon is electrophilic in Fischer carbene and nucleophilic in Schrock carbene The correct statements are

- **A** A, B and C
- **B** A, B and D
- **C** B. C and D
- **D** A, C and D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Fischer vs Schrock carbenes, M=C reactivity

PYQ FREQUENCY
Moderate · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Correct Answer B A, B and D

CONCEPT

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

↓

LOGIC / WORKING

- Refer to the governing principle for this topic; the correct option follows directly from it.

FINAL: (B) A, B and D

SHORTCUT / EXAM TRICK

Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

COMMON MISTAKE

Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.

EXAM TIP

Fischer C is attacked by nucleophiles; Schrock C by electrophiles. Carbynes M≡CR are Fischer-type.

MEMORY TRICK

Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Why the Other Options Are Wrong

Correct answer: **B**

A **A, B and C**
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (B). See the worked explanation.

C **B. C and D**
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (B). See the worked explanation.

D **A, C and D**
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (B). See the worked explanation.

Q79

Match column A (coupling reactions) with column B (reagents) Column-A Column-B (1) Suzuki coupling (I) H_2C=CHCO CH (2) Heck coupling (II) RB(OH), (3) Sonagashira coupling (III) PhCO(CH) Znl (4) Negeshi coupling (IV) CHECR (V) SnR The correct match is:

A. I-II, 2-1, 3-IV, 4-III

B. 1-1, 2-V. 3-III, 4-IV

C. 1-IV, 2-III, 3-11, 4-1

D. 1-11.2-111, 3-IV,4-V

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Fischer vs Schrock carbenes, M=C reactivity

PYQ FREQUENCY
Moderate · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Correct Answer A I-II, 2-1, 3-IV, 4-III

CONCEPT

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

↓

LOGIC / WORKING

Suzuki coupling-Palladium catalyzed cross coupling between organoboranic acid and halides.
Heck coupling-Palladium catalyzed C-C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base.
Sonogashira coupling-This coupling terminal alkynes with aryl or vinyl halides is performed with a palladium catalyst, Cu(I) cocatalyst and amine base.

- Negeshi coupling-This reaction is the organic reaction of an organohalide with an organic-zinc compound Pd and Ni catalyst.

FINAL: (A) I-II, 2-1, 3-IV, 4-III

SHORTCUT / EXAM TRICK

Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

COMMON MISTAKE

Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.

EXAM TIP

Fischer C is attacked by nucleophiles; Schrock C by electrophiles. Carbynes M≡CR are Fischer-type.

MEMORY TRICK

Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Why the Other Options Are Wrong

Correct answer: **A**

B **1-1, 2-V. 3-III, 4-IV**
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See the worked explanation.

C **1-IV, 2-III, 3-11, 4-1**
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See the worked explanation.

D **1-11.2-111, 3-IV,4-V**
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See the worked explanation.

Q105 **Reaction of $Cr(CO)_6$ with LiC_6H_5 gives A which reacts with $[MeO][BF_4]$ to give B. The structures of A and B respectively, are**

A $[Cr(CO)_5(COPh)]^-$ and $(CO)_5Cr=C(OMe)Ph$

B $[(CO)_5Cr–Ph]^-$ and $(CO)_5Cr=C(OMe)Ph$

C $[Cr(CO)_5(COPh)]^-$ and $[Cr(CO)_5(COPh)(OMe)]$

D $[(CO)_5Cr–Ph]^-$ and $[Cr(CO)_5Ph(OMe)]$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Fischer vs Schrock carbenes, M=C reactivity

PYQ FREQUENCY
Moderate · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Correct Answer A $[Cr(CO)_5(COPh)]^-$ and $(CO)_5Cr=C(OMe)Ph$

CONCEPT

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

↓

LOGIC / WORKING

LiPh attacks $Cr(CO)_6$ at a CO to give lithium acylchromate A = $Li[(CO)_5Cr–C(=O)Ph]$. Methylation with $[MeO]^+$ at the O gives Fischer carbene B = $(CO)_5Cr=C(OMe)Ph$.

FINAL: (A) $[Cr(CO)_5(COPh)]^-$ and $(CO)_5Cr=C(OMe)Ph$

SHORTCUT / EXAM TRICK

Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

COMMON MISTAKE

Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.

EXAM TIP

Fischer C is attacked by nucleophiles; Schrock C by electrophiles. Carbynes M≡CR are Fischer-type.

MEMORY TRICK

Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Why the Other Options Are Wrong

Correct answer: **A**

B **$[(CO)_5Cr–Ph]^-$ and $(CO)_5Cr=C(OMe)Ph$**

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See worked explanation.

C **$[Cr(CO)_5(COPh)]^-$ and $[Cr(CO)_5(COPh)(OMe)]$**

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See worked explanation.

D **$[(CO)_5Cr–Ph]^-$ and $[Cr(CO)_5Ph(OMe)]$**

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See worked explanation.

Q115

Product A in the following reaction is:
$(CO)_5W{=}CD_2 \rightarrow[h\nu,\ -CO]\ A$

A $D_2C{=}CD_2$

B $D_3C{-}CD_3$

C $[W(CO)_4(CD_2)]$ (η^2-carbene complex)

D $[W(CO)_4]{=}CD_2$ (16e carbene)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Fischer vs Schrock carbenes, M=C reactivity

PYQ FREQUENCY
Moderate · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Correct Answer C $[W(CO)_4(CD_2)]$ (η^2-carbene complex)

CONCEPT

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

↓

LOGIC / WORKING

Photolysis loses one CO from the Fischer carbene $(CO)_5W{=}CD_2$ to give a 16e η^1-carbene intermediate that rearranges to the η^2-carbene complex $[W(CO)_4(CD_2)]$ with side-on coordination of the carbene.

FINAL: (C) $[W(CO)_4(CD_2)]$ (η^2-carbene complex)

SHORTCUT / EXAM TRICK

Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

COMMON MISTAKE

Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.

EXAM TIP

Fischer C is attacked by nucleophiles; Schrock C by electrophiles. Carbynes M≡CR are Fischer-type.

MEMORY TRICK

Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Why the Other Options Are Wrong

Correct answer: **C**

A $D_2C=CD_2$

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (C). See worked explanation.

B $D_3C–CD_3$

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (C). See worked explanation.

D $[W(CO)_4]=CD_2$ (16e carbene)

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (C). See worked explanation.

Q119

Reaction of $Na[Mn(CO)_5]$ with $H_2C=CH-CH_2Cl$ gives A along with NaCl. Photolysis of compound A results in compound B together with elimination of CO. The correct structural formulations of compounds A and B are respectively

A $(CO)_5Mn–CH_2–CH=CH_2$ and $(CO)_4Mn(\eta^3\text{-allyl})$

B $(CO)_5Mn–CH_2–CH=CH_2$ and $(CO)_4Mn–CH_2–CH=CH_2$

C $(CO)_4Mn(\eta^3\text{-allyl})$ and $(CO)_5Mn–CH_2–CH=CH_2$

D $Na[(CO)_4Mn–CH_2–CH=CH_2]$ and $(CO)_4Mn(\eta^3\text{-allyl})$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Fischer vs Schrock carbenes, M=C reactivity

PYQ FREQUENCY
Moderate · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Correct Answer A $(CO)_5Mn–CH_2–CH=CH_2$ and $(CO)_4Mn(\eta^3\text{-allyl})$

CONCEPT

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

↓

LOGIC / WORKING

S_N2 displacement of Cl^- by $[Mn(CO)_5]^-$ gives A = σ-allyl complex $(CO)_5Mn–CH_2CH=CH_2$. Photolysis removes one CO, allowing the allyl to haptotropically shift to η^3, giving B = $(CO)_4Mn(\eta^3\text{-allyl})$.

FINAL: (A) $(CO)_5Mn–CH_2–CH=CH_2$ and $(CO)_4Mn(\eta^3\text{-allyl})$

SHORTCUT / EXAM TRICK

Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

COMMON MISTAKE

Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.

EXAM TIP

Fischer C is attacked by nucleophiles; Schrock C by electrophiles. Carbynes M≡CR are Fischer-type.

MEMORY TRICK

Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Why the Other Options Are Wrong

Correct answer: **A**

B $(CO)_5Mn–CH_2–CH=CH_2$ and $(CO)_4Mn–CH_2–CH=CH_2$

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See worked explanation.

C $(CO)_4Mn(\eta^3\text{-allyl})$ and $(CO)_5Mn–CH_2–CH=CH_2$

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See worked explanation.

D $Na[(CO)_4Mn–CH_2–CH=CH_2]$ and $(CO)_4Mn(\eta^3\text{-allyl})$

Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (A). See worked explanation.

Q130 The correct **increasing order** of C–C bond length in the following molecules: ethane (A), ethylene (B), acetylene (C), ferrocene ring C–C (D)

A. C < B < D < A

B. C < B < A < D

C. D < C < B < A

D. C < D < B < A

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Fischer vs Schrock carbenes, M=C reactivity

PYQ FREQUENCY
Moderate · 7 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Correct Answer D C < D < B < A

CONCEPT

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

↓

LOGIC / WORKING

- C≡C (1.20 Å) < C(ferrocene, aromatic 1.43 Å) < C=C (1.34 Å) < C–C (1.54 Å). So: C < D < B < A.

FINAL: (D) C < D < B < A

SHORTCUT / EXAM TRICK

Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

COMMON MISTAKE

Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.

EXAM TIP

Fischer C is attacked by nucleophiles; Schrock C by electrophiles. Carbynes M≡CR are Fischer-type.

MEMORY TRICK

Fischer has a heteroatom helper (electrophilic C); Schrock's carbon is a nucleophile.

Why the Other Options Are Wrong

Correct answer: D

A C < B < D < A
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (D). See worked explanation.

B C < B < A < D
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (D). See worked explanation.

C D < C < B < A
Inconsistent with the Fischer vs Schrock electronic description; the correct choice is (D). See worked explanation.

TOPIC REVISION

Carbenes, Carbynes & M=C

8 PYQs · Last-minute revision

TOPIC SUMMARY

Fischer carbenes: low-valent late metal + π-donor heteroatom (OR/NR_2), electrophilic carbene C. Schrock alkylidenes: high-valent early metal, no heteroatom, nucleophilic carbene C and active in metathesis.

IMPORTANT FORMULA SHEET

Fischer: $(CO)_5W{=}C(OMe)Ph$

Schrock: $Ta(=CH\text{-}tBu)(CH_2\text{-}tBu)_3$

Fischer C: δ+ (electrophilic)

- Schrock C: δ− (nucleophilic)

FREQUENTLY ASKED CONCEPTS

Fischer carbene
Schrock alkylidene
carbyne M≡CR

- metathesis-active carbenes

COMMON MISTAKES & QUICK NOTES

Watch out:
Swapping the electrophilic/nucleophilic carbene carbon between Fischer and Schrock.
Last-minute:
Heteroatom on the carbene carbon ⇒ Fischer (electrophilic). Just H/alkyl + early metal ⇒ Schrock (nucleophilic).

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q35 Q69 Q72 Q79 Q105 Q115 Q119 Q130

Expect **2 question(s)** next session on **Fischer vs Schrock carbenes, M=C reactivity.**

TOPIC 6

Oxidative Addition & Reductive Elimination

9 questions · Easy 0 | Medium 9 | Hard 0 · PYQ frequency: High

Q1

The oxidative addition and reductive elimination steps are favoured by

A. Electron rich metal centres.

B. Electron deficient metal centers

C. Electron deficient and electron rich metal centers respectively.

D. Electron rich and electron deficient metal centers respectively

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Oxidative Addition & Reductive Elimination

Correct Answer D Electron rich and electron deficient metal centers respectively

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

- Oxidation of metal is easier for electron rich systems, so electron rich metals undergo oxidative addition and as reduction is easier for electron-deficient metal, so it undergoes reductive elimina tion.

FINAL: (D) Electron rich and electron deficient metal centers respectively

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **D**

A **Electron rich metal centres.**

Why (D) is the key — Oxidation of metal is easier for electron rich systems, so electron rich metals undergo oxidative addition and as reduction is easier for electron-deficient metal, so it undergoes reductive elimina tion. Explanation as extracted from the printed page; notation may be imperfect.

B **Electron deficient metal centers**

Option (B) is ruled out by the same reasoning: Oxidation of metal is easier for electron rich systems, so electron rich metals undergo oxidative addition and as reduction is easier for electron-deficient…

C **Electron deficient and electron rich metal centers respectively.**

Option (C) is ruled out by the same reasoning: Oxidation of metal is easier for electron rich systems, so electron rich metals undergo oxidative addition and as reduction is easier for electron-deficient…

Q31

Consider the following reaction mechanism The steps A, B and C, respectively, are

A. Oxidative addition; transmetallation; reductive elimination.

B. Oxidative addition; carbopalladation; β-hydride elimination.

C. Carbopalladation; transmetallation; reductive elimination.

D. Metal halogen exchange; transmetallation; metal extrusion.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Oxidative Addition & Reductive Elimination

Correct Answer A Oxidative addition; transmetallation; reductive elimination.

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

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Step (A) is O.A. because the oxidation state of the metal is increased by two units.

- Step(B) is transmetallation because the ligand is transferring from one metal to another metal. Step(C) is reductive elimination because the oxidation state of the metal is increased by two units

FINAL: (A) Oxidative addition; transmetallation; reductive elimination.

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **A**

B **Oxidative addition; carbopalladation; β-hydride elimination.**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See the worked explanation.

C **Carbopalladation; transmetallation; reductive elimination.**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See the worked explanation.

D **Metal halogen exchange; transmetallation; metal extrusion.**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See the worked explanation.

Q32

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

A $[Rh(CO)_2I_2]^-$

B $[Ir(PPh_3)_2(CO)Cl]$

C $[(\eta^2\text{-}CpRu(CO)_2]$

D $[(\eta^5\text{-}Cp_2Ti(Me)Cl]$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Correct Answer D $[(\eta^5\text{-}Cp_2Ti(Me)Cl]$

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

(a)$[Rh(CO)_2I_2]^-$ →16e- and a better coordinate for O.A.

(b) $[Ir(PPh_3)_2(CO)Cl]$ →16e- species (Vaska's complex) O.A. is possible.

(c) $[(\eta^2\text{-}CpRu(CO)_2]$ →16e- system O.A. is not possible because metal in high oxidation state.

(d) $[(\eta^5\text{-}Cp_2Ti(Me)Cl]$ →18e- species as such O.A. is not possible but after the dissociation of ligand 'CO', O.A. is possible.

FINAL: (D) $[(\eta^5\text{-}Cp_2Ti(Me)Cl]$

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **D**

A $[Rh(CO)_2I_2]^-$

Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

B $[Ir(PPh_3)_2(CO)Cl]$

Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

C $[(\eta^2\text{-}CpRu(CO)_2]$

Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

Q52

The typical electronic configurations of the transition metal centre for oxidative addition

A. d_0 and d_8

B. d_6 and d_8

C. d_8 and d_{10}

D. d_5 and d_{10}

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Oxidative Addition & Reductive Elimination

Correct Answer C d_8 and d_{10}

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

Most commonly the metal in the complexes in their low oxidation state with d_8 or d_{10} configuration undergo oxidative addition.

FINAL: (C) d_8 and d_{10}

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **C**

A d_0 and d_8

Why (C) is the key — Oxidative addition is typical of d^8 (Rh(I), Ir(I), Pd(II), Pt(II)) and d^{10} (Pd(0), Pt(0), Ni(0)) centres, which have a stable two-units-higher oxidation state.

B d_6 and d_8

Option (B) is ruled out by the same reasoning: Oxidative addition is typical of d^8 (Rh(I), Ir(I), Pd(II), Pt(II)) and d^{10} (Pd(0), Pt(0), Ni(0)) centres, which have a stable two-units-higher oxidation

D d_5 and d_{10}

Option (D) is ruled out by the same reasoning: Oxidative addition is typical of d^8 (Rh(I), Ir(I), Pd(II), Pt(II)) and d^{10} (Pd(0), Pt(0), Ni(0)) centres, which have a stable two-units-higher oxidation

Q65

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

A. $[Mn(CO)_5]^-$

B. $[(\eta^5\text{-}C_5H_5)MCO_3]^-$

C. $[IrCl(CO)(PPh_3)_2]$

D. $[(\eta^5\text{-}C_5H_5)_2ReH]$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Correct Answer C $[IrCl(CO)(PPh_3)_2]$

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

16 electron stable complex 18 electron stable complex $[IrCl(CO)(PPh_3)_2]$ is a 16 electron complex called as Vaska complex. Only show oxidative addition in the presence of H_2

FINAL: (C) $[IrCl(CO)(PPh_3)_2]$

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **C**

A **$[Mn(CO)_5]^-$**

Why (C) is the key — Vaska's complex, trans-$[IrCl(CO)(PPh_3)_2]$ (d^8, 16 e), adds H_2 oxidatively to give the Ir(III) dihydride; the anionic 18-electron species and the rhenium hydride do not.

B **$[(\eta^5\text{-}C_5H_5)MCO_3]^-$**

Option (B) is ruled out by the same reasoning: Vaska's complex, trans-$[IrCl(CO)(PPh_3)_2]$ (d^8, 16 e), adds H_2 oxidatively to give the Ir(III) dihydride; the anionic 18-electron species and the rhenium hydride…

D **$[(\eta^5\text{-}C_5H_5)_2ReH]$**

Option (D) is ruled out by the same reasoning: Vaska's complex, trans-$[IrCl(CO)(PPh_3)_2]$ (d^8, 16 e), adds H_2 oxidatively to give the Ir(III) dihydride; the anionic 18-electron species and the rhenium hydride…

Q82

The reductive elimination of Ar-R (coupled product) from A is facile when

A. R = CH_3

B. R = CH_2Ph

C. R CH_2COPh

D. R = CH_2CF_3

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Oxidative Addition & Reductive Elimination

Correct Answer A R = CH_3

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

- For reductive elimination, the eliminating group should be electron releasing group and also the eliminating product should be neutral.So, only Me group is electron releasing group among all the given option.

FINAL: (A) R = CH_3

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **A**

B **R = CH_2Ph**

Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See the worked explanation.

C **R CH_2COPh**

Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See the worked explanation.

D **R = CH_2CF_3**

Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See the worked explanation.

