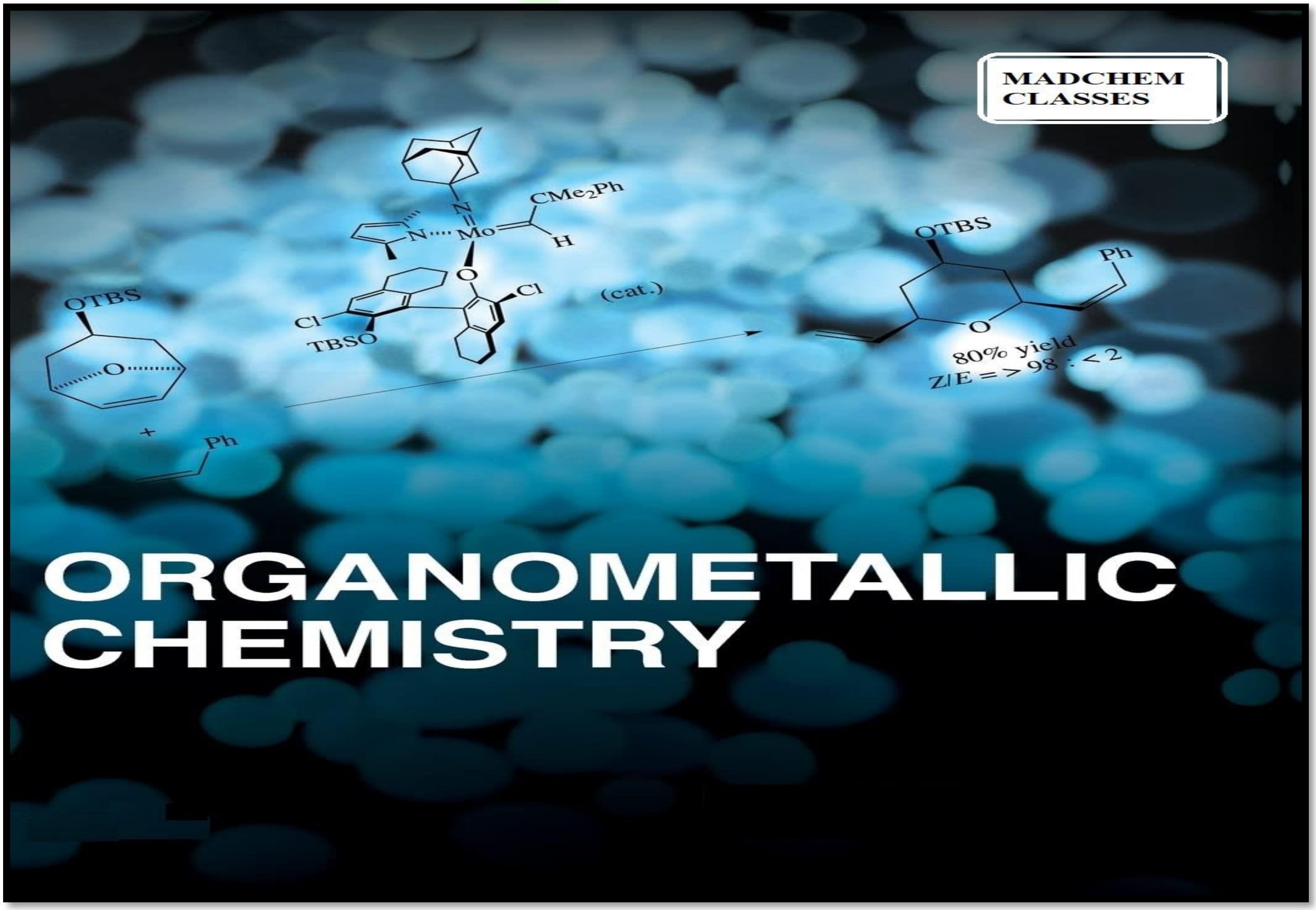
MadChem Classes

CSIR NET CHEMICAL SCIENCE



Organometallic Compound NET PYQ Ass. With Solution

1. In Ziegler–Natta catalysis the commonly used catalyst system is ? **[NET JUNE 2011]**
(a) $TiCl_4$, $Al(C_2H_5)_3$ (b) $(\eta^5\text{–}Cp)_2\ TiCl_2Al(OEt)_3$
(c) $VO(acac)_2$, $Al_2(CH_3)_6$ (d) $TiCl_4$, BF_3

2. Oxidation occurs very easily in case of: **[NET JUNE 2011]**
(a) $(\eta^5\text{-}C_5H_5)_2Fe$ (b) $(\eta^5\text{-}C_5H_5)_2Co$ (c) $(\eta^5\text{-}C_5H_5)_2Ru$ (d) $(\eta^5\text{-}C_5H_5)_2Co^+$

3. Complex in which organic ligand is having only σ–bond with metal is : **[NET JUNE 2011]**
(a) $W(CH_3)_6$ (b) $(\eta^5\text{–}C_5H_5)_2Fe$ (c) $K[PtCl_3(C_2H_4)]$ (d) $(\eta^6\text{–}C_6H_6)_2Ru$

4. The oxidative addition and reductive elimination steps are favoured by **[NET JUNE 2011]**
(a) Electron rich metal centres.
(b) Electron deficient metal centers
(c) Electron deficeint and electron rich metal centers respectively.
(d) Electron rich and electron deficient metal centers respectively.

5. Identify the order according to increasing stability of the following organometallic compounds, $TiMe_4$, $Ti(CH_2Ph)_4$, $Ti(i\text{–}Pr)_4$ and $TiEt_4$. **[NET JUNE 2011]**
(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) $TiMe_4 < TiEt_4 < Ti(i\text{–}Pr)_4\ ,\ Ti(CH_2Ph)_4$

6. 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 : **[NET JUNE 2011]**
(a) Co and Mn (b) Mn and Fe (c) Fe and Ni (d) Ni and Co

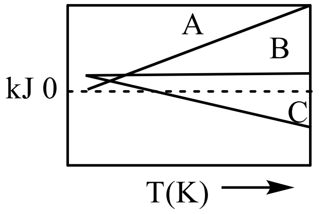
7. In the $H_2Ru_6(CO)_{18}$ cluster, containing 8–coordinated Ru centers, the hydrogen atoms are
(a) Both terminal **[NET JUNE 2011]**
(b) One terminal and the other bridging
(c) Both bridging between two Ru centers
(d) Both bridging between three Ru centers.

8. In the hydroformylation reaction, the intermediate $CH_3CH_2CH_2Co(CO)_4$: **[NET JUNE 2011]**
(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.

9. The correct combination of metal, number of carbonyl ligands and the charge for a metal carbonyl complex $[M(CO)_x]^{2-}$ that satisfies the 18 electron rule is **[NET DEC 2011]**
(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

10. The stable cyclopentadienyl complex of beryllium is **[NET DEC 2011]**
(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) $[Be(\eta^1\text{–}C_5H_5)\ (\eta^5\text{–}C_5H_5)]$

11. For the reaction $H_2O(g) + C(graphite) \rightleftharpoons CO(g) + H_2O(g)$, the variation of energy parameter ΔG^o, ΔH^o and T ΔS^o of the reaction over a large temperature range is shown below. The correct identification of the curves is given by **[NET DEC 2011]**



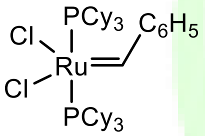
(a) $A \to \Delta G^o, B \to \Delta H^o, C \to T\Delta S^o$
(b) $A \to \Delta H^o, B \to \Delta G^o, C \to T\Delta S^o$
(c) $A \to \Delta G^o, B \to T\Delta S^o, C \to \Delta H^o$
(d) $A \to T\,\Delta S^o, B \to \Delta H^o, C \to \Delta G^o$

12. The number of metal–metal bonds in the dimers, $[CpFe(CO)(NO)]_2$ and $[CpMo(CO)_3]_2]$ respectively, are **[NET DEC 2011]**

(a) two and two
(b) two and three
(c) one and two
(d) zero and one

13. In the trans–$PtCl_2L(CO)$ complex, the CO stretching frequency for L = NH_3, pyridine, NMe_3 de–creases in the order. **[NET DEC 2011]**

14. The catalyst involved in carrying out the metathesis of 1–butene to give ethylene and 2–hexene is : **[NET DEC 2011]**

(a) 

(b) Na_2PdCl_4 **(c)** $Co_2(CO)_8$, H_2 **(d)** $RhCl(PPh_3)_3$

15. The greater stability of $(Me_3CCH_2)_4$–Ti (A) compared to that of $(Me_3CCH_2\,CH_2)_4$-Ti (B) is due to:
(a) Hyperconjugation present in complex (A) **[NET DEC 2011]**
(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)

16. A compound A having the composition $FeC_8H_8O_2$ 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 1900 and 1680 cm^{-1}. The compound follows the 18-electron rule of the following statements for A, the correct one is/are: **[NET DEC 2011]**

(I) It has $\eta^5 - C_p$ group
(II) It has terminal CO ligand
(III) It has CH_3 ligand
(IV) It has Fe–H bond

(a) I, II, III (b) II and III (c) I and IV (d) I and III

17. The reactions of $Ni(CO)_4$ with the ligand L (L = PMe_3 or $P(OMe)_3$) yields $Ni(CO)_3L$. The reaction is: **[NET JUNE 2012]**

(a) Associative (b) Dissociative (c) Interchange (Ia) (d) Interchange (Id)

18. For the reaction, trans $\left[IrCl(CO)(Ph_3)_2\right] + Cl_2 \to$ trans $-\left[IrCl_3(CO)(Phh_3)_2\right]$,the correct observation. **[NET JUNE 2012]**

(a)$V_{CO}(product) > V_{CO}(reac\,tant)$
(b) $V_{CO}(product) < V_{CO}(reac\,tant)$

(c) $V_{CO}(\text{product}) = V_{CO}(\text{reactant})$ (d) $V_{CO}(\text{product}) = V_{CO}(\text{free CO})$

19. The cluster having archano type structure is: **[NET JUNE 2012]**
(a) $[Os_5(CO)_{36}]$ (b) $[Os_3(CO)_{12}]$ (c) $[Ir_4(CO)_{12}]$ (d) $[Rh_5(CO)_{36}]$

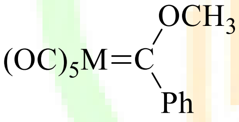
20. The complex that does not obey 18-electron rule is: **[NET JUNE 2012]**
(a) $[(\eta^5-C_5H_5)\,RuCl(CO)(PPh_3)]$ (b) $[W(CO)_3(SiMe_3)(Cl)(NCMe)_2]$
(c) $[IrCl_3(PPh_3)_2(AsPh_2)]^-$ (d) $[Os(N)Br_2(Pme_3)(Nme_2)]^-$

21. The final product of the reaction $[Mn(CO)_6]^+ + MeLi \rightarrow$ is: **[NET JUNE 2012]**
(a) $[Mn(CO)_6]^+Me^-$ (b) $[Mn(CO)_5Me]$ (c) $[Mn(CO)_6]$ (d) $[MeCO)Mn(CO)_5]$

22. The reaction $3[Rh_4(CO)_{12}) \rightarrow 2[Rh_6(CO)_{16}] + 4CO$ [25°C, 500 atm CO] is: **[NET JUNE 2012]**
(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 $\Delta G = 0$
(d) Thermodynamically unfavorable ($\Delta G > 0$)

23. In $[Mo_2(S_2)_6]^{2-}$ cluster the number of bridging S_2^{2-} and coordination number of Mo respectively, are: **[NET DEC 2012]**
(a) 2 and 8 (b) 2 and 6 (c) 1 and 8 (d) 1 and 6

24. The substitution of η^5-Cp group with nitric oxide is the easiest for: **[NET DEC 2012]**
(a) η^5-Cp_2Fe (b) η^5-Cp_2CoCl (c) η^5-Cp_2Ni (d) η^5-Cp_2Co

25. The molecule, 
$(OC)_5M{=}C(OCH_3)(Ph)$ **[NET DEC 2012]**

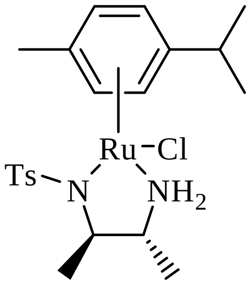
Obeys 18 e^- rule. The two 'M' satisfying the condition are:
(a) Cr, Re^+ (b) Mo, V (c) V, Re^+ (d) Cr, V

26. Complex of general formula, fac-$[Mo(CO)_3(\text{phosphine})_3]$ have the C—O stretching bands as given below. **[NET DEC 2012]**
Phosphines: PF_3(A); PCl_3(B); $P(Cl)Ph_2$(C); PMe_3(D)
ν(CO), cm^{-1}: 2090 (i); 2040 (ii); 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

27. Structure of a carborane with formula, $C_2B_4H_8$ is formally derived from: **[NET DEC 2012]**
(a) Closo-borane (b) Nido-borane (c) Arachno-borane (d) Conjuncto-borane

28. In the cluster $[Co_3(CH)(CO)_9]$ obeying 18 e^- rule, the number of metal-metal bonds and the bridging ligands respectively, as: **[NET DEC 2012]**
(a) 3 and 1 CH (b) 0 and 3 CO (c) 3 and 1 CO (d) 6 and 1 CH

29. Consider the catalyst in column I and reaction in column II **[NET DEC 2012]**

Column I	**Column II**
(a) $[(R)\text{-BINAP}]Ru^{2-}$	(I) Hydroformylation
(b) $HRh(CO)(PPh_3)_3$	(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 under Column II is:

(a) (a)-II, (b)-I, (c)-IV, (d)-III (b) (a)-I, (b)-II, (c)-III, (d)-IV

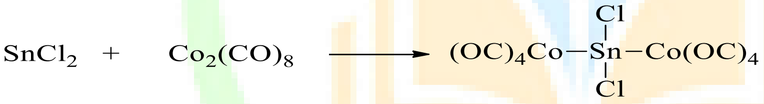
(c) (a)-III, (b)-I, (c)-IV, (d)-II (d) (a)-IV, (b)-III, (c)-II, (d)-I

30. In hydroformylation reaction using $[Rh(PPh_3)_3(CO)(H)]$ as the catalyst, addition of excess PPh_3 would: **[NET DEC 2012]**

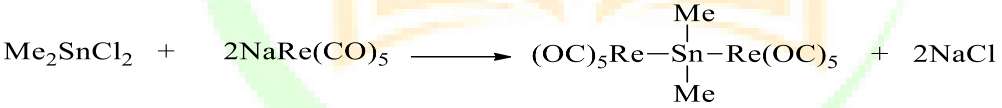
(a) Increase the rate of reaction (b) Decrease the rate of reaction

(c) Not influence of the reaction (d) Stop the reaction

31. Reactions A and B are termed as respectively **[NET DEC 2012]**

(A) 

$$SnCl_2 + Co_2(CO)_8 \longrightarrow (OC)_4Co-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Sn}}-Co(OC)_4$$

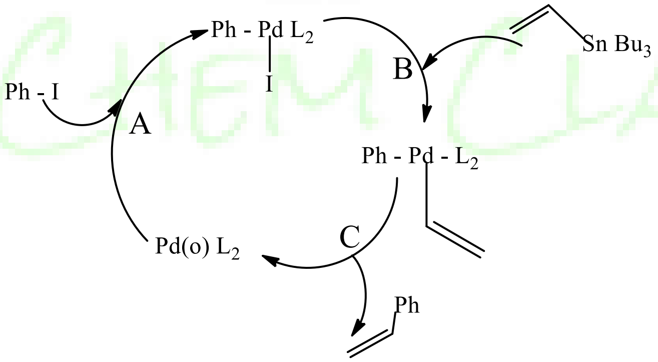
(B) 

$$Me_2SnCl_2 + 2NaRe(CO)_5 \longrightarrow (OC)_5Re-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Sn}}-Re(OC)_5 + 2NaCl$$

(a) Insertion, Metathesis (b) Metathesis, insertion

(c) Oxidative addition, metathesis (d) Oxidative addition, insertion

32. Consider the following reaction Mechanism: **[NET DEC 2012]**



The steps A, B and C, respectively, are:

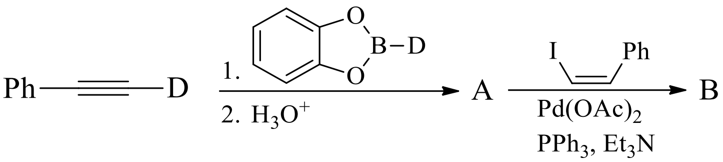
(a) Oxidative addition ; transmetallation; reductive elimination.

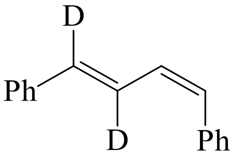
(b) Oxidative addition; Carbopalladation; $\beta-Hydride$ elimination.

(c) Carbopalladation; transmetallation; reductive elimination.

(d) Metal halogen exchange; transmetallation; metal extrusion.

33. The major product B formed in the following reaction sequence is: **[NET DEC 2012]**



(a)


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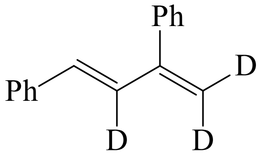

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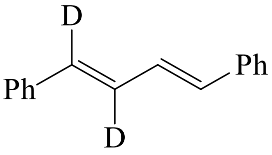
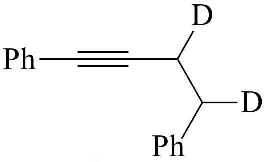


(d)


34. The oxidation state of molybdenum in $[(\eta^7\text{–tropylium}) Mo(CO)_3]^+$ is : **[NET JUNE 2013]**
(a) +2 (b) +1 (c) 0 (d) −1

35. The number of metal–metal bonds in $[W_2(OPh)_6]$ is **[NET JUNE 2013]**
(a) 1 (b) 2 (c) 3 (d) 4

36. The reaction: **[NET JUNE 2013]**
$[(CO)_5Mn(Me)] + CO \rightarrow [(CO)_5Mn\{C(O)Me\}]$ is an example of:
(a) Oxidative addition (b) Electrophilic substitution
(c) Nucleophilic substitution (d) Migratory insertion

37. Though cyclobutadiene (C_4H_4) is highly unstable and readily polymerizes in its free state, its transition metal complexes could be isolated because : **[NET JUNE 2013]**
(a) It engages in long-range interaction with transition metals
(b) It gains stability due to formation of $C_4H_4^{2+}$ on binding to transition metals
(c) Its polymerization ability reduces in presence of transition metal
(d) It becomes stable in presence of transition metals due to formation of $C_4H_4^{2+}$

38. The number of metal-metal bonds in $Ir_4(CO)_{12}$ is: **[NET JUNE 2013]**
(a) 4 (b) 6 (c) 10 (d) 12

39. The bond order of the metal-metal bond in the dimeric complex $[Re_2Cl_4(PMe_2Ph)_4]^+$ is: **[NET DEC 2013]**
(a) 4.0 (b) 3.5 (c) 3.0 (d) 2.5

40. Which of the following is not suitable as catalyst for hydroformylation: **[NET DEC 2013]**
(a) $HCo(CO)_4$ (b) $HCo(CO)_3PBu_3$
(c) $HRh(CO)(PPh_3)_3$ (d) $H_2Rh(CO)(PPh_3)_2Cl$

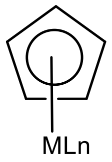
41. In a cluster, $H_3CoRu_3(CO)_{12}$, total number of electrons considered to be involved in its formation is: **[NET DEC 2013]**
(a) 57 (b) 60 (c) 63 (d) 72

42. On reducing $Fe_3(CO)_{12}$ with an excess of sodium, a carbonylate ion is formed. The iron is isoelectronic with: **[NET DEC 2013]**
(a) $[Mn(CO)_5]^-$ (b) $[Ni(CO)_4]$ (c) $[Mn(CO)_5]^+$ (d) $[V(CO)_6]^-$

43. The electrophile Ph_3C^+ reacts with $[(\eta^5-C_5H_5)Fe(CO)_2(CDMe_2)]^+$ to give a product A. The product A is formed because: **[NET DEC 2013]**

(a) Fe is oxidized
(b) Alkyl is substituted with Ph_3C
(c) Fe—Ph bond is formed
(d) Alkyl is converted to alkene

44. Substitution of L with other ligands will be easiest for the species: **[NET DEC 2013]**

(a)


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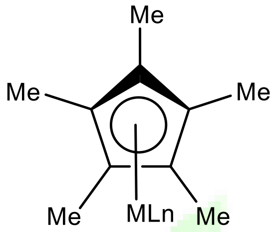

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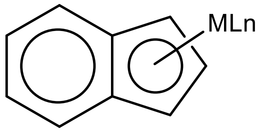


(d)


45. The ligand(s) that is /are fluxional in $\left[(\eta^5-C_5H_5)(\eta^1-C_5H_5)Fe(CO)_2\right]$ in the temperature range 221-298 K, is- **[NET JUNE 2014]**

(a) $\eta^5-C_5H_5$
(b) $\eta^1-C_5H_5$
(c) $\eta^5-C_5H_5$ & CO
(d) $\eta^1-C_5H_5$ & CO

46. The oxidation state of Ni and the number of metal–metal bonds in $[Ni_2(CO)_6]^{2-}$ that are consistent with the 18 electron rule are: **[NET JUNE 2014]**

(a) Ni(–II), 1 bond
(b) Ni(–IV), 2bonds
(c) Ni(–I), 1 bond
(d) Ni(–IV), 3 bonds

47. The compound $[Re_2(Me_2PPh)_4Cl_4]$ (M) having a configuration of $\sigma^2\pi^4\delta^2\delta^{*2}$ can be oxidized to M^+ and M^{2+}. The formal metal–metal bond order in M, M^+ andM^{2+} respectively, are: **[NET JUNE 2014]**

(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

48. The total valence electron count and the structure type adopted by the complex $[Fe_5(CO)_{15}C]$ respectively, are: **[NET JUNE 2014]**

(a) 74 and closo
(b) 60 and closo
(c) 74 and nido
(d) 62 and nido

49. ^1H NMR spectrum of $\left[(\eta^5-C_5H_5)Rh(C_2H_4)_2\right]$ at –20 ^0C shows a typical AA 'XX' pattern in the olefinic region. On increasing the temperatue to 70^o**C,** The separate lines collapse into a single line which is due to. **[NET JUNE 2014]**

(a) Free rotation of the ethylene ligand about the metal – olefin bond
(b) Intramolecular exchange between the ethylene ligands
(c) Intermolecular exchange between the ethylene ligands
(d) Change in hapticity of the cyclopentadienyl ligand

50. Reaction of nitrosyl tetrafluoroborate to Vaska's complex gives complex A with $\angle M-N-O=124^0$. The complex A and its NO stretching frequency are, respectively- **[NET JUNE 2014]**

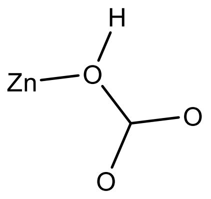
(a) $[IrCl(CO)(NO)(PPh_3)_2]BF_4, 1620\,cm^{-1}$
(b) $[IrCl(NO)_2(CO)(PPh_3)](BF_4)_2, 1730\,cm^{-1}$
(c) $[IrCl(CO)(NO)_2(PPh_3)](BF_4)_2 1520\,cm^{-1}$
(d) $[IrCl(CO)(NO)(PPh_3)_2], 1820\,cm^{-1}$

51. A 1 : 2 mixture of $Me_2NCH_2CH_2CH_2PPh_2$ and KSCN with $K_2[PdCl_4]$ gives a square planar complex A. Identify the correct pairs of donor atoms trans to each other in complex A from the following combinations. **[NET JUNE 2014]**

I. P, N
II. N, S
III. P, S
IV. N, N

(a) I and II (b) I and IV (c) II and III (d) III and IV

52. At pH 7, the zinc (II) ion in carbonic anhydrase reacts with CO_2 to give **[NET JUNE 2014]**

(a)


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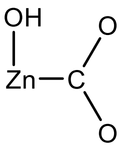

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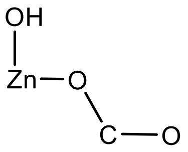

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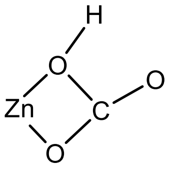
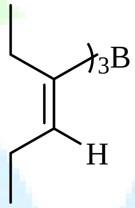


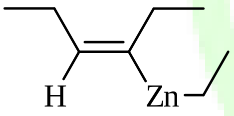
53. Amongst the following which are not isolobal pairs: **[NET JUNE 2014]**

(a) $Mn(CO)_5$, CH_3 (b) $Fe(CO)_4$, O (c) $Co(CO)_3$, R_2Si (d) $Mn(CO)_5$, RS

54. The organoborane X, when reacted with Et_2Zn followed by *p*-iodotoluene in the presence of catalytic amount of $Pd(PPh_3)_4$ furnishes a trisubstituted alkene. The intermediate and the product of the reaction, respectively, are: **[NET JUNE 2014]**



X

(a)


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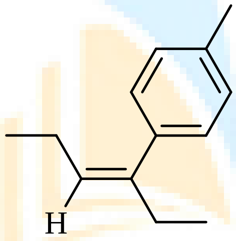
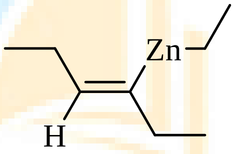


(b)


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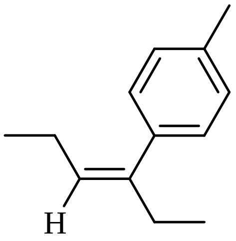

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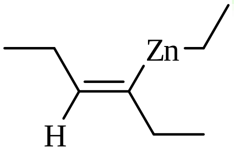

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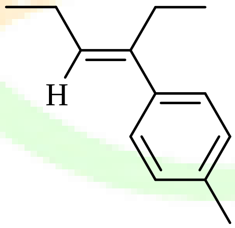

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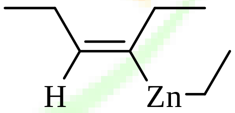