Q126 In the complex [Pd(L-L)(Me)(Ph)], the bisphosphine (L-L) that does not allow reductive elimination of PhMe is

A

B

C

D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Oxidative Addition & Reductive Elimination

Correct Answer D

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

According to reductive elimination reaction mechanism cis-complex can give the product but trans- complex is not suitable for reaction and does not give reductive elimination product. Since, ligand given in option (d) forms a trans-complex with Pd(II) due to the presence of flexible methylene ($-CH_{2}-$)

groups. Therefore, reductive elimination not occured.

- Actually formed but does not give reaction This can give reaction but not formed

FINAL: (D)

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **D**

A Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

B Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

C Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

Q133 For the following reaction (Vaska's complex + H_2), correct statement(s) is/are: (A) Oxidation state of Ir increases from I to III (B) Coordination number of Ir increases from 4 to 6 (C) The product is paramagnetic (D) H_2 adds in a cis fashion

A. A, B and D

B. B, C and D

C. A and C

D. A, C and D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Correct Answer A A, B and D

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

Oxidative addition of H_2 to Vaska's complex [IrCl(CO)(PPh_3)$_2$] (16e, Ir^I) gives [IrH_2Cl(CO)(PPh_3)$_2$] (18e, Ir^III). OS increases +I → +III (A✓), CN 4 → 6 (B✓), product is diamagnetic d^6 (C×), H_2 adds cis (D✓). A, B, D correct.

FINAL: (A) A, B and D

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **A**

B — **B, C and D**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See worked explanation.

C — **A and C**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See worked explanation.

D — **A, C and D**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (A). See worked explanation.

Q146

For the reaction of trans-$[IrX(CO)(PPh_3)_2]$ (X= F, Cl , Br , I) with O_2, correct order of variation of rate with X is

A. Br>I>F>Cl

B. F>Cl>Br>I

C. F≈Cl≈Br≈1

D. I>Br>Cl> F

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
OA/RE book-keeping, cis requirement, metal electron richness

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
OA opens two and oxidises two; RE closes two and needs a cis couple.

Correct Answer D I>Br>Cl> F

CONCEPT

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

↓

LOGIC / WORKING

- Electron withdrawing group present on the metal decreases the electron density and hence decreases the rate of oxidative addition because the rate of oxidative addition is directly proportional to the electron density on the metal.

FINAL: (D) I>Br>Cl> F

SHORTCUT / EXAM TRICK

OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

COMMON MISTAKE

Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.

EXAM TIP

Vaska's 16e Ir(I) → 18e Ir(III) on H_2 OA. Electron-rich metals oxidatively add; electron-poor reductively eliminate.

MEMORY TRICK

OA opens two and oxidises two; RE closes two and needs a cis couple.

Why the Other Options Are Wrong

Correct answer: **D**

A **Br>I>F>Cl**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

B **F>Cl>Br>I**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

C **F≈Cl≈Br≈1**
Inconsistent with the oxidation-state / electron-count book-keeping; the correct choice is (D). See the worked explanation.

TOPIC REVISION

Oxidative Addition & Reductive Elimination

9 PYQs · Last-minute revision

TOPIC SUMMARY

Oxidative addition (OA) raises oxidation state, coordination number and electron count each by 2; reductive elimination (RE) is the exact reverse and needs the two groups mutually cis.

IMPORTANT FORMULA SHEET

OA: ΔOS +2, ΔCN +2, Δe +2
RE: ΔOS −2, ΔCN −2, Δe −2
Vaska: $IrCl(CO)(PPh_3)_2$ (16e)

- Concerted OA retains stereochemistry

FREQUENTLY ASKED CONCEPTS

oxidative addition
reductive elimination
cis requirement

- Vaska's complex

COMMON MISTAKES & QUICK NOTES

Watch out:
Forgetting the coordination number also changes by 2, or letting trans groups reductively eliminate.
Last-minute:
OA: +2/+2/+2 (favoured by electron-rich ≤16e metals). RE: cis-only, favoured by bulky ligands and high OS.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q1 Q31 Q32 Q52 Q65 Q82 Q126 Q133 Q146

Expect **2 question(s)** next session on **OA/RE book-keeping, cis requirement, metal electron richness.**

TOPIC 7

Insertion, β-Elimination & Agostic

6 questions · Easy 0 | Medium 6 | Hard 0 · PYQ frequency: Moderate

Q15

The greater stability of $((CH_3)_3$ C-$CH_{2-})_4$ Ti(A) compared to that of $((CH_3)_2$CH-CH_2 -$)_4$ Ti(B) is due to

(A) Hyperconjugation present in complex (A)

(B) β-hydride elimination is not possible in complex (A)

(C) Steric protection of titanium from reactive species in complex (A)

(D) The stronger nature of Ti-C bond in complex (A).

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Migratory insertion, β-H elimination, agostic interaction

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Correct Answer B β-hydride elimination is not possible in complex (A)

CONCEPT

1,1-CO insertion gives an acyl (no OS change, opens a site); 1,2-alkene insertion grows a chain. β-Hydride elimination needs a β-H and a vacant cis site; an agostic M···H–C is a 3-centre–2-electron interaction.

↓

LOGIC / WORKING

- Neopentyl groups have no Î²-hydrogen, so the usual Î²-hydride elimination decomposition path is blocked; isobutyl groups have Î²-H and decompose readily.
- Therefore the answer is (B).

FINAL: (B) β-hydride elimination is not possible in complex (A)

SHORTCUT / EXAM TRICK

Stable alkyls have NO β-hydrogens (–CH_3, neopentyl, –CH_2SiMe_3, aryl).

COMMON MISTAKE

Choosing alkyls that contain β-H when stability is needed, or calling agostic a hydrogen bond.

EXAM TIP

CO insertion → acyl with no oxidation-state change; β-H elimination is the main alkyl decomposition route.

MEMORY TRICK

Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Why the Other Options Are Wrong

Correct answer: **B**

A

Hyperconjugation present in complex (A)

Why (B) is the key — Neopentyl groups have no Î²-hydrogen, so the usual Î²-hydride elimination decomposition path is blocked; isobutyl groups have Î²-H and decompose readily.

C

Steric protection of titanium from reactive species in complex (A)

Option (C) is ruled out by the same reasoning: Neopentyl groups have no Î²-hydrogen, so the usual Î²-hydride elimination decomposition path is blocked; isobutyl groups have Î²-H and decompose

D

The stronger nature of Ti-C bond in complex (A).

Option (D) is ruled out by the same reasoning: Neopentyl groups have no Î²-hydrogen, so the usual Î²-hydride elimination decomposition path is blocked; isobutyl groups have Î²-H and decompose

Q37

The reaction, $[(CO)_5 Mn (Me)]^+ CO \rightarrow [(CO)_5 Mn \{C(O)Me\}]$ is an example for

A. oxidative addition

B. electrophilic substitution

C. nucleophilic substitution

D. migratory insertion

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Migratory insertion, β-H elimination, agostic interaction

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Correct Answer D migratory insertion

CONCEPT

1,1-CO insertion gives an acyl (no OS change, opens a site); 1,2-alkene insertion grows a chain. β-Hydride elimination needs a β-H and a vacant cis site; an agostic M···H–C is a 3-centre–2-electron interaction.

↓

LOGIC / WORKING

- The above reaction is an example of 1,1-migratory insertion

FINAL: (D) migratory insertion

SHORTCUT / EXAM TRICK

Stable alkyls have NO β-hydrogens (–CH_3, neopentyl, –CH_2SiMe_3, aryl).

COMMON MISTAKE

Choosing alkyls that contain β-H when stability is needed, or calling agostic a hydrogen bond.

EXAM TIP

CO insertion → acyl with no oxidation-state change; β-H elimination is the main alkyl decomposition route.

MEMORY TRICK

Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Why the Other Options Are Wrong

Correct answer: **D**

A **oxidative addition**

Why (D) is the key — The methyl group migrates onto an adjacent coordinated CO to give the acetyl ligand; the vacant site is then filled by external CO — CO migratory insertion.

B **electrophilic substitution**

Option (B) is ruled out by the same reasoning: The methyl group migrates onto an adjacent coordinated CO to give the acetyl ligand; the vacant site is then filled by external CO — CO migratory

C **nucleophilic substitution**

Option (C) is ruled out by the same reasoning: The methyl group migrates onto an adjacent coordinated CO to give the acetyl ligand; the vacant site is then filled by external CO — CO migratory

Q68

The final product in the reaction of [Cp ThH] with CO in an equimolar ratio is

A

B

C

D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Migratory insertion, β-H elimination, agostic interaction

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Correct Answer D

CONCEPT

1,1-CO insertion gives an acyl (no OS change, opens a site); 1,2-alkene insertion grows a chain. β-Hydride elimination needs a β-H and a vacant cis site; an agostic M···H–C is a 3-centre–2-electron interaction.

↓

LOGIC / WORKING

- It is a kind of insertion reaction of M-H (metalhydride bond between CO)

FINAL: (D)

SHORTCUT / EXAM TRICK

Stable alkyls have NO β-hydrogens (–CH_3, neopentyl, –CH_2SiMe_3, aryl).

COMMON MISTAKE

Choosing alkyls that contain β-H when stability is needed, or calling agostic a hydrogen bond.

EXAM TIP

CO insertion → acyl with no oxidation-state change; β-H elimination is the main alkyl decomposition route.

MEMORY TRICK

Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Why the Other Options Are Wrong

Correct answer: **D**

A Inconsistent with the migratory-insertion / β-H elimination requirement; the correct choice is (D). See the worked explanation.

B Inconsistent with the migratory-insertion / β-H elimination requirement; the correct choice is (D). See the worked explanation.

C Inconsistent with the migratory-insertion / β-H elimination requirement; the correct choice is (D). See the worked explanation.

Q74

The β-hydrogen elimination will be facile in

A

B

C

D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Migratory insertion, β-H elimination, agostic interaction

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Correct Answer A

CONCEPT

1,1-CO insertion gives an acyl (no OS change, opens a site); 1,2-alkene insertion grows a chain. β-Hydride elimination needs a β-H and a vacant cis site; an agostic M···H–C is a 3-centre–2-electron interaction.

↓

LOGIC / WORKING

β-hydrogen elimination mechanism.
Since C-H, σ bond pair electron donate to the metal for this elimination. Therefore, as the donor ability of the σ electron pair increases rate of β-elimination increases.
In option D, the unit is anti-periplanar and thus β-H elimination not possible.
For β hydride elimination reaction β hydrogen should be closer to metal in option B,C all hydrogen atoms are far so elimination not possible (sp_2 carbon)

So, more facile β-elimination occur in option (a)
Electron donor ability at a bond is C-H (sp^3) > C-H (sp_2) >C-H (sp)

- So, more facile β-elimination occur in option (a)

FINAL: (A)

SHORTCUT / EXAM TRICK

Stable alkyls have NO β-hydrogens (–CH_3, neopentyl, –CH_2SiMe_3, aryl).

COMMON MISTAKE

Choosing alkyls that contain β-H when stability is needed, or calling agostic a hydrogen bond.

EXAM TIP

CO insertion → acyl with no oxidation-state change; β-H elimination is the main alkyl decomposition route.

MEMORY TRICK

Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Why the Other Options Are Wrong

Correct answer: **A**

B Inconsistent with the migratory-insertion / β-H elimination requirement; the correct choice is (A). See the worked explanation.

C Inconsistent with the migratory-insertion / β-H elimination requirement; the correct choice is (A). See the worked explanation.

D Inconsistent with the migratory-insertion / β-H elimination requirement; the correct choice is (A). See the worked explanation.

Q78

The following statements are given regarding the agostic interaction C-H----Ir observed in $[Ir(Ph_3P)_3Cl]$. (A) Upfield shift of C-H proton in 1H NMR spectrum (B) Increased acid character of C-H (C) ῡ co- in IR spectrum shifts to higher wavenumber The correct answer is/are:

A. A and C

B. B and C

C. A and B

D. C only

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Migratory insertion, β-H elimination, agostic interaction

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Correct Answer C A and B

CONCEPT

1,1-CO insertion gives an acyl (no OS change, opens a site); 1,2-alkene insertion grows a chain. β-Hydride elimination needs a β-H and a vacant cis site; an agostic M···H–C is a 3-centre–2-electron interaction.

↓

LOGIC / WORKING

Due to this agostic interaction C-H bond becomes weak and hydrogen flanked in between M and C.As proton come in contact with metal becomes shielded and upfield shift in 1H NMR.

- Since $v \propto K$,bond strength of C-H bond decreases, in IR spectrum shift to lower wave number.

FINAL: (C) A and B

SHORTCUT / EXAM TRICK

Stable alkyls have NO β-hydrogens (–CH_3, neopentyl, –CH_2SiMe_3, aryl).

COMMON MISTAKE

Choosing alkyls that contain β-H when stability is needed, or calling agostic a hydrogen bond.

EXAM TIP

CO insertion → acyl with no oxidation-state change; β-H elimination is the main alkyl decomposition route.

MEMORY TRICK

Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Why the Other Options Are Wrong

Correct answer: **C**

A

A and C

Why (C) is the key — An agostic C–H···M interaction moves the proton upfield in ^{1}H NMR and weakens/acidifies the C–H bond; [Ir(PPh$_3$)$_3$Cl] has no CO, so statement C does not apply. A and B.

B

B and C

Option (B) is ruled out by the same reasoning: An agostic C–H···M interaction moves the proton upfield in ^{1}H NMR and weakens/acidifies the C–H bond; [Ir(PPh$_3$)$_3$Cl] has no CO, so statement C does not apply. A…

D

C only

Option (D) is ruled out by the same reasoning: An agostic C–H···M interaction moves the proton upfield in ^{1}H NMR and weakens/acidifies the C–H bond; [Ir(PPh$_3$)$_3$Cl] has no CO, so statement C does not apply. A…

Q86

For the reaction of $[Fe(\eta^5\text{-}C_5H_5)(CH_3)(CO)_2]$ with PMe_3, the main intermediate is

A $[Fe(\eta^5\text{-}C_5H_5)(CH_3)(CO)_2(PMe_3)]$

B $[Fe(\eta^5\text{-}C_5H_5)(COCH_3)(CO)]$

C $[Fe(\eta^3\text{-}C_5H_5)(CH_3)(CO)_2]$

D) $[Fe(\eta^3\text{-}C_5H_5)(COCH_3)(CO)(PMe_3)]$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Migratory insertion, β-H elimination, agostic interaction

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Correct Answer B $[Fe(\eta^5\text{-}C_5H_5)(COCH_3)(CO)]$

CONCEPT

1,1-CO insertion gives an acyl (no OS change, opens a site); 1,2-alkene insertion grows a chain. β-Hydride elimination needs a β-H and a vacant cis site; an agostic M···H–C is a 3-centre–2-electron interaction.

↓

LOGIC / WORKING

- Example of migratory insertion reaction in which alkyl group insert to CO. A new ligand create acycl a vaccancy is created which is occupied by new ligand.

FINAL: (B) $[Fe(\eta^5\text{-}C_5H_5)(COCH_3)(CO)]$

SHORTCUT / EXAM TRICK

Stable alkyls have NO β-hydrogens (–CH_3, neopentyl, –CH_2SiMe_3, aryl).

COMMON MISTAKE

Choosing alkyls that contain β-H when stability is needed, or calling agostic a hydrogen bond.

EXAM TIP

CO insertion → acyl with no oxidation-state change; β-H elimination is the main alkyl decomposition route.

MEMORY TRICK

Insert CO to make an acyl; remove the β-H to stop elimination; a C–H leaning on a hungry metal is agostic.

Why the Other Options Are Wrong

Correct answer: **B**

A $[Fe(\eta^5\text{-}C_5H_5)(CH_3)(CO)_2(PMe_3)]$

Why (B) is the key — The methyl migrates onto CO first, giving the 16-electron acetyl intermediate $[CpFe(COCH_3)(CO)]$, which PMe_3 then traps.

C $[Fe(\eta^3\text{-}C_5H_5)(CH_3)(CO)_2]$

Option (C) is ruled out by the same reasoning: The methyl migrates onto CO first, giving the 16-electron acetyl intermediate $[CpFe(COCH_3)(CO)]$, which PMe_3 then

D) $[Fe(\eta^3\text{-}C_5H_5)(COCH_3)(CO)(PMe_3)]$

Option (D) is ruled out by the same reasoning: The methyl migrates onto CO first, giving the 16-electron acetyl intermediate $[CpFe(COCH_3)(CO)]$, which PMe_3 then

TOPIC REVISION

Insertion, β-Elimination & Agostic

6 PYQs · Last-minute revision

TOPIC SUMMARY

1,1-CO insertion gives an acyl (no OS change, opens a site); 1,2-alkene insertion grows a chain. β-Hydride elimination needs a β-H and a vacant cis site; an agostic M···H–C is a 3-centre–2-electron interaction.

IMPORTANT FORMULA SHEET

1,1-CO insertion → M–C(=O)R (acyl)
1,2-alkene insertion → M–CH_2CH_2R
β-H elim needs syn-coplanar M–C–C–H
- Agostic = 3c–2e M···H–C

FREQUENTLY ASKED CONCEPTS

migratory insertion
β-hydride elimination
stable alkyl design
- agostic interaction

COMMON MISTAKES & QUICK NOTES

Watch out:
Choosing alkyls that contain β-H when stability is needed, or calling agostic a hydrogen bond.
Last-minute:
Stable alkyls have NO β-hydrogens (–CH_3, neopentyl, –CH_2SiMe_3, aryl).

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q15 Q37 Q68 Q74 Q78 Q86

Expect **1 question(s)** next session on **Migratory insertion, β-H elimination, agostic interaction.**

TOPIC 8

Homogeneous Catalysis

10 questions · Easy 0 | Medium 10 | Hard 0 · PYQ frequency: High

Q7

In the hydroformylation reaction, the intermediate $CH_3CH_2CH_2$ $Co(Co)_4$:

A. Forms are acyl intermediate $CH_3CH_2CH_2COCo\ (CO)_3$

B. Forms an adduct with an olefin reactant.

C. Reacts with H_2

D. Eliminates propane.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer A Forms are acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

During hydroformylation the intermediate CH_3-CH_2-CH_2-$Co(CO)_4$ gets transformed to acyl intermediate $CH_3CH_2CH_2$ -$COCo(CO)_3$

FINAL: (A) Forms are acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **A**

B **Forms an adduct with an olefin reactant.**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (A). See the worked explanation.

C **Reacts with H_2**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (A). See the worked explanation.

D **Eliminates propane.**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (A). See the worked explanation.

Q30

Consider the catalyst in column-I and reaction in column-II Column-I Column-II A [(R)-BINAP] Ru-2 i. Hydroformylation. B $[Rh(CO)_2I_2]^-$ ii. asymmetric hydrogenation C $[Pd(PPh_3)_4]$ iii. Asymmetric hydrogen transfer D iv heck coupling The best match of a catalyst of column-I with the reaction nuclear column-II is

A (A-ii), (B-i), (C-iv), (D-iii)

B (A-i), (B-ii), (C-iii), (D-iv)

C (A-iii), (B-i), (C-iv), (D-ii)

D (A-iv), (B-iii), (C-ii), (D-i)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer B (A-i), (B-ii), (C-iii), (D-iv)

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

$[Rh(CO)_2I_2]^-$ → Hydroformylation.

$[Pd(PPh_3)_4]$ → Heck coupling (It is a catalyst for Heck coupling)

FINAL: (B) (A-i), (B-ii), (C-iii), (D-iv)

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **B**

A **(A-ii), (B-i), (C-iv), (D-iii)**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See the worked explanation.

C **(A-iii), (B-i), (C-iv), (D-ii)**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See the worked explanation.

D **(A-iv), (B-iii), (C-ii), (D-i)**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See the worked explanation.

Q33

In hydrofomylation reaction using $[Rh(PPh_3)_2(CO)(H)]$ as the catalyst, addition of excess PPh_3, would

A. increase the rate of reaction

B. decrease the rate of reaction.

C. not influence of the rate of reaction

D. stop the reaction.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer B decrease the rate of reaction.

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

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18 electron species in excess PPh_3 it becomes 20 electron species but the active catalyst is 16 electron species. So, in presence of excess PPh_3 the rate of hydroformylation will be decreases.

FINAL: (B) decrease the rate of reaction.

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **B**

A **increase the rate of reaction**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See the worked explanation.

C **not influence of the rate of reaction**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See the worked explanation.

D **stop the reaction.**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See the worked explanation.

Q42

Which of the following in NOT suitable as catalyst for hydroformylation?

A. $HCo(CO)_4$

B. $HCo(CO)_3PBu_3$

C. $HRh(CO)(PPh_3)_3$

D. $H_2Rh(PPh_3)_2Cl$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer D $H_2Rh(PPh_3)_2Cl$

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

$HCo(CO)_4$, $HCo(CO)_3PBu_3$, $HRh(CO)(PPh_3)_3$. These all are the catalyst for hydroformylation process.

FINAL: (D) $H_2Rh(PPh_3)_2Cl$

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **D**

A $HCo(CO)_4$

Why (D) is the key — $HCo(CO)_4$, $HCo(CO)_3PBu_3$ and $HRh(CO)(PPh_3)_3$ are the classical hydroformylation catalysts; $H_2Rh(PPh_3)_2Cl$ is a hydrogenation intermediate (Wilkinson), not a carbonyl catalyst.

B $HCo(CO)_3PBu_3$

Option (B) is ruled out by the same reasoning: $HCo(CO)_4$, $HCo(CO)_3PBu_3$ and $HRh(CO)(PPh_3)_3$ are the classical hydroformylation catalysts; $H_2Rh(PPh_3)_2Cl$ is a hydrogenation intermediate (Wilkinson), not a…

C $HRh(CO)(PPh_3)_3$

Option (C) is ruled out by the same reasoning: $HCo(CO)_4$, $HCo(CO)_3PBu_3$ and $HRh(CO)(PPh_3)_3$ are the classical hydroformylation catalysts; $H_2Rh(PPh_3)_2Cl$ is a hydrogenation intermediate (Wilkinson), not a…

Q59

The rate of the reaction $Ni(CO)_4 + PPh_3$ $[Ni(CO)_3(PPh_3)]^+ CO$ depends on

A. Concentration of both the reactants

B. Concentration of $Ni(CO)_4$ only

C. Concentration of PPh_3 only

D. The steric bulk of PPh_3

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer B Concentration of $Ni(CO)_4$ only

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

- Substitution on the 18-electron $Ni(CO)_4$ is dissociative: rate = $k[Ni(CO)_4]$, independent of the phosphine concentration.
- Therefore the answer is (B).

FINAL: (B) Concentration of $Ni(CO)_4$ only

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **B**

A **Concentration of both the reactants**

Why (B) is the key — Substitution on the 18-electron $Ni(CO)_4$ is dissociative: rate = $k[Ni(CO)_4]$, independent of the phosphine concentration.

C **Concentration of PPh_3 only**

Option (C) is ruled out by the same reasoning: Substitution on the 18-electron $Ni(CO)_4$ is dissociative: rate = $k[Ni(CO)_4]$, independent of the phosphine

D **The steric bulk of PPh_3**

Option (D) is ruled out by the same reasoning: Substitution on the 18-electron $Ni(CO)_4$ is dissociative: rate = $k[Ni(CO)_4]$, independent of the phosphine

Q63

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

A. T-shaped $[Rh(PPh_3)_2Cl]$

B. Trigonal-planar $[Rh(PPh_3)_2Cl]^{2+}$

C. T-shaped $[Rh(H)(PPh_3)Cl]^{+}$

D. Trigonal-planar $[Rh(H)(PPh_3)_2]$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer A T-shaped $[Rh(PPh_3)_2Cl]$

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

$Rh(PPh_3)_3Cl$ is a Wilkinson catalyst in hydrogenation step one PPh_3 loss due to steric factor and form Rh $(PPh_3)_2Cl$ Shape = T-shaped

FINAL: (A) T-shaped $[Rh(PPh_3)_2Cl]$

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **A**

B **Trigonal-planar $[Rh(PPh_3)_2Cl]^{2+}$**

Why (A) is the key — After reductive elimination of the alkane the catalyst returns as the 14-electron T-shaped $[RhCl(PPh_3)_2]$, which re-adds H_2 (solvent completes the coordination sphere).

C **T-shaped $[Rh(H)(PPh_3)Cl]^{+}$**

Option (C) is ruled out by the same reasoning: After reductive elimination of the alkane the catalyst returns as the 14-electron T-shaped $[RhCl(PPh_3)_2]$, which re-adds H_2 (solvent completes the coordination…

D **Trigonal-planar $[Rh(H)(PPh_3)_2]$**

Option (D) is ruled out by the same reasoning: After reductive elimination of the alkane the catalyst returns as the 14-electron T-shaped $[RhCl(PPh_3)_2]$, which re-adds H_2 (solvent completes the coordination…

Q71 The role of copper salt as co-catalyst in Wacker process is

A. oxidation of Pd(0) by Cu(II)

B. oxidation of Pd(0) by Cu(I)

C. oxidation of Pd(II) by Cu(I)

D. oxidation of Pd(II) by Cu(II)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer A oxidation of Pd(0) by Cu(II)

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

$[PdCl_4]$-2+$C_2H_{4+}H_2O$ CH_3CHO+Pd+2HC_{1+2}Cl- Pd(II) Pd(0)

$2CuCl_{2+1}$/2 $O_{2+2}HCl \rightarrow 2CuCl_2 + H_2O$

FINAL: (A) oxidation of Pd(0) by Cu(II)

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **A**

B **oxidation of Pd(0) by Cu(I)**

Why (A) is the key — In the Wacker process Cu(II) reoxidises the Pd(0) formed after acetaldehyde release back to Pd(II); the Cu(I) produced is reoxidised by O_2.

C **oxidation of Pd(II) by Cu(I)**

Option (C) is ruled out by the same reasoning: In the Wacker process Cu(II) reoxidises the Pd(0) formed after acetaldehyde release back to Pd(II); the Cu(I) produced is reoxidised by

D **oxidation of Pd(II) by Cu(II)**

Option (D) is ruled out by the same reasoning: In the Wacker process Cu(II) reoxidises the Pd(0) formed after acetaldehyde release back to Pd(II); the Cu(I) produced is reoxidised by

Q110 **Consider the following statements, I and II: I: $[Rh(CO)_2I_2]^-$ catalytically converts CH_3I and CO to CH_3COI II: $[Rh(CO)_2I_2]^-$ is diamagnetic in nature The correct from the following is**

A. I and II are correct and II is an explanation of I

B. I and II are correct and II is not an explanation of I

C. I is correct and II is incorrect

D. I and II are incorrect

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer B I and II are correct and II is not an explanation of I

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

Statement I →$[Rh(CO)_2 I_2]^-$ Converts CH-I and CO into CH_3COI Statement → $[Rh(CO)_2 I_2]^-$ is diamagnetic in nature.
I and II are correct but II is not correct explanation of I.

- Correct explanation: Monsanto process occurs via oxidative reaction, migratory insertion and re ductive elimination reaction for that the starting compound must be square planar.

FINAL: (B) I and II are correct and II is not an explanation of I

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **B**

A **I and II are correct and II is an explanation of I**

Why (B) is the key — $[Rh(CO)_2I_2]^-$ is the Monsanto acetic-acid catalyst (I true) and, as a d^8 square-planar complex, is diamagnetic (II true); its diamagnetism is not the reason for its catalysis.

C **I is correct and II is incorrect**

Option (C) is ruled out by the same reasoning: $[Rh(CO)_2I_2]^-$ is the Monsanto acetic-acid catalyst (I true) and, as a d^8 square-planar complex, is diamagnetic (II true); its diamagnetism is not the reason for…

D **I and II are incorrect**

Option (D) is ruled out by the same reasoning: $[Rh(CO)_2I_2]^-$ is the Monsanto acetic-acid catalyst (I true) and, as a d^8 square-planar complex, is diamagnetic (II true); its diamagnetism is not the reason for…

Q136 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(O) is oxidized to Pd(II) by Cu(II) (C) Cu(II) promotes the reductive elimination correct answer is

A. A and C

B. B and C

C. A and B

D. B Only

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer D B Only

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

In Wacker process, a Co catalyst $CuCl_2$ which could re-oxidise Pd(0) back to Pd(II)

$[PdCl_4]$-2 +C_2H_4 +H_2O → CH_3CHO+ Pd+ 2HCl+2Cl- Pd + 2$CuCl_2$ + 2Cl-→$[PdCl_4]$-2 +2CuCl

2CuCl + ½ O_2 + 2HCl →→2$CuCl_2$ + H_2O C_2H_{4+1}/2 O_2 →CH_3CHO [CSIR DEC 2018]

FINAL: (D) B Only

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **D**

A **A and C**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (D). See the worked explanation.

B **B and C**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (D). See the worked explanation.

C **A and B**
Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (D). See the worked explanation.

Q155 The rate-determining step in the catalytic synthesis of acetic acid by the Monsanto process is

A Migratory insertion of CO into Rh–CH_3

B Oxidative addition of CH_3I to $[Rh(CO)_2I_2]^-$

C Reductive elimination to give CH_3COI

D Transmetalation of CH_3 from CH_3I

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Catalytic cycles and rate-determining steps

PYQ FREQUENCY
High · 8 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Correct Answer B Oxidative addition of CH_3I to $[Rh(CO)_2I_2]^-$

CONCEPT

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

↓

LOGIC / WORKING

In the Monsanto process, $[Rh(CO)_2I_2]^-$ undergoes oxidative addition of CH_3I as the rate-determining step (RDS). This is confirmed by the rate law: rate $\propto [Rh][CH_3I]$. Subsequent CO insertion and RE are faster.

FINAL: (B) Oxidative addition of CH_3I to $[Rh(CO)_2I_2]^-$

SHORTCUT / EXAM TRICK

Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I. Wacker key step = water on coordinated alkene.

COMMON MISTAKE

Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

EXAM TIP

Wilkinson $RhCl(PPh_3)_3$ is 16e and selective for less-hindered alkenes; Rh + bulky phosphine gives linear aldehydes.

MEMORY TRICK

Oxo adds CHO; Monsanto makes vinegar from MeOH+CO; Wacker uses a Pd–Cu redox team.

Why the Other Options Are Wrong

Correct answer: **B**

A **Migratory insertion of CO into Rh–CH_3**

Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See worked explanation.

C **Reductive elimination to give CH_3COI**

Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See worked explanation.

D **Transmetalation of CH_3 from CH_3I**

Inconsistent with the accepted catalytic cycle and its key step; the correct choice is (B). See worked explanation.

TOPIC REVISION

Homogeneous Catalysis

10 PYQs · Last-minute revision

TOPIC SUMMARY

Catalytic cycles thread the same elementary steps: ligand loss, oxidative addition, migratory insertion and reductive elimination. Wilkinson (hydrogenation), the oxo process (hydroformylation), Monsanto/Cativa (acetic acid) and Wacker (acetaldehyde) are the canonical cycles.

IMPORTANT FORMULA SHEET

Hydroformylation: alkene + CO + H_2 → RCHO

Monsanto: $CH_3OH + CO \rightarrow CH_3COOH$; cat. $[Rh(CO)_2I_2]^-$

Wacker: $C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3CHO$ ($PdCl_2/CuCl_2$)

Wilkinson: $RhCl(PPh_3)_3$ (16e)

FREQUENTLY ASKED CONCEPTS

hydroformylation
Monsanto/Cativa
Wacker process
- Wilkinson hydrogenation

COMMON MISTAKES & QUICK NOTES

Watch out:
Calling hydroformylation's product an alcohol, or naming CO insertion (not CH_3I OA) as the Monsanto slow step.

Last-minute:
Hydroformylation = aldehyde (one extra C). Monsanto RDS = OA of CH_3I.

Wacker key step = water on coordinated alkene.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q7 Q30 Q33 Q42 Q59 Q63 Q71 Q110 Q136 Q155

Expect **2 question(s)** next session on **Catalytic cycles and rate-determining steps.**

TOPIC 9

Olefin Metathesis & Polymerisation

2 questions · Easy 0 | Medium 2 | Hard 0 · PYQ frequency: Rare

Q8

In Ziegler-Natta catalysis the commonly used catalyst system is:

A. $TiCl_4$, $Al(C_2H_5)_3$

B. $(\eta^5\text{-}Cp)_2TiCl_2$, $Al(OEt)_3$

C. $VO(acac)_2$, $Al_2(CH_3)_6$

D. $TiCl_4$, BF_3

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Metathesis mechanism, Ziegler–Natta polymerisation

PYQ FREQUENCY
Rare · 2 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
A four-membered metallacycle swaps the alkene ends; Ziegler–Natta inserts monomers one at a time.

Correct Answer A $TiCl_4$, $Al(C_2H_5)_3$

CONCEPT

Olefin metathesis redistributes C=C through a metallacyclobutane (Chauvin mechanism, Grubbs/Schrock catalysts). Ziegler–Natta polymerises α-olefins by repeated 1,2-migratory insertion (Cossee–Arlman).

↓

LOGIC / WORKING

Ziegler-Natta catalyst is $TiCl_4$, $Al(C_2H_5)_3$ [CSIR DEC 2011]

FINAL: (A) $TiCl_4$, $Al(C_2H_5)_3$

SHORTCUT / EXAM TRICK

Metathesis = carbene chemistry (metallacyclobutane). Z–N = insertion chemistry (no radicals).

COMMON MISTAKE

Choosing metallacyclopentane for metathesis, or calling Ziegler–Natta a radical mechanism.

EXAM TIP

Grubbs catalysts are Ru carbenes; metallocene/MAO single-site systems give stereocontrolled polyolefins.

MEMORY TRICK

A four-membered metallacycle swaps the alkene ends; Ziegler–Natta inserts monomers one at a time.

Why the Other Options Are Wrong

Correct answer: **A**

B $(\eta^5\text{-Cp})_2TiCl_2$, $Al(OEt)_3$

Inconsistent with the metathesis / insertion mechanism; the correct choice is (A). See the worked explanation.

C $VO(acac)_2$, $Al_2(CH_3)_6$

Inconsistent with the metathesis / insertion mechanism; the correct choice is (A). See the worked explanation.

D $TiCl_4$, BF_3

Inconsistent with the metathesis / insertion mechanism; the correct choice is (A). See the worked explanation.

Q14 The catalyst involved in carrying out the metathesis of 1-butene to give ethylene and 3-hexene is:

A

B Na_2PdCl_4

C $Co_2(CO)_2$,H_2

D $RhCl(PPh_3)_2$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Metathesis mechanism, Ziegler–Natta polymerisation

PYQ FREQUENCY
Rare · 2 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
A four-membered metallacycle swaps the alkene ends; Ziegler–Natta inserts monomers one at a time.

Correct Answer A

CONCEPT

Olefin metathesis redistributes C=C through a metallacyclobutane (Chauvin mechanism, Grubbs/Schrock catalysts). Ziegler–Natta polymerises α-olefins by repeated 1,2-migratory insertion (Cossee–Arlman).

↓

LOGIC / WORKING

.

Explanation:

- Option A is Ruthenium(II) carbenoid complexes, also known as Grubb's Catalysts, they are widely used for olefin methathesis.

FINAL: (A)

SHORTCUT / EXAM TRICK

Metathesis = carbene chemistry (metallacyclobutane). Z–N = insertion chemistry (no radicals).

COMMON MISTAKE

Choosing metallacyclopentane for metathesis, or calling Ziegler–Natta a radical mechanism.

EXAM TIP

Grubbs catalysts are Ru carbenes; metallocene/MAO single-site systems give stereocontrolled polyolefins.

MEMORY TRICK

A four-membered metallacycle swaps the alkene ends; Ziegler–Natta inserts monomers one at a time.

Why the Other Options Are Wrong

Correct answer: **A**

B Na_2PdCl_4

Inconsistent with the metathesis / insertion mechanism; the correct choice is (A). See the worked explanation.

C $Co_2(CO)_2$,H_2

Inconsistent with the metathesis / insertion mechanism; the correct choice is (A). See the worked explanation.

D $RhCl(PPh_3)_2$

Inconsistent with the metathesis / insertion mechanism; the correct choice is (A). See the worked explanation.

TOPIC REVISION

Olefin Metathesis & Polymerisation

2 PYQs · Last-minute revision

TOPIC SUMMARY

Olefin metathesis redistributes C=C through a metallacyclobutane (Chauvin mechanism, Grubbs/Schrock catalysts). Ziegler–Natta polymerises α-olefins by repeated 1,2-migratory insertion (Cossee–Arlman).