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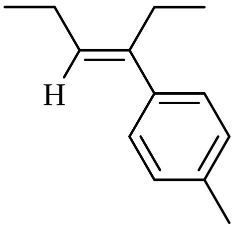


55. The hapticities X and Y of the arene moieties in the diamagnetic complex **[NET DEC 2014]**
$\left[\left(\eta^{x}-C_6H_6\right)Ru\left(\eta^{y}-C_6H_6\right)\right]$, respectively, are-

(a) 6 & 6 (b) 4& 4 (c) 4 & 6 (d) 6 & 2

56. The rate of the reaction **[NET DEC 2014]**

$Ni(CO)_4 + PPh_3 \xrightarrow{hv} [Ni(CO)_3(PPh_3)] + CO$ 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

57. The product of the reaction of propene, CO and H_2 in the presence of $Co_2(CO)_8$ as a catalyst is: **[NET DEC 2014]**

(a) Butanoic acid (b) Butanal (c) 2-butanone (d) Methylpropanoate

58. $Co_4(CO)_{12}$ adopts the : **[NET DEC 2014]**

(a) *closo*-structure (b) *nido*-structure (c) *arachno*-structure (d) *hypho*-structure

59. Reductive elimination step in hydrogenation of alkenes by Wilkinson catalyst results in (neglecting solvent in coordination sphere of Rh) **[NET DEC 2014]**

(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 $[Rh(H)(PPh_3)_2]$

60. $Na[(\eta^5-C_5H_5)Fe(CO)_2]$ 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: **[NET DEC 2014]**

(a) $(\eta^5-C_5H_5)$ Fe $(CO)_2Br$ and $(\eta^5-C_5H_5)Fe(CO)_2H$

(b) $(\eta^4-C_5H_5)$ Fe $(CO)_2Br_2$ and $(\eta^4-C_5H_5)Fe(CO)_2HBr$

(c) $(\eta^5-C_5H_5)$ Fe $(CO)_2Br$ and $(\eta^4-C_5H_5)Fe(CO)_2(H)_2$

(d) $(\eta^5-C_5H_5)$ Fe $(CO)_2Br$ and $(\eta^5-C_5H_5)Fe(CO)_2HBr$

61. The compound that undergoes oxidative addition reaction in presence of H_2 is: **[NET DEC 2014]**

(a) $[Mn(CO)_5]^-$ (b) $[(\eta^5-C_5H_5)Mo(CO)_3]^-$

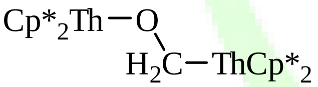
(c) $[IrCl(CO)(PPh_3)_2]$ (d) $[(\eta^5-C_5H_5)_2ReH]$

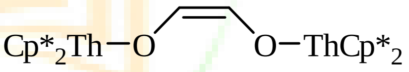
62. The reaction of phosphorus trichloride with phenyllithium in 1:3 molar ratio yields product ‘X’, which on further treatment with methyl iodide produces ‘Y’. The reaction of B with “BuLi gives product ‘Z’. The products X, Y and Z, respectively, are: **[NET DEC 2014]**

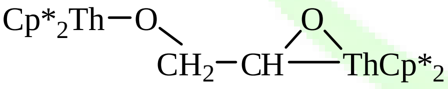
(a) $[PPh_4]Cl$, $[Ph_2P{=}CH_2]I$, $Ph_2P(n\text{Bu})$ (b) PPh_3, $[Ph_3PI]Me$, $Ph_2P(n\text{Bu})_3$

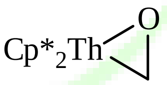
(c) PPh_3, $[PPh_3PMe]I$, $Ph_3P{=}CH_2$ (d) $[PPh_4]Cl$, $[Ph_3P{=}CH_2]I$, $[Ph_3P(n\text{Bu})]Li$

63. The final product in the reaction of $[Cp^*_2ThH]$ with CO in an equimolar ratio is: **[NET DEC 2014]**

(a) 

(b) 

(c) 

(d) 

64. Complexes $HM(CO)_5$ and $[(\eta^5-C_5H_5)M'(CO)_3]_2$ obey the 18-electron rule. Identify M and M’ and their ^1H NMR chemical shifts relative to TMS: **[NET DEC 2014]**

(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

65. The binding modes of NO in 18 electron compounds $[Co(CO)_3(NO)]$ and $[Ni(\eta^5—Cp)(NO)]$, respectively, are : **[NET JUNE 2015]**

(a) linear and bent (b) bent and linear (c) linear and linear (d) bent and bent

66. The role of copper salt as co-catalyst in Wacker process is: **[NET JUNE 2015]**

(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)

67. For typical Fischer and Schrock carbenes, consider the following statements: **[NET JUNE 2015]**

(I) Oxidation state of metal is low in Fischer carbene and high in Schrock carbene

(II) Auxilliary ligands are π-acceptor in Fischer carbene and non-π-acceptor in Schrock carbene

(III) Substituents on carbene carbon are non-π-donor in Fischer carbene and π-donor in Schrock carbene

(IV) Carbene carbon is electrophilic in Fischer carbene and nucleophilic in Schrock carbene

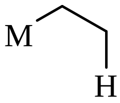
The correct statements are:

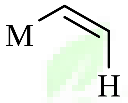
(a) I, II and III (b) I, II and IV (c) II, III and IV (d) I, III and IV

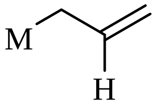
68. The refluxing of $RhCl_3.3H_2O$ with an excess of PPh_3 in ethanol gives a complex A. Complex A and the valence electron count on rhodium are, respectively: **[NET JUNE 2015]**

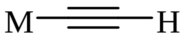
(a) $[RhCl(PPh_3)_3]$, 16 (b) $[RhCl(PPh_3)_5]$, 16 (c) $[RhCl(PPh_3)_3]$, 18 (d) $[RhCl(PPh_3)_5]$, 18

69. The β-hydrogen elimination will be facile in **[NET JUNE 2015]**

(a) 

(b) 

(c) 

(d) 

70. Match the column A(coupling reactions) with column B(Reagents): **[NET JUNE 2015]**

Column – A	**Column-B**
(a) Suzuki coupling	(I) $CH_2 = CHCO_2\,CH_3$
(b) Heck coupling.	(II) $RB\,(OH)_2$
(c) Sonogashira coupling.	(III) $PhCO(CH_2)_3\,Zn\,I$
(d) Negishi coupling	(IV) $HC \equiv CR$
	(V) SnR_4

(a) a-II, b-I, c-IV, d-III (b) a-I, b-V, c-III, d-IV (c) a-IV, b-III, c-II, d-I (d) a-II, b-III, c-IV, d-V

71. According to Wade's theory the anion $[B_{12}H_{12}]^{2-}$ adopts **[NET JUNE 2015]**

(a) closo-structure (b) arachno-structure (c) hypo-structure (d) nido-structure

72. The following statements are given regarding the agostic interaction C—H—Ir observed in $[Ir(Ph_3P)_3Cl]$. **[NET JUNE 2015]**

I. Upfield shift of C—H proton in 1H NMR spectrum

II. Increased acid character of C—H

III. V_{C-H} in IR spectrum shifts to higher wave number

The correct answer is/are:

(a) I and II (b) II and III (c) I and II (d) III only

73. Amongst the following: (I) $[Mn(\eta^5\text{-}Cp)(CO)_3]$, (II) $[Os(\eta^5\text{-}Cp)_2]$, (III) $[Ru(\eta^5\text{-}Cp)_2]$ and (IV) $[Fe(\eta^5\text{-}Cp)_2]$ the compounds with most shielded and deshielded Cp protons respectively, are: **[NET JUNE 2015]**

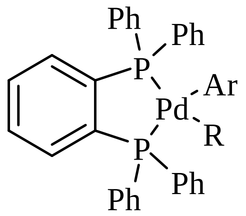
(a) IV and I (b) IV and II (c) III and I (d) III and II

74. Total number of vertices in metal clusters $[Ru_6(C)(CO)_{17}]$, $(Os_5C(CO)_{15}]$ and $[Ru_5C(CO)_{16}]$ are 6, 5 and 5, respectively. The predicted structures of these complexes, respectively, are: **[NET JUNE 2015]**

(a) closo, nido and nido (b) closo, nido and arachno

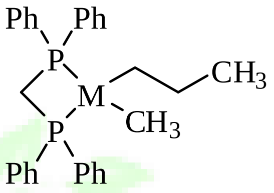
(c) arachno, closo and nido (d) arachno, nido and closo

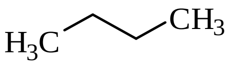
75. The reductive elimination of Ar—R (coupled product) from A is facile when **[NET JUNE 2015]**



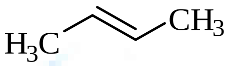
(a) R = CH_3 (b) R = CH_2Ph (c) R = CH_2COPh (d) R = CH_2CF_3

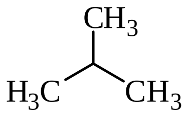
76. The least probable product from A on reductive elimination is: **[NET JUNE 2015]**



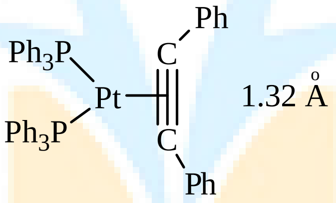
(a)


(b) CH_4

(c)


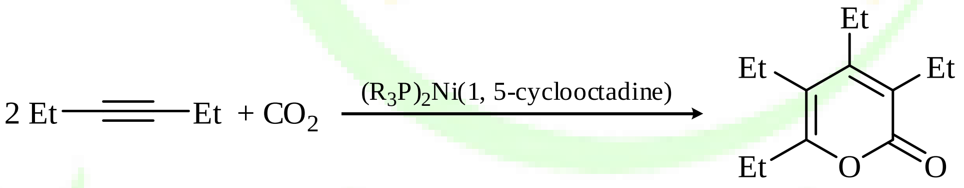
(d)


77. With respect to σ and π bonding in Pt—III in the structure given below, which of the following represent the correct bonding : **[NET JUNE 2015]**



(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*)

78.  **[NET JUNE 2015]**

For the above conversion, which of the following statements are correct?

I. CO_2 combines with $Ni(PR_3)_2$ (1,5-cyclooctadiene)

II. Insertion of CO_2 occurs

III. Insertion of $\mathrm{Et}{-}{\equiv}{-}\mathrm{Et}$ takes place

The correct answer is

(a) I and II (b) II and III (c) III and I (d) I, II and III

79. For the reaction of $\left[Fe\left(\eta^5-C_5H_5\right)(CH_3)(CO)_2\right]$ with PMe_3, the main intermediate is:

[NET DEC 2015]

(a) $\left[Fe\left(\eta^5\text{-}C_5H_5\right)(CH_3)(CO)_2(PMe_3)\right]$ (b) $\left[Fe\left(\eta^5\text{-}C_5H_5\right)(COCH_3)(CO)\right]$

(c) $\left[Fe\left(\eta^3-C_5H_5\right)(CH_3)(CO)_2\right]$ (d) $\left[Fe\left(\eta^3\text{-}C_5H_5\right)(COCH_3)(CO)(PMe_3)\right]$

80. The molecule C_3O_2 has a linear strcuture. This compound has **[NET DEC 2015]**

(a) 4σ and 4π bonds (b) 3σ and 2 π bonds

(c) 2σ and 3π bonds (d) 3σ and 4π bonds.

81. [(η^3-C_3H_5)Mn(CO)$_4$ shows fluxional behavior. The ^{1}H NMR spectrum of this compound when it is in the non-fluxional state shows: **[NET DEC 2015]**

(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

82. Using Wade's rules predict the structure type of [$C_2B_5H_7$] **[NET DEC 2015]**

(a) Nido (b) Closo (c) Arachno (d) Hypho

83. For uranocene, the correct statements (s) is /are: **[NET DEC 2015]**

(I) Oxidation state of uranium is '+4' (II) It has cyclooctatetraenide ligands

(III) It is a bent sandwich compound (IV) It has '–2' charge.

Correct answer is:

(a) I and II (b) II and III (c) I and IV (d) II only

84. The final products of the reaction of carbonyl metalates [V(CO)$_6$]$^-$and [Co(CO)$_4$]$^-$ with H_3PO_4, respectively, are: **[NET DEC 2015]**

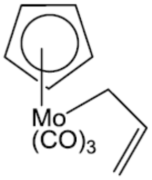
(a) V(CO)$_6$ and HCo(CO)$_4$ (b) HV (CO)$_6$ and Co_2(CO)$_8$

(c) H_2V(CO)$_6$]$^+$and HCo(CO)$_4$ (d) V(CO)$_6$ and Co_2(CO)$_8$

85. The number of valence electrons provided by [Ru(CO)$_3$] fragment towards cluster bonding is: **[NET DEC 2015]**

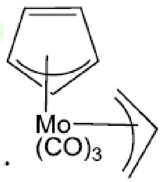
(a) 1 (b) 14 (c) 6 (d) 2

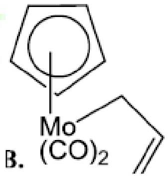
86. The intermediate and the final major product of photolysis of Z **[NET DEC 2015]**

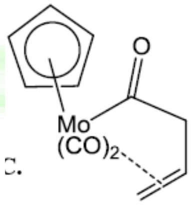


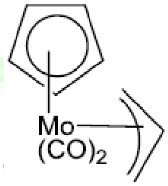
Z

from the following:

(I)


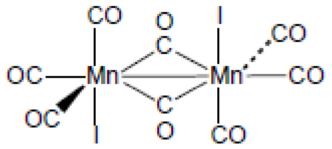
(II)


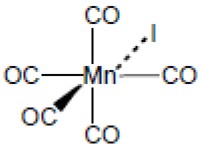
(III)


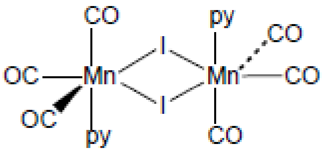
(IV)


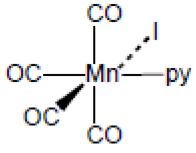
(a) I and IV (b) II and IV (c) II and III (d) I and III

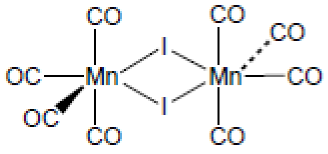
87. Reaction of [Mn_2(CO)$_{10}$] with I_2 results in A without loss of CO. Compound A, on heating to 120°C loses a CO ligand to give B, which does not have a Mn—Mn bond. Compound B reacts with pyridine to give 2 equivalents of C. Compounds A, B and C from the following respectively, are: **[NET DEC 2015]**


I


II


III


IV


V

(a) II, V and IV (b) II, III and IV (c) V, III and IV (d) II, V and III

88. The approximate positions of ν_{CO} bands (cm^{-1}) in the solid–state infrared spectrum and the Fe–Fe bond order in $[Fe(\eta^5-C_5H_5)(\mu-CO)(CO)]_2$ (non-centrosymmetric) respectively, are: **[NET DEC 2015]**

(a) (2020, 1980, 1800) and one (b) (2020, 1980, 1800) and Two

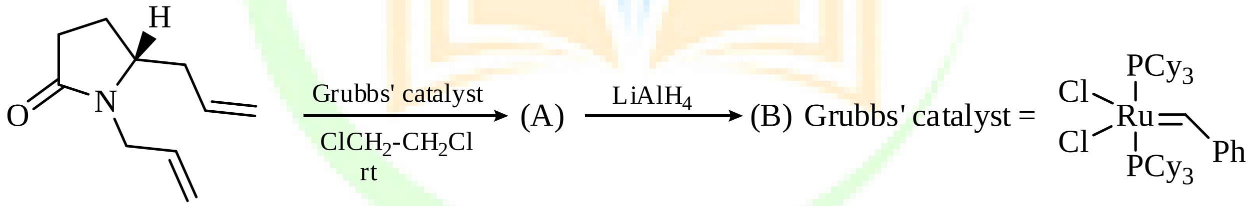
(c) (2020, 1980) and one (d)(2143) and one

89. Protonated form of ZSM-5 catalyzes the reaction of ethene with benzene to produce ethylbenzene. The correct statement for this catalytic process is **[NET DEC 2015]**

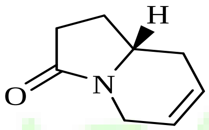
(a) alkyl carbocation is formed (b) carbanion is formed

(c) benzene is converted to $(C_6H_5)^+$ group (d) vinyl radical is formed

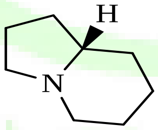
90. The major products A and B in the following reaction sequence are: **[NET DEC 2015]**



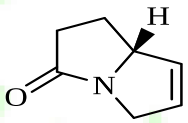
(a) A =



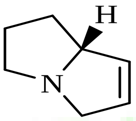
B =



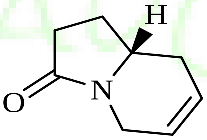
(b) A =



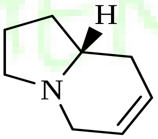
B =



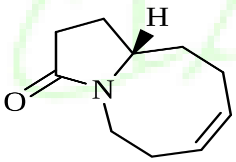
(c) A =



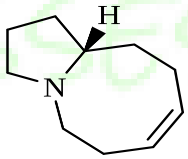
B =



(d) A =

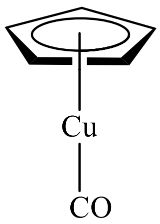


B =

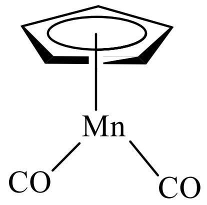


91. Identify the species, those obey the 18-electron rule, from the following: **[NET JUNE 2016]**

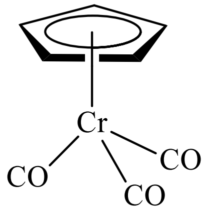
(I)



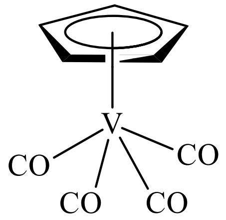
(II)



(III)

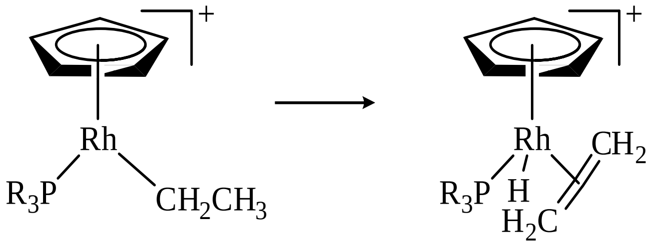


(IV)



(a) I and II (b) II and III (c) III and IV (d) I and IV

92. The following transformation is an example of: **[NET JUNE 2016]**



(a) Oxidative addition (b) Insertion

(c) β-hydride elimination (d) Reductive elimination

93. $C_pM[C_p is(\eta^5-C_5H_5)]$ fragment isolobal with a BH fragment is: **[NET JUNE 2016]**

(a) C_pGe (b) C_pMn (c) C_pRu (d) C_pCo

94. The number of metal–metal bonds in $[Co_2Fe_2(CO)_{11}(\mu_4-PPh)_2]$ is: **[NET JUNE 2016]**

(a) 3 (b) 4 (c) 5 (d)6

95. Correct order of M—C bond length of metallocenes (a-c) **[NET JUNE 2016]**

(I) $[Fe(\eta^5\text{-}Cp)_2]$ (II) $[Ni(\eta^5\text{-}Cp)_2]$ (III) $[Co(\eta^5\text{-}Cp)_2]$ is:

(a) I > II > III (b) II > III > I (c) III > II > I (d) I > III > II

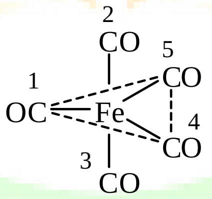
96. The ^1H NMR spectrum of $[Ru(\eta^4\text{-}C_8H_8)(CO)_3]$ at 23°C consists of a sharp single line. The number of signals observed at low temperature (–140°C) in its spectrum is: **[NET JUNE 2016]**

(a) 8 (b) 6 (c) 4 (d) 2

97. The numbers of skeletal electrons present in the compounds $C_2B_3H_5$, C_2B_4 **[NET JUNE 2016]**

(a) 10, 12 and 12 (b) 12,14 and 14 (c)10, 12 and 14 (d)12, 14 and 12

98. For fluxional $Fe(CO)_5$ (structure given below) in solution, the exchange of numbered CO groups will be between: **[NET JUNE 2016]**



(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

99. In the following reaction sequence: **[NET JUNE 2016]**

$$HNEt_2 + CS_2 \xrightarrow{KOH} P \xrightarrow[I_2]{\text{aq soln}} R \xrightarrow{[CpMo(CO)_3]_2} S$$

where dtc = dithiocarbamate and tds = thiuramdisulfide.

Identify P, R and S. Cp = $\eta^5\text{-}C_5H_5$

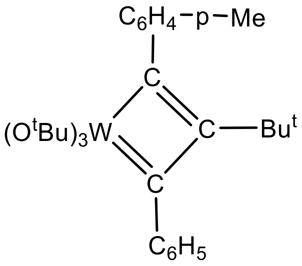
P	**R**	**S**
(a) $Et_2dtc^-K^+$	Et_4tds	$CpMo(Et_2dtc)(CO)_2$
(b) $Etdtc^-K^+$	Et_3tds	$CpMo(Et_3dtc)(CO)_2$
(c) $Et_4dtc^-K^+$	Et_2tds	$CpMo(Et_4dtc)(CO)$
(d) $Etdtc^-K^+$	Ettds	CpMo(Etdtc)(CO)

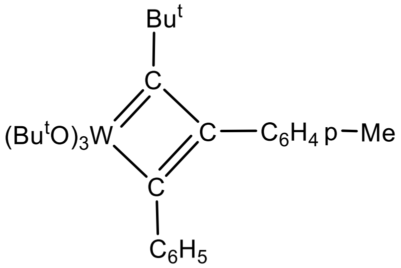
100. Heating a sample of $[(\eta^5-C_5H_5)Mo(CO)_3]_2$ results in the formation of $[(\eta^5-C_5H_5)Mo(CO)_2]_2$ with elimination of 2 equivalents of CO. The Mo–Mo bond order in this reaction changes from:

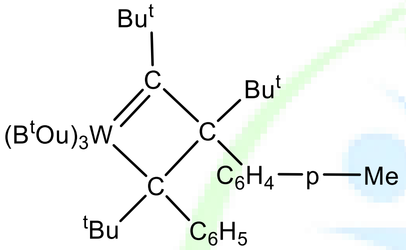
[NET JUNE 2016]

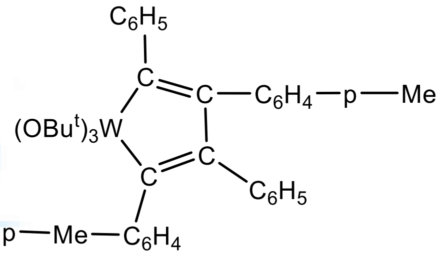
(a) 2 to 3 (b) 1 to 2 (c) 1 to 3 (d) 2 to 4

101. A plausible intermediate involved in the self-metathesis reaction of **[NET JUNE 2016]**
$C_6H_5-C\equiv C-C_6H_4\text{-p-Me}$ catalyzed by $[({}^tBuO)_3W\equiv C\text{-}{}^tBu]$ is:

(a)


(b)


(c)


(d)


102. The correct reagent combination to effect the following reaction is **[NET JUNE 2016]**

(a) (i) $NaBH_4$, $CeCl_3$, MeOH, 0°C; (ii) H_2, $[Ir(COD)(py)P(Cy)_3]PF_6$, (iii) Ph_3P, $PhCO_2H$, DEAD; (iv) $LiAlH_4$.

(b) (i) Li, liquid NH_3; (ii) H_2, $[Ir(COD)(py)P(Cy)_3]PF_6$; (iii) Ph_3P, $PhCO_2H$, DIAD; (iv) $NaBH_4$, $CeCl_3$, MeOH, 0°C.

(c) (i) H_2, Pd/C; (ii) $LiAlH_4$, −78°C

(d) (i) H_2, Pd/C; (ii) Li, liquid NH_3.

103. The number of bridging ligand(s) and metal-metal bond(s) present in the complex $[Ru_2(\eta^5\text{-}Cp)_2(CO)_2(Ph_2PCH_2PPh_2)]$ (obeys 18-electron rule), respectively, are: **[NET DEC 2016]**

(a) 0 and 1 (b) 2 and 1 (c) 3 and 1 (d) 1 and 2

104. The rate of alkene coordination to $[PtCl_4]^{2-}$ is highest for: **[NET DEC 2016]**

(a) norbornene (b) ethylene (c) cyclohexene (d) 1-butene

105. According to isolobal analogy, the right set of fragments that might replace $Co(CO)_3$ in $[Co_4(CO)_{12}]$ is: **[NET DEC 2016]**

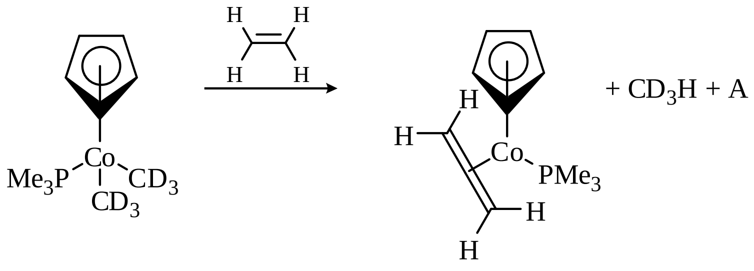
(a) CH, BH and $Mn(CO)_5$ (b) P, CH and $Ni(\eta^5\text{-}C_5H_5)$

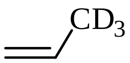
(c) $Fe(CO)_4$, CH_2 and $SiCH_3$ (d) BH, $SiCH_3$ and P

106. 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: **[NET DEC 2016]**

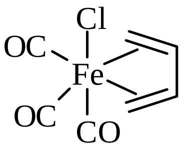
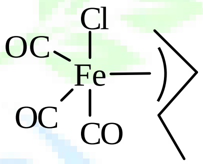
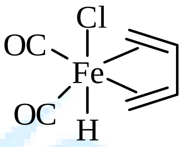
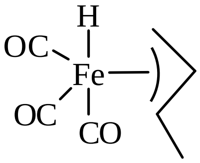
(a) closo and nido (b) nido and arachno (c) closo and arachno (d) nido and nido

107. Product A in the following reaction is: **[NET DEC 2016]**



(a) $D_2C{=}CD_2$ (b) $D_3C{-}CD_3$ (c)  (d) $H_2C{=}CD$

108. Treatment of $Fe(CO)_5$ with 1,3-butadiene gives B that shows two signals in its ^1H NMR spectrum. B on treatment with HCl yields C which shows four signals in its ^1H NMR spectrum. The compound C is: **[NET DEC 2016]**

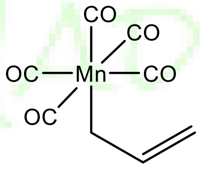
(a)  (b)  (c)  (d) 

109. The correct statement for a Fischer carbene complex is: **[NET DEC 2016]**
(a) The carbene carbon is electrophilic in nature (b) Metal exists in high oxidation state
(c) Metal fragment and carbene are in the triplet states. (d) CO ligands destabilize the complex

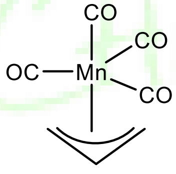
110. Choose the isoelectronic pair among the following : **[NET JUNE 2017]**
A. $[V(CO)_6]$
B. $[Cu(\eta^5{-}C_5H_5)(CO)]$
C. $[Co(CO)_4]^-$
D. $[IrCl(CO)(PPh_3)_2]$
(a) A and B (b) B and C (c) C and D (d) A and D

111. An organometallic fragment that is isolobal to CH_3^+ is: **[NET JUNE 2017]**
(a) $[Fe(CO)_5]$ (b) $[Mn(CO)_5]$ (c) $[Cr(CO)_5]$ (d) $[Ni(CO)_3]^+$

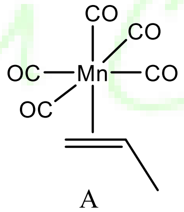
112. Reaction of $Na[Mn(CO)_5]$ with $H_2C = CHCH_2Cl$ gives A along with NaCl. Photolysis of compound A results in compound B together with elimination of CO. The correct structural formulations of compound A and B are respectively: **[NET JUNE 2017]**

(a) 

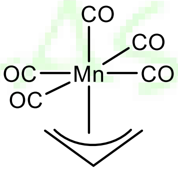
A



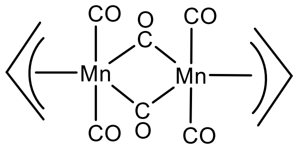
B

(b) 

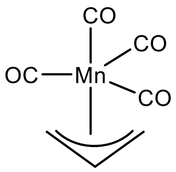
A



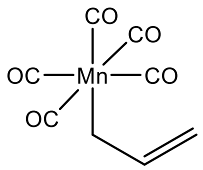
B

(c) 

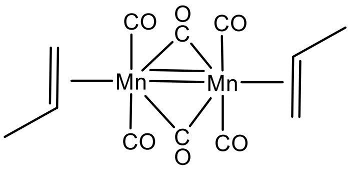
A



B

(d) 

A



B

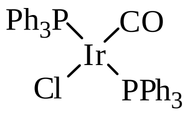
113. The number of bonding molecular orbitals and the number of available skeletal electrons in $[B_6H_6]^{2-}$, respectively, are : **[NET JUNE 2017]**

(a) 7 and 14 (b) 6 and 12 (c) 18 and 12 (d) 11 and 14

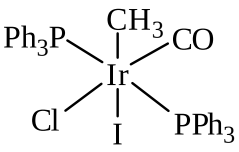
114. Addition of $NaBH_4$ to $[(\eta^5\text{-Cp})Fe(\eta^6\text{-}C_6H_6)]^+$ will give: **[NET JUNE 2017]**

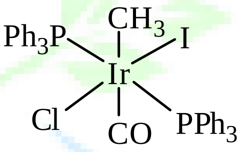
(a) $[(\eta^5\text{-Cp})Fe(H)_2]^-$ (b) $[(\eta^5\text{-Cp})Fe(H)(\eta^6\text{-}C_6H_6)]$

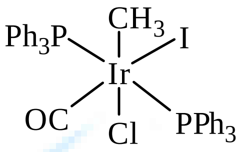
(c) $[(\eta^5\text{-Cp})Fe(\eta^6\text{-}C_6H_6)]$ (d) $[(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_6H_7)]$

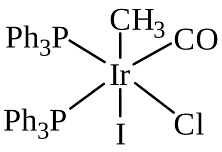
115. Identify the product in the reaction between 

and CH_3I going at room temperature *via* S_N2 mechanism: **[NET JUNE 2017]**

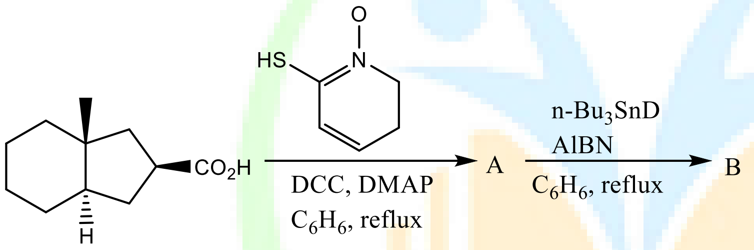
(a) 

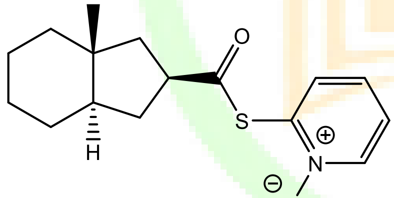
(b) 

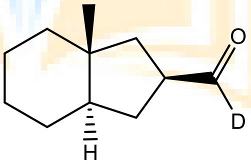
(c) 

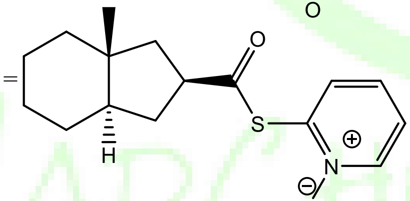
(d) 

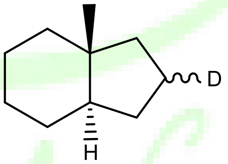
116. The intermediate A and product B formed in the following reaction sequence are **[NET JUNE 2017]**

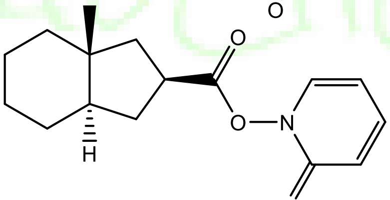


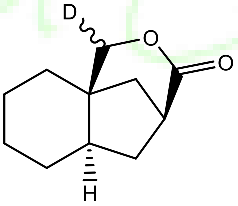
(a) A = 

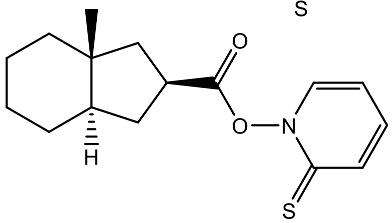
B = 

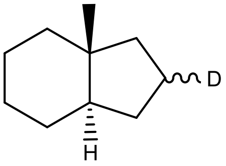
(b) A = 

B = 

(c) A = 

B = 

(d) A = 

B = 

117. Among the following, species isolobal to CH_2 are: **[NET DEC 2017]**

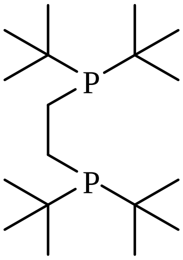
(I) $CpCr(CO)_2$ (II) CpCu (III) $Ni(CO)_2$ (IV) $Cr(CO)_4$

(V) $Fe(CO)_4$

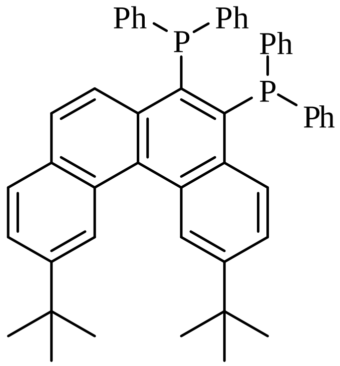
(a) I, III and V (b) II, III and IV (c) II, III and V (d) I, II and IV

118. In the complex $[Pd(L\text{-}L)(Me)(Ph)]$, the disphosphine (L-L) that does not allow reductive elimination of PhMe, is: **[NET DEC 2017]**

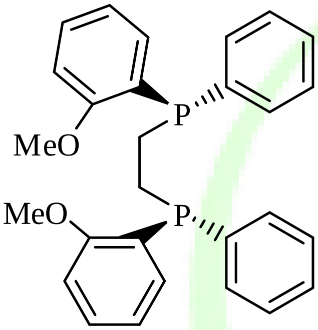
(a)



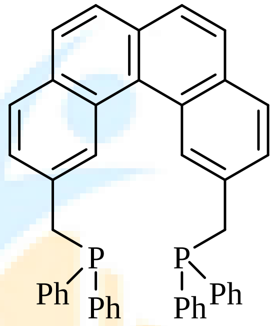
(b)



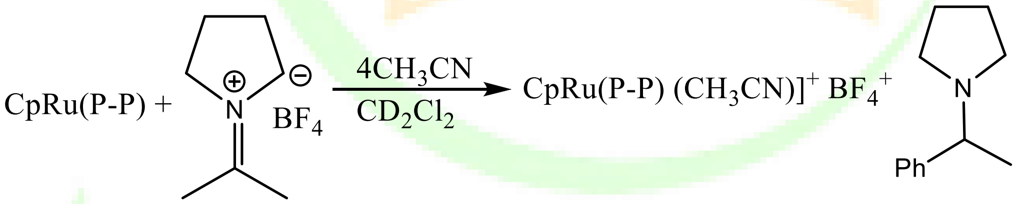
(c)



(d)



119. In the reacion given below, the bisphosphine (P–P) that is in effective for transfer hydrogenation reaction is **[NET DEC 2017]**



(a) Diphenylphosphinomethane (b) 1, 2- Diphenylphosphinoethane

(c) 1, 3-Diphenylphosphinopropane (d) 1, 4-Diphyenylphosphinobutane

120. According to Wade's rules, the *cluster type* and geometry of $[Sn_9]^{4-}$, respectively, are: **[NET DEC 2017]**

(a) *closo* and tricapped trigonal prismatic (b) *nido* and monocapped square-antiprismatic

(c) *arachno* and heptagonal bipyramidal (d) *closo* and monocapped square antiprismatic

121. The correct of C–O bond length is – **[NET JUNE 2018]**

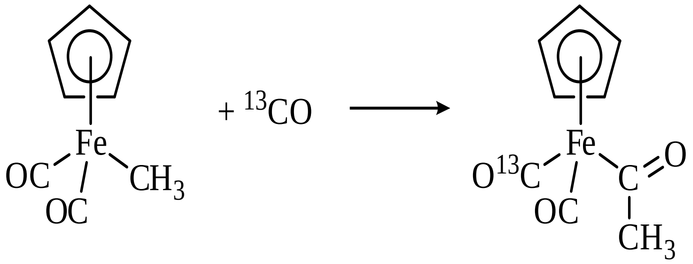
(a) $H_3B.CO > [Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^-$

(b) $[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+ > H_3B.CO$

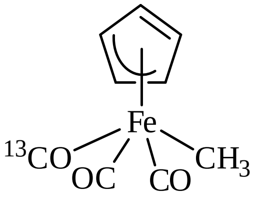
(c) $[Mn(CO)_6]^+ > H_3B.CO > V(CO)_6]^- > [Cr(CO)_6]$

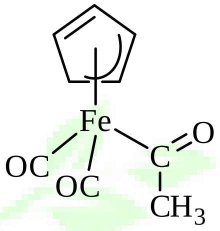
(d) $[Cr(CO)_6] > [V(CO)_6]^- > H_3B.CO > [Mn(CO)_6]^+$

122. For the following reaction **[NET JUNE 2018]**



The structure of the intermediate is:

(a)


(b)


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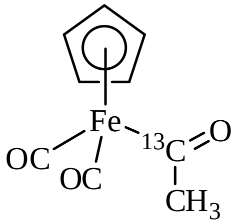

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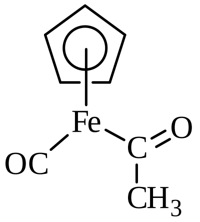
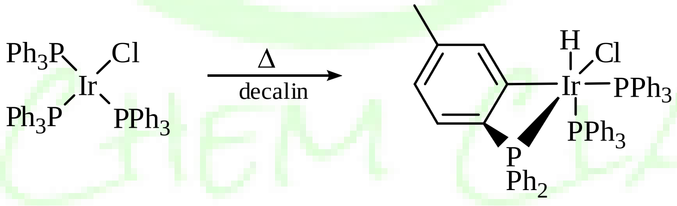


123. The correct increasing order of C-C bond length in the following molecules (A–D)
$[PtCl_3(C_2H_4)]^-$(A), $[Pt(PPh_3)_2(C_2H_4)]$(B), $[Pt(PPh_3)_2 \{C_2(CH_4)\}]$ (C) **[NET JUNE 2018]**
(a) (C) < (A) < (B) (b) (A) < (B) < (C) (c) (B) < (C) < (A) (d) (C) < (B) < (A)

124. Which of the following are not *closo* clusters: **[NET JUNE 2018]**
$[\{Co(\eta^5\text{-}C_5H_5)\}_2(C_2B_6H_8)]$ (A), $[B_4C_2H_8]$ (B), $[B_{10}H_{13}\{Au(PPh_3)\}]$ (C), $[C_2B_8H_{10}]$ (D)
The correct answer is:
(a) C and D (b) A and B (c) A and C (d) B and C

125. Identify the pair of molecules which are isoelectronic as well as isostructural from the following: **[NET JUNE 2018]**
$[Pd(PPh_3)_4]^-$(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

126. For the following reaction, correct statement(s) is/are: **[NET JUNE 2018]**

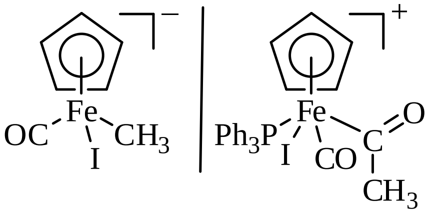


(I) (II)

(a) Oxidation state of iridium increases from I to III
(b) It is β-hydride elimination reaction
(c)I and II both are diamagnEtic
(d) It is migratory insertion reaction
The correct answer is:
(a) (a) only (b) (a) and (c) (c) (c) and (d) (d) (b), (c) and (d)

127. The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ with CH_3I gives compound A. The ^1H NMR spectrum of A shows two singlets in an integrated intensity ratio of 3:5. Compound A upon reaction with PPh_3

gives compound B. The ^{1}H NMR spectrum of B shows 3 sets of signals in an integrated intensity ratio of 3:5:15. Compounds A and B respectively, are: **[NET JUNE 2018]**

(a)


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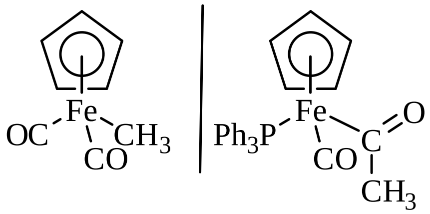
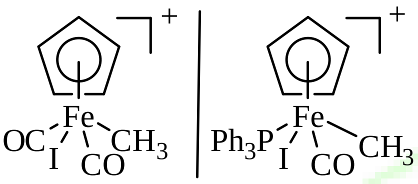
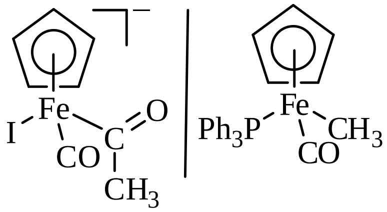


(c)


(d)


128. The structures of $[Re_2Cl_8]^{2-}$ (A) and $[Os_2Cl_8]^{2-}$ (B) are made up of two MCl_4 units. For these structures, which statement is correct? **[NET JUNE 2018]**

(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.

129. The correct order of acceptor ability of the phosphrous ligands is **[NET DEC 2018]**

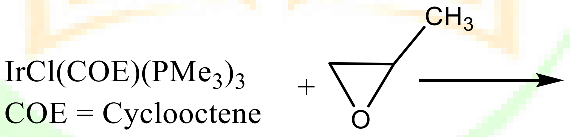
(a) $PMe_3 > PPh_3 > P(OPh)_3 > PF_3$

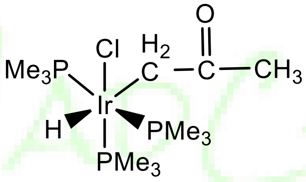
(b) $PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

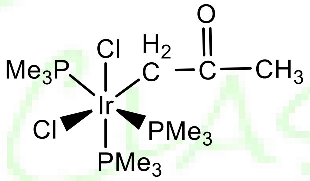
(c) $PF_3 > PMe_3 > PPh_3 > P(OPh)_3$

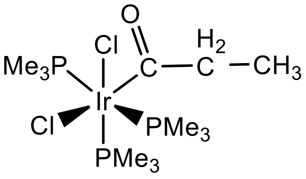
(d) $P(OPh)_3 > PF_3 > PMe_3 > PPh_3$

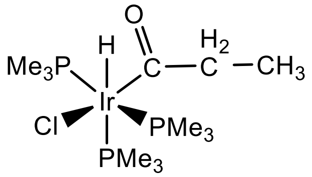
130. The product for the reaction given below is **[NET JUNE 2018]**



(a)


(b)


(c)


(d)


131. Match the following complexes with their ν_{CO} stretching frequency **[NET JUNE 2018]**

Complex	$\nu_{CO}(cm^{-1})$ values
(A) $Mo(PF_3)_3(CO)_3$	(I) 1835, 1934
(B) $Mo\{P(OMe)_3\}_3(CO)_3$	(II) 1888, 1977

(C) $Mo(PPh_3)_3(CO)_3$	(III) 2055, 2090
(D) $Mo(pyridine)_3(CO)_3$	(IV) 1746, 1888

The correct match is

(a) A-I, B-IV, C-II, D-III (b) A-III, B-II, C-I, D-IV

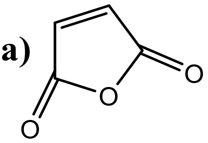
(c) A-IV, B-III, C-I, D-II (d) A-I, B-II, C-III, D-IV

132. The ν_{CN} in $[Fe(CN)_6]^{3-}$ (A) and $[Fe(CN)_6]^{4-}$ (B) and ν_{CO} in $[Cr(CO)_3(NH_3)_3]$ (C) and $[Cr(CO)_6]$ (D) are compared below. The pair with correct order is **[NET JUNE 2018]**

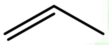
(a) A > B ; C > D (b) A > B ; C < D (c) A < B ; C > D (d) A < B ; C < D

133. The ligand that bins strongly to the nickel center in (2, 2'-bipyridine) Ni(0) complex is **[NET JUNE 2018]**

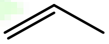
(a)



(b)



(c)



(d)

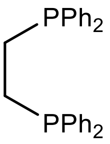
134. The cluster type and geometry of the species $[Rh_9P(CO)_{21}]^{2-}$ are **[NET JUNE 2018]**

(a) closo, tricapped trigonal prism (b) arachno, trigonal prism

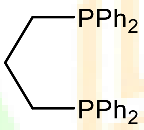
(c) nido, capped square antiprism (d) nido, bicapped trigonal prism

135. Hydroformylation of 1-propene with $[HRh(CO)L_2]$ leads to linear and branched formlated products. The linear hydroformylated product is formed with highest selectivity when 'L' in the rhodium complex is **[NET JUNE 2018]**

(a)



(b)



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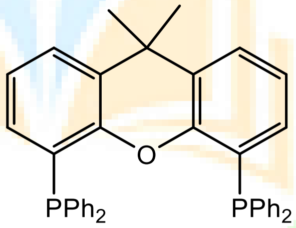
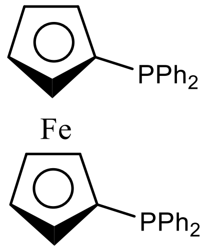


(d)



136. The hydrocarbon having an analogous structure to that of P_4O_6 is **[NET JUNE 2018]**

(a) $[(CH)_4(\mu\text{–}CH_2)_6]$ (b) $[(CH)_6(\mu\text{–}CH_2)_4]$ (c) $[(CH_2)_4(\mu\text{–}CH)_6]$ (d) $[(CH_2)_4(\mu\text{–}CH)_4]$

137. 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 **[NET JUNE 2019]**

138. 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 **[NET JUNE 2019]**

(a) Br > I > F > Cl (b) F > Cl > Br > I (c) F ≈ Cl ≈ Br ≈ I (d) I > Br > Cl > F

139. The organic species isolobal to $[Fe(CO)_2(PPh_3)]^-$ is **[NET JUNE 2019]**

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

140. The correct statements about $[Ru_6C(CO)_{17}]$ cluster from the following **[NET JUNE 2019]**

(1) itis an 86 electron cluster

(2) it is a closo structure type

(3) its shape is capped square pyramid

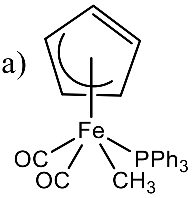
(4) carbon interacts with all the Ru centres in the cluster are

(a) 1, 2, 3 and 4 (b) 1 and 2 only (c) 1, 2 and 3 (d) 1, 2 and 4

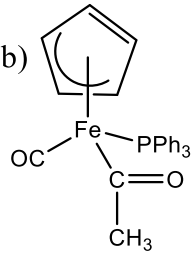
141. A plausible structure of the intermediate involved in the following reaction **[NET JUNE 2019]**

$[Fe(\eta^5–C_5H_5)(CH_3)(CO)_2] + PPh_3 \rightarrow [Fe(\eta^5–C_5H_5)(C=O)CH_3)(CO)(PPh_3)]$ is

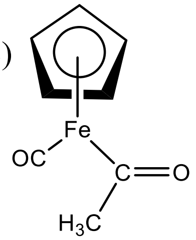
(a)



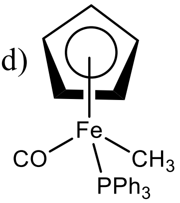
(b)



(c)

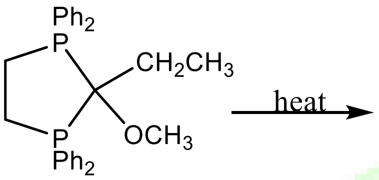


(d)

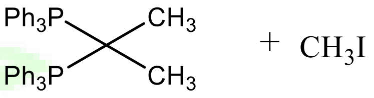


142. Consider the following reactions: **[NET JUNE 2019]**

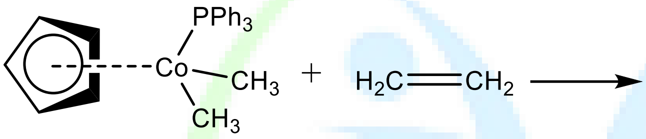
(A)



(B)



(C)



The reaction(s) which will NOT produce ethane as a product is/are

(a) A (b) B (c)C (d) A and C

143. Donor mode of NO ligand depends on the metal. Now, consider the following complexes(in gaseous state). **[NET JUNE 2019]**

(A) $[IrCl(CO)(PPh_3)_2(NO)]^+$ (B) $[RuCl(PPh_3)_2(NO)_2]^+$

(C) $[Co(NCS)(diars)_2(NO)]^+$, where diars = o –$(Me_2As)_2C_6H_4$

(D) $[Cr(CN)_5(NO)]^{3-}$

The complex (es) that do NOT exhibit bent NO coordination mode is/are

(a) A and B (b) C and D (c) D only (d) B only

144. The expected number of ν_{co} bands in the IR spectra of fac–$[Mo(PPh_3)_3(CO)_3]$ and trans–$[Mo(PPh_3)_2(CO)_4]$ are, respectively **[NET DEC 2019]**

(a) one and one (b) two and two (c) two and one (d) three and one

145. The rate-determining step in the catalytic synthesis of acetic acid by Monsanto process is

(a) Oxidative addition of CH_3I to $[RhI_2(CO)_2]^–$ **[NET DEC 2019]**

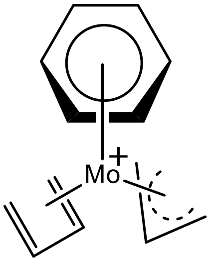
(b) migration of CH_3 group to CO of $[RhI_3(CO)_2(CH_3)]^–$

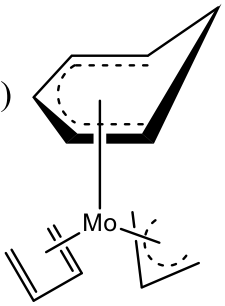
(c) loss of CH_3COI from $[RhI_3(CO)_2(COCH_3)]^–$

(d) coordination of CO to $[RhI_3CO(COCH_3)]^–$

146. The main product of nucleophillic attack of H– on the complex ion given below is :

[NET DEC 2019]



(a)


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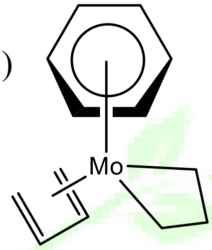
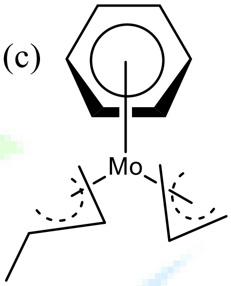
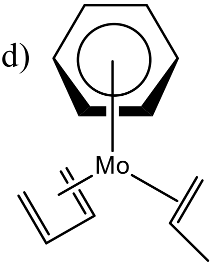


(c)


(d)