IMPORTANT FORMULA SHEET

Metathesis: $M{=}CR_2$ + alkene ⇌ metallacyclobutane

Grubbs: Ru=CHPh carbene

Z–N: $TiCl_4$ / $AlEt_3$ (Cossee–Arlman)

Single-site: Cp_2ZrCl_2 / MAO

FREQUENTLY ASKED CONCEPTS

Chauvin mechanism

metallacyclobutane

Ziegler–Natta

- stereoregular polymers

COMMON MISTAKES & QUICK NOTES

Watch out:

Choosing metallacyclopentane for metathesis, or calling Ziegler–Natta a radical mechanism.

Last-minute:

Metathesis = carbene chemistry (metallacyclobutane). Z–N = insertion chemistry (no radicals).

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q8 Q14

Expect **1 question(s)** next session on **Metathesis mechanism, Ziegler–Natta polymerisation.**

TOPIC 10

Metal Clusters & M–M Bonding

36 questions · Easy 0 | Medium 0 | Hard 36 · PYQ frequency: Very High

Q6

In the $H_2Ru_6(CO)_{18}$ cluster, containing 8-coordinated Ru centers, the hydrogen atoms are

A. Both terminal

B. One terminal and the other bridging

C. Both bridging between two Ru centers

D. Both bridging between three Ru centers.

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer D Both bridging between three Ru centers.

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

Electron cluster $H_2Ru_6(CO)_{18}$ displays a distorted octahedral metal geometry.

- Here each hydride ligand is connected to 3-Ru atoms.

FINAL: (D) Both bridging between three Ru centers.

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **D**

A **Both terminal**

Why (D) is the key — In $H_2Ru_6(CO)_{18}$ the hydrides cap triangular faces of the octahedron (μ_3-H), which is what makes the Ru centres formally eight-coordinate.

B **One terminal and the other bridging**

Option (B) is ruled out by the same reasoning: In $H_2Ru_6(CO)_{18}$ the hydrides cap triangular faces of the octahedron (μ_3-H), which is what makes the Ru centres formally

C **Both bridging between two Ru centers**

Option (C) is ruled out by the same reasoning: In $H_2Ru_6(CO)_{18}$ the hydrides cap triangular faces of the octahedron (μ_3-H), which is what makes the Ru centres formally

Q12

The number of metal-metal bonds in the dimers, $[CpFe(CO)(NO)]_2$ and $[CpMo(CO)_3]_2$ respectively, are

A. two and two

B. two and three

C. one and two

D. zero and one

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer D zero and one

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

. $[CpFe(CO)(NO)]_2$ Step-1: Determine the total valence electron (TVE) = A

A=[5+8+2+3]×2=[18]×2=36 Step-2: B=(18n –A) where n number of metal.
B (2×18)-36 =36-36=0 No metal-metal bond found. $[CpMo(CO)_3]_2$ Step-1: A

[5+6+2×3]×2=[17]×2=34 Step-2: B= (18n-A)=2×18-34 = 36-34 = 2 Step-3: B/2 gives the total number of M-M bonds in the complex B =2/2=1 In this complex, the total number of M-M bonds is one

FINAL: (D) zero and one

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **D**

A — **two and two**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

B — **two and three**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

C — **one and two**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

Q21 The cluster having arachno type structure is:

A $[Os_5(CO)_{16}]$

B $[Os_3(CO)_{12}]$

C $[Ir_4(CO)_{12},]$

D $[Rh_6(CO)_{16}]$ Corret answer is (b) $[Os_3(CO)_{12}]$

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B $[Os_3(CO)_{12}]$

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

FINAL: (B) $[Os_3(CO)_{12}]$

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A $[Os_5(CO)_{16}]$

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See worked explanation.

C $[Ir_4(CO)_{12},]$

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See worked explanation.

D $[Rh_6(CO)_{16}]$ Corret answer is (b) $[Os_3(CO)_{12}]$

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See worked explanation.

Q23

The reaction $3[Rh_4(CO)_{12}] \rightarrow 2[Rh_6(CO)_{16}] + 4CO$ [25°C, 500 atm CO] is:

A Exothermic as more metal-metal bonds are formed.

B Endothermic as stronger metal-carbonyl bonds are cleaved while weaker metal-metal bonds are formed.

C Is entropically favorable but enthalpically unfavorable such that (ΔG=0)

D Thermodynamically unfavourable (ΔG>0). Because metal carbonyls are stronger bond , to break this bond huge amount of energy are required. But metal-metal bonds are weaker bond. So, reaction is endothermic and enthalpy predominant and entropy unfavourable.

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B Endothermic as stronger metal-carbonyl bonds are cleaved while weaker metal-metal bonds are formed.

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

- .

FINAL: (B) Endothermic as stronger metal-carbonyl bonds are cleaved while weaker metal-metal bonds are formed.

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A **Exothermic as more metal-metal bonds are formed.**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

C **Is entropically favorable but enthalpically unfavorable such that (ΔG=0)**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

D **Thermodynamically unfavourable (ΔG>0). Because metal carbonyls are stronger bond , to break this bond huge amount of energy are required. But metal-metal bonds are weaker bond. So, reaction is endothermic and enthalpy predominant and entropy unfavourable.**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

Q28

In the cluster $[Co_3(CH)(CO)_9]$ obeying 18e rule, the number of metal-metal bonds and the bridging ligands respectively, are

A. 3 and 1 CH

B. 0 and 3 CO

C. 3 and 1 CO

D. 6 and 1 CH

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A 3 and 1 CH

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

The structure of cluster $[Co_3(CH)(CO)_9]$ So, the number of M-M bond = 3 and bridging ligand=1 CH 29 For the following molecule :
Consider the following statements about its room temperature spectral data.
$(A)_1$H NMR has singlets at 5.48 and 3.18 ppm $(B)_1$H NMR has multiplet at 5.48 and singlet at 3.18 ppm (C) IR has CO stretching bands at 1950 and 1860 cm-1 (D) IR has only one CO stretching band at 1900 cm-1 The correct pair of statement is, (a) A and C (b) B and C (c) A and D (d) B and D Correct answer is (a)
Since, the molecule is C_2 -symmetric. So, two CO's will give two absorption band in IR spectrum.

FINAL: (A) 3 and 1 CH

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B — **0 and 3 CO**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

C — **3 and 1 CO**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

D — **6 and 1 CH**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

Q34

Reactions A and B are, termed as respectively.

A. Insertion, Metathesis

B. Metathesis, insertion

C. Oxidative, addition, metathesis

D. Oxidative addition, insertion

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A Insertion, Metathesis

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

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Since $SnCl_2$ will behaves as a carbene and it insert into the M-M bond. So, it is a kind of insertion reaction. [CSIR JUNE 2013]

FINAL: (A) Insertion, Metathesis

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B **Metathesis, insertion**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

C **Oxidative, addition, metathesis**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

D **Oxidative addition, insertion**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

Q39

The number of metal-metal bonds in $[W_2(OPh)_6]$ is:

A 1

B 2

C 3

D 4

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer C 3

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

- $W_2(OR)_6$ compounds are ethane-like d^3–d^3 dimers with a W≡W triple bond ($\sigma^2\pi^4$).
- Therefore the answer is (C).

FINAL: (C) 3

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **C**

A — **1**

Why (C) is the key — $W_2(OR)_6$ compounds are ethane-like d^3–d^3 dimers with a W≡W triple bond ($\sigma^2\pi^4$).

B — **2**

Option (B) is ruled out by the same reasoning: $W_2(OR)_6$ compounds are ethane-like d^3–d^3 dimers with a W≡W triple bond

D — **4**

Option (D) is ruled out by the same reasoning: $W_2(OR)_6$ compounds are ethane-like d^3–d^3 dimers with a W≡W triple bond

Q40

The number of metal-metal bonds in $Ir_4(CO)_{12}$ is

A. 4

B. 6

C. 10

D. 12

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B 6

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

- A= TVE =60 B (n×18) – TVE= 72 – 60= 12 metal-metal bond= B/2 =12/2= 6 [CSIR DEC 2013]

FINAL: (B) 6

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A — **4**

Why (B) is the key — Six Ir–Ir bonds (b).

C — **10**

Option (C) is ruled out by the same reasoning: Six Ir–Ir bonds

D — **12**

Option (D) is ruled out by the same reasoning: Six Ir–Ir bonds

Q41

The bond order of the metal-metal bond in the dimeric complex [$Re_2Cl_4(PMe_2Ph)_4$] is

A. 4.0

B. 3.5

C. 3.0

D. 2.5

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B 3.5

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

- #$%#&)%* Bond order = = = 3.5 ((

FINAL: (B) 3.5

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A **4.0**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

C **3.0**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

D **2.5**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

Q43

In a cluster, $H_3CoRu_3(CO)_{12}$ total number of electrons considered to be involved in its formation is

A. 57

B. 60

C. 63

D. 72

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B 60

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$H_3CoRu_3(CO)_{12}$ = 3+9+8×3+12×2 = 60 electron

FINAL: (B) 60

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A **57**
Why (B) is the key — 60 cluster valence electrons (b).

C **63**
Option (C) is ruled out by the same reasoning: 60 cluster valence electrons

D **72**
Option (D) is ruled out by the same reasoning: 60 cluster valence electrons

Q44

Among the following clusters, A=[(H)Co_6 $(CO)_{15}$] B =[$(H)_2Os_6$ $(CO)_{18}$] C=[$(H)_2$ Os_5 $(CO)_{16}$] H is encapsulated in

A. A only

B. B only

C. B and C only

D. A and B only

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A A only

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[(H)Co_6(CO)_{15}]$ has H encapsulated.

The image shows solid state structure of $HCo_6(CO)_{15}$, obtained using neutron diffraction technique. The blue spheres are Co molecules, white spheres are CO ligands whereas black sphere is H, encapsulated in the crystal.

Source: Journal of the Chemical Society Dalton Transactions, Oct. 1999 (DOI: 10.1039/a_{810025}j)

FINAL: (A) A only

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B

B only

Why (A) is the key — $[HCo_6(CO)_1]^-$ has an interstitial hydride at the centre of the Co_6 octahedron; in $H_2Os_6(CO)_{18}$ and $H_2Os(CO)_{16}$ the hydrides bridge edges/faces on the surface.

C

B and C only

Option (C) is ruled out by the same reasoning: $[HCo_6(CO)_1]^-$ has an interstitial hydride at the centre of the Co_6 octahedron; in $H_2Os_6(CO)_{18}$ and $H_2Os(CO)_{16}$ the hydrides bridge edges/faces on the

D

A and B only

Option (D) is ruled out by the same reasoning: $[HCo_6(CO)_1]^-$ has an interstitial hydride at the centre of the Co_6 octahedron; in $H_2Os_6(CO)_{18}$ and $H_2Os(CO)_{16}$ the hydrides bridge edges/faces on the

Q45

The correct statement regarding terminal/bridging CO groups in solid $Co_4(CO)_{12}$ and $Ir_4(CO)_{12}$ is

A. both have equal number of bridging CO groups

B. number of bridging CO groups in $Co_4(CO)_{12}$ is 4

C. the number of terminal CO groups in $Co_4(CO)_{12}$ is 8

D. the number of bridging CO groups in $Ir_4(CO)_{12}$ is zero.

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer D the number of bridging CO groups in $Ir_4(CO)_{12}$ is zero.

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

- Due to increase in size of Ir, compared to Co, the Metal-Metal bond length also increases, thus the ability to form bridge carbonyl decreases with increase in M-M bond No of bridging CO= 3 No of bridging CO = 0 No of Terminal CO= 9 No of terminal CO =12 +

FINAL: (D) the number of bridging CO groups in $Ir_4(CO)_{12}$ is zero.

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **D**

A **both have equal number of bridging CO groups**

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

B **number of bridging CO groups in $Co_4(CO)_{12}$ is 4**

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

C **the number of terminal CO groups in $Co_4(CO)_{12}$ is 8**

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

Q53

The oxidation state of Ni and the number of metal–metal bonds in $[Ni_2(CO)_6]^{2-}$ consistent with the 18-electron rule are

A. Ni(–II), 1 bond

B. Ni(IV), 2 bonds

C. Ni(–I), 1 bond

D. Ni(IV), 3 bonds

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer C Ni(–I), 1 bond

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

2x + 0 (CO neutral) = −2 → x = −1, so Ni(−I). Each Ni(−I) (d^{10+1}): 10 + 2×2(CO each = 2e) + 1(M–M bond) = 10 + 6 + 1 = 17. Wait — Ni(−I) has 11e + 3×CO(6e) + M–M(1e) = 18e. One M–M bond is required.

FINAL: (C) Ni(–I), 1 bond

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **C**

A **Ni(–II), 1 bond**

Why (C) is the key — $[Ni_2(CO)_6]^{2-}$: each Ni(−I) has 11 + 6 = 17 electrons, so one Ni–Ni bond completes 18.

B **Ni(IV), 2 bonds**

Option (B) is ruled out by the same reasoning: $[Ni_2(CO)_6]^{2-}$: each Ni(−I) has 11 + 6 = 17 electrons, so one Ni–Ni bond completes

D **Ni(IV), 3 bonds**

Option (D) is ruled out by the same reasoning: $[Ni_2(CO)_6]^{2-}$: each Ni(−I) has 11 + 6 = 17 electrons, so one Ni–Ni bond completes

Q54 The compound $[Re_2(Me_2PPh)_2Cl_4]$ (M) having a configuration of σ π δ δ* can be oxidized to M and 2+ + +2 M . The formal metal-metal order in M ,M and M respectively, are

A. 3.0, 3.5 and 4.0

B. 3.5, 4.0 and 3.0

C. 4.0, 3.5 and 3.0

D. 3.0, 4.0 and 3.5 $[Re_2(Me_2PPh)_2Cl_4]$ = (M)

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A 3.0, 3.5 and 4.0

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

- Refer to the governing principle for this topic; the correct option follows directly from it.

FINAL: (A) 3.0, 3.5 and 4.0

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B **3.5, 4.0 and 3.0**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

C **4.0, 3.5 and 3.0**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

D **3.0, 4.0 and 3.5 $[Re_2(Me_2PPh)_2Cl_4]$ = (M)**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

Q56

1H NMR spectrum of $[\eta^5\text{-}C_5H_5Rh)(C_2H_4)_2]$ at -20°C shows a typical AA' XX' pattern in the olefinic region. On increasing the temperature to -70°C, the separate lines collapse into a single line which is due to

A. free rotation of the ethylene ligand about the metal-olefin bond

B. interamolecular exchange between the ethylene ligands

C. intermolecular exchange between the ethylene ligands

D. change in hapticity of the cyclopentadienyl ligand

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A free rotation of the ethylene ligand about the metal-olefin bond

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[\eta^5\text{-}C_5H_5Rh)(C_2H_4)_2]$ at -20°C shows a typical AA' XX' pattern in the olefinic region due to free rotation of the ethylene ligand about the metal-olefin bond

FINAL: (A) free rotation of the ethylene ligand about the metal-olefin bond

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B **interamolecular exchange between the ethylene ligands**

Why (A) is the key — Warming allows the ethylene ligands to rotate about the Rh–olefin axis, exchanging the inner and outer protons of each C_2H_4 and collapsing the AA′XX′ pattern into a singlet.

C **intermolecular exchange between the ethylene ligands**

Option (C) is ruled out by the same reasoning: Warming allows the ethylene ligands to rotate about the Rh–olefin axis, exchanging the inner and outer protons of each C_2H_4 and collapsing the AA′XX′ pattern…

D **change in hapticity of the cyclopentadienyl ligand**

Option (D) is ruled out by the same reasoning: Warming allows the ethylene ligands to rotate about the Rh–olefin axis, exchanging the inner and outer protons of each C_2H_4 and collapsing the AA′XX′ pattern…

Q61

The point group symmetries for trans-$[Cr(en)_2F_2]^+$ and $[TiCl_6]$ -3, respectively, are

A. D_4d and D_3d

B. D_3d and D_4d

C. D_4h and D_3h

D. D_3h and D_4h Correct answer is (*), none of the given option is correct . 62 $Co_4(CO)_{12}$ adopts the (a)closo-structure (b) nido-structure (c) arachno-structure (d) hypho-structure

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B D_3d and D_4d

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$Co_4(CO)_{12}$ TVE =36+ 24 = 60 PEC=TVE-(nx_{12})=60-48=12 PEC/2=12/2 = 6 = 4+2 (n+2=Nido)

FINAL: (B) D_3d and D_4d

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A — **D_4d and D_3d**

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

C — **D_4h and D_3h**

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

D — **D_3h and D_4h Correct answer is (*), none of the given option is correct . 62 $Co_4(CO)_{12}$ adopts the (a)closo-structure (b) nido-structure (c) arachno-structure (d) hypho-structure**

Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

Q67

According to Wade's rule, anion $C_2B_9H_{12}$ adopts

A. closo-structure

B. nido-structure

C. arachno-sturcture

D. hypho-structure

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B nido-structure

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

The $C_2B_9H_{12}$ is carborane anion.

$C_2B_9H_{12\text{-}1}$ follow wade rule as C ≡ BH ↓ ↓ (4e-) (4e-)

$C_2B_9H_{12\text{-}1} \equiv (BH)_2B_9H_{12\text{-}1} \equiv B_2H_2B_9H_{12\text{-}1} \equiv B_{11}H_{14\text{-}1}$ Now, $B_{11}H_{14\text{-}1}$ is equivalent to $B_{11}H_{15}$ neutral borane which follows the formula BnHn-4 which is the general formula of nidoborane.

$B_{11}H_{14\text{-}1} \equiv B_{11}H_{15} \equiv$ BnHn-4 ≡ Nido.

FINAL: (B) nido-structure

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A — **closo-structure**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

C — **arachno-sturcture**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

D — **hypho-structure**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

Q76

According to Wade's theory the anion $[B_{12}H_{12}]^{2-}$ adopts

A. closo-structure

B. arachno-structure

C. hypo-structure

D. nido-structure

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A closo-structure

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[B_{12}H_{12}]^{2-} \equiv [BnHn]^{2-}$ Therefore, it is closo structure

FINAL: (A) closo-structure

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B **arachno-structure**
Why (A) is the key — $[B_{12}H_{12}]^{2-}$ is closo (a).