147. The correct order of metal-carbon distance is **[NET DEC 2019]**

(a) Fe(η^5–Cp)$_2$ > Co(η^5–Cp)$_2$ > Ni(η^5–Cp)$_2$

(b) Fe(η^5–Cp)$_2$ > Ni(η^5–Cp)$_2$ > Co(η^5–Cp)$_2$

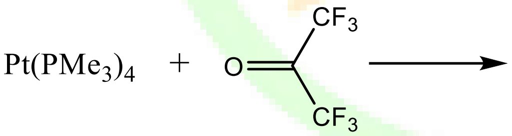
(c) Ni(η^5–Cp)$_2$ > Fe(η^5–Cp)$_2$ > Co(η^5–Cp)$_2$

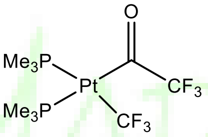
(d) Ni(η^5–Cp)$_2$ > Co(η^5–Cp)$_2$ > Fe(η^5–Cp)$_2$

148. The cluster types of $[Fe_5(CO)_{14}N]^-$ and $[Co_6(CO)_{13}N]^-$ are, respectively : **[NET DEC 2019]**

(a) nido-, nido- (b) nido, closo- (c) closo-, nido- (d) closo-, closo–

149. The major product formed in the following reaction is : **[NET DEC 2019]**



(a)


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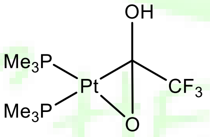

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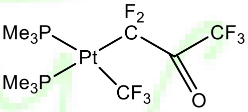
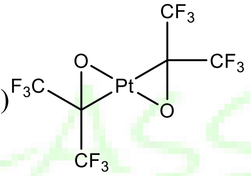


(d)


150. The number of Ni–Ni bonds in $[CpNi(\mu\text{-}PPh_2)]_2$ complex obeying the 18 electron rule is **[NET DEC 2019]**

(a) 0 (b) 1 (c) 2 (d) 3

151. 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 **[NET DEC 2019]**

(a) Br > I > F > Cl (b) F > Cl > Br > I (c) F ≈ Cl ≈ Br ≈ I (d) I > Br > Cl > F

152. The organic species isolobal to $[Fe(CO)_2(PPh_3)]^-$ is **[NET DEC 2019]**

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

153. The correct statements about $[Ru_6C(CO)_{17}]$ cluster from the following **[NET DEC 2019]**

(1) itis an 86 electron cluster

(2) it is a closo structure type

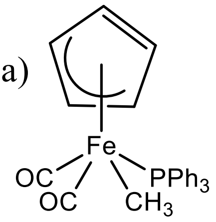
(3) its shape is capped square pyramid

(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

154. A plausible structure of the intermediate involved in the following reaction$[Fe(\eta^5–C_5H_5)(CH_3)(CO)_2] + PPh_3 \rightarrow [Fe(\eta^5–C_5H_5)(C{=}O)CH_3)(CO)(PPh_3)]$ is **[NET DEC 2019]**

(a)



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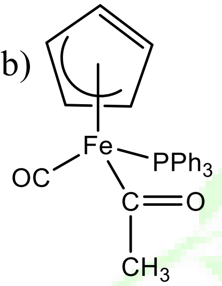
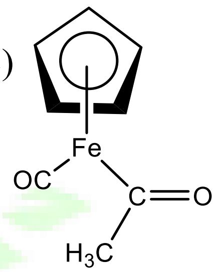


(c)



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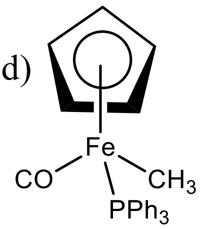
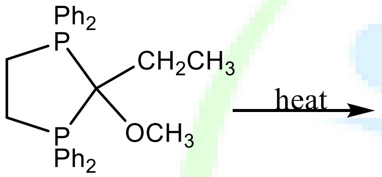
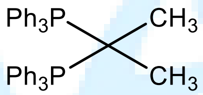


155. Consider the following reactions: **[NET DEC 2019]**

(A)

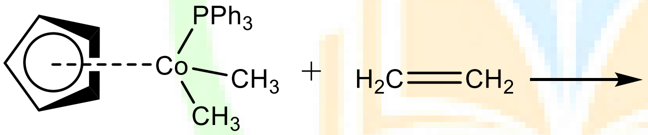


(B)



+ CH_3I

(C)



The reaction(s) which will NOT produce ethane as a product is/are

(a) A (b) B (c)C (d) A and C

156. Donor mode of NO ligand depends on the metal. Now, consider the following complexes (in gaseous state). **[NET DEC 2019]**

(A) $[IrCl(CO)(PPh_3)_2(NO)]^+$

(B) $[RuCl(PPh_3)_2(NO)_2]^+$

(C) $[Co(NCS)(diars)_2(NO)]^+$, where diars = o –$(Me_2As)_2C_6H_4$

(D) $[Cr(CN)_5(NO)]^{3-}$

The complex (es) that do NOT exhibit bent NO coordination mode is/are

(b) A and B (b) C and D (c) D only (d) B only

157. Consider the nuclear reaction **[NET NOV 2020]**

$_{92}X^{234} + \beta + \alpha \rightarrow Y + y + 2\beta^+$

Y is

(a) $_{92}Y^{236}$ (b) $_{91}Y^{238}$ (c)$_{93}Y^{236}$ (d) $_{94}Y^{238}$

158. The reason for significantly high solubility of $AgClO_4$ in benzene than in alkane solvents is **[NET NOV 2020]**

(a) Alkane solvents are non-polar. (b) Benzene is an aprotic solvent

(c) PhAg is formed (d) Benzene acts as a soft base

159. I_2 is violet in the solid as well as in gas phase. However in acetone or ethanol. it turns brown. Choose the correct statement(s) for this colour change. **[NET NOV 2020]**

(a) Dissociation of I_2 in atomic state

(b) Interaction of low-lying σ*–orbital of iodine with lone pair of O (solvent)

(c) Formation of a charge-transfer complex

(a) (a) only (b) (b) Only (c) (a) and (b) only (d) (b) and (c) only

160. Correct statement/s among the following with respect to ionization energy (IE) is/are

(i) ($IE_1 + IE_2 + IE_3$) for indium is more than that of aluminium **[NET NOV 2020]**

(ii) IE_1 of scandium is higher than that of cobalt

(iii) IE_1 of gallium is lower than that of selenium

(iv) IE_1 of nitrogen is greater than that of oxygen

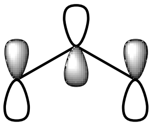
(a) (ii) and (iv) (b) (iii) and (iv) (c)(i) and (iv) (d)(ii)and(iii)

161. The natural product that gives a signal at δ 218 ppm in its ^{13}C NMR spectrum is**[NET NOV 2020]**

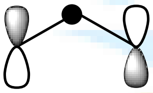
(a) α–pinene (b) camphor (c) geraniol (d) carvone

162. The HOMO of π-molecular orbitals of methylazide is **[NET NOV 2020]**

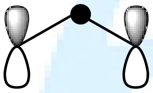
(a)



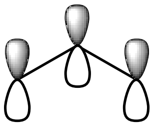
(b)



(c)



(d)



163. The energies of interaction for (i) ion pair (ii) ion-dipole and (iii) dipole-dipole interactions are inversely proportional to **[NET NOV 2020]**

(a) r, r^2 and r^3 respectively (b) r^2, r and r^3 respectively

(c) r, r^2 and r^6 respectively (d) r^2, r and r^6 respectively

164. Of the following statements regarding dissociative substitution in an octahedral transition metal complex, **[NET FEB 2022]**

(a) High steric hindrance between in the metal complex favors fast dissociation of ligand.

(b) Increased charge on the metal complex fast dissociation of ligand.

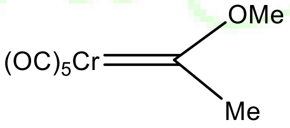
(c) A pentacoordinated intermediate is observed.

(d) Nature of the entering ligand significantly influences the reaction.

Which are correct ?

(a) a and d (b) a and c (c) a, c and d (d) a, b, c and d

165. Consider the following statement(s) in the context of organometallic complex (X): **[NET FEB 2022]**



A. The carbene ligand donates two electrons to the metal and accepts d electrons to make a π-bond

B. The C (carbene) is nucleophilic

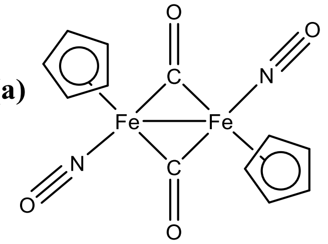
C. Rotation around the Cr=C(OMe) Me double bond has low barrier (< 10 kcl/mol)

Correct statement(s) is/are:

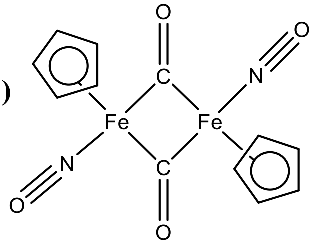
(a) A and B (b) A only (c) A and C (d) B and C

166. Identify the thermodynamically stable structure of $[(\eta^5\text{–}C_5H_5)\,Fe(\mu_2\text{–}CO)(NO)]_2$ **[NET FEB 2022]**

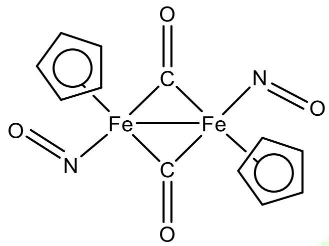
(a)



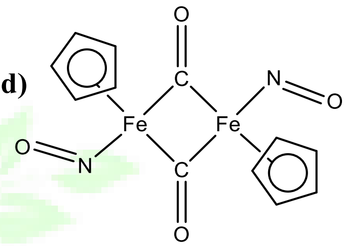
(b)



(c)



(d)

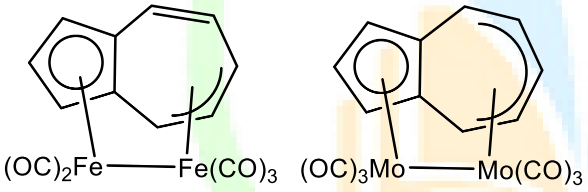


167. The type of molecular orbitals in the allyl ligand ($CH_2{=}CH{-}CH_2^-$) that are used for σ-donation and σ-back donation with metal d-orbitals, respectively are **[NET FEB 2022]**

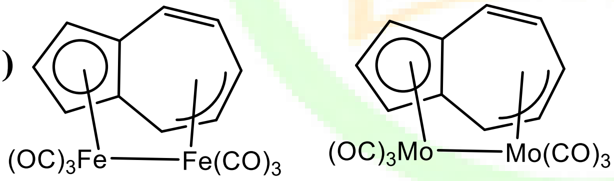
(a) 2σ and 3σ (b) 1σ and 3σ (c) 3σ and 2σ (d) 1σ and 2σ

168. The set of structures showing the correct hapticity of azulene on the basis of the 18 e⁻ rule, is **[NET FEB 2022]**

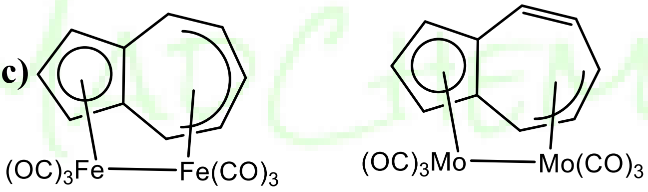
(a)



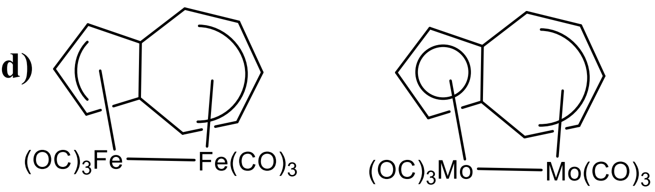
(b)



(c)



(d)



169. The correct geometries for the metal carbonyl clusters, A-C **[NET FEB 2022]**

A. $[Ru_6(CO)_{17}B]^-$ B. $[Os_6(CO)_{18}P]^-$ C. $[Os_4(CO)_{16}]$

are

(a) A : pentagonal bipyramidal, B: trigonal prismatic, and C: tetrahedral

(b) A: pentagonal bipyramidal, B: Octahedral, and square

(c) A: Octahedral, B : Trigonal prismatic, and C : tetrahedral

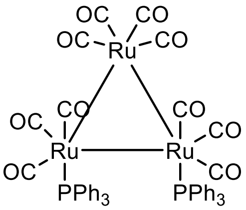
(d) A :Octahedral, B : Trigonal prismatic, and C : square

170. The ^{1}H-NMR spectrum of $[(C_5H_5)_2Fe(CO)_2]$ exhibits two peaks of equal intensity at room temperature , but four resonances of relative intensities 5:2:2:1 at lower temperature. The hapticities of $C_5H_5^-$ are **[NET SEP 2022]**

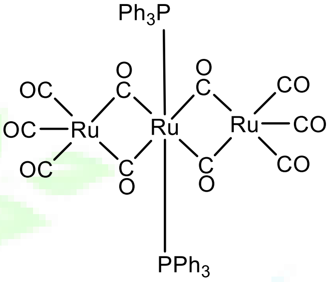
(a) η^5andη^1 (b)$\eta^5$and η^3 (c)$\eta^3$and η^1 (d) $\eta^3$and η^3

171. In the Solid state, structure of the metal cluster $[Ru_3(CO)_{10}(PPh_3)_2]$ is **[NET SEP 2022]**

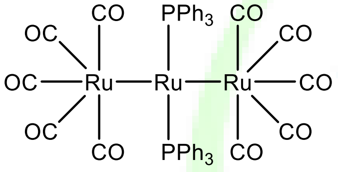
(a)



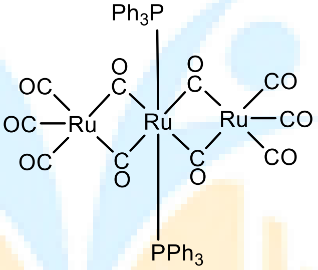
(b)



(c)



(d)



ANSWER KEY

1. A	2. B	3. A	4. D	5. C	6. C	7. D	8. A	9. B	10.D
11. D	12. D	13. A	14. A	15. B	16. A	17. B	18. A	19. B	20. D
21. D	22. B	23. A	24. C	25. A	26. A	27. B	28. A	29. A	30. B
31. A	32. A	33.A	34. C	35. C	36. D	37. C	38. B	39. B	40. D
41. B	42. B	43. D	44. C	45. B	46. C	47. A	48. A	49. A	50. A
51. C	52. A	53. C	54. D	55. C	56. B	57. B	58. B	59. A	60. A
61. C	62. C	63. D	64. A	65. C	66. A	67. B	68. A	69. A	70. A
71. A	72. C	73. A	74. B	75. A	76. C	77. D	78. B	79. B	80. A
81. C	82. B	83. A	84. A	85. D	86. B	87. A	88. A	89. A	90. C
91. D	92. C	93. D	94. B	95. B	96. C	97. B	98. A	99. A	100. C
101. B	102. A	103. C	104. A	105. B	106. B	107. C	108. B	109. A	110. B
111. C	112.	113. A	114. D	115. A	116. D	117. C	118. D	119. D	120. B
121. B	122. D	123. B	124. D	125. B	126. B	127. B	128. D	129. B	130. B
131. B	132. B	133. A	134. C	135. C	136. A	137. A	138. D	139. D	140. D
141. C	142.	143. C	144. C	145. D	146. A	147. B	148. D	149. B	150. A
151. D	152. D	153. D	154. C	155.	156. C	157. B	158. D	159. D	160. B
161. B	162. B	163. A	164. B	165. A & C	166. B	167. A	168. A	169. C	170. A
171. A									

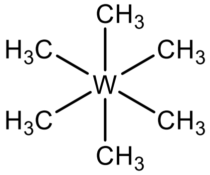
SOLUTION

1.
Ans. **(a)**
Sol. Ziegler–Natta catalyst is $Al(C_2H_5)_3 + TiCl_4$.
2.
Ans. **(b)**
Sol.

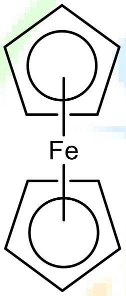
Compound	Number of electron in outer shell of central atom
$(\eta^5\text{–}C_5H_5)_2$ Fe	$18e^-$ (Stable) ;
$(\eta^5 – C_5H_5)_2$ Co	$19e^-$ (unstable)
$(\eta^5\text{–}C_5H_5)_2Ru$	$18e^-$ (stable)
$(\eta^5\text{–}C_5H_5)_2$ Co*	$18e^-$ (stable)

Oxidation of $(\eta^5\text{–}C_5H_5)_2$ Co to $(\eta^5\text{–}C_5H_5)_2Co^*$ gives an 18 electron compound, so easier to oxidise.

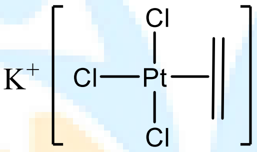
3.
Ans. **(a)**
Sol.

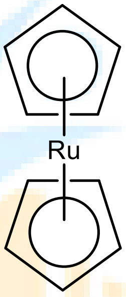


$W(CH_3)_6$



$(\eta^5 - C_5H_5)_2Fe$





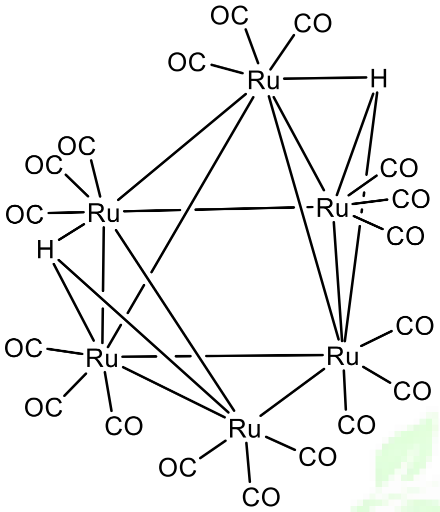
$(\eta^6 - C_6H_6)_2Ru$

4.
Ans. **(d)**
Sol. 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 elimination.
5.
Ans. **(c)**
Sol. $Ti(i\text{–}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$. Thus is correct stability order because $Ti(CH_2Ph)_4$ has no β-elimination but $Ti(i\text{–}Pr)_4$ has more β–elimination. More β-elimination less stable.

6.
Ans. **(c)**
Sol. $Ni + 4CO \xrightarrow[25^oC]{1\ atm} Ni\ (CO)_4$

$Fe + 5CO \xrightarrow[200^oC]{200\ atm} Fe(CO)_5$

7.
Ans. **(d)**
Sol.



86–elecron cluster $H_2Ru_6(CO)_{18}$ displays a distorted octahedral metal geometry .

Here each hydride ligand is connected to 3–Ru atoms.

8.

Ans. **(a)**

Sol. During hydroformylation the intermediate $CH_3–CH_2–CH_2–Co(CO)_4$ gets transformed to acyl inter mediate $CH_3CH_2CH_2–COCo(CO)_3$.

9.

Ans. **(b)**

Sol. M = V, X = 6, Z = 1

i.e. $[V(CO)_6]^{-1} = 5 + 2 \times 6 + 1 = 18$

10.

Ans. **(d)**

Sol. Because main group element follows octet rule.

2+5 + 1 = 8

11.

Ans. **(d)**

Sol. $H_2O\ (g) + C(graphite) \rightleftharpoons Co(g) + H_2O(g)$

As the number of mole of gaseous product is more than reactant ($\Delta n_g = 1$),

So there is overall increase in entropy

$\therefore\ \Delta S^0 = +\text{ ve}$

$\therefore$ T ΔS^0 will increase with increase in temperature ($\therefore$ A $\rightarrow$ TΔS^0)

Enthalpy of reaction (ΔH^0) is independent of temperature

$\therefore$ ΔH^0 = constant ($-B \rightarrow \Delta H^0$)

$\because$ $\Delta G = \Delta H^0 - T\,\Delta S^0 = \text{const} - T\Delta S^0$

So with increases of temperature ΔG^0 decreases because $\Delta S^0 = +$ Ve (C $\rightarrow \Delta G^0$)

12.

Ans. **(d)**

Sol. $[CpFe(CO)(NO)]_2$

Step–1: Determine the total valence electron (TVE) = A

A = [5+8+2+3] × 2 = [18] × 2 = 36

Step -2 ; B = (n × 18)–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 = (n × 18)–A = 2 × 18 – 34 = 36 – 34 = 2

Step –3: B/2 = gives the total number of M–M bonds in the complex

B = 2 and B/2 = 2/2 = 1

In this complex, the total number of M–M bonds is one.

13.

Ans. **(a)**

Sol. Order of σ donor ability $NMe_3 > NH_3 > Py$

Order of ν_{CO}, $Py > NH_3 > NMe_3$

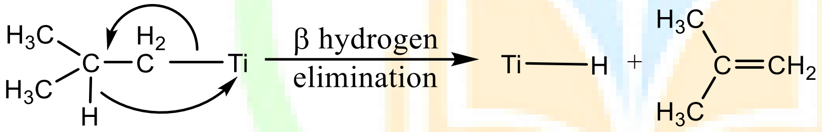
14.

Ans. **(a)**

15.

Ans. **(b)**

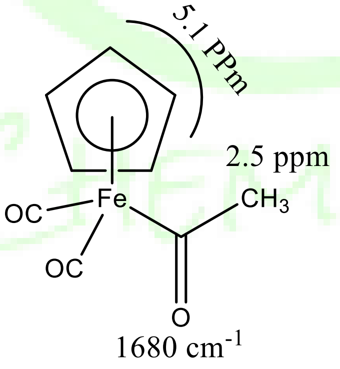
Sol.



16.

Ans. **(a)**

Sol.



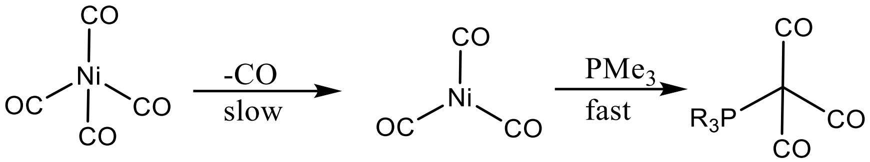
17.

Ans. **(b)**

Sol.

$Ni(CO)_4$	[L = PMe_3, $P(OMe)_3$]
$Ni(CO)_4$	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.

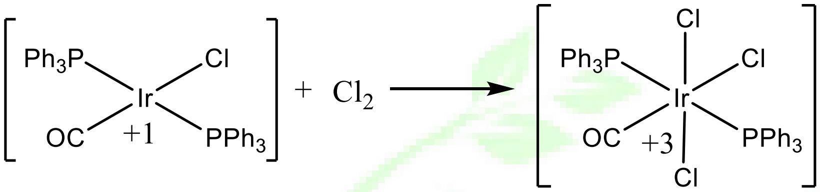


Since rate does not depend upon the concentration and nature of the ligand suggesting a dissociative mechanism.

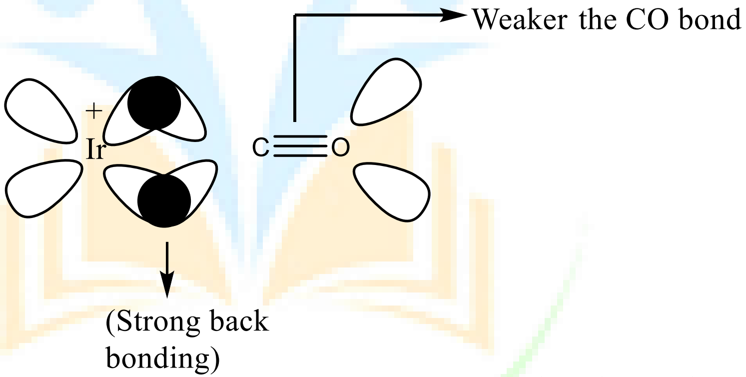
18.

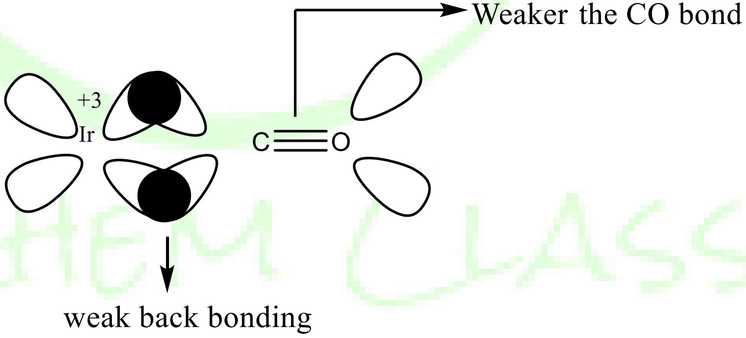
Ans. **(a)**

Sol.



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





Hence, v(CO) product > v (CO) reactant

19.

Ans. **(b)**

Sol. Step–I : Calculate T.V.E. (total valency electron)

$$= 8 \times 3 + 2 \times 12 = 48$$

Step-II : Polyhedral electron count

$$= \text{T.V.E.} - (n \times 12) = 48 - 36 = 12 \qquad n = \text{number of the metal atom}$$

Step – III : = P.E.C./2 = 12/2 = 6 = (n + 3) = Archano.

20.

Ans. **(d)**

Sol. $[\eta^5 C_5H_5^- \ Ru^{+2}\ Cl^{-1}\ (CO)(PPh_3)]$

T.V.E. = 6 + 6 + 2 + 2 + 2 = 18

$[W^{+2}(CO)_3\ (Si^{-1}\ Me_3)\ Cl^{-1}\ (NCMe)_2]$

Total valence electron = 4 + 6 + 2 + 2 +4 = 18

$[Ir^{+3}\ Cl_3^{-3}\ (PPh_3)_2(AsPh_2^-)]^-$

Total valence electron = 6 + 6 + 4 + 2 =18

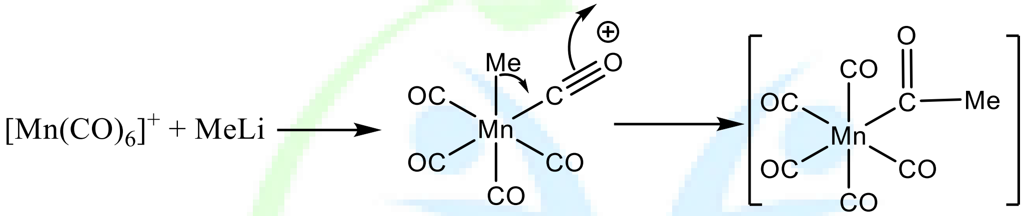
$[Os{+}5(N^{-3})\ Br_2^{-2}\ (PMe_3)\ (N^{-1}Me_2)]^-$

Total valence electron – 8 + 3 + 2 + 2 +1 + 1 –17

21.

Ans. **(d)**

Sol.



22.

Ans. **(b)**

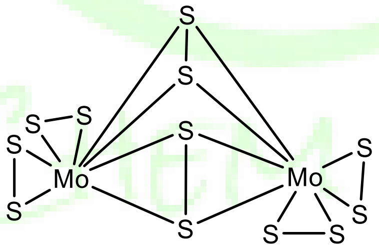
Sol. Because metal carbonyls are stronger bond then break this bond huge amount of energy are required. But metal-metal bonds are weaker bond. So, reaction is endothermic and enthalpy predominant and entropy unfavourable.

23.

Ans. **(a)**

Sol. $[Mo_2(S_2)_6]^{2-}$

The structure of $[Mo_2(S_2)_6]^{2-}$ cluster is:

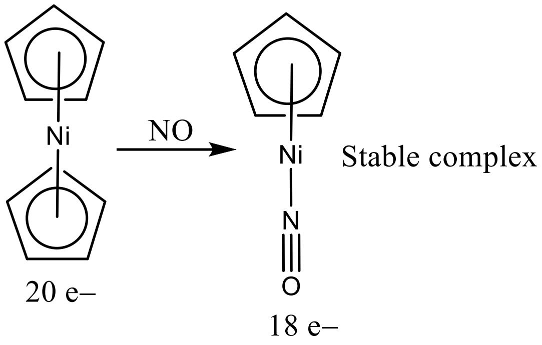


So, the bridging S_2^{2-} is two and co-ordination number of Mo is 8.

24.

Ans. **(c)**

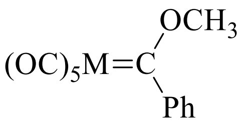
Sol.



25.

Ans. **(a)**

Sol.



$$(OC)_5M{=}C(OCH_3)(Ph)$$

$2 \times 5 + M + 2 = 18$, $M = 18 - 12 = 6$

So, M = Cr, and Re^+.

26.

Ans. **(a)**

Sol. As the π–accepting abilities of phosphine increases $\nu_{C\text{-}O}$ stretching frequency of the complex increases. So, the order of π–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 $\nu_{C\text{-}O}$ stretching is :

A → 2090 C → 1977

B → 2040 D→ 1945

27.

Ans. **(b)**

Sol. $C_2B_4H_8$

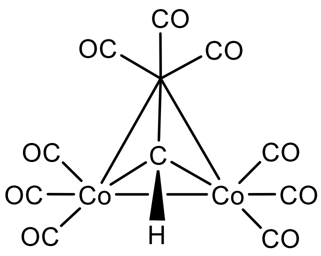
$(BH)_2B_4H_8$; $B_2H_2B_4H_8$

Or, $B_6H_{10} \xrightarrow{-4H} [B_6H_6]^{4-} \rightarrow$ nido borane

28.

Ans. **(a)**

Sol. The structure of cluster $[Co_3(CH)(CO)_9]$



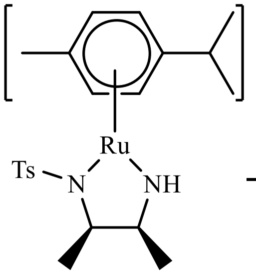
So, the number of M–M bond = 3 bridging ligand = 1 CH

29.

Ans. **(a)**

Sol. $[Rh(CO)_2I_2]^-$ → Hydroformylation.

$[Pd(PPh_3)_4]$ → Heck coupling (It is a catalyst for Heck

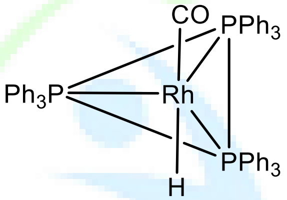


→ Asymmetry hydrogen transfer.

30.

Ans. **(b)**

Sol.

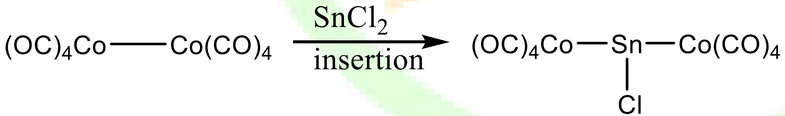


18 electron species in excess PPh_3 it becomes 20 electron species but the active catalyst is 16 electron species. So, in presence of excess PPh_3. The rate of hydroformylation will be decreases.

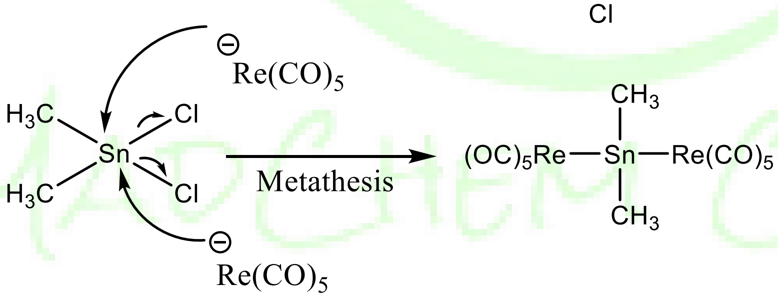
31.

Ans. **(a)**

Sol. Since $SnCl_2$ will behaves are a carbene and it insert into the M-M bond. So, it is a kind of insertion reaction.



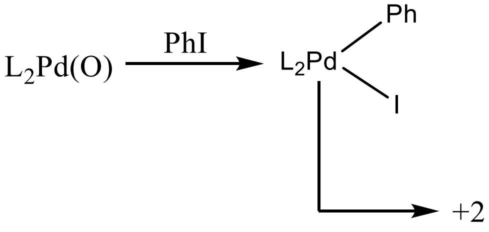
$$(OC)_4Co—Co(CO)_4 \xrightarrow[\text{insertion}]{SnCl_2} (OC)_4Co—\underset{\underset{Cl}{|}}{Sn}—Co(CO)_4$$



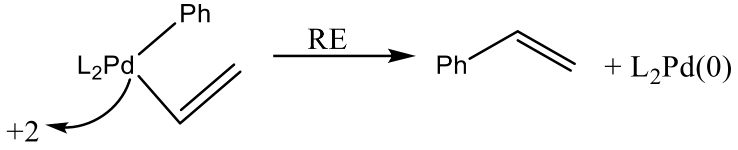
32.

Ans. **(a)**

Sol. Step (A) is O.A. because the oxidation state of the metal is increased by two units.



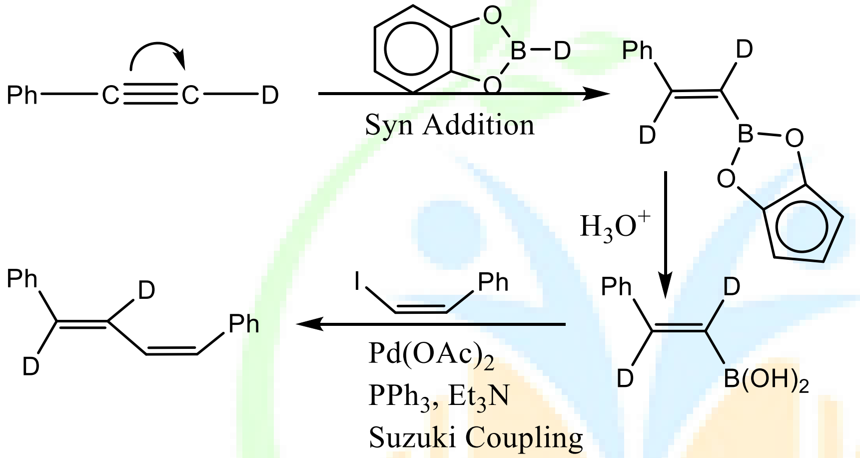
Step (B) is transmetallation because the ligand is transferring from one metal to another metal.
Step (C) is reductive elimination because the oxidation state of the metal is increased by two units.



33.

Ans. **(a)**

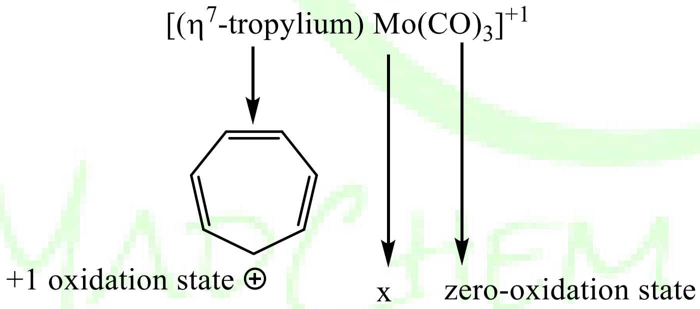
Sol. Chemical reaction involved in the above transformation can be illustrated as



34.

Ans. **(c)**

Sol.



$+1 + x + 0 = +1 \qquad \Rightarrow x = 1 - 1 = 0$

Mo in zero oxidation state.

35.

Ans. **(c)**

Sol. Total valency electron = 12 + 18 = 30 (A) [(OPh) in bridging donate 3 electron]

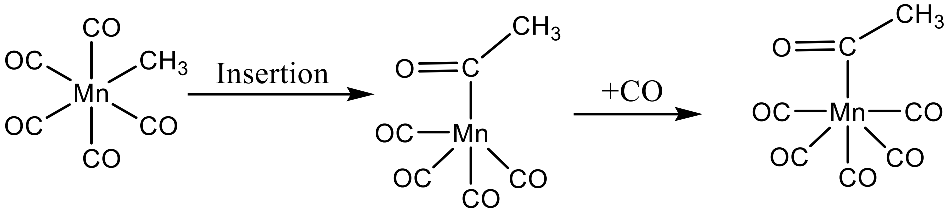
$B = (n \times 18 - A) = 36 - 30 = 6$

Metal –metal bond = B/2 = 6/2 = 3

36.

Ans. **(d)**

Sol.

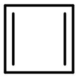


Insertion reaction

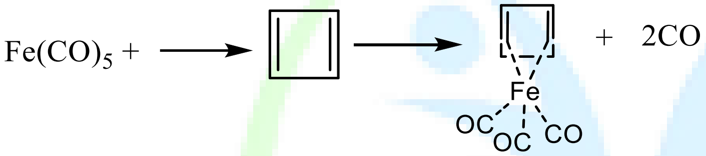
37.

Ans. (c)

Sol.

Cyclobutadiene is 

which is antiaromatic and unstable due to this reasons it dimerizes, but when it attached with metal such as

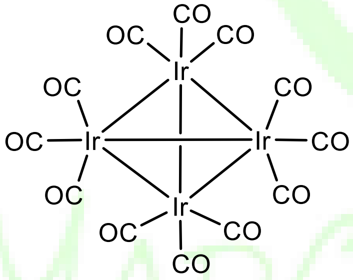


The back π-bonding occurs from metal to cylobutadienes due to this it gain electro from the metal and converted, into cyclobutadiene anion which aromatic and hence stables.

38.

Ans. (b)

Sol.



A = TVE = 60

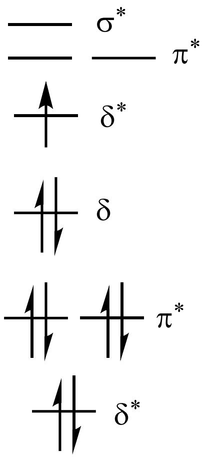
B = (n × 18)–TVE = 72 – 60 = 12

Metal metal bond = B/2 = 12/2 = 6

39.

Ans. (b)

Sol.



$[Re_2Cl_4(PMe_2Ph)_4]^+$

$C = M + L$

$+1 = 2M - 4$

$\therefore \quad 2M = 5$

Total valence electron = 14 - 5 = 9 ($\because$ 2M = 2 x 7 = 14)

M = Number of valence electron present in the metal

Bond order = $\frac{N_b - N_a}{2} = \frac{8-1}{2} = 3.5$

40.

Ans. **(d)**

Sol. $HCo(CO)_4$, $HCo(CO)_3PBu_3$ and $HRh\,(CO)(PPh_3)_3$. These all are the catalyst for hydroformylation process.

41.

Ans. **(b)**

Sol. $H_3CoRu_3(CO)_{12}$

$3 + 9 + 8 \times 3 + 12 \times 2 = 60$ electron.

42.

Ans. **(b)**

Sol. $Fe_3(CO)_{12} \xrightarrow{Na} [Fe(CO)_4]^{2-}$

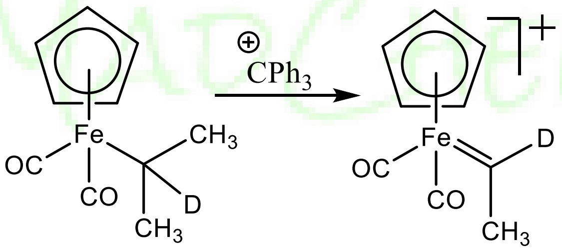
$8 + 8 + 2 = 18$ electron

$[Fe(CO)_4]^{2-}$ is isoelectronic with $Ni(CO)_4$

43.

Ans. **(d)**

Sol.



$5 + 8 + 4 + 1 = 18$ electron

44.

Ans. **(c)**

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

45.

Ans. **(b)**

Sol. $[(\eta^5\text{–}C_5H_5)(\eta^1\text{–}C_5H_5)Fe(CO)_2 \xrightarrow{221-298K} [(\eta^5\text{–}C_5H_5)(\eta^5\text{–}C_5H_5)Fe]$

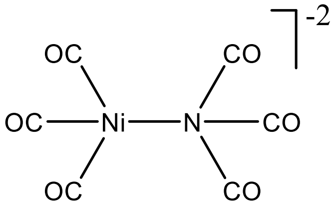
46.

Ans. **(c)**

Sol.

$[Ni_2(CO)_6]^{2-}$

$2\times + 0 = 2$



M-M bond = 1

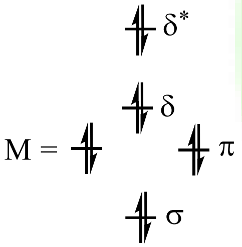
$x = -\frac{2}{2}$

$x = -1$

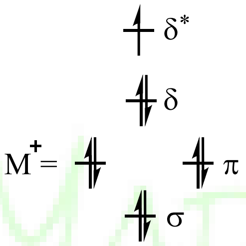
47.

Ans. **(a)**

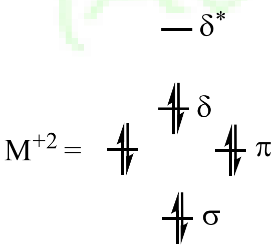
Sol. $[Re_2(Me_2PPh)_4Cl_4]$ – (M)



$\text{B.O.} = \frac{8-2}{2} = \frac{6}{2} = 3$



$\text{B.O.} = \frac{8-1}{2} = \frac{7}{2} = 3.5$



$\text{B.O.} = \frac{8}{2} = 4$

48.

Ans. **(a)**

Sol. $[Fe_5(CO)_{15}C)]$

Total valency electron = $8 \times 5 + 15 \times 2 + 4 = 74$

PEC = TEC – $n \times 12$

PEC = 74 – 5 × 12 = 74 – 60= 14

$\frac{PEC}{2} = \frac{14}{2} = 7$

7 = n + 2 where, n = number of metal in electron.

= 5 + 2 = (n + 2) Nido

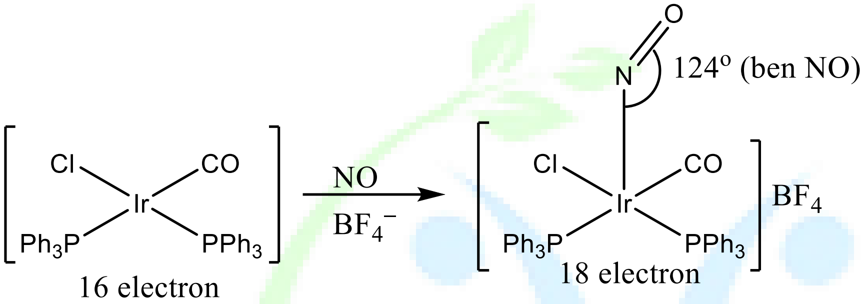
49.

Ans. **(a)**

50.

Ans. **(a)**

Sol.



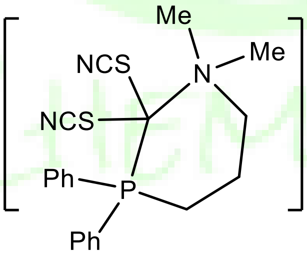
Terminal NO = 1672 cm^{-1}

Bridging NO = 1505 cm^{-1}

51.

Ans. **(c)**

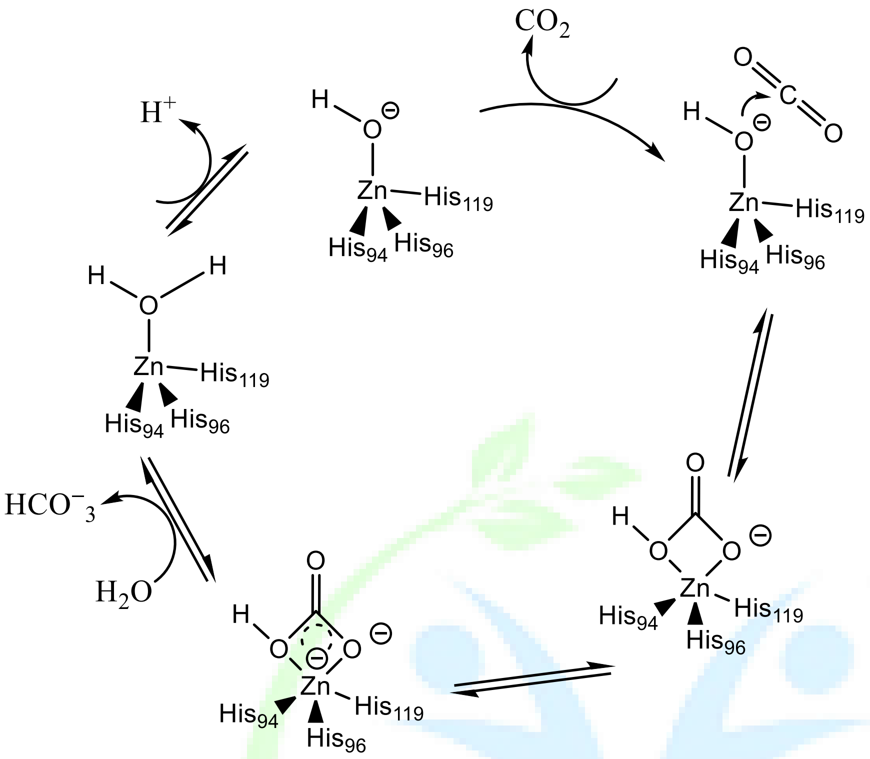
Sol. S and P both form π–bonding with complex and π–bonding capacity of sulphur is greater than phosphours due to smaller size of d-orbital of sulphur. Hence, in presence of sulphur trans to phosphorus donor atom phosphorus-metal bond will be weak hence they do not lie trans to each other in the complex. As nitrogen does not involment in π-bonding with complex hence when nitrogen atom is trans to phosphorus, phosphorus become able to form efficient π-bond with metal hence become stable thats why P and N are trans to each other.



52.

Ans. **(a)**

Sol.



53.

Ans. **(c)**

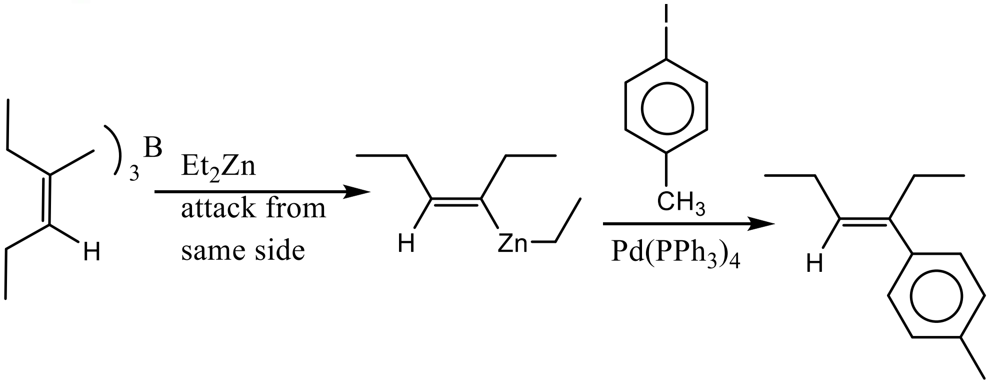
Sol. Total electron

Co(CO)3	15 electron	Not isolbal
R2Si	6 electron	
Mn(CO)5	17 electron	isolobal
CH3	7 electron	
Fe(CO)4	16 electron	isolobal
O	6 electron	
Mn(CO)5	17 electron	isolobal
RS	7 electron	

54.

Ans. **(d)**

Sol.



55.

Ans. **(c)**

Sol. $[(\eta^x - C_6H_6)Ru(\eta^y - C_6H_6)]$

$x = 4, y = 6$

$[(\eta^4 - C_6H_6)Ru(\eta^6 - C_6H_6)]$

Total electron = 4 + 8 + 6 = 18 electron. (Diamagnetic complex)

Example : $^{57}Fe = 3d^64s^2$

56.

Ans. **(b)**

Sol. $Ni(CO)_4 + PPh_3 \xrightarrow{hv} [Ni(CO)_3(PPh_3)] + CO$

$(18e^-)$

Since $Ni(CO)_4$ follows 18 electron rule. So, it follow substitution via dissociation mechanism i.e.

Step-1 : $Ni(CO)_4 \xrightarrow{CO} Ni(CO)_3$ (slow)

$(18e^-)$ $(16e^-)$

Step–2: $Ni(CO)_3 + PPh_3 \xrightarrow{CO} Ni(CO)_3(PPh_3)$

$(16e^-)$

So, the rate of reaction depends upon the concentration of $Ni(CO)_4$ only because this step is slowest step.

57.

Ans. **(b)**

Sol.

$$H_3C-\overset{H}{C}{=}CH_2 + CO + H_2 \xrightarrow{CO_2(CO)_8} H_3C-\overset{H_2}{C}-\overset{H_2}{C}-CHO$$

(butanal)

Hydroformylation.

58.

Ans. **(b)**

Sol. $CO_4(CO)_{12}$

TVE = 36 + 24 = 60

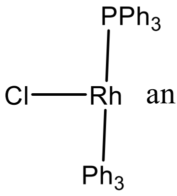
PEC = TVE – (n × 12) = 60–48=12

$\frac{PEC}{2} = \frac{12}{2} = 6 = 4 + 2$ (n +2 = Nido)

59.

Ans. **(a)**

Sol. $Rh(PPh_3)_3$ Cl is a Wilkinson catalyst in hydrogenation step one PPh3 loss due to steric factor and form $Rh(PPh_3)_2$ Cl

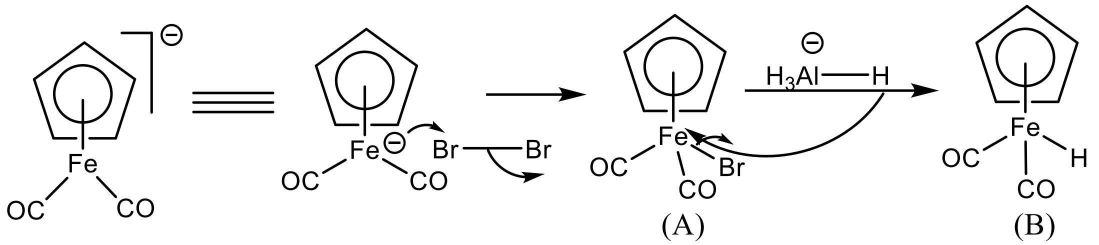


and shape is T-shaped

60.

Ans. **(a)**

Sol.

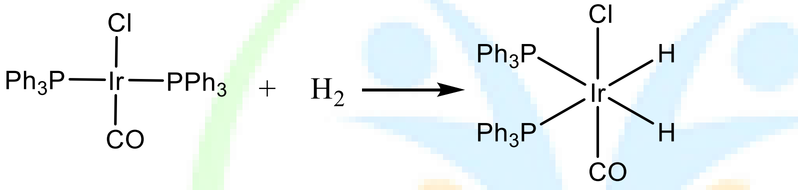


So, in the product (B) it shows two signals in ^1H NMR one for 5H of Cp ring and one for Fe–H proton with intensity ratio 5 : 1.

61.

Ans. **(c)**

Sol. $[IrCl(CO)(PPh_3)_2]$ is a 16 electron complex called as Vaska complex. Only show oxidative addition in the presence of



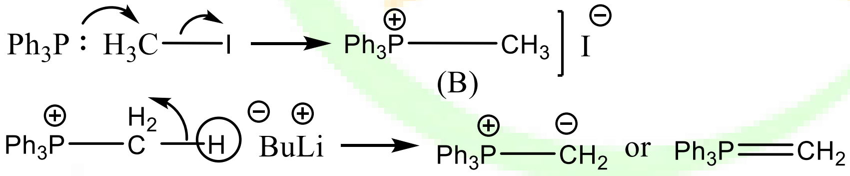
16 electron stable complex 18 electron stable complex

62.

Ans. **(c)**

Sol. $PCl_3 + PhLi \rightarrow PPh_3 + 3LiCl$

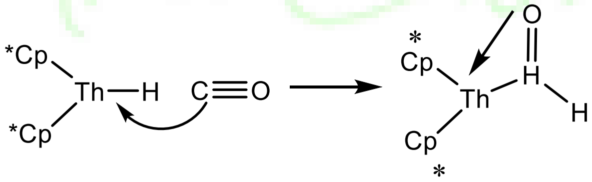
(A)



63.