C **hypo-structure**
Option (C) is ruled out by the same reasoning: $[B_{12}H_{12}]^{2-}$ is closo

D **nido-structure**
Option (D) is ruled out by the same reasoning: $[B_{12}H_{12}]^{2-}$ is closo

Q81

Total number of vertices in metal clusters $[Ru_6(C)(CO)_{17}]$ $[Os_5(C)(CO)_{15}]$ and $[Ru_5(C)(CO)_{16}]$ are 6, 5 and 5, respectively. The predicted structures of these complexes, respectively are

(A) closo, nido and nido

(B) closo, nido and arachno

(C) arachno, closo and nido

(D) arachno, nido and closo

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B closo, nido and arachno

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[Ru_6(C)(CO)_{17}]$ TEC =8×6+4+17×2 = 86 PEC= 86 - 6×12 = 14 PEC/2= 14/2 = 7 Therefore, 7=6+1=(n+1) closo $[Os_5(C)(CO)_{15}]$ TEC= 8×5+4 +15×2 = 74 PEC =74-12×5 PEC = 74-60= 14/2 =7= (5+2)=(n+2) .Therefore, nido $[Ru_5(C)(CO)_{16}]$ TEC= 8×5+4+16×2 TEC=76 PEC =76-60=16 PEC/2=16/2 =8= (5+3)=(n+3) Arachno

FINAL: (B) closo, nido and arachno

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A **closo, nido and nido**

Why (B) is the key — $Ru_6C(CO)_{17}$: 48 + 4 + 34 = 86 = 14n + 2 → closo; Os $C(CO)_1$: 40 + 4 + 30 = 74 = 14n + 4 → nido; Ru $C(CO)_{16}$: 76 = 14n + 6 → arachno.

C **arachno, closo and nido**

Option (C) is ruled out by the same reasoning: $Ru_6C(CO)_{17}$: 48 + 4 + 34 = 86 = 14n + 2 → closo; Os $C(CO)_1$: 40 + 4 + 30 = 74 = 14n + 4 → nido; Ru $C(CO)_{16}$: 76 = 14n + 6 →

D **arachno, nido and closo**

Option (D) is ruled out by the same reasoning: $Ru_6C(CO)_{17}$: 48 + 4 + 34 = 86 = 14n + 2 → closo; Os $C(CO)_1$: 40 + 4 + 30 = 74 = 14n + 4 → nido; Ru $C(CO)_{16}$: 76 = 14n + 6 →

Q88

Using Wade's rules predict the structure type of $[C_2B_5H_7]$

A. nido

B. closos

C. arachno

D. hypho

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B closos

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$C_2B_5H_7$ C ≡ BH $(BH)_2$ B_5H_7 ≡B_7H_9 ≡ (B_7H_7)-2, (closo)

- (BnHn -2)

FINAL: (B) closos

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A **nido**

Why (B) is the key — $C_2B\ H_7$: 7 vertices; skeletal electrons 2×3 (CH) + 5×2 (BH) = 16 = 8 pairs = n + 1 → closo (pentagonal bipyramid).

C **arachno**

Option (C) is ruled out by the same reasoning: $C_2B\ H_7$: 7 vertices; skeletal electrons 2×3 (CH) + 5×2 (BH) = 16 = 8 pairs = n + 1 → closo (pentagonal

D **hypho**

Option (D) is ruled out by the same reasoning: $C_2B\ H_7$: 7 vertices; skeletal electrons 2×3 (CH) + 5×2 (BH) = 16 = 8 pairs = n + 1 → closo (pentagonal

Q91

The number of valence electrons provided by $[Ru(CO)_3]$ fragment towards cluster bonding is

A. 1

B. 14

C. 6

D. 2

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer D 2

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

Number of electron involving in metal cluster = T.V.E - 12 T.V.E in $Ru(CO)_3$ = 8 + 6 = 14 (T.V.E = total valence electron)

- Hence, number of electron provided for cluster bonding = 14-12=2

FINAL: (D) 2

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **D**

A **1**

Why (D) is the key — $Ru(CO)_3$ supplies 8 + 6 − 12 = 2 electrons to cluster bonding (isolobal with BH).

B **14**

Option (B) is ruled out by the same reasoning: $Ru(CO)_3$ supplies 8 + 6 − 12 = 2 electrons to cluster bonding (isolobal with

C **6**

Option (C) is ruled out by the same reasoning: $Ru(CO)_3$ supplies 8 + 6 − 12 = 2 electrons to cluster bonding (isolobal with

Q94

The approximate positions of νco bands (cm) in the solid-state infrared spectrum and the Fe- Fe bond order in $[Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)(CO)]_2$ (non-centrosymmetric) respectively,are

A (2020, 1980, 1800) and one

B (2020, 1980, 1800) and two

C (2020, 1980) and one

D (2143) and one

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A (2020, 1980, 1800) and one

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

- -1 Terminal CO=2120-1850 cm -1 μ2 CO=1850-1750 cm 2 In this complex M-M bond order = 1 and two types of CO's terminal as well as -bridging. So, νco band lies in both range. [CSIR-JUNE 2016]

FINAL: (A) (2020, 1980, 1800) and one

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B **(2020, 1980, 1800) and two**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

C **(2020, 1980) and one**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

D **(2143) and one**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

Q98

The number of metal-metal bonds in $[Co_2Fe_2(CO)_{11}(\eta^4\text{-}PPh)_2]$ is

A. 3

B. 4

C. 5

D. 6

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B 4

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

TVE= 9×2 + 8×2 + 2×11 + (4×2)

- TVE = 18+ 16+ 22+8 = 64 = A B = (n ×18) –A = (4×18) – 64 = 72-64 =8 Number of metal-metal bond = B/2=8/2 = 4

FINAL: (B) 4

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A **3**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

C **5**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

D **6**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

Q102

The numbers of skeletal electrons present in the compounds $C_2B_3H_5$, $C_2B_4H_6$, and B_5H_9 are, respectively

A. 10, 12 and 12

B. 12, 14 and 14

C. 10, 12 and 14

D. 12, 14 and 12

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B 12, 14 and 14

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$C_2B_3H_5 = (B\text{-}H)_2B_3H_5 = B_5H_7$ Each B-H unit give 2 electron. For cage bonding.
Hence, 5(B-H)= 5×2= 10 electron. Each hydrogen one electron, Hence, 2H=2×1= 2 electron
Total =12 electrons $C_2B_4H_6 = (BH)_2B_4H_6 = B_6H_8$ $6(B\text{-}H)_6$×2=12e- 2H= 2×1=2e- Total = 14 electron B_5H_9 5(B-H)=5×2=10 4H = 4×1= 4 Total =14 e-

FINAL: (B) 12, 14 and 14

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A **10, 12 and 12**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

C **10, 12 and 14**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

D **12, 14 and 12**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See the worked explanation.

Q106

Heating a sample of $[(\eta^5\text{- } C_5H_5)Mo(CO)_3]_2$ results in the formation of $[(\eta^5\text{- } C_5H_5)Mo(CO)_2]$ with elimination of 2 equivalents of CO. The Mo- Mo bond order in this reaction changes from

A. 2 to 3.

B. 1 to 2

C. 1 to 3

D. 2 to 4

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer C 1 to 3

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

TVE = 10+12+12=34= A.
B= (n×18) -A B=(2×18)-34 = 36-34=2 Number of metal-metal bond =2/2=1 On heating :

- TVE 10+12+8 = 30 =A B=(n×18)-A= 36-30=6 Number of metal-metal bond = B/2=6/2 =3

FINAL: (C) 1 to 3

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **C**

A **2 to 3.**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See the worked explanation.

B **1 to 2**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See the worked explanation.

D **2 to 4**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See the worked explanation.

Q108 The number of bridging ligand(s) and metal-metal bond(s) present in the complex Ru_2 (η^5-Cp)$_2$(CO)$_2$($Ph_2PCH_2PPh_2$)] (obeys 18-electron rule), respectively, are

A. 0 and 1

B. 2 and 1

C. 3 and 1

D. 1 and 2

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer C 3 and 1

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

T.V.E. = 8×2 + 5×2 +2×2 + 4= 34 = A B = (nx_{18})-A=36-34= 2 Number of M-M bonds=B/2=2/2=1

3-bridging, 1-M-M bonds.

FINAL: (C) 3 and 1

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **C**

A **0 and 1**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See the worked explanation.

B **2 and 1**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See the worked explanation.

D **1 and 2**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See the worked explanation.

Q113 According to Wade's rules, the correct structural types of $[Co(\eta^5\text{-}C_5H_5)B_4H_8]$ and $[Mn(\eta^2\text{-}B_3H_8)(CO)_4]$ are

A. closo and nido

B. nido and arachno

C. closo and arachno

D. nido and nido

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B nido and arachno

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[Co(\eta^5\text{-}C_5H_5)B_4H_8]$ $Co(\eta^5\text{-}C_5H_5)$ ↔ BH 14 4 $[BHB_4H_8] = [B_5H_5]$-4 = [BnHn]-4 → nido $[Mn(\eta^2\text{-}B_3H_8)(CO)_4]$ $[Mn(CO)_4]$ ↔ $[BH_2]$ 7+8=15 5 $[B_3H_8BH_2] = [B_4H_{10}] = [B_4H_4]$-6 = [BnHn]-6 → Arachno

FINAL: (B) nido and arachno

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A — **closo and nido**

Why (B) is the key — [$CpCoB_4H_8$]: CpCo gives 2 e, four BH 8 e, four extra H 4 e = 14 = 2n + 4 for five vertices → nido. [$Mn(\eta^2\text{-}B_3H_8)(CO)_4$]: $Mn(CO)_4$ 3 e + B_3H_8 11 e = 14 = 2n + 6 for four vertices → arachno.

C — **closo and arachno**

Option (C) is ruled out by the same reasoning: [$CpCoB_4H_8$]: CpCo gives 2 e, four BH 8 e, four extra H 4 e = 14 = 2n + 4 for five vertices → nido. [$Mn(\eta^2\text{-}B_3H_8)(CO)_4$]: $Mn(CO)_4$ 3 e + B_3H_8 11 e = 14 = 2n + 6 for…

D — **nido and nido**

Option (D) is ruled out by the same reasoning: [$CpCoB_4H_8$]: CpCo gives 2 e, four BH 8 e, four extra H 4 e = 14 = 2n + 4 for five vertices → nido. [$Mn(\eta^2\text{-}B_3H_8)(CO)_4$]: $Mn(CO)_4$ 3 e + B_3H_8 11 e = 14 = 2n + 6 for…

Q114 The correct geometry of $[Rh_6C(CO)_{15}]^{-2}$ is

A. octahedron

B. pentagonal pyramid

C. trigonal prism

D. monocapped square pyramid

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer C trigonal prism

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[Rh_6C(CO)_{15}]$-2 TVE = 9×6 + 4 + 15×2 +2 =54+4+2+30 = 90 Hence, it has trigonal prism geometry.

FINAL: (C) trigonal prism

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **C**

A — **octahedron**

Why (C) is the key — $[Rh_6C(CO)_{1}]^{-}$ has 90 electrons (14n + 6), one more pair than the closo octahedron, and adopts a trigonal prism with the carbide at its centre.

B — **pentagonal pyramid**

Option (B) is ruled out by the same reasoning: $[Rh_6C(CO)_{1}]^{-}$ has 90 electrons (14n + 6), one more pair than the closo octahedron, and adopts a trigonal prism with the carbide at its

D — **monocapped square pyramid**

Option (D) is ruled out by the same reasoning: $[Rh_6C(CO)_{1}]^{-}$ has 90 electrons (14n + 6), one more pair than the closo octahedron, and adopts a trigonal prism with the carbide at its

Q120 The number of bonding molecular orbitals and the number of available skeletal electrons in $[B_6H_6]^{-2}$, respectively, are:

A 7 and 14

B 6 and 12

C 18 and 12

D 11 and 14

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A 7 and 14

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[B_6H_6]$-2 has 6 + 1 = 7 bonding molecular orbital $[B_6H_6]$-2 = B-H=2×6=12 e- for 2 negative charge, hence 12e- +2e- =14e-

FINAL: (A) 7 and 14

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B **6 and 12**

Why (A) is the key — closo-$[B_6H_6]^{2-}$: n + 1 = 7 bonding skeletal MOs filled by 6×2 + 2 = 14 skeletal electrons.

C **18 and 12**

Option (C) is ruled out by the same reasoning: closo-$[B_6H_6]^{2-}$: n + 1 = 7 bonding skeletal MOs filled by 6×2 + 2 = 14 skeletal

D **11 and 14**

Option (D) is ruled out by the same reasoning: closo-$[B_6H_6]^{2-}$: n + 1 = 7 bonding skeletal MOs filled by 6×2 + 2 = 14 skeletal

Q127

According to Wade's rules, the cluster type and geometry of $[Sn_9]$-4 , respectively, are

A. closo and tricapped trigonal prismatic

B. nido and monocapped square-antiprismatic

C. arachno and heptagonal bipyramidal

D. closo and monocapped square antiprismatic

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B nido and monocapped square-antiprismatic

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

Sn_{9-4} = 9×4+4=40 , thus it follow 4n+4. Hence, it has nido structure [CSIR JUNE 2018]

FINAL: (B) nido and monocapped square-antiprismatic

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A — **closo and tricapped trigonal prismatic**

Why (B) is the key — $[Sn_9]^{4-}$: 9×2 + 4 = 22 = 2n + 4 skeletal electrons → nido, a monocapped square antiprism (C_4v).

C — **arachno and heptagonal bipyramidal**

Option (C) is ruled out by the same reasoning: $[Sn_9]^{4-}$: 9×2 + 4 = 22 = 2n + 4 skeletal electrons → nido, a monocapped square antiprism

D — **closo and monocapped square antiprismatic**

Option (D) is ruled out by the same reasoning: $[Sn_9]^{4-}$: 9×2 + 4 = 22 = 2n + 4 skeletal electrons → nido, a monocapped square antiprism

Q131

Which of the following are NOT closo clusters?
$[\{Co(\eta^5\text{-}C_5H_5)\}_2(C_2B_6H_8)]$ (A),
$[Fe_2(CO)_6(C_2B_4H_6)]$ (B), $[B_6H_6]^{2-}$ (C), $[B_5H_9]$ (D)

A. A and B

B. B and D

C. A and C

D. C and D

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer B B and D

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[B_6H_6]^{2-}$ is closo (n+1=7 SEP); $[\{Co(Cp)\}_2(C_2B_6H_8)]$ is closo. $[Fe_2(CO)_6(C_2B_4H_6)]$ is nido and $[B_5H_9]$ is nido (n+2 SEP) — neither is closo. So B and D are NOT closo.

FINAL: (B) B and D

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **B**

A **A and B**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See worked explanation.

C **A and C**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See worked explanation.

D **C and D**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (B). See worked explanation.

Q142

The cluster type and geometry of the species $[Rh_9P(CO)_{21}]$-2 are

A. closo, tricapped trigonal prism

B. arachno, trigonal prism

C. nido, capped square antiprism

D. nido, bicapped trigonal prism

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer C nido, capped square antiprism

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[Rh_9P(CO)_{21}]^{-2}$ → TEC = 9×9+5+2×21+2=130 PEC=130 - 9×12=22 PEC/2 = 22/2 =11→ 9+2=(n+2)=nido

FINAL: (C) nido, capped square antiprism

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **C**

A **closo, tricapped trigonal prism**

Why (C) is the key — $[Rh_9P(CO)_{21}]^{2-}$: 9×9 + 5 + 42 + 2 = 130 = 14n + 4 for n = 9 → nido, a monocapped square antiprism with the phosphide at its centre.

B **arachno, trigonal prism**

Option (B) is ruled out by the same reasoning: $[Rh_9P(CO)_{21}]^{2-}$: 9×9 + 5 + 42 + 2 = 130 = 14n + 4 for n = 9 → nido, a monocapped square antiprism with the phosphide at its

D **nido, bicapped trigonal prism**

Option (D) is ruled out by the same reasoning: $[Rh_9P(CO)_{21}]^{2-}$: 9×9 + 5 + 42 + 2 = 130 = 14n + 4 for n = 9 → nido, a monocapped square antiprism with the phosphide at its

Q145

The number of Ni-Ni bonds in $[CpNi(\mu\text{-}PPh_2)]_2$ complex obeying the 18 electron rule is

A. 0

B. 1

C. 2

D. 3

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer A 0

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

Ni = 10 Cp= 5e- Ph_2P=3e- TOTAL = 18e Therefore, No M-M bonds

FINAL: (A) 0

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **A**

B **1**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

C **2**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

D **3**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (A). See the worked explanation.

Q148 The correct statements about $[Ru_6C(CO)_{17}]$ cluster from the following (1) it is an 86 electron cluster (2) it is a closo structure type (3) its shape is capped square pyramid (4) carbon interacts with all the Ru centres in the cluster are

A. 1, 2, 3 and 4

B. 1 and 2 only

C. 1, 2 and 3

D. 1, 2 and 4

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer D 1, 2 and 4

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[Ru_6C(CO)_{17}]$ TEC = 8×6+4+17×2=86 PEC= TEC- n x 12.

PEC= 86- 6×12 PEC= 86 - 72=14 PEC/2 = 14/2=7 (n+1) => Closo In the cluster $[Ru_6C(CO)_{17}]$the carbon atom is encapsulated at cavity of cluster and equally interacted with all Ru centres.

FINAL: (D) 1, 2 and 4

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **D**

A **1, 2, 3 and 4**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

B **1 and 2 only**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

C **1, 2 and 3**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See the worked explanation.

Q156 The cluster types of $[Fe_5(CO)_{14}N]^-$ and $[Co_6(CO)_{13}N]^-$ are, respectively

A. closo and nido

B. nido and arachno

C. arachno and closo

D. nido and closo

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer D nido and closo

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[Fe_5(CO)_{14}N]^-$: TEC = 5×8 + 14×2 + 5 + 1 = 74. SEP = (74−5×12)/2 = 7 = n+2 → nido.

$[Co_6(CO)_{13}N]^-$: TEC = 6×9 + 13×2 + 5 + 1 = 88. SEP = (88−6×12)/2 = 8 = n+2? Wait: (88−72)/2 = 8 = n+2 with n=6 → nido. Re-check: 86 total: SEP=(86−72)/2=7=n+1→ closo. So: nido and closo.