Ans. **(d)**

Sol. It is a kind of insertion reaction of M–H (metalhydride bond between CO)



64.

Ans. **(a)**

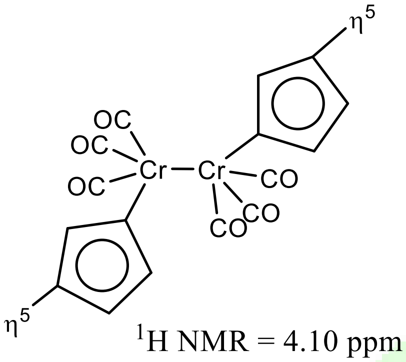
Sol. Complex (A) $HM(CO)_5$

M = Mn [7 electron]

Complex (B) $[(\eta^5C_5H_5)M(CO)_3]_2$

$[(\eta^5\text{–}C_5H_5)\ Cr(CO)_3]_2$ M’ = Cr = $6e^-$

10 + 12 + 12 + 2 (M–M) bond = 36 electron.



^1H NMR = 4.10 ppm

65.

Ans. **(c)**

Sol. $[Co(CO)_3(NO)]$

9 + 6 + 3 = 18 electron

$[Ni(\eta^5\text{–}Cp)(NO)]$

10 + 5 + 3 = 18 electron

In both complexes NO donating three electron. So, NO is in linear form.

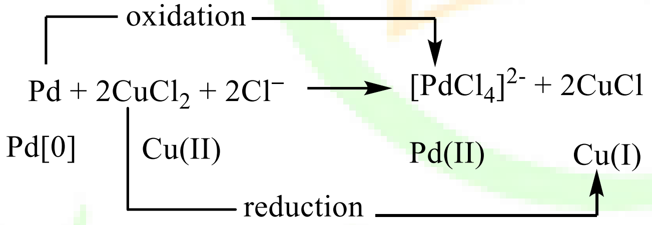
Note : When NO in bent form donating 1 electron.

66.

Ans. **(a)**

Sol. $[PdCl_4]^{2-} + C_2H_4 + H_2O \rightarrow CH_3CHO + Pd + 2HCl + 2Cl^-$

Pd(II) Pd(0)



$$2CuCl_2 + \frac{1}{2}O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

67.

Ans. **(b)**

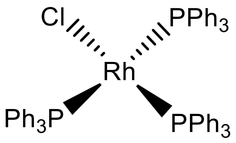
68.

Ans. **(a)**

Sol. The refluxing of $RhCl_3.\ 3H_2O$ with an excess of PPh_3 in boiling ethanol gives a $RhCl(PPh_3)_3^-$ chlorotris (triphenyl phosphine) rhodium (I) is known as wilkinson catalyst.

$$RhCl_3.\ 3H_2O + \text{excess } PPh_3 \xrightarrow{\textit{bonding ethanol}} \underset{(A)}{RhCl(PPh_3)_3} + Ph_3P = O + \underbrace{2HCl + 2H_2O}_{\text{oxidized solvent}}$$

PPh_3 serves as the reducing agent.



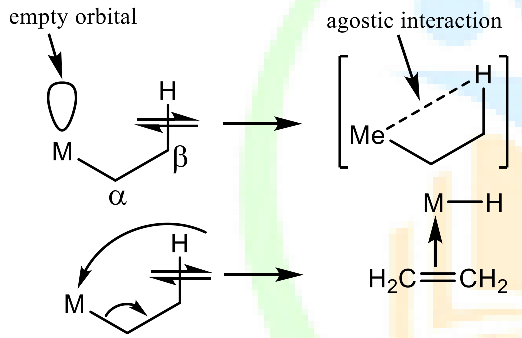
It is a square planer 16-electron complex. Valence electron counting on rhodium metal centre.
(i) there is no overall charge on complex
(ii) there is one anionic ligand (Cl^-)
(iii) Rh metal atom must have +1 charge to compensate for the one negatively charged ligand.
So, the oxidation state of Rh is +1.
Now, we can do our electron counting.

Rh(+1)	d^9(9electron)
$3PPh_3$	6 electron
Cl–	1 electron
Total	16 electron

69.

Ans. **(a)**

Sol. 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.
Electron donor ability at σ bond is
C––H(sp^3) > C––H(sp^2) > C––H(sp)
So, more facile β–elimination occur in option (a)

70.

Ans. **(a)**

Sol. For Suzuki coupling boron is required.
For Heck coupling alkene is required
For Sonagashira coupling terminal alkyne is required
For Negeshi coupling organo zinc is required.

71.

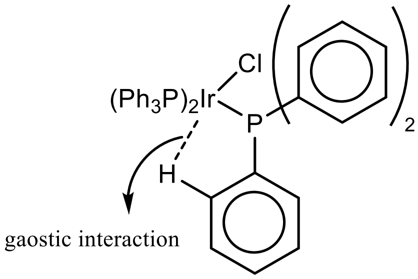
Ans. **(a)**

Sol. $B_{12}H_{12}^{2-} \equiv B_n H_n^{2-}$
Therefore, it is closo structure

72.

Ans. **(c)**

Sol.

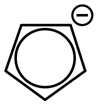


Due to this agostic interaction C–H bond becomes weak and hydrogen flanked in between M and C. As proton come in contact with metal becomes shielded and upfield shift in ^{1}H NMR. Since $v \propto \sqrt{k}$, bond strength of C–H bond decreases, in IR spectrum shift to lower wave number.

73.

Ans. **(a)**

Sol. Here, Cp is cyclopentadienyl ligand is one of the most common and popular ligands in organometallic chemistry.


6 electron donor

It is an anionic ligand that nornally coordinates in an n5 mode as a 6 electron donor. Now, 18–electron rule apply on the complexes

(A) $[Mn(\eta^5–Cp)(CO)_3]$

Mn(II)	d^5(5 electron)
Cp	6 electron
3CO	6 electron
Total	17 electron

(B) $[Os(\eta^5–Cp)_2]$

Os(II)	d^6(6 electron)
2Cp	12 electron
Total	18 electro

(C) $[Ru(\eta^5–Cp)_2]$

Ru(II)	d^6(6 electron)
2Cp	12 electron
Total	18 electron

(D) $[Fe(\eta^5–Cp)_2]$

Fe(II)	d^6 (6 electron)
2 Cp	12 electron
Total	18 electron

$[Mn(\eta^5–Cp)(CO)_2]$ does not follow 18–electron rule. So, this complex is most deshielded compound whne we 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, $[Fe(\eta^5–Cp)_2]$ is more shielded than other.

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

74.

Ans. **(b)**

Sol. $[Ru_6(C)(CO)_{17}]$

TEC = 8 × 6 + 4 + 17 × 2 = 86

PEC = 86 – 6 × 12 = 14

$\frac{PEC}{2} = \frac{14}{2} = 7$

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 = $\frac{14}{2}$ = 7 =(5+2) = (n+2). Therefore, nido

$[Ru_5(C)(CO)_{16}]$

TEC = 8 × 5 + 4 + 16 ×2

TEC = 76

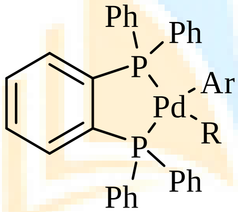
PEC = 76 – 60 = 16

$\frac{PEC}{2} = \frac{16}{2} = 8 = (5+3) Arachno$

75.

Ans. **(a)**

Sol.



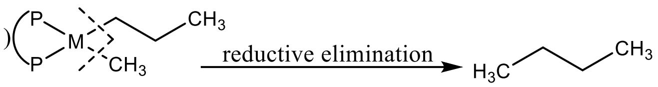
For reductive elimination, the eliminating group should be electron releasing group and also the eliminating product should be neutral.

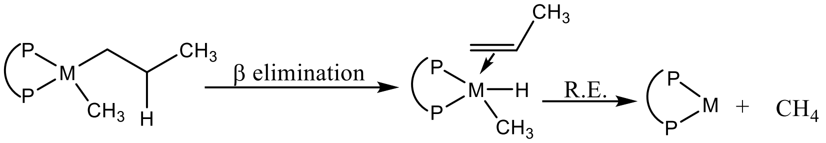
So, only Me group is electron releasing group among all the given option.

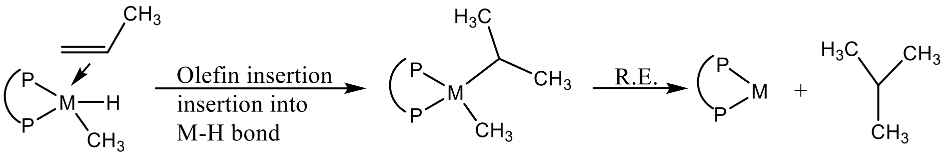
76.

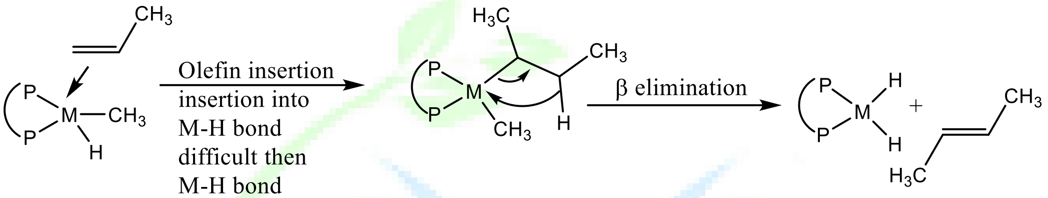
Ans. **(c)**

Sol.

(1) 

(2) 

(3) 

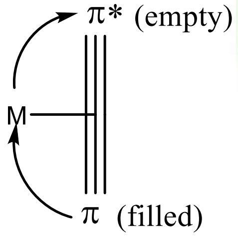
(4) 

All the product is possible but possibility (4) is least probable.

77.

Ans. **(d)**

Sol. Step–2 (π-bond formed)

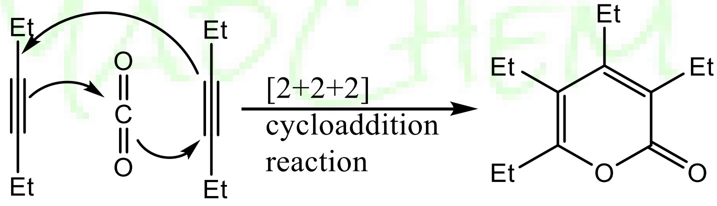


Step-1 (σ-bond formed)

78.

Ans. **(b)**

Sol.

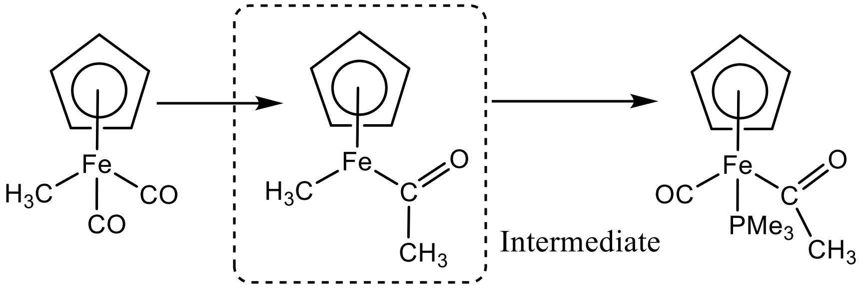


The preparation of tetraethyl pyrone via [2+2+2] cycloaddition of dynes and CO_2. The reaction employs catalytic amounts of Ni(0), PR_3 ligand, CO_2(1 atm).

79.

Ans. **(b)**

Sol.



Example of migratory insertion reaction in which alkyl group insert to CO. A new ligand create acycl a vaccancy is creasted which is occupied by new ligand.

80.

Ans. **(a)**

Sol. The structure of C_3O_2 (carbon suboxide) is

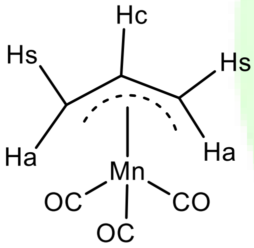
$$O\underset{\pi}{\overset{\sigma}{=\!=}}C\underset{\pi}{\overset{\sigma}{=\!=}}C\underset{\pi}{\overset{\sigma}{=\!=}}C\underset{\pi}{\overset{\sigma}{=\!=}}O \quad \text{(Linear)}$$

4σ and 4π

81.

Ans. **(c)**

Sol.



H_C = central proton

H_a = is anti with respect to Hc

H_s = syn with respect to Hc

H_a, H_s, H_c environment are different new intensity ratio 2: 2 : 1. When allyl is non-fluxional.

82.

Ans. **(b)**

Sol. $C_2B_5H_7$ $\qquad$ $C \equiv BH$

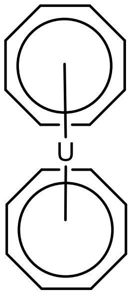
$(BH)_2B_5H_7 \equiv B_7H_9 \equiv B_7H_7^{2-}$ (closo)

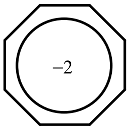
$(B_nH_n^{-2})$

83.

Ans. **(a)**

Sol. Structure of Uranocane





$= C_8H_8^{2-}$

Cyclooctatetraenide

Hence, oxidation state of U = +4

Thus in uranocene U is in +4 oxidation state and have cyclooctatetraenide ligand.

84.

Ans. **(a)**

Sol. $[V(CO)_6]^- \xrightarrow{H_3PO_4} [V(CO)_6]$

$[Co(CO)_4]^- \xrightarrow{H_3PO_5} [HCo(CO)_4]$

85.

Ans. **(d)**

Sol. Number of electron involving in metal cluster = T.V.E – 12

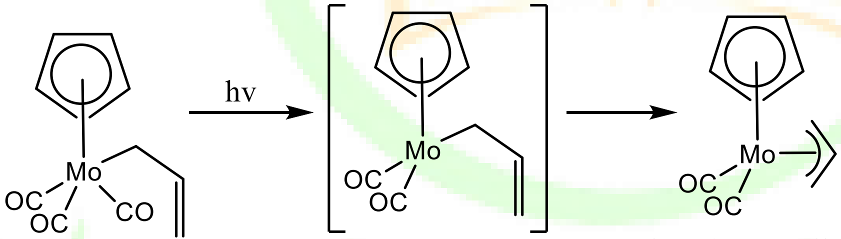
T.V.E. in $Ru(CO)_3$ = 8 + 6 = 14 (T.V.E = total valence electron)

Hence, number of electron provided for cluster bonding = 14 – 12 = 2

86.

Ans. **(b)**

Sol.



18 electron

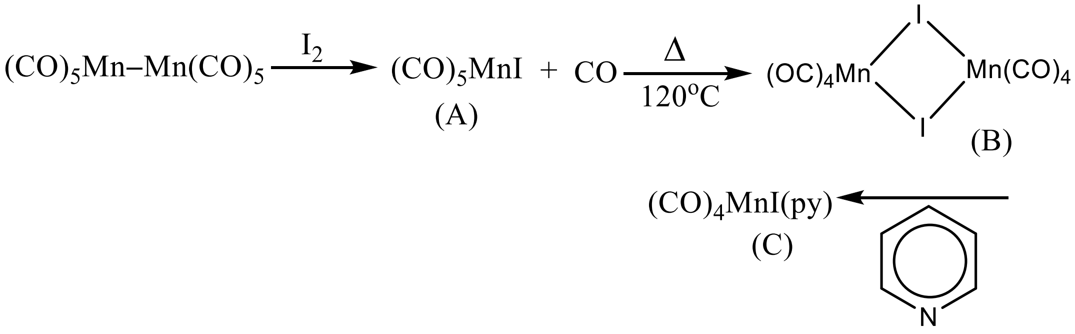
16 electron intermediate

therefore, η' allyl converted into η^3 allyl

87.

Ans. **(a)**

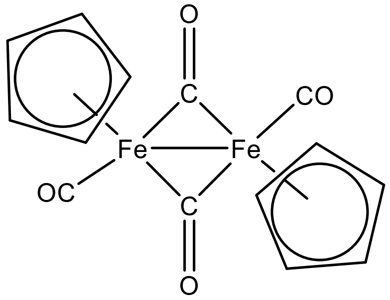
Sol.



88.

Ans. **(a)**

Sol.



Terminal CO = 2120 – 1850 cm^{-1}

μ^2. CO = 1850–1750 cm^{-1}

In this complex M–M bond order = 1 and two types of CO's terminal as well as μ^2–bridging. So, ν_{C-O} band lies in both range.

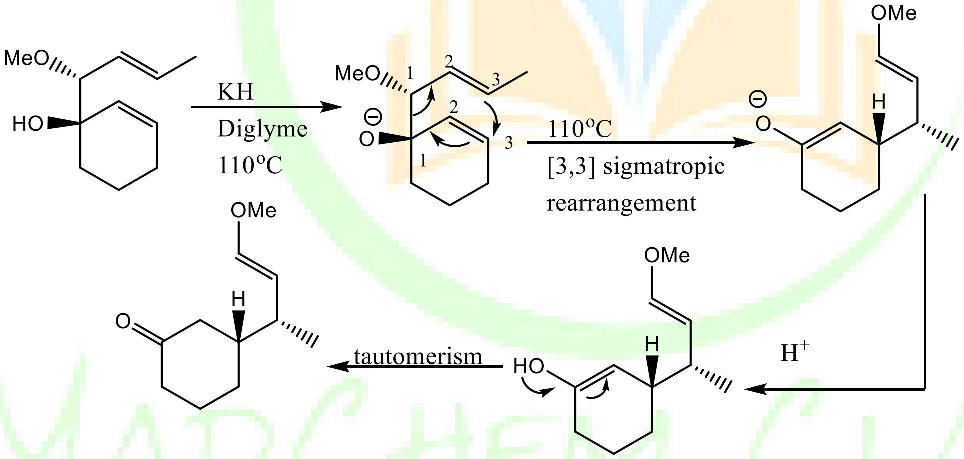
89.

Ans. **(a)**

90.

Ans. **(c)**

Sol.

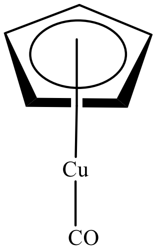


91.

Ans. **(d)**

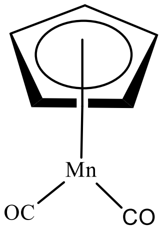
Sol.

(I)



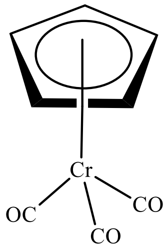
TVE = 5 + 11 + 2 = 18 electron

(II)

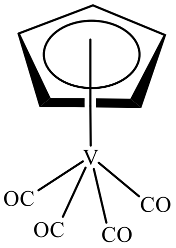


TVE = 5 + 7 + 4 = 16 electron

(III)



TVE = 5 + 6 + 6 = 17 electron

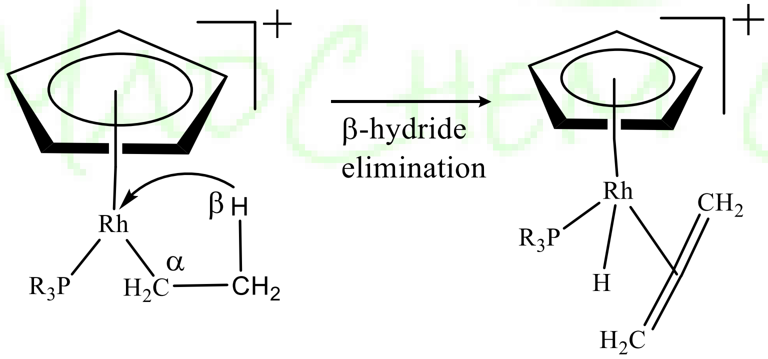


TVE = 5 + 5 + 8 = 18 electron

92.

Ans. **(c)**

Sol.



93.

Ans. **(d)**

Sol. B–H = 4e⁻ fragment isolobal fragment should have 14 electron.

Cp + Co = 5 + 9 = 14

94.

Ans. **(b)**

Sol. TVE = 18 + 16 + 22 + 8 = 64 = A

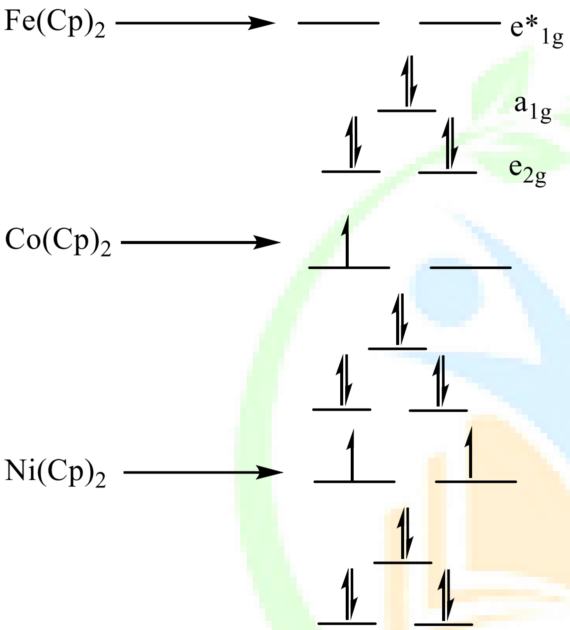
B = (n × 18)–A = (4 × 18) – 64 = 72 – 64 = 8

Number of metal–metal bond = $\frac{B}{2} = \frac{8}{2} = 4$

95.

Ans. **(b)**

Sol. As the electron goes to e_{1g}^{*} (d_{xz}, d_{yz}), orbital of metallocene bond length increases as they are anologous e_g set orbital of an octahedral complex.



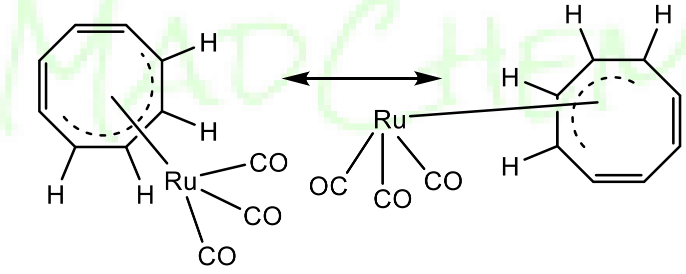
Thus, in $Ni(Cp)_2$ there are highest number of electrons in e_{1g}^{*}. Hence , it has highest M–C bond length.

$Ni(Cp)_2 > Co(Cp)_2 > Fe(Cp)_2$

96.

Ans. **(c)**

Sol.



Therefore, total protons 8, but in η4–mode COT attached to the four carbon and all 4 protons show different environment at –140°C because fluxonial behaviour slow down and hence, 4 signals will be observed.

97.

Ans. **(b)**

Sol. $C_2B_3H_5 = (B–H)_2\ B_3H_5 = B_5H_7$

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

= 12 electrons

$C_2B_4H_6 = (BH)_2B_4H_6 = B_6H_8$ B_5H_9

6(B–H) = 6 × 2 = 12 e^- 5(B–H) = 5 × 2 = 10

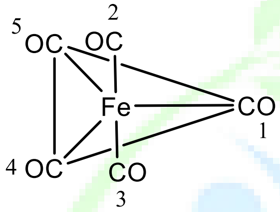
2H =2 × 1 = $2e^-$ 4H = 4 × 1 = 4

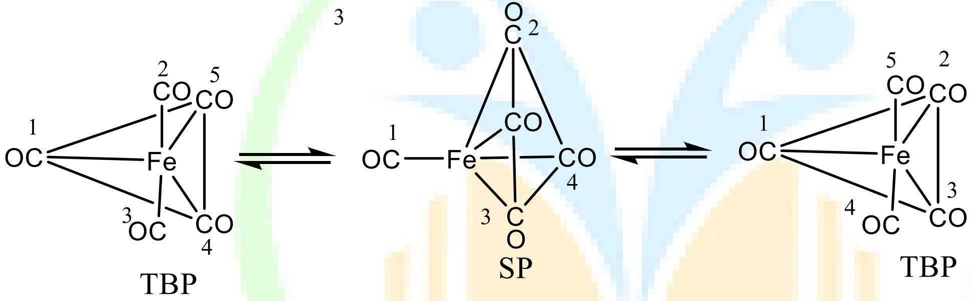
= 14 electron $14e^-$

98.

Ans. **(a)**

Sol. During fluxional axial ligands are exchanged with equatorial ligand. Hence,

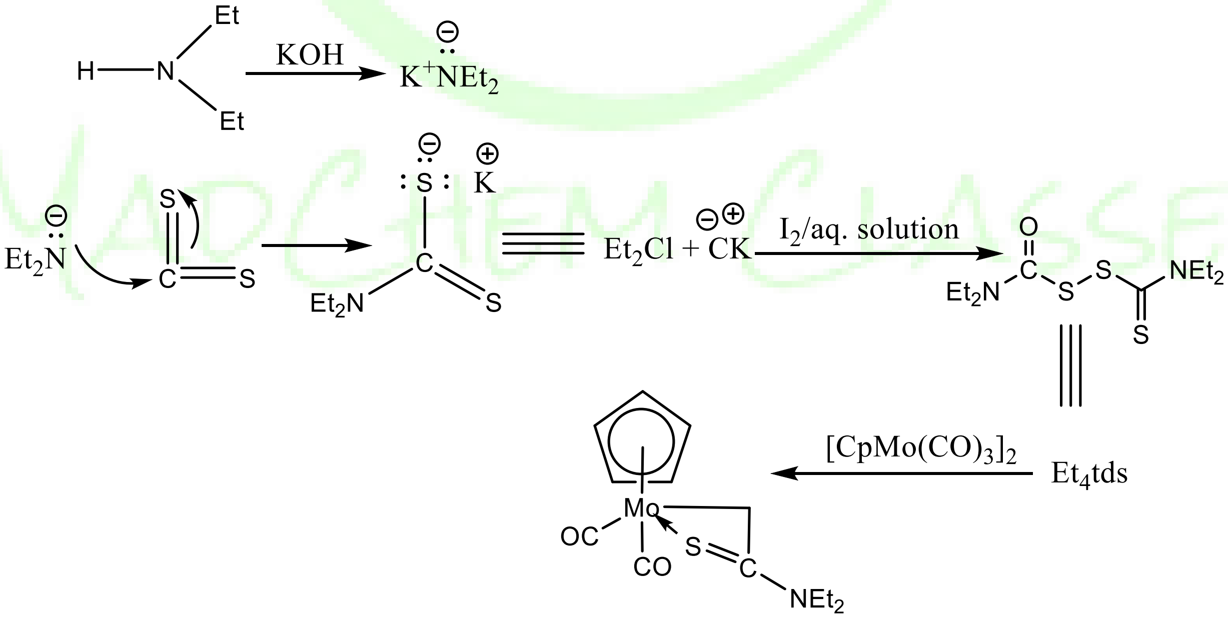




99.

Ans. **(a)**

Sol.



100.

Ans. **(c)**

Sol. TVE = 10 + 12 + 12 = 34 = A

B = (n × 18) – A

B = (2 × 18) – 34 = 36 – 34 = 2

Number of metal-metal bond = $\frac{2}{2} = 1$

TVE = 10 +12 +8 = 30 = A

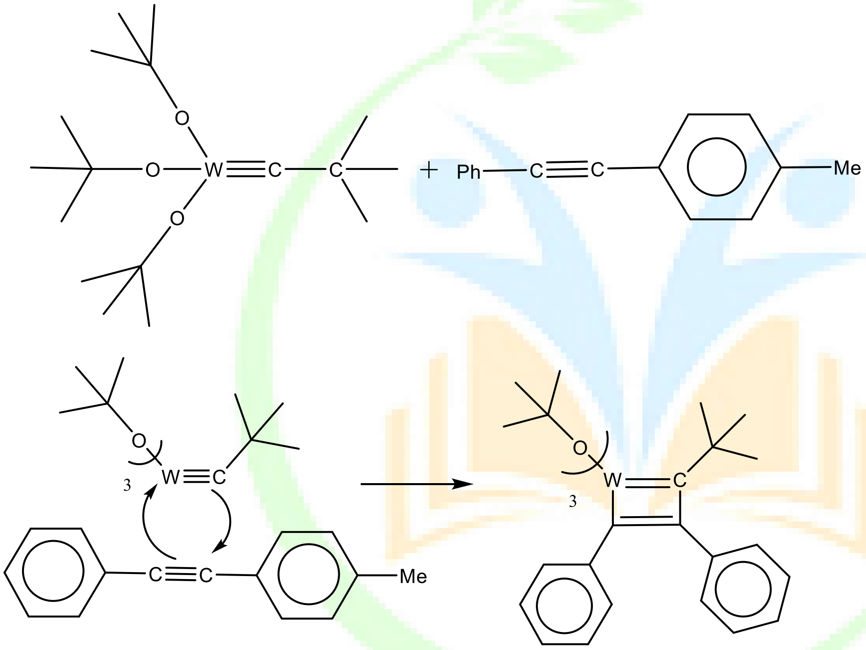
B = (n × 18) – A = 36–30=6

Number of metal-metal bond = $\frac{B}{2} = \frac{6}{2} = 3$

101.

Ans. (b)

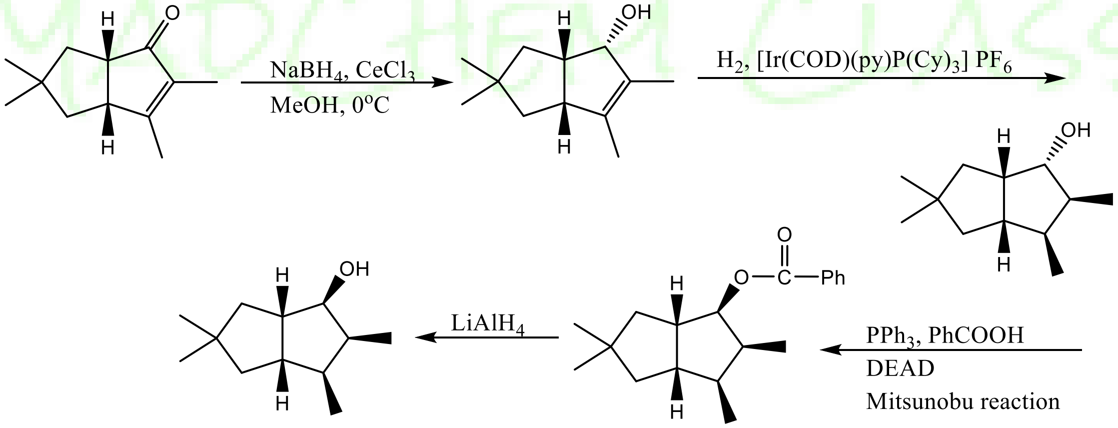
Sol.



102.

Ans. (a)

Sol.



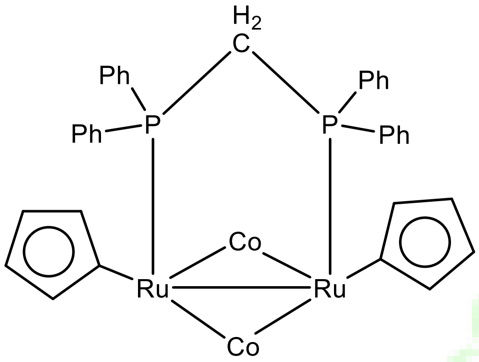
103.

Ans. (c)

Sol. T.V.E. = 8 × 2 + 5 × 2 + 2 × 2 + 4 = 34 = A

B = (n × 18) – A = 36 – 34 = 2

Number of M–M bonds = $\frac{B}{2} = \frac{2}{2} = 1$



3– bridging, 1–M–M bonds

104.

Ans. **(a)**

Sol. When the norvornene is strained molecule because the hyberdizaton is sp^2 when the metal attached with norborene back π-bonding takes place and due to this back π-bonding the hyberdization changes to sp^2–sp^3 and hence relief to strain.

105.

Ans. **(b)**

Sol. $Co(CO)_3$

9 + 6 = 15 (for 18 electron require 3 electron)

P ↔ BH_2

5   3 + 2 = 5 (for 8 electron require 3 electron)

CH ↔ BH_2 (for 8 electron require 3 electron)

4 + 1 = 5 3 + 2 = 5

$Ni(\eta^5–C_5H_5)$ for 18 electron require 3 electron)

10 + 5 = 15

$Co(CO)_3 \leftrightarrow P \leftrightarrow CH \leftrightarrow Ni(\eta^5–C_5H_5)$

106.

Ans. **(b)**

Sol. $[Co(\eta^5–C_5H_5)B_4H_8]$

$Co(\eta^5–C_5H_5) \leftrightarrow (BH)$

14   4

$[BHB_4H_8] = [B_5H_5]^{-4} \equiv [BnHn]^{-4} \rightarrow$ nido

$[Mn(\eta^2–B_3H_8)(CO)_4]$; $[Mn(CO)_4] \leftrightarrow [BH_2]$

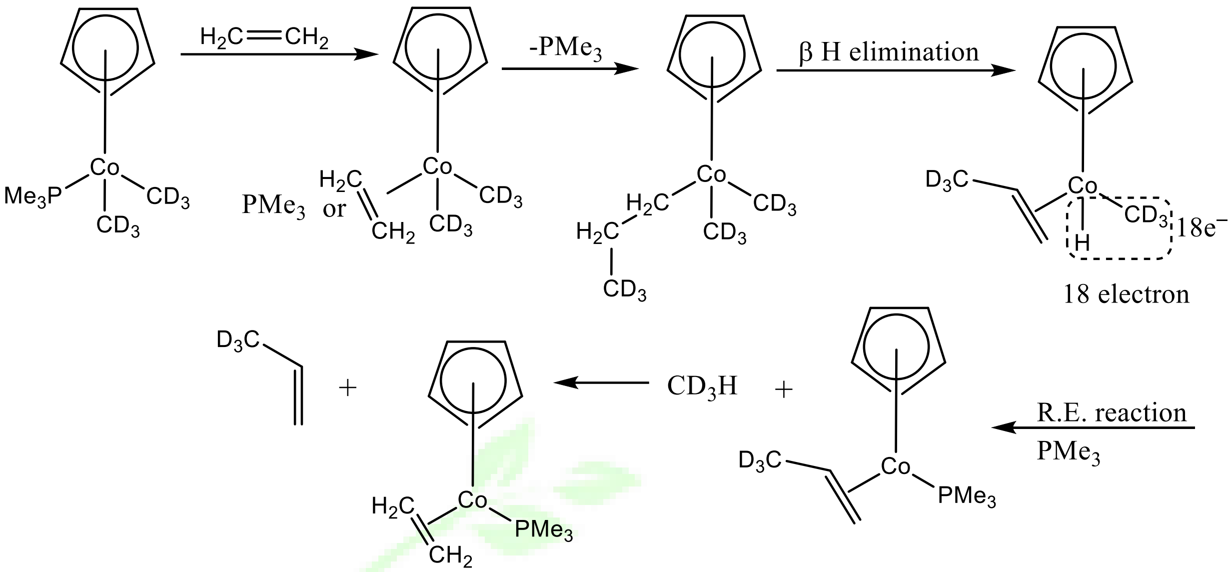
7 + 8 = 15   5

$[B_3H_8BH_2] = [B_4H_{10}] = [B_4H_4]^{-6} \equiv [BnHn]^{-6} \rightarrow$ Arachno

107.

Ans. **(c)**

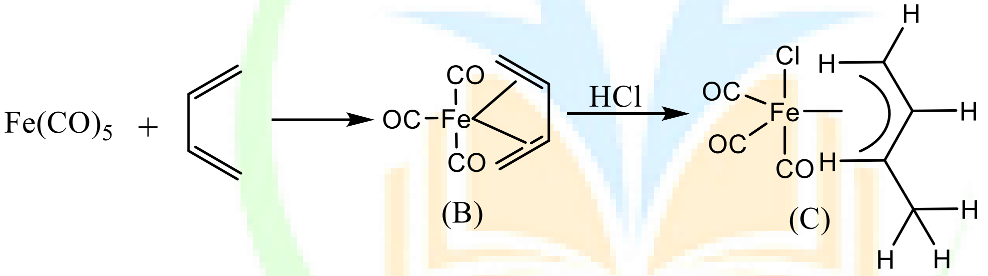
Sol.



108.

Ans. **(b)**

Sol.



Compound (C) has show four ^{1}H NMR signal

109.

Ans. **(a)**

Sol. Fischer carbene carbon is electrophilic in nature due to strong π-acceptor ligands

110.

Ans. **(b)**

Sol. 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 = 16 e$^-$

111.

Ans. **(c)**

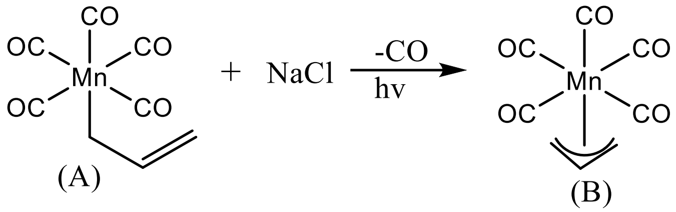
Sol. CH_3^+ = 4 + 3 – 1 = 6

$[Cr(CO)_5]$ = 6 + 10 = 16

112.

Ans.

Sol. $[Na[Mn(CO)_5] + CH_2 = CH\text{–}CH_2\text{–}Cl \rightarrow$



113.

Ans. **(a)**

Sol. $[B_6H_6]^{2-}$ has 6 + 1 = 7 binding moleculas orbital

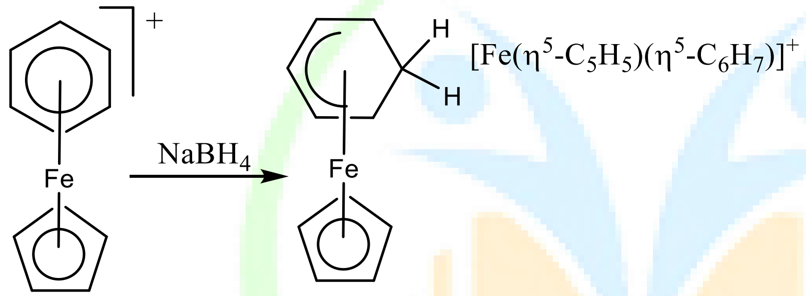
$[B_6H_6]^{2-}$ B–H = 2 × 6 = 12 e^-

for 2 negative charge, hence 12e– + 2e^- = 14e^-

114.

Ans. **(d)**

Sol.

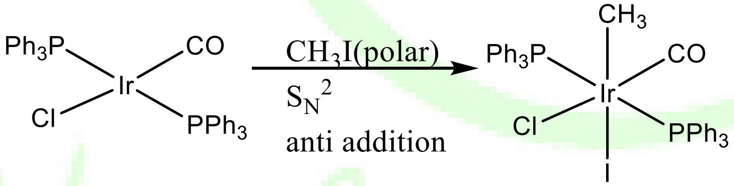


$[Fe(\eta^5–C_6H_6)(\eta^5–C_5H_5)]^+$

115.

Ans. **(a)**

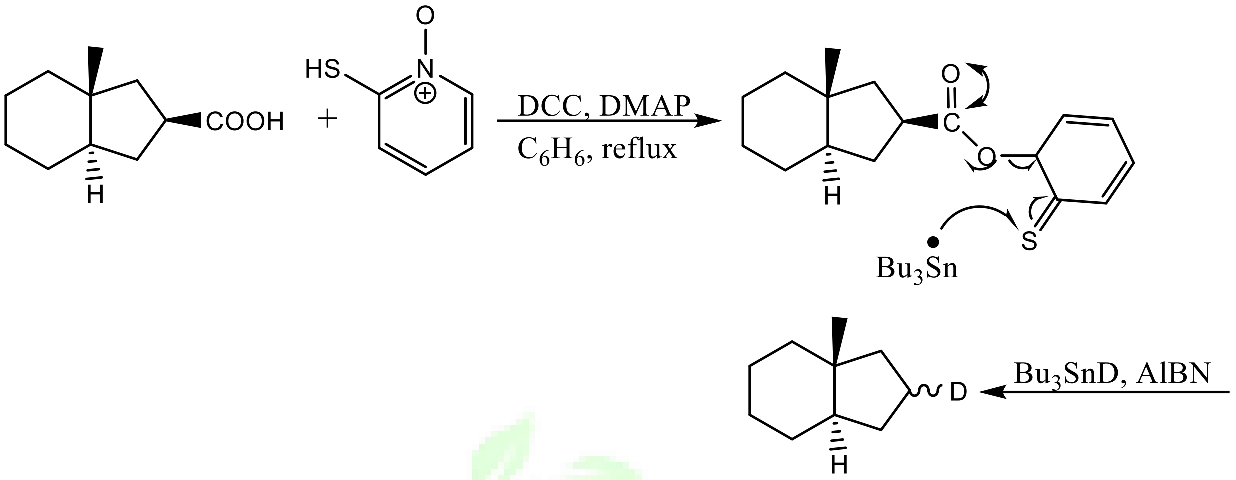
Sol.



116.

Ans. **(d)**

Sol.



117.

Ans. (c)

Sol. Number of valence electron in CH$_2$ = 6

Hence, fragment having 16 electon will be isolobal to this fragment.

A → CpCr(CO)$_2$ ⇒ 5 + 6 +4 = 15

B → CpCu ⇒ 5 + 11 = 16

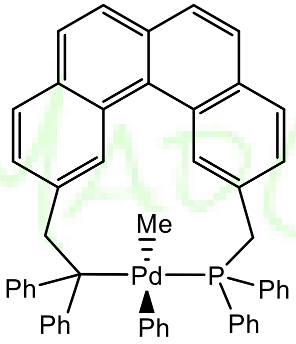
C → Ni(CO)$_2$ ⇒ 10 + 4 = 14

D → Cr(CO)$_4$ ⇒ 6 + 8 = 14; E → Fe(CO)4 ⇒ 8+8=16

118.

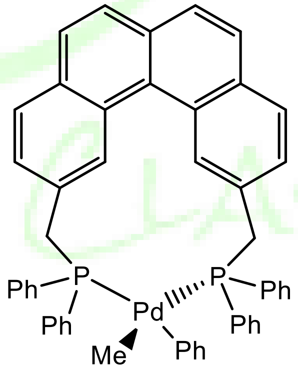
Ans. (d)

Sol. Accroding to reductive elimination reaction mechanism cis-complex can give the product but trans-complex is notr 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.



(trans)

Actually formd but does not give reaction



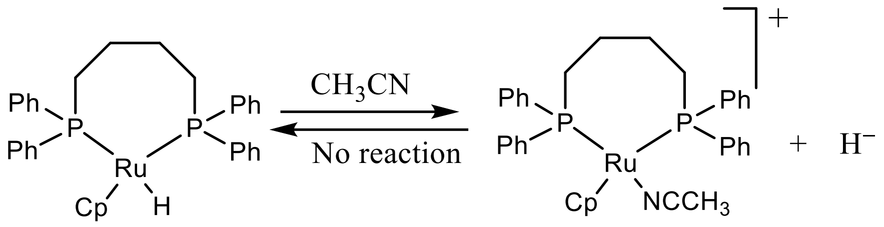
(cis)

This can give the reaction but not formed

119.

Ans. (d)

Sol. As the chelate ring size increases (in case of (d)), the energy of LUMO of complex cation CpRu(P–P)$^+$ (which formed after H– transfer) decreases and makes the complex cation better H– acceptor and therefore decreasing the rate of H– transfer from CpRu(P–P) H.



High steric crowding due to large chelating ring

Low energy LUMO so, better H^- acceptro

120.

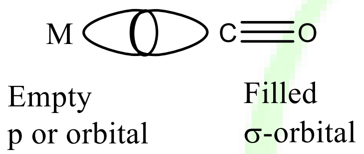
Ans. **(b)**

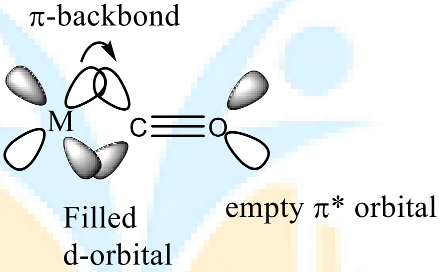
Sol. $Sn_9^{4-} \Rightarrow 9 \times 4 + 4 - 40$, thus it follow 4n + 4. Hence, it has nido structure

121.

Ans. **(b)**

Sol.





back bonding (synergic bonding) $\propto \frac{1}{\nu_{CO}(\text{streching frequency})} \propto$ C–O bond length

Compound	$[V(CO)_6]^-$	$Cr(CO)_6$	$[Mn(CO)_6]^+$	$H_3B.CO$
$\nu_{C-O}(cm^{-1})$	1860	2000	2098	2164

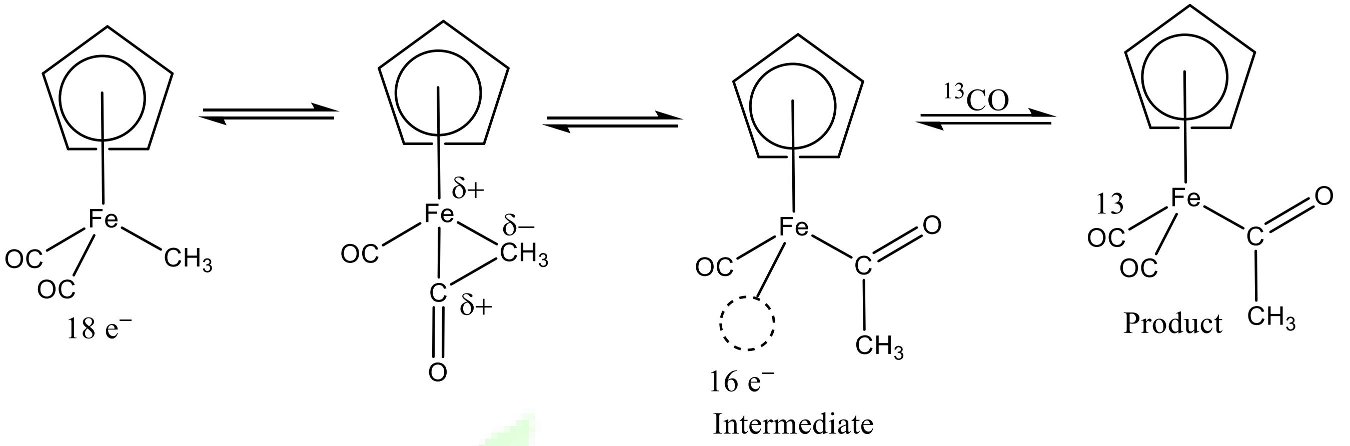
$$[V(CO)_6]^- < Cr(CO)_6 < [Mn(CO)_6]^+ < H_3B-CO$$
$$\xrightarrow[\text{Order of } \nu_{CO} \text{ streching frequency}]{}$$

$$[V(CO)_6]^- > Cr(CO)_6 > [Mn(CO)_6]^+ > H_3B-CO$$
$$\xrightarrow[\text{Order of } C-O \text{ bond length}]{}$$

122.

Ans. **(d)**

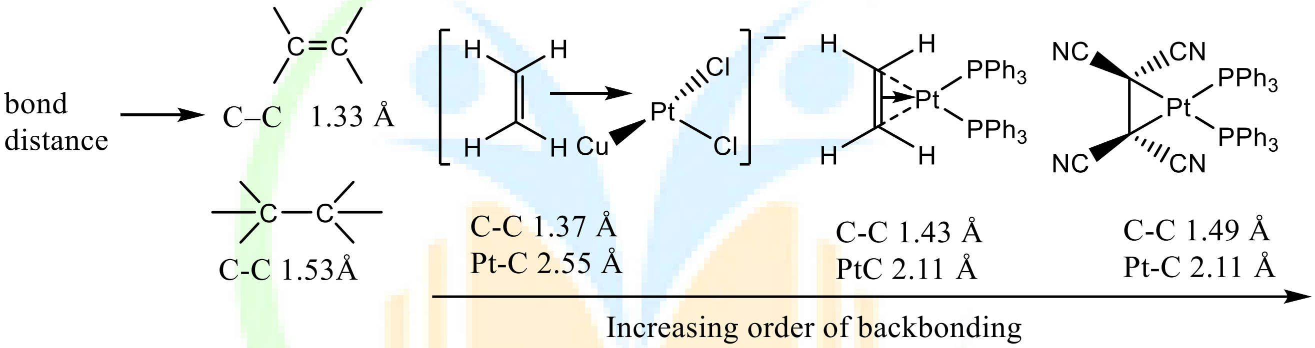
Sol. The insertion of carbon monoxide into a metal carbon bond to form an acyl group is the basis of carbonylation reaction.



123.

Ans. **(b)**

Sol.



Donation of π–electron of the C = C to empty σ orbital of the metal acompanied by back donation from a filled metal dπ orbital into an empty C = C π* orbital

Synergic bonding ∝ C–C bond length

124.

Ans. **(d)**

Sol. (A) $[(Co(\eta^5\text{–}C_5H_5))_2(C_2B_6H_8)]$

$[Co(\eta^5\text{–}C_5H_5)]_2 \rightarrow 18 + 10 = 28$ is isolobal with (B_7H_7)

$[(BH)_7(BH)_2B_6H_8]$

$B_{15}H_{17} \rightarrow B_{15}\,H_{15}^{2-} \rightarrow$ closo

(B) $B_4C_2H_8 \rightarrow [(BH)_2B_4H_8] \rightarrow B_6H_{10}$ or $B_6H_6^{4-} \rightarrow$ nido

$[B_10H_{13}(Au(PPh_3))]$

(C) $Au(PPh_3) \rightarrow 11 + 2 = 13$ is isolobal with B_3H_4

$[B_{13}H_{17}] \rightarrow B_{13}\,H_{13}^{4-} \rightarrow$ nido

(D) $C_2B_8H_{10} \rightarrow (BH)_2\,B_8H_{10} \rightarrow B_{10}H_{12} \rightarrow B_{10}H_{10}^{2-} \rightarrow$ closo

125.

Ans. **(b)**

Sol. $[Pd(PPh_3)_4]$ and $Ni(CO)_4$ compound are isoelectronic (follow 18 electron rule) and isotructural in natural (tetrahedral structure)

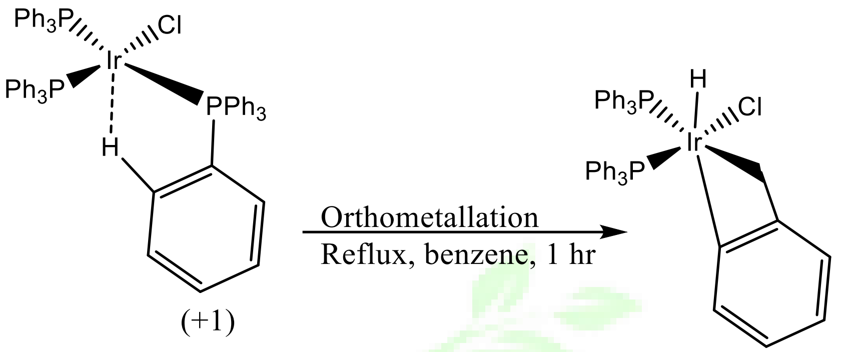
$[Pd(PPh_3)_4]$ $[Ni(CO)_4]$

$10 + 8 = 18e^-$ $10 + 8 = 18e^-$

126.

Ans. **(b)**

Sol.