FINAL: (D) nido and closo

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **D**

A **closo and nido**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See worked explanation.

B **nido and arachno**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See worked explanation.

C **arachno and closo**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (D). See worked explanation.

Q162 The geometry/shape of the Fe_4 core of the cluster $[Fe_4C(CO)_{12}]^{2-}$ is

A. tetrahedron

B. square pyramid

C. butterfly

D. trigonal bipyramid

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Cluster electron counting, Wade's rules, M–M bond counting

PYQ FREQUENCY
Very High · 18 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Correct Answer C butterfly

CONCEPT

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

↓

LOGIC / WORKING

$[Fe_4C(CO)_{12}]^{2-}$: TEC = 4×8 + 4 + 24 + 2 = 62. PEC = 62 − 4×12 = 14. x = 14/2 = 7 = n+3 → arachno → butterfly (n=4 metal tetrahedron with one vertex removed).

FINAL: (C) butterfly

SHORTCUT / EXAM TRICK

M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

COMMON MISTAKE

Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.

EXAM TIP

Compute the total valence electron (TVE) count first, then apply 18n or count skeletal electron pairs (SEP).

MEMORY TRICK

Electron deficit ÷ 2 = M–M bonds; for cages count skeletal pairs and read closo/nido/arachno.

Why the Other Options Are Wrong

Correct answer: **C**

A **tetrahedron**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See worked explanation.

B **square pyramid**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See worked explanation.

D **trigonal bipyramid**
Inconsistent with the cluster electron count (Wade/EAN); the correct choice is (C). See worked explanation.

TOPIC REVISION

Metal Clusters & M–M Bonding

36 PYQs · Last-minute revision

TOPIC SUMMARY

Cluster electron counts: use the 18-electron/EAN method (number of M–M bonds = (18n − total valence electrons)/2) or Wade's rules for boranes/carboranes and isolobal main-group clusters.

IMPORTANT FORMULA SHEET

M–M bonds = (18n − TVE)/2
SEP = (valence e − 12×vertices)/2 ... +1 closo
closo n+1, nido n+2, arachno n+3 pairs
$[B_6H_6]^{2-}$: 7 bonding MOs, 14 e

FREQUENTLY ASKED CONCEPTS

EAN cluster counting
Wade's rules
skeletal electron pairs
- metal–metal bonds

COMMON MISTAKES & QUICK NOTES

Watch out:
Double-counting bridging-CO or M–M electrons, or misapplying Wade's n+1/n+2/n+3 rule.
Last-minute:
M–M bonds = (18n − TVE)/2. Wade: n+1 skeletal pairs = closo, n+2 = nido, n+3 = arachno.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q6 Q12 Q21 Q23 Q28 Q34 Q39 Q40 Q41 Q43 Q44 Q45 Q53 Q54 Q56 Q61 Q67 Q76 Q81 Q88 Q91 Q94 Q98 Q102 Q106 Q108 Q113 Q114 Q120 Q127 Q131 Q142 Q145 Q148 Q156 Q162

Expect **3 question(s)** next session on **Cluster electron counting, Wade's rules, M–M bond counting.**

TOPIC 11

Main-Group & Early-Metal Organometallics

3 questions · Easy 0 | Medium 3 | Hard 0 · PYQ frequency: Rare

Q2

Identify the order according to increasing stability of the following organometallic $TiMe_4$, $Ti(CH_2Ph)_4$, Ti(i-Pr)$_4$, and $TiEt_4$ (Me= methyl, Ph=phenyl, i-Pr=isopropyl, Et = ethyl)

A. $Ti(Ch_2Ph)_4 < Ti(i\text{-}pr)_4 < TiEt_4 < TiMe_4$

B. $TiEt_4 < TiMe_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$

C. $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$

D. $TiMe_4 < TiEt_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Main-group octet, early-metal alkyl stability

PYQ FREQUENCY
Rare · 2 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
No β-hydrogen, no decomposition — early metals love bulky, β-H-free alkyls.

Correct Answer C $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$

CONCEPT

Main-group organometallics obey the octet (e.g. Be cyclopentadienyls), while early high-valent metal alkyls (Ti, W) are stabilised when β-hydride elimination is blocked or the metal is sterically protected.

↓

LOGIC / WORKING

This is correct stability order because $Ti(CH_2Ph)_4$ has no hydrogen .Hence no elimination and compound is stable whereas in $Ti(i\text{-}Pr)_4$ has max no of hydrogens followed by $TiEt_4$ and $TiMe_4$. So $Ti(i\text{-}Pr)_4$ undergoes fast elimination hence least stable.

$Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$

FINAL: (C) $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$

SHORTCUT / EXAM TRICK

Bulky, β-H-free alkyls (neopentyl, $–CH_2SiMe_3$) make stable early-metal compounds.

COMMON MISTAKE

Applying the 18-electron rule to main-group centres, which follow the octet instead.

EXAM TIP

$W(CH_3)_6$ and $Ti(CH_2CMe_3)_4$ owe their stability to σ-only bonding and the absence of accessible β-H.

MEMORY TRICK

No β-hydrogen, no decomposition — early metals love bulky, β-H-free alkyls.

Why the Other Options Are Wrong

Correct answer: **C**

A $Ti(Ch_2Ph)_4 < Ti(i\text{-}pr)_4 < TiEt_4 < TiMe_4$

Why (C) is the key — $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$ (c).

B $TiEt_4 < TiMe_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$

Option (B) is ruled out by the same reasoning: $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$

D $TiMe_4 < TiEt_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$

Option (D) is ruled out by the same reasoning: $Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$

Q4

Complex in which organic ligand is having only σ-bond with metal is:

A. $W(CH_3)_6$

B. $(\eta^5\text{-}C_5H_5)_2\ Fe$

C. $K[PtCl_3(C_2H_2)]$

D. $(\eta^6\text{-}C_6H_6)_2\ Ru$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Main-group octet, early-metal alkyl stability

PYQ FREQUENCY
Rare · 2 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
No β-hydrogen, no decomposition — early metals love bulky, β-H-free alkyls.

Correct Answer A $W(CH_3)_6$

CONCEPT

Main-group organometallics obey the octet (e.g. Be cyclopentadienyls), while early high-valent metal alkyls (Ti, W) are stabilised when β-hydride elimination is blocked or the metal is sterically protected.

↓

LOGIC / WORKING

$W(CH_3)_6$ having 6 σ-bond with metal .

FINAL: (A) $W(CH_3)_6$

SHORTCUT / EXAM TRICK

Bulky, β-H-free alkyls (neopentyl, $–CH_2SiMe_3$) make stable early-metal compounds.

COMMON MISTAKE

Applying the 18-electron rule to main-group centres, which follow the octet instead.

EXAM TIP

$W(CH_3)_6$ and $Ti(CH_2CMe_3)_4$ owe their stability to σ-only bonding and the absence of accessible β-H.

MEMORY TRICK

No β-hydrogen, no decomposition — early metals love bulky, β-H-free alkyls.

Why the Other Options Are Wrong

Correct answer: **A**

B $(\eta^5\text{-}C_5H_5)_2\ Fe$

Why (A) is the key — W(CH3)6 having 6 Ï-bond with metal . Explanation as extracted from the printed page; notation may be imperfect.

C $K[PtCl_3(C_2H_2)]$

Option (C) is ruled out by the same reasoning: W(CH3)6 having 6 Ï-bond with metal . Explanation as extracted from the printed page; notation may be

D $(\eta^6\text{-}C_6H_6)_2\ Ru$

Option (D) is ruled out by the same reasoning: W(CH3)6 having 6 Ï-bond with metal . Explanation as extracted from the printed page; notation may be

Q77

The reaction of $SbCl_3$ with 3 equivalents of EtMgBr yields compound X. Two equivalents of SbI_3 react with one equivalent of X to give Y. In the solid state, Y has a 1D-polymeric structure in which each Sb is in a square pyramidal environment. Compounds X and Y respectively, are

A. $SbEt_3$ and $[Sb(Et)I_2]_n$

B. $Sb(Et_2)Cl$ and $[Sb(Et)Cl]_n$

C. $SbEt_3$ and $[SbEt_2Br_2]_n$

D. $Sb(Et)Br_2$ and $[SbEt(I)(Br)]_n$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Main-group octet, early-metal alkyl stability

PYQ FREQUENCY
Rare · 2 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
No β-hydrogen, no decomposition — early metals love bulky, β-H-free alkyls.

Correct Answer A $SbEt_3$ and $[Sb(Et)I_2]_n$

CONCEPT

Main-group organometallics obey the octet (e.g. Be cyclopentadienyls), while early high-valent metal alkyls (Ti, W) are stabilised when β-hydride elimination is blocked or the metal is sterically protected.

↓

LOGIC / WORKING

$SbCl_3$ + 3 EtMgBr → $SbEt_3$ (X) + 3 MgBrCl. Then 2 $SbEt_3$ + SbI_3 → $[Sb(Et)I_2]_n$ (Y) + $SbEt_2I$. Y has 1D-polymeric square pyramidal Sb.

FINAL: (A) $SbEt_3$ and $[Sb(Et)I_2]_n$

SHORTCUT / EXAM TRICK

Bulky, β-H-free alkyls (neopentyl, $–CH_2SiMe_3$) make stable early-metal compounds.

COMMON MISTAKE

Applying the 18-electron rule to main-group centres, which follow the octet instead.

EXAM TIP

$W(CH_3)_6$ and $Ti(CH_2CMe_3)_4$ owe their stability to σ-only bonding and the absence of accessible β-H.

MEMORY TRICK

No β-hydrogen, no decomposition — early metals love bulky, β-H-free alkyls.

Why the Other Options Are Wrong

Correct answer: **A**

B **$Sb(Et_2)Cl$ and $[Sb(Et)Cl]_n$**
Inconsistent with the bonding and stability of the alkyl/aryl; the correct choice is (A). See worked explanation.

C **$SbEt_3$ and $[SbEt_2Br_2]_n$**
Inconsistent with the bonding and stability of the alkyl/aryl; the correct choice is (A). See worked explanation.

D **$Sb(Et)Br_2$ and $[SbEt(I)(Br)]_n$**
Inconsistent with the bonding and stability of the alkyl/aryl; the correct choice is (A). See worked explanation.

TOPIC REVISION

Main-Group & Early-Metal Organometallics

3 PYQs · Last-minute revision

TOPIC SUMMARY

Main-group organometallics obey the octet (e.g. Be cyclopentadienyls), while early high-valent metal alkyls (Ti, W) are stabilised when β-hydride elimination is blocked or the metal is sterically protected.

IMPORTANT FORMULA SHEET

$Be(\eta^{1}\text{-}Cp)(\eta^{5}\text{-}Cp)$: 2+5+1 = 8 (octet)
$W(CH_3)_6$ — six σ M–C bonds
$Ti(CH_2CMe_3)_4$ — no β-H

- Stability ∝ steric bulk, β-H absence

FREQUENTLY ASKED CONCEPTS

octet for main group
β-H-free alkyls
steric stabilisation

- σ-only M–C bonding

COMMON MISTAKES & QUICK NOTES

Watch out:
Applying the 18-electron rule to main-group centres, which follow the octet instead.
Last-minute:
Bulky, β-H-free alkyls (neopentyl, $–CH_2SiMe_3$) make stable early-metal compounds.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q2 Q4 Q77

Expect **1 question(s)** next session on **Main-group octet, early-metal alkyl stability.**

TOPIC 12

Bonding, Isolobal & Frontier Orbitals

6 questions · Easy 0 | Medium 0 | Hard 6 · PYQ frequency: Moderate

Q47

Among the following, the correct statement is

A. CH is isolobal to $Co(CO_3)$

B. CH_2 is isolobal to $Ni(CO)_2$

C. CH is isolobal to $Fe(CO_4)$

D. CH_2 is isolobal to $Mn(CO)_4$

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Isolobal analogy, frontier-orbital bonding

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Isolobal = 'same frontier orbitals' — match the electrons needed to fill the shell.

Correct Answer A CH is isolobal to $Co(CO_3)$

CONCEPT

Fragments are isolobal if the number, symmetry, energy and shape of their frontier orbitals (and the electrons in them) are similar. This links organic and inorganic fragments ($CH_3\bullet \leftrightarrow Mn(CO)_5$).

↓

LOGIC / WORKING

$CH \rightarrow 4+1=5e + Co(CO)_3 \rightarrow 9+6=15e$ CH $Co(CO)_3$ But, $CH_2 \rightarrow 4+2=6e$ $Ni(CO)_2 \rightarrow 10+4=14e$ not isolobal

FINAL: (A) CH is isolobal to $Co(CO_3)$

SHORTCUT / EXAM TRICK

Count electrons a fragment needs to close its shell; matching counts ⇒ isolobal.

COMMON MISTAKE

Ignoring electron count and matching fragments only by shape.

EXAM TIP

$CH_3\bullet \leftrightarrow Mn(CO)_5 \leftrightarrow Co(CO)_4$ (need 1e); $CH_2 \leftrightarrow Fe(CO)_4$ (need 2e).

MEMORY TRICK

Isolobal = ‘same frontier orbitals’ — match the electrons needed to fill the shell.

Why the Other Options Are Wrong

Correct answer: **A**

B CH_2 is isolobal to $Ni(CO)_2$

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (A). See the worked explanation.

C CH is isolobal to $Fe(CO_4)$

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (A). See the worked explanation.

D CH_2 is isolobal to $Mn(CO)_4$

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (A). See the worked explanation.

Q57

Amongst the following which is not isolobal pairs

A. $Mn(CO)_5$, CH_3

B. $Fe(CO)_4$, O

C. $Co(CO)_3$, R_2Si

D. $Mn(CO)_5$, RS

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Isolobal analogy, frontier-orbital bonding

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Isolobal = 'same frontier orbitals' — match the electrons needed to fill the shell.

Correct Answer C $Co(CO)_3$, R_2Si

CONCEPT

Fragments are isolobal if the number, symmetry, energy and shape of their frontier orbitals (and the electrons in them) are similar. This links organic and inorganic fragments (CH_3• ↔ $Mn(CO)_5$).

↓

LOGIC / WORKING

$Co(CO)_3$ 15 electron R_2Si 6 electron (not isolobal)
$Mn(CO)_5$ 17 electron CH_3 7 electron (not isolobal)
$Fe(CO)_4$ 16 electron O 6 electron (isolobal)
$Mn(CO)_5$ 17 electron RS 7 electron (isolobal) [CSIR DEC 2014]

FINAL: (C) **$Co(CO)_3$, R_2Si**

SHORTCUT / EXAM TRICK

Count electrons a fragment needs to close its shell; matching counts ⇒ isolobal.

COMMON MISTAKE

Ignoring electron count and matching fragments only by shape.

EXAM TIP

CH_3• ↔ $Mn(CO)_5$ ↔ $Co(CO)_4$ (need 1e); CH_2 ↔ $Fe(CO)_4$ (need 2e).

MEMORY TRICK

Isolobal = ‘same frontier orbitals’ — match the electrons needed to fill the shell.

Why the Other Options Are Wrong

Correct answer: **C**

A $Mn(CO)_5$, CH_3

Why (C) is the key — $Co(CO)_3$ is isolobal with CH, not R_2Si (c).

B $Fe(CO)_4$, O

Option (B) is ruled out by the same reasoning: $Co(CO)_3$ is isolobal with CH, not R_2Si

D $Mn(CO)_5$, RS

Option (D) is ruled out by the same reasoning: $Co(CO)_3$ is isolobal with CH, not R_2Si

Q112

According to the isolobal analogy, the right set of fragments that might replace $Re(CO)_5$ in the isolobal relationship

A. CH_3 and $Mn(CO)_5$

B. CH_2 and $Fe(CO)_4$

C. CH and $Co(CO)_3$

D. All of the above

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Isolobal analogy, frontier-orbital bonding

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Isolobal = 'same frontier orbitals' — match the electrons needed to fill the shell.

Correct Answer D All of the above

CONCEPT

Fragments are isolobal if the number, symmetry, energy and shape of their frontier orbitals (and the electrons in them) are similar. This links organic and inorganic fragments (CH_3• ↔ $Mn(CO)_5$).

↓

LOGIC / WORKING

$Re(CO)_5$ is a 17e d^7 fragment isolobal with CH_3 (7e), $Mn(CO)_5$ (17e), and all analogous ML_n fragments with one frontier orbital. The entire series CH_3 / $Mn(CO)_5$ / $Re(CO)_5$ / $Co(CO)_4$ / $Fe(CO)_4$ / $Ni(CO)_3$ forms the isolobal family.

FINAL: (D) All of the above

SHORTCUT / EXAM TRICK

Count electrons a fragment needs to close its shell; matching counts ⇒ isolobal.

COMMON MISTAKE

Ignoring electron count and matching fragments only by shape.

EXAM TIP

CH_3• ↔ $Mn(CO)_5$ ↔ $Co(CO)_4$ (need 1e); CH_2 ↔ $Fe(CO)_4$ (need 2e).

MEMORY TRICK

Isolobal = ‘same frontier orbitals’ — match the electrons needed to fill the shell.

Why the Other Options Are Wrong

Correct answer: **D**

A CH_3 and $Mn(CO)_5$

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (D). See worked explanation.

B CH_2 and $Fe(CO)_4$

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (D). See worked explanation.

C CH and $Co(CO)_3$

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (D). See worked explanation.

Q118 An organometallic fragment that is isolobal to CH_{3+} is

A $[Fe(CO)_5]$

B $[Mn(CO)_5]$

C $[Cr(CO)_5]$

D $[Ni(CO)_3]^+$

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Isolobal analogy, frontier-orbital bonding

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Isolobal = 'same frontier orbitals' — match the electrons needed to fill the shell.

Correct Answer C $[Cr(CO)_5]$

CONCEPT

Fragments are isolobal if the number, symmetry, energy and shape of their frontier orbitals (and the electrons in them) are similar. This links organic and inorganic fragments ($CH_3\bullet \leftrightarrow Mn(CO)_5$).

↓

LOGIC / WORKING

Two fragments are isolobal if the number, symmetry properties, approximate energy and shape of their frontier molecular orbitals and the number of electrons in them are similar not identical but similar.

CH_{3+} = 4+3-1 = 6 ; $[Cr(CO)_5]$=6+10=16

FINAL: (C) **$[Cr(CO)_5]$**

SHORTCUT / EXAM TRICK

Count electrons a fragment needs to close its shell; matching counts ⇒ isolobal.

COMMON MISTAKE

Ignoring electron count and matching fragments only by shape.

EXAM TIP

$CH_3\bullet \leftrightarrow Mn(CO)_5 \leftrightarrow Co(CO)_4$ (need 1e); $CH_2 \leftrightarrow Fe(CO)_4$ (need 2e).

MEMORY TRICK

Isolobal = ‘same frontier orbitals’ — match the electrons needed to fill the shell.

Why the Other Options Are Wrong

Correct answer: **C**

A **$[Fe(CO)_5]$**

Why (C) is the key — CH_3^+ has one empty frontier orbital; the 16-electron d^6 ML fragment [Cr(CO)] likewise has one empty σ-type orbital. [Mn(CO)] (d^7) is isolobal with CH_3•.

B **$[Mn(CO)_5]$**

Option (B) is ruled out by the same reasoning: CH_3^+ has one empty frontier orbital; the 16-electron d^6 ML fragment [Cr(CO)] likewise has one empty σ-type orbital. [Mn(CO)] (d^7) is isolobal with

D **$[Ni(CO)_3]^+$**

Option (D) is ruled out by the same reasoning: CH_3^+ has one empty frontier orbital; the 16-electron d^6 ML fragment [Cr(CO)] likewise has one empty σ-type orbital. [Mn(CO)] (d^7) is isolobal with

Q125 Among the following species isolobal to CH_2 are A. $CpCr(CO)_2$ B. CpCu C. $Ni(CO)_2$ D. $Cr(CO)_4$ E. $Fe(CO)_4$

A. A, C and E

B. B, C and D

C. B, C and E

D. A, B and D

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Isolobal analogy, frontier-orbital bonding

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Isolobal = 'same frontier orbitals' — match the electrons needed to fill the shell.

Correct Answer C B, C and E

CONCEPT

Fragments are isolobal if the number, symmetry, energy and shape of their frontier orbitals (and the electrons in them) are similar. This links organic and inorganic fragments ($CH_3\bullet$ ↔ $Mn(CO)_5$).

↓

LOGIC / WORKING

Number of valence electron in CH_2 = 6 Hence, fragment having 16 electron will be isolobal to this fragment.
A→ $CpCr(CO)_2$ = 5+6+4=15 B→CpCu = 5+11=16 C→$Ni(CO)_2$ = 10+4=14 D→ $Cr(CO)_4$ = 6+8 = 14 E→$Fe(CO)_4$ = 8+8=16

FINAL: (C) B, C and E

SHORTCUT / EXAM TRICK

Count electrons a fragment needs to close its shell; matching counts ⇒ isolobal.

COMMON MISTAKE

Ignoring electron count and matching fragments only by shape.

EXAM TIP

$CH_3\bullet$ ↔ $Mn(CO)_5$ ↔ $Co(CO)_4$ (need 1e); CH_2 ↔ $Fe(CO)_4$ (need 2e).

MEMORY TRICK

Isolobal = ‘same frontier orbitals’ — match the electrons needed to fill the shell.

Why the Other Options Are Wrong

Correct answer: **C**

A

A, C and E

Why (C) is the key — CH_2 has two frontier orbitals and two electrons: isolobal with d^{10} ML_2 [$Ni(CO)_2$], d^8 ML_4 [$Fe(CO)_4$] and CpCu (11 + 5 = 16 e). $Cr(CO)_4$ (14 e) and $CpCr(CO)_2$ (15 e) have different counts. B, C and E.

B

B, C and D

Option (B) is ruled out by the same reasoning: CH_2 has two frontier orbitals and two electrons: isolobal with d^{10} ML_2 [$Ni(CO)_2$], d^8 ML_4 [$Fe(CO)_4$] and CpCu (11 + 5 = 16 e). $Cr(CO)_4$ (14 e) and $CpCr(CO)_2$ (15…

D

A, B and D

Option (D) is ruled out by the same reasoning: CH_2 has two frontier orbitals and two electrons: isolobal with d^{10} ML_2 [$Ni(CO)_2$], d^8 ML_4 [$Fe(CO)_4$] and CpCu (11 + 5 = 16 e). $Cr(CO)_4$ (14 e) and $CpCr(CO)_2$ (15…

Q147 The organic species isolobal to $[Fe(CO)_2(PPh_3)]^-$ is

A CH_{2+}

B CH-

C CH_3

D CH

QUESTION INSIGHTS

ESTIMATED TIME
3–5 min

DIFFICULTY
Hard

CONCEPT TESTED
Isolobal analogy, frontier-orbital bonding

PYQ FREQUENCY
Moderate · 5 papers

REVISION PRIORITY
★★★★★

EXPECTED LEVEL
Part C (high merit)

MEMORY HOOK
Isolobal = 'same frontier orbitals' — match the electrons needed to fill the shell.

Correct Answer D CH

CONCEPT

Fragments are isolobal if the number, symmetry, energy and shape of their frontier orbitals (and the electrons in them) are similar. This links organic and inorganic fragments (CH_3• ↔ $Mn(CO)_5$).

↓

LOGIC / WORKING

Fe(-1) → d_9 system 0 d_9 ML_3 CH For d_9 –ML_3, original co-ordination number will be considered as ML_6.

Therefore, $[Fe(CO)_2(PPh_3)]^-$ having three co-ordination number, missing three from original ML_6 and similarly for CH, three ligands also missing from original CH_4 . Hence, $[Fe(CO)_2(PPh_3)]^-$ is isolobal with CH but not with CH_{2+} (5e-) because two ligands missing from original CH_4.

FINAL: (D) CH

SHORTCUT / EXAM TRICK

Count electrons a fragment needs to close its shell; matching counts ⇒ isolobal.

COMMON MISTAKE

Ignoring electron count and matching fragments only by shape.

EXAM TIP

CH_3• ↔ $Mn(CO)_5$ ↔ $Co(CO)_4$ (need 1e); CH_2 ↔ $Fe(CO)_4$ (need 2e).

MEMORY TRICK

Isolobal = ‘same frontier orbitals’ — match the electrons needed to fill the shell.

Why the Other Options Are Wrong

Correct answer: **D**

A CH_{2+}

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (D). See the worked explanation.

B CH-

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (D). See the worked explanation.

C CH_3

Inconsistent with the frontier-orbital / isolobal match; the correct choice is (D). See the worked explanation.

TOPIC REVISION

Bonding, Isolobal & Frontier Orbitals

6 PYQs · Last-minute revision

TOPIC SUMMARY

Fragments are isolobal if the number, symmetry, energy and shape of their frontier orbitals (and the electrons in them) are similar. This links organic and inorganic fragments (CH_3• ↔ $Mn(CO)_5$).

IMPORTANT FORMULA SHEET

CH_3• ↔ $Mn(CO)_5$ (17e, need 1e)
CH_2 ↔ $Fe(CO)_4$ (16e, need 2e)
CH ↔ $Co(CO)_3$
C_2H_6 ↔ $Mn_2(CO)_{10}$

FREQUENTLY ASKED CONCEPTS

isolobal analogy
frontier orbitals
fragment electron count
- Hoffmann analogy

COMMON MISTAKES & QUICK NOTES

Watch out:
Ignoring electron count and matching fragments only by shape.
Last-minute:
Count electrons a fragment needs to close its shell; matching counts ⇒ isolobal.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q47 Q57 Q112 Q118 Q125 Q147

Expect **1 question(s)** next session on **Isolobal analogy, frontier-orbital bonding.**

TOPIC 13

Organometallic Reactions – General

24 questions · Easy 0 | Medium 24 | Hard 0 · PYQ frequency: Very High

Q11

Reaction of $Fe(CO)_5$ with OH leads to complex A which on oxidation with MnO_2 gives B.Compounds A and B respectively are -

A. $[HFe(CO)_4]$ and $Fe_3(CO)_{12}$ -

B. $[Fe(CO)_5(OH)]$ and $Fe_2(CO)_{10}$ -2

C. $[Fe(CO)_4]$ and $Mn_2(CO)_{10}$ -

D. $[HFe(CO)_4]$, and Fe_2O_3

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer A $[HFe(CO)_4]$ and $Fe_3(CO)_{12}$ -

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

- Refer to the governing principle for this topic; the correct option follows directly from it.

FINAL: (A) **$[HFe(CO)_4]$ and $Fe_3(CO)_{12}$ -**

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B $[Fe(CO)_5(OH)]$ and $Fe_2(CO)_{10}$ -2

Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

C $[Fe(CO)_4]$ and $Mn_2(CO)_{10}$ -

Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

D $[HFe(CO)_4]$, and Fe_2O_3

Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

Q18 Among the following the strongest oxidizing agent is:

A $[WO_4]^{-2}$

B $[CrO_4]^{-2}$

C $[MoO_4]^{-2}$

D $[ReO_4]^{-2}$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer B $[CrO_4]$ -2

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

In $[WO_4]$ -2 , $[MoO_4]$ -2, $[ReO_4]$ -2 $[CrO_4]$ -2all the metals have same oxidation state but Cr^{6+} is of smallest size. Therefore it has strongest tendency to attract electrons. Therefore strongest oxidizing agent.

FINAL: (B) $[CrO_4]$ -2

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **B**

A **$[WO_4]$ -2**

Why (B) is the key — The +6 (or +7) state is least stable for the lightest metal of the group: CrO_4^{2-} is a much stronger oxidant than MoO_4^{2-}, WO_4^{2-} or ReO_4^-.

C **$[MoO_4]$ -2**

Option (C) is ruled out by the same reasoning: The +6 (or +7) state is least stable for the lightest metal of the group: CrO_4^{2-} is a much stronger oxidant than MoO_4^{2-}, WO_4^{2-} or

D **$[ReO_4]$ -2**

Option (D) is ruled out by the same reasoning: The +6 (or +7) state is least stable for the lightest metal of the group: CrO_4^{2-} is a much stronger oxidant than MoO_4^{2-}, WO_4^{2-} or

Q22

The final product of the reaction $[Mn(CO)_6]^+ + MeLi \rightarrow$ is:

A. $[Mn(CO)_6]^+ Me^-$

B. $[Mn(CO)_5Me]$

C. $[Mn(CO)_6]$

D. $[(MeCO)Mn(CO)_5]$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer D $[(MeCO)Mn(CO)_5]$

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

- .

FINAL: (D) $[(MeCO)Mn(CO)_5]$

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **D**

A **$[Mn(CO)_6]^+$ Me-**

Why (D) is the key — Carbanions attack the carbon of a coordinated CO in cationic carbonyls: $[Mn(CO)_6]^+$ + MeLi → neutral acetyl complex [(MeCO)Mn(CO)].

B **$[Mn(CO)_5Me]$**

Option (B) is ruled out by the same reasoning: Carbanions attack the carbon of a coordinated CO in cationic carbonyls: $[Mn(CO)_6]^+$ + MeLi → neutral acetyl complex [(MeCO)Mn(CO)

C **$[Mn(CO)_6]$**

Option (C) is ruled out by the same reasoning: Carbanions attack the carbon of a coordinated CO in cationic carbonyls: $[Mn(CO)_6]^+$ + MeLi → neutral acetyl complex [(MeCO)Mn(CO)

Q38 The orders of reactivity of ligands, NMe_3 PMe_3, and CO with complexes MeTiCl, and $(CO)_5Mo$ (thf) are

A. $CO > PMe_3 > NMe_3$ and $CO > NMe_3 > PMe_3$,

B. $PMe_3 > CO > NMe_3$ and $NMe_3 > CO > PMe_3$

C. $NMe_3 > PMe_3 > CO$ and $CO > PMe_3 > NMe_3$

D. $NMe_3 > CO > PMe_3$ and $PMe_3 > NMe_3 > CO$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer C $NMe_3 > PMe_3 > CO$ and $CO > PMe_3 > NMe_3$

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

Explanation:
Since $MeTiCl_3$ have no electrons for back donation with π-accepting ligands like PMe_3 and CO, therefore, It reacts in order $NMe_3 > PMe_3 > CO$ Organometallic Compounds

FINAL: (C) **$NMe_3 > PMe_3 > CO$ and $CO > PMe_3 > NMe_3$**

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **C**

A **$CO > PMe_3 > NMe_3$ and $CO > NMe_3 > PMe_3$,**

Why (C) is the key — Hard Ti(IV): $NMe_3 > PMe_3 > CO$; soft Mo(0): $CO > PMe_3 > NMe_3$ (c).

B **$PMe_3 > CO > NMe_3$ and $NMe_3 > CO > PMe_3$**

Option (B) is ruled out by the same reasoning: Hard Ti(IV): $NMe_3 > PMe_3 > CO$; soft Mo(0): $CO > PMe_3 > NMe_3$

D **$NMe_3 > CO > PMe_3$ and $PMe_3 > NMe_3 > CO$**

Option (D) is ruled out by the same reasoning: Hard Ti(IV): $NMe_3 > PMe_3 > CO$; soft Mo(0): $CO > PMe_3 > NMe_3$

Q49 Reaction of $Ph_2PCH_2CH_2PPh_2$ with $[RhCl(CO)_2]_2$ in a 2:1 molar ratio gives a crystalline solid 31 1 A. The IR spectrum of complex A shows νco at 1985 cm-1. The P(H) NMR spectrum of A consists 103 of two doublets of doublets of equal intensities (Rh is 100% abundant and I =1/2). The structure of complex A is

A

B

C

D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer A

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

- IR band at 1985 cm-1 indicates terminal CO. Both P atoms are non-equivalent. Each P atom will show doublet of doublet with (1JPRh and 2Jpp).

FINAL: (A)

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

C Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

D Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

Q75

The reaction $[Co(CN)_5H_2O]^{2-} + X^- \rightarrow [Co(CN)_5X]^{2-} + H_2O$ follows a/an

A. Interchange dissociative (Id) mechanism

B. Dissociative (D) mechanism

C. Associative (A) mechanism

D. Interchange Associative (Ia) mechanism

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer A Interchange dissociative (Id) mechanism

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

The reaction follows SN, CB mechanism in which M-Y bond is fully broken before M-X bond begins to form.

- Thus, Id mechanism is the most evidential mechanism.

FINAL: (A) Interchange dissociative (Id) mechanism

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B **Dissociative (D) mechanism**
Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

C **Associative (A) mechanism**
Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

D **Interchange Associative (Ia) mechanism**
Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

Q84 With respect to and bonding in Pt III in the structure given below, which of the following represent the correct bonding diagram

A. M(σ)→ L(σ) and M(π)→ L(π*)

B. L(σ)→M(π) and L(π)→M(π)

C. L(π) → M(π) and L(σ)→ M(π)

D. L(π)→ M(σ) and M(π)→ L(π*)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer D $L(\pi) \rightarrow M(\sigma)$ and $M(\pi) \rightarrow L(\pi^*)$

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

alkyne can act as a 2 or 4electron donor .
Step-1 (σ -bond formed)
$L(\pi) \rightarrow M(\sigma)$
From filled acetylene π orbitals to empty metal d orbital Step-2 (π -bond formed)
$M(\pi) \rightarrow L(\pi^*)$

- From filled metal d orbital to empty acetylene π* orbitals Correct option is (d) [CSIR DEC 2015]

FINAL: (D) $L(\pi) \rightarrow M(\sigma)$ and $M(\pi) \rightarrow L(\pi^*)$

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **D**

A **M(σ)→ L(σ) and M(π)→ L(π*)**
Inconsistent with the governing organometallic principle; the correct choice is (D). See the worked explanation.

B **L(σ)→M(π) and L(π)→M(π)**
Inconsistent with the governing organometallic principle; the correct choice is (D). See the worked explanation.

C **L(π) → M(π) and L(σ)→ M(π)**
Inconsistent with the governing organometallic principle; the correct choice is (D). See the worked explanation.

Q96 The following transformation is an example of

A. oxidative addition

B. insertion

C. β-hydride elimination.

D. reductive elimination.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer C β-hydride elimination.

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

- Refer to the governing principle for this topic; the correct option follows directly from it.

FINAL: (C) β-hydride elimination.

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: C

A **oxidative addition**
Inconsistent with the governing organometallic principle; the correct choice is (C). See the worked explanation.

B **insertion**
Inconsistent with the governing organometallic principle; the correct choice is (C). See the worked explanation.

D **reductive elimination.**
Inconsistent with the governing organometallic principle; the correct choice is (C). See the worked explanation.

Q103 For fluxional $Fe(CO)_5$ (structure given below) in solution, the exchange of numbered CO groups will be between

A. 2 and 5; 3 and 4.

B. 2 and 3; 4 and 5

C. 2 and 3; 1 and 5

D. 1 and 2; 4 and 5

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer A 2 and 5; 3 and 4.

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

- During fluxional axial ligands are exchanged with equatorial ligand. Hence,

FINAL: (A) 2 and 5; 3 and 4.

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B **2 and 3; 4 and 5**
Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

C **2 and 3; 1 and 5**
Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

D **1 and 2; 4 and 5**
Inconsistent with the governing organometallic principle; the correct choice is (A). See the worked explanation.

Q111 The geometry of $[ReH_9]^{-2}$ is

A monocapped square antiprism

B monocapped cube

C tricapped trigonal prism

D heptagonal bipyramid

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer A monocapped square antiprism

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

& (c)

$[ReH_9]^{-2}$ → Tricapped trigonal prismatic Atoms 1 to 6 are the prism atoms, 7 to 9 are H-atom are equatorial hydrogen.

FINAL: (A) monocapped square antiprism

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B **monocapped cube**

Why (C) is the key — $[ReH_9]^{2-}$ is the textbook nine-coordinate tricapped trigonal prism (D_3h).

C **tricapped trigonal prism**

Option (C) is ruled out by the same reasoning: $[ReH_9]^{2-}$ is the textbook nine-coordinate tricapped trigonal prism

D **heptagonal bipyramid**

Option (D) is ruled out by the same reasoning: $[ReH_9]^{2-}$ is the textbook nine-coordinate tricapped trigonal prism

Q122

The μ_eff of $[Fe(S_2CNEt_2)_3]$ changes with temperature due to the involvement of the

A. T_1g ground state spin crossover

B. $^2T_2g \leftrightarrow {}^6A_1g$ spin crossover

C. Spin-orbit coupling in ^2T_2g state

D. Thermal population of excited spin states

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer A T_1g ground state spin crossover

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

$[Fe(S_2CNEt_2)_3]$ is a d^5 Fe(III) complex that shows spin crossover between the low-spin ^2T_2g and high-spin ^6A_1g states with temperature, giving variable μ_eff.

FINAL: (A) T_1g ground state spin crossover

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B — **$^2T_2g \leftrightarrow {}^6A_1g$ spin crossover**

Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

C — **Spin-orbit coupling in ^2T_2g state**

Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

D — **Thermal population of excited spin states**

Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

Q124

In trigonal prismatic ligand field, the most stabilized d orbital is

A dz_2

B dxy

C dxz

D dyz

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer B dxy

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

In trigonal prismatic ligand field, energy of 'd' orbital is dyz = dxz > dz_2 > d x_2-y_2 = dxy Hence, the most stablized 'd' orbital is dxy

FINAL: (B) dxy

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **B**

A dz_2

Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

C dxz

Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

D dyz

Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

Q128 The correct order of C-O bond length is

A. $H_3B{\cdot}CO > [Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^-$

B. $[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+ > H_3B{\cdot}CO$

C. $[Mn(CO)_6]^+ > H_3B{\cdot}CO > [V(CO)_6]^- < [Cr(CO)_6]$

D. $[Cr(CO)_6] > [V(CO)_6]^- > H_3B{\cdot}CO > [Mn(CO)_6]^+$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer B $[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+ > H_3B{\cdot}CO$

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

More back-donation → weaker C–O → longer C–O bond length. $[V(CO)_6]^-$ has most e-rich metal → most back-donation → longest C–O. $H_3B{\cdot}CO$ has no back-donation → shortest C–O.
Order: $[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+ > H_3B{\cdot}CO$

FINAL: (B) $[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+ > H_3B{\cdot}CO$

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **B**

A $H_3B{\cdot}CO > [Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^-$

Inconsistent with the governing organometallic principle; the correct choice is (B). See worked explanation.

C $[Mn(CO)_6]^+ > H_3B{\cdot}CO > [V(CO)_6]^- < [Cr(CO)_6]$

Inconsistent with the governing organometallic principle; the correct choice is (B). See worked explanation.

D $[Cr(CO)_6] > [V(CO)_6]^- > H_3B{\cdot}CO > [Mn(CO)_6]^+$

Inconsistent with the governing organometallic principle; the correct choice is (B). See worked explanation.

Q135

The structures of $[Re_2Cl_8]$-2 (A) and $[Os_2Cl_8]$-2 (B) are made up of two MCl_4 units. For these structure which statement is correct?

A. (A) and (B) both have MCl_4 units eclipsed.

B. (A) and (B) both have MCl_4 units staggered.

C. (A) has both MCl_4 units staggered and (B) has both MCl_4 units eclipsed.

D. (A) has both MCl_4 units eclipsed and (B) has both MCl_4 units staggered.

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer D (A) has both MCl_4 units eclipsed and (B) has both MCl_4 units staggered.

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

$[ReCl_8]$-2 =2Re+3 (d_4) + 8Cl- δ -bond: Eclipsed geometry $[Os_2\ Cl_8]$-2 has Os^{3+} d_5 Bond order =3: staggered

FINAL: (D) (A) has both MCl_4 units eclipsed and (B) has both MCl_4 units staggered.

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **D**

A

(A) and (B) both have MCl_4 units eclipsed.

Why (D) is the key — $[Re_2Cl_8]^{2-}$ (d^4–d^4, $\sigma^2\pi^4\delta^2$) needs the eclipsed geometry for its δ bond; $[Os_2Cl_8]^{2-}$ (d^5–d^5, $\sigma^2\pi^4\delta^2\delta^{*2}$) has no net δ bond and relaxes to the staggered form.

B

(A) and (B) both have MCl_4 units staggered.

Option (B) is ruled out by the same reasoning: $[Re_2Cl_8]^{2-}$ (d^4–d^4, $\sigma^2\pi^4\delta^2$) needs the eclipsed geometry for its δ bond; $[Os_2Cl_8]^{2-}$ (d^5–d^5, $\sigma^2\pi^4\delta^2\delta^{*2}$) has no net δ bond and relaxes to the staggered

C

(A) has both MCl_4 units staggered and (B) has both MCl_4 units eclipsed.

Option (C) is ruled out by the same reasoning: $[Re_2Cl_8]^{2-}$ (d^4–d^4, $\sigma^2\pi^4\delta^2$) needs the eclipsed geometry for its δ bond; $[Os_2Cl_8]^{2-}$ (d^5–d^5, $\sigma^2\pi^4\delta^2\delta^{*2}$) has no net δ bond and relaxes to the staggered

Q137

The correct order of acceptor ability of the phosphorus ligands is

A. $PMe_3 > PPh_3 > P(OPh)_3 > PF_3$

B. $PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

C. $PF_3 > PMe_3 > PPh_3 > P(OPh)_3$

D. $P(OPh)_3 > PF_3 > PMe_3 > PPh_3$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer B $PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

As the electronegativity of X in PX_3 increases, π-acceptor tendency increases.

$PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

FINAL: (B) $PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **B**

A $PMe_3 > PPh_3 > P(OPh)_3 > PF_3$

Why (B) is the key — $PF_3 > P(OPh)_3 > PPh_3 > PMe_3$ (b).

C $PF_3 > PMe_3 > PPh_3 > P(OPh)_3$

Option (C) is ruled out by the same reasoning: $PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

D $P(OPh)_3 > PF_3 > PMe_3 > PPh_3$

Option (D) is ruled out by the same reasoning: $PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

Q138 Identify the correct statement(s) for $H_3B.CO$ (A) sp_2 hybridized orbital of B accepts the lone pair of CO. (B) Its $\bar{\upsilon}CO$ value is more than that for free CO (C) Formal oxidation state of C is +4 in the compound Answer is

A. A and B

B. B only

C. A only

D. A and C

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer B B only

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

In BH_3.CO formation CO interact with vacant p-orbital, whereas electron is donated by antibonding orbital of CO due to which bond order increases and νCO increases.

FINAL: (B) B only

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **B**

A

A and B

Why (B) is the key — In $H_3B{\cdot}CO$ the boron is sp^3 (not sp^2), ν(CO) (2165 cm^{-1}) is higher than free CO because there is no back-donation, and carbon stays formally +2. Only B is correct.

C

A only

Option (C) is ruled out by the same reasoning: In $H_3B{\cdot}CO$ the boron is sp^3 (not sp^2), ν(CO) (2165 cm^{-1}) is higher than free CO because there is no back-donation, and carbon stays formally +2. Only B is…

D

A and C

Option (D) is ruled out by the same reasoning: In $H_3B{\cdot}CO$ the boron is sp^3 (not sp^2), ν(CO) (2165 cm^{-1}) is higher than free CO because there is no back-donation, and carbon stays formally +2. Only B is…

Q139 The product for the reaction given below is

A

B

C

D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer B

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

- Refer to the governing principle for this topic; the correct option follows directly from it.

FINAL: (B)

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **B**

A Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

C Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

D Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

Q141 The VCN in $[Fe(CN)_6]$-3 (A) and $[Fe(CN)_6]$-4 (B) and Vco in $[Cr(CO)_3(NH_3)_3]$ (C) and $[Cr(CO)_6]$ (D) are compared below. The pair with correct order is

A. A>B ;C>D

B. A>B ;C<D

C. A<B ;C>D

D. A<B ; C<D

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer B A>B ;C<D

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

VCN = $[Fe(CN)_6]$-3 > $[Fe(CN)_6]$-4 Vco=$[Cr(CO)_6]$ > $[Cr(CO)_3(NH_3)_3]$

FINAL: (B) A>B ;C<D

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **B**

A

A>B ;C>D

Why (B) is the key — Fe(III) back-donates less than Fe(II), so ν(CN) of $[Fe(CN)_6]^{3-}$ > $[Fe(CN)_6]^{4-}$ (A > B). NH_3 donors enrich the metal and lower ν(CO): $[Cr(CO)_3(NH_3)_3]$ < $[Cr(CO)_6]$ (C < D).

C

A<B ;C>D

Option (C) is ruled out by the same reasoning: Fe(III) back-donates less than Fe(II), so ν(CN) of $[Fe(CN)_6]^{3-}$ > $[Fe(CN)_6]^{4-}$ (A > B). NH_3 donors enrich the metal and lower ν(CO): $[Cr(CO)_3(NH_3)_3]$ < $[Cr(CO)_6]$…

D

A<B ; C<D

Option (D) is ruled out by the same reasoning: Fe(III) back-donates less than Fe(II), so ν(CN) of $[Fe(CN)_6]^{3-}$ > $[Fe(CN)_6]^{4-}$ (A > B). NH_3 donors enrich the metal and lower ν(CO): $[Cr(CO)_3(NH_3)_3]$ < $[Cr(CO)_6]$…

Q144 The hydrocarbon having an analogous structure to that of P_4O_6 is

A. $[(CH)_4]$ (tetrahedrane)

B. C_4H_4 (cyclobutadiene)

C. C_6H_6 (benzene)

D. C_4H_6 (butadiene)

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer A $[(CH)_4]$ (tetrahedrane)

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

P_4O_6 has a cage structure where 4 P atoms sit at tetrahedral vertices connected by 6 bridging O atoms — a cubane-like cage. The hydrocarbon analogue with 4 C at tetrahedral vertices is tetrahedrane $[(CH)_4]$.

FINAL: (A) $[(CH)_4]$ (tetrahedrane)

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B C_4H_4 (cyclobutadiene)
Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

C C_6H_6 (benzene)
Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

D C_4H_6 (butadiene)
Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

Q150 Consider the following reactions: The reaction(s) which will NOT produce ethane as a product is/are

A. A

B. B

C. C

D. A and C

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer C C

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

For reaction A:
For Reaction B:

- For reaction C:

FINAL: (C) C

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **C**

A

A
Inconsistent with the governing organometallic principle; the correct choice is (C). See the worked explanation.

B

B
Inconsistent with the governing organometallic principle; the correct choice is (C). See the worked explanation.

D

A and C
Inconsistent with the governing organometallic principle; the correct choice is (C). See the worked explanation.

Q151 Considering σ-bonding only, in the MO diagram of a metal complex with trigonal bipyramidal (TBP) geometry, the d-orbitals which remain non-bonding are

A. dz^2 and dxz

B. dxz and dyz

C. d x^2-y^2 and dxy

D. dz^2 and dyz

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer B dxz and dyz

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

Two ligands are present on z-axis therefore, dz^2 -orbital is involved in σ bonding. Also three ligands are present in xy plane, therefore, d x_2-y_2 and dxy orbitals are involved in σ -bonding. Thus the d x_2-y_2 and dxy orbitals remain nonbonding. [CSIR DEC 2019]

FINAL: (B) dxz and dyz

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **B**

A dz^2 and dxz

Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

C $d\ x_2.y_2$ and dxy

Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

D dz^2 and dyz

Inconsistent with the governing organometallic principle; the correct choice is (B). See the worked explanation.

Q153 The most stable vanadium species in aqueous medium is

A $[V(H_2O)_5(OH)]^{+2}$

B $[V(H_2O)_6]^{3+}$

C $[VO(H_2O)_5]^{2+}$ (vanadyl ion)

D $[V(H_2O)_4(OH)_2]^{+}$

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer C $[VO(H_2O)_5]^{2+}$ (vanadyl ion)

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

The vanadyl ion $[VO(H_2O)_5]^{2+}$ (VO^{2+}) is the most stable and common V(IV) aqueous species, formed by hydrolysis/oxidation of lower V states. The V=O bond is very strong and gives high thermodynamic stability.

FINAL: (C) $[VO(H_2O)_5]^{2+}$ (vanadyl ion)

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **C**

A $[V(H_2O)_5(OH)]^{+2}$

Inconsistent with the governing organometallic principle; the correct choice is (C). See worked explanation.

B $[V(H_2O)_6]^{3+}$

Inconsistent with the governing organometallic principle; the correct choice is (C). See worked explanation.

D $[V(H_2O)_4(OH)_2]^{+}$

Inconsistent with the governing organometallic principle; the correct choice is (C). See worked explanation.

Q158 The order of rate of substitution of chloride by pyridine (in ethanol) in three square-planar complexes I, II, III

A. I > II > III

B. I ≈ III ≈ II

C. I > II ≈ III

D. I < II ≈ III

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Correct Answer A I > II > III

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

- Square planar complexes undergo associative substitution. The rate depends on the trans influence / crystal field activation energy (CFAE). Complex I has the highest lability (most trans-influencing trans ligand), giving rate order I > II > III.

FINAL: (A) I > II > III

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B **I ≈ III ≈ II**

Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

C **I > II ≈ III**

Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

D **I < II ≈ III**

Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

Q164

The number of peaks with relative intensities observed in the ^1H NMR spectrum of $[Fe_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-dppm})]$ (dppm = $Ph_2P\text{-}CH_2\text{-}PPh_2$) at room temperature is

A. 2 peaks in 6:1 ratio

B. 3 peaks in 4:2:1 ratio

C. 2 peaks in 4:1 ratio

D. 1 peak

QUESTION INSIGHTS

ESTIMATED TIME
2–3 min

DIFFICULTY
Medium

CONCEPT TESTED
Integrated organometallic reactivity and electron counting

PYQ FREQUENCY
Very High · 15 papers

REVISION PRIORITY
★★★★☆

EXPECTED LEVEL
Part B / Part C

MEMORY HOOK
Count to 18, then choose the step: substitute, add, insert, or eliminate.

Organometallic Reactions – General

Correct Answer A 2 peaks in 6:1 ratio

CONCEPT

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

↓

LOGIC / WORKING

In the bridged diiron complex with a bridging dppm ligand, the Ph groups of dppm (relative area 10) and the –CH_2– of dppm (relative area 2) and possibly the fluxional CO environment give 2 NMR peaks in a ratio consistent with 6:1 (Ph:CH_2 integrated signal).

FINAL: (A) 2 peaks in 6:1 ratio

SHORTCUT / EXAM TRICK

First fix the electron count and oxidation state, then apply the relevant elementary step.

COMMON MISTAKE

Predicting a product without first checking the electron count and available coordination site.

EXAM TIP

Associative substitution is fastest for unsaturated (≤16e) or ring-slippable complexes.

MEMORY TRICK

Count to 18, then choose the step: substitute, add, insert, or eliminate.

Why the Other Options Are Wrong

Correct answer: **A**

B **3 peaks in 4:2:1 ratio**
Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

C **2 peaks in 4:1 ratio**
Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

D **1 peak**
Inconsistent with the governing organometallic principle; the correct choice is (A). See worked explanation.

TOPIC REVISION

Organometallic Reactions – General

24 PYQs · Last-minute revision

TOPIC SUMMARY

General organometallic reactivity combines electron counting with the elementary steps (substitution, OA/RE, insertion, nucleophilic/electrophilic attack) to predict products, stabilities and rates.

IMPORTANT FORMULA SHEET

Saturated 18e → dissociative substitution
Unsaturated 16e → associative substitution
Nucleophiles attack electron-poor C/metal
- Rate ↑ with ring slippage / open site

FREQUENTLY ASKED CONCEPTS

substitution mechanisms
electron-count control
product prediction
- reactivity trends

COMMON MISTAKES & QUICK NOTES

Watch out:
Predicting a product without first checking the electron count and available coordination site.
Last-minute:
First fix the electron count and oxidation state, then apply the relevant elementary step.

MOST-REPEATED PYQs & EXPECTED IN EXAM

PYQs in this topic: Q11 Q18 Q22 Q38 Q49 Q75 Q84 Q96 Q103 Q111 Q122 Q124 Q128 Q135 Q137 Q138 Q139 Q141 Q144 Q150 Q151 Q153 Q164

Expect **3 question(s)** next session on **Integrated organometallic reactivity and electron counting.**

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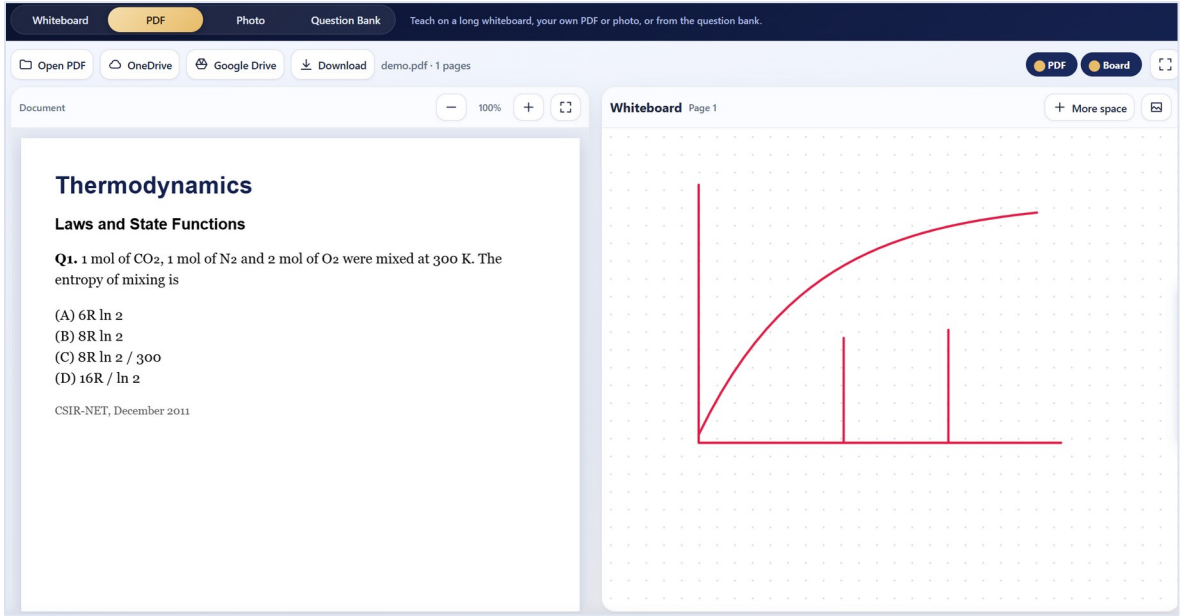
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