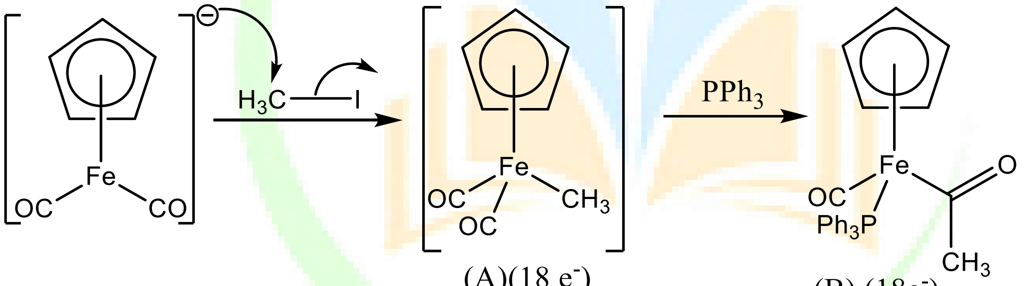
(+1)
$16e^-$
(diamagnetic)

(+3)
$18e^-$
(diamagnetic)

127.

Ans. **(b)**

Sol.



$(18e^-)$

(A)$(18\ e^-)$
two signals with
3:5 intensity ratio

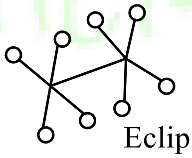
(B) $(18e^-)$
three signal with
3:5:15 intensity ratio

128.

Ans. **(d)**

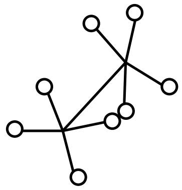
Sol.

$[ReCl_8]^{2-} = 2Re^{3+}\ (d^4) + 8Cl^-$
δ-bond : Eclipsed geometry



Eclipsed

$[Os_2Cl_8]^{2-}$ has $Os^{3+}d^5$
Bonjd order = 3 : staggered



Staggered

129.

Ans. **(b)**

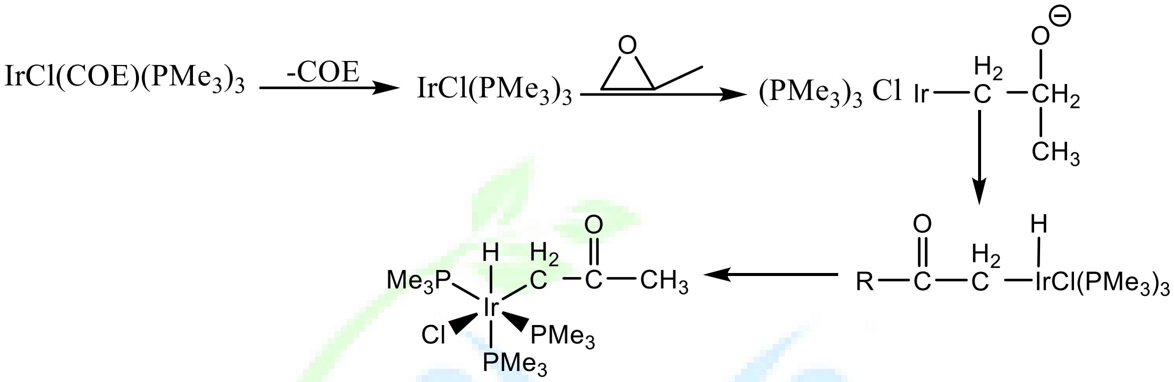
Sol. As the electrongativity of X in PX_3 increases, π–acceptor tendency increases.

$PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

130.

Ans. **(b)**

Sol.



131.

Ans. **(b)**

Sol. **Comlex :**

$Mo(PF_3)_3(CO)_3$	2055, 2090
$Mo\{P(OMe_3)_3\}(CO)_3$	1888, 1977
$Mo(PPh_3)_3(CO)_3$	1835, 1934
$Mo(pyridine)_3(CO)_3$	1746, 1888

π-acceptro tendency of spectator ligand is $PF_3 > POMe_3 > PPh_3 >$ Pyridine. Therefore, PF_3 reduce more electron density from the metal in complex to pyridine consequently. As the electron density on metal decreases, M-C bond strength decreases, C–O bond strength increases. Hence, ν_{CO} increases,

132.

Ans. **(b)**

Sol. $\nu CN = [Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-}$

$\nu CO = [Cr(CO)_6] > [Cr(CO)_3(NH_3)_3]$

133.

Ans. **(a)**

Sol. The ligand which have strong electron withdrawing group have strong π–acceptor tendency. So, binds strongly.

134.

Ans. **(c)**

Sol. $[Rh_9P(CO)_{21}]^{2-} \rightarrow \text{TEC} = 9 \times 9 + 5 + 2 \times 21 + 2 = 130$

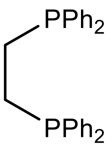
$$\text{PEC} = 130 - 9 \times 12 = 22$$

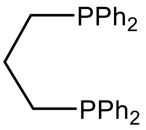
$$\frac{PEC}{2} = \frac{22}{2} = 11 \Rightarrow 9 + 2 \Rightarrow (n + 2) = nido$$

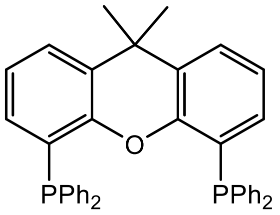
135.

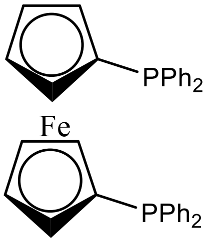
Ans. **(c)**

Sol.

(i) 

(ii) 

(iii) 

(iv) 

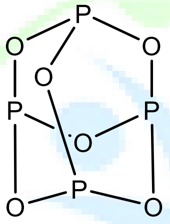
Blte angle 85° 91° > 120° 96°

The linear and brached formylated product is depends upon natural bite angle of biphosphines. As the natural bite angle increases selectivity for linear product increases.

136.

Ans. **(a)**

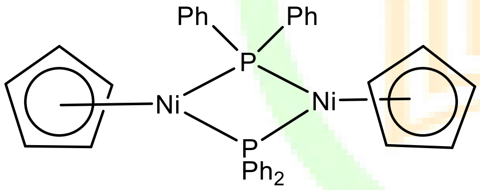
Sol.



137.

Ans. **(a)**

Sol.



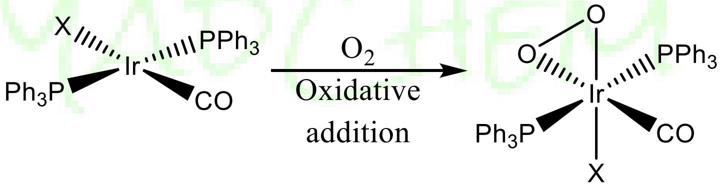
Ni = 10
Cp = 5e$^-$
Ph$_2$P = 3e$^-$
$\underline{18e^-}$

Therefore, No M–M bonds

138.

Ans. **(d)**

Sol.



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.

X =	F	Cl	Br	I
Rate ($M^{-1}S^{-1}$)	1.48×10^{-2}	3.4×10^{-2}	7.4×10^{-2}	0.34

139.

Ans. **(d)**

Sol. Fe(−1) → d^9 ststem

$d^9ML_3 \xleftrightarrow{O} CH$

For d^9–ML_3, original co-ordination number will be considered as ML_6.

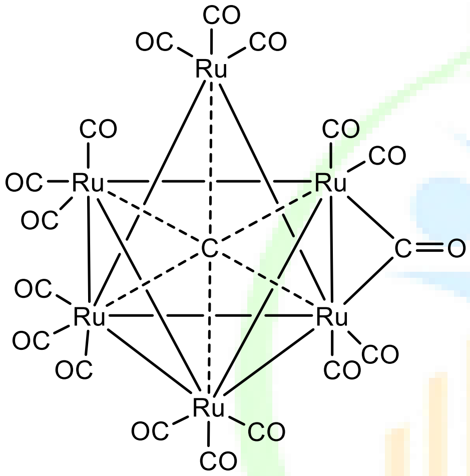
Therefore, $[Fe(CO)_2(PPh_3)]^-$ having three co-ordination number, missing three from original ML_6 and similarly for CH, three ligands also missing from original CH_4.

Hence, $[Fe(CO)_2(PPh_3)]^-$ is isolobal with CH but not with CH_2^+ ($5e^-$) because two ligands missing from original CH_4.

140.

Ans. **(d)**

Sol. $[Ru_6C(CO)_{17}]$



TEC = 8 × 6 + 4 + 17 × 2 = 86

PEC = TEC – n × 12

PEC = 86 – 6 × 12

PEC = 86 – 72 = 14

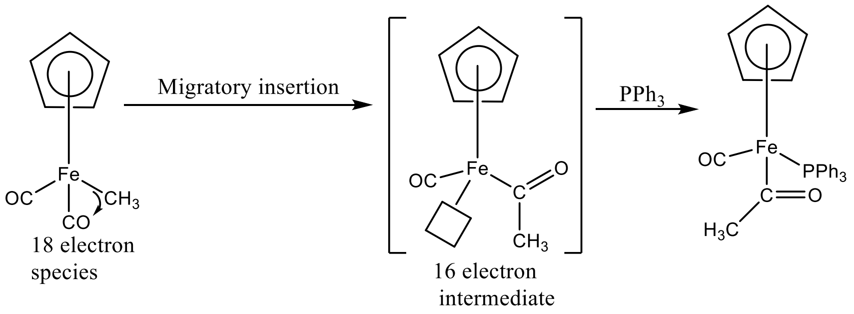
$\frac{PEC}{2} = \frac{14}{2} = 7$ (n+1) ⇒ Closo

In the cluster $[Ru_6C(CO)_{17}]$, the carbon atom is encapsulated at cavity of cluster and equally interacted with all Ru centres.

141.

Ans. **(c)**

Sol.



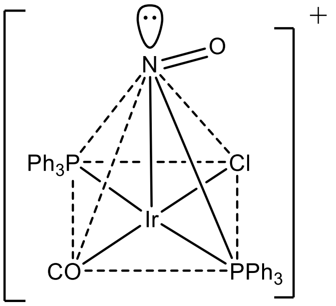
142.

Ans.

143.

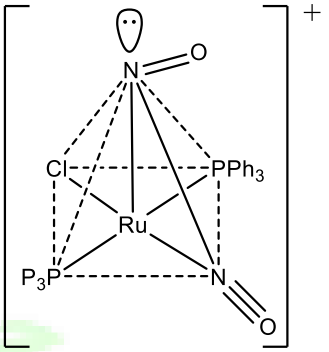
Ans. **(c)**

Sol.



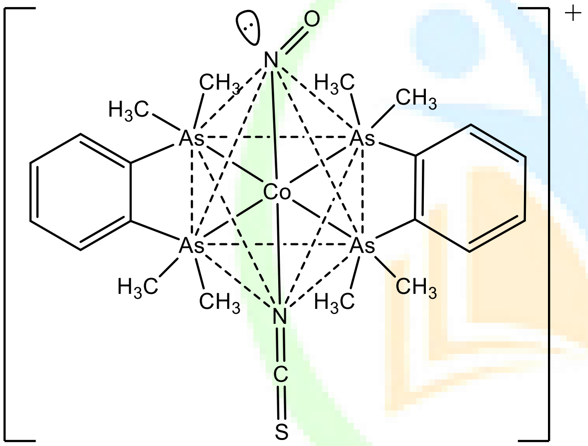
$2e^- + 2e^- + 2e^- + 1e^- + 1e^- + 9e^- - 1e^- = 16e^-$

NO Present in bent mode



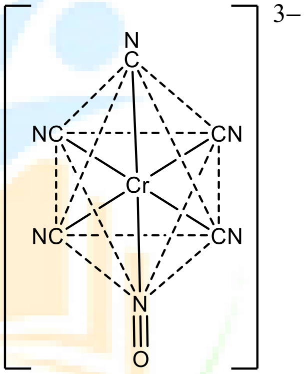
$1e^- + 3e^- + 1e^- + 4e^- + 8e^- - 1e^- = 16e^-$

One NO is in bent mode and other in linear mode



$4e^- + 4e^- + 1e^- + 1e^- + 9e^- - 1e^- = 18e^-$

NO (Nitrosyl) Present in bent mode



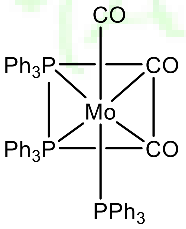
$5e^- + 3e^- + 3e^- + 6e^- = 17e^-$

No (Nitrosyl) Presetnt in linear mode

144.

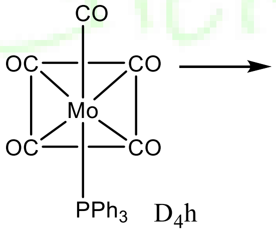
Ans. **(c)**

Sol.



Fac-C_3V

2 Peaks



symmetrical

D_4h

Trans

1 Peaks

145.

Ans. **(d)**

Sol.

	Expected	observed
Sm^{+3}	0.5	1.9

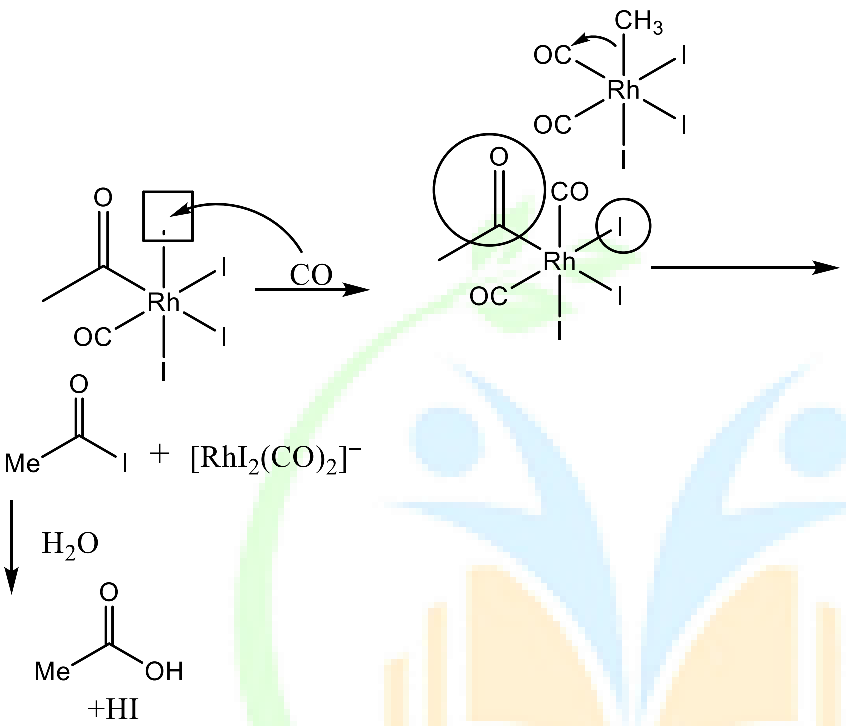
Eu^{+3} 0 0.9

146.

Ans. **(a)**

Sol. $CH_3OH + HI \rightarrow CH_3I + H_2O$

$[Rh\,I_2(CO)_2]^- + CH_3I \xrightarrow[R.D.S]{O.A} CO$



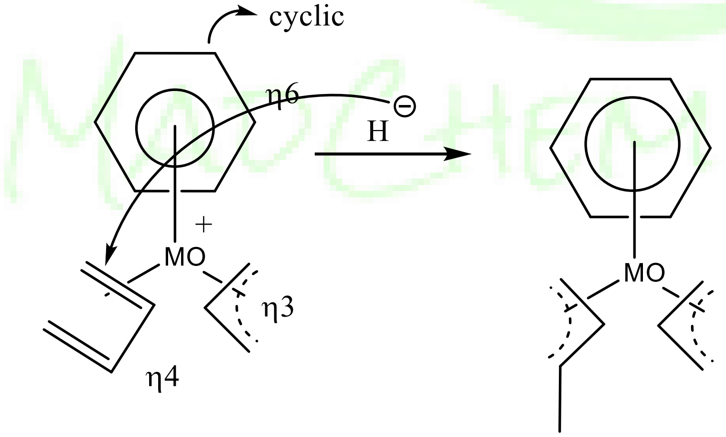
147.

Ans. **(b)**

Sol. DMG : (1) 18e– complex ⇒ polyene

(2) even polyne > odd polyene

(3) alyclic polyene > cyclec polyene



148.

Ans. **(d)**

Sol. M–e bond length ↑. no. of unpaired 2–↑es

unpaired –(η)

$Ni(cp)_2 = 2Oe^{-} - 12 = 8 = n = 2$

—— —— eng $CO(cp)_2 \Rightarrow 19e^- - 12 = 7 = n = 1$

dxz dyz $Fe(cp)_2 = 18e^- - 12 = 6 = n = 0$

—— e1g

—— —— e_2g

dxy dx_2y_2

149.

Ans. **(b)**

Sol. $[Fe_5(CO)_{14}N]^-$ $[CO_6(CO)_{13}N]^-$

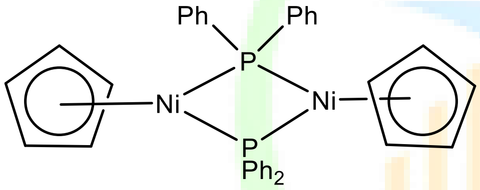
$TVE = 8 \times 5 + 14 \times 2 + 5 + 1$
$= 40 + 28 + 6$
$= 74$
$14 \times 5 = 70$ n + 2
14n + 4
nido

$TVE = 9 \times 6 + 13 \times 2 + 5 + 1$
$= 54 + 26 + 6$
$= 86$
$14 \times 6 = 84$
14n + 2
closo
n + 1

150.

Ans. **(a)**

Sol.



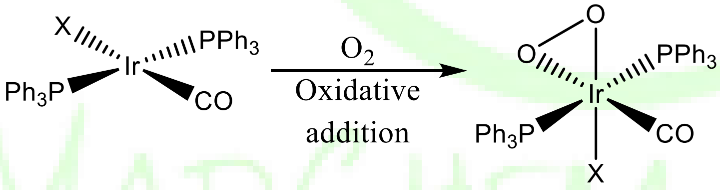
Ni = 10
Cp = $5e^-$
$Ph_2P = 3e^-$
$\overline{\underline{18e^-}}$

Therefore, No M–M bonds

151.

Ans. **(d)**

Sol.



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 proportionalto the electron density on the metal.

X =	F	Cl	Br	I
Rate $(M^{-1}S^{-1})$	1.48×10^{-2}	3.4×10^{-2}	7.4×10^{-2}	0.34

152.

Ans. **(d)**

Sol. Fe(–1) → d^9 ststem

$d^9ML_3 \xleftrightarrow{o} CH$

For d^9–ML_3, original co-ordination number will be considered as ML_6.

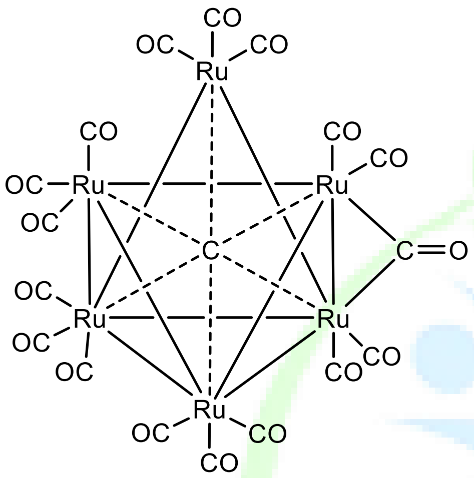
Therefore, $[Fe(CO)_2(PPh_3)]^-$ having three co-ordination number, missing three from original ML_6 and similarly for CH, three ligands also missing from original CH_4.

Hence, $[Fe(CO)_2(PPh_3)]^-$ is isolobal with CH but not with CH_2^+ (5e⁻) because two ligands missing from original CH_4.

153.

Ans. **(d)**

Sol. $[Ru_6C(CO)_{17}]$



TEC = 8 × 6 + 4 + 17 × 2 = 86

PEC = TEC – n × 12

PEC = 86 – 6 × 12

PEC = 86 – 72 = 14

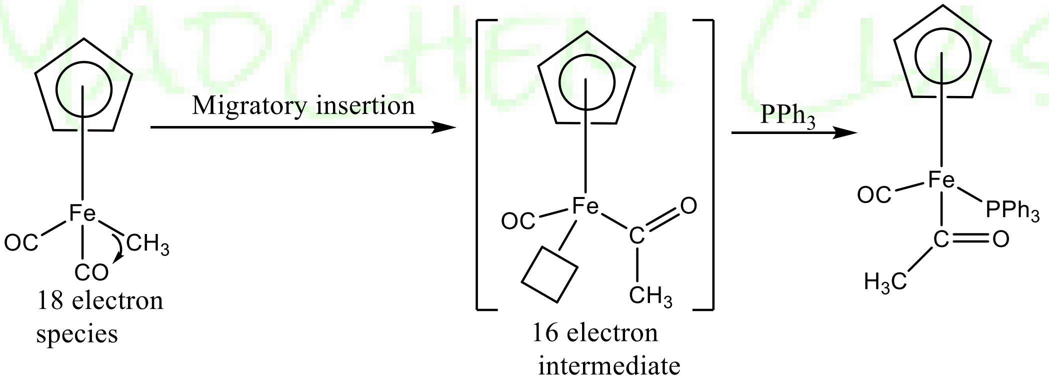
$\frac{PEC}{2} = \frac{14}{2} = 7\ (n+1) \Rightarrow$ Closo

In the cluster $[Ru_6C(CO)_{17}]$, the carbon atom is encapsulated at cavity of cluster and equally interacted with all Ru centres.

154.

Ans. **(c)**

Sol.



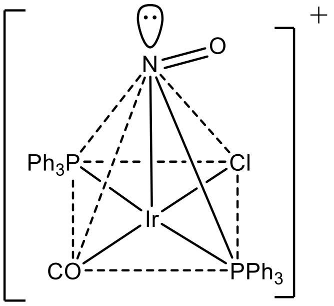
155.

Ans.

156.

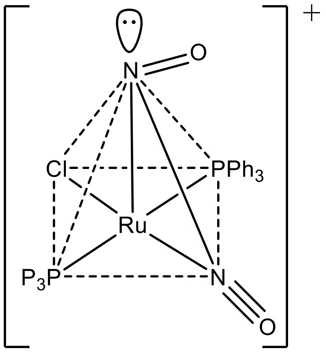
Ans. **(c)**

Sol.



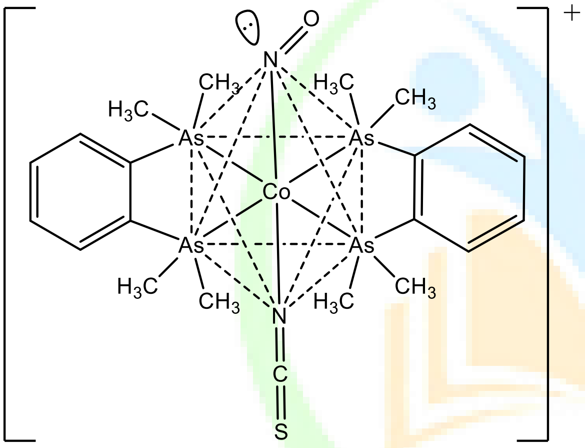
$2e^- + 2e^- + 2e^- + 1e^- + 1e^- + 9e^- - 1e^- = 16e^-$

NO Present in bent mode



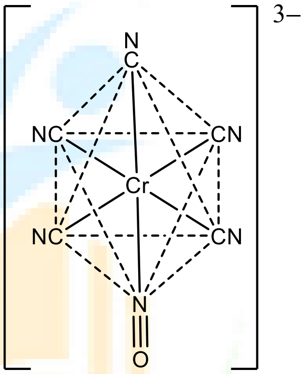
$1e^- + 3e^- + 1e^- + 4e^- + 8e^- - 1e^- = 16e^-$

One NO is in bent mode and other in linear mode



$4e^- + 4e^- + 1e^- + 1e^- + 9e^- - 1e^- = 18e^-$

NO (Nitrosyl) Present in bent mode



$5e^- + 3e^- + 3e^- + 6e^- = 17e^-$

No (Nitrosyl) Presetnt in linear mode

157.

Ans. **(b)**

Sol. $X_{92}^{234} + \beta + \alpha \rightarrow \gamma + \alpha + 2\beta +$

$\beta \rightarrow {}^{0}_{-1} \quad \alpha = {}^{4}_{2} \quad \underset{\downarrow}{B^+} = {0 \atop +1} \quad \gamma = {}^{0}_{0}$

positron

238

91 γ

$\gamma = \frac{238}{93-2} \rightarrow {}^{238}_{91}\gamma$

158.

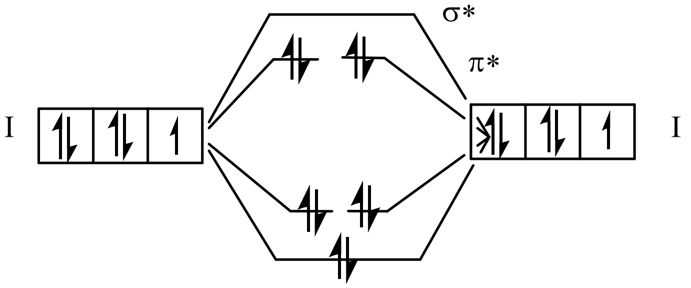
Ans. **(d)**

Sol. $AgClO_4$ is more soluble in benzene because Benzene has a electrons which act as soft base. coupled plasma Atomic Emission oxide formation lowers atomization of metals.

159.

Ans. **(d)**

Sol. I_2 molecular orbital diagram



acetone and
ethanol have
cone pair on oxygen
donokes of σ* orobital

160.

Ans. **(b)**

Sol. As we go to right ionization energy increase

IE_1 gallium < IE_1 of selenium

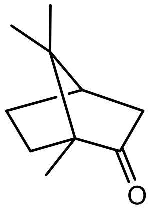
As nitrogen have half filled shell so they have higher ionization potential

Statement (III) and (iv) are correct (2) iii and iv.

161.

Ans. **(b)**

Sol. 219 ppm–carbonyl peak

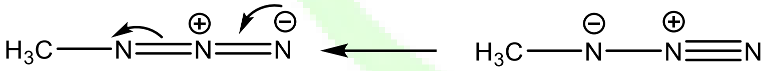


δ = 219 ppm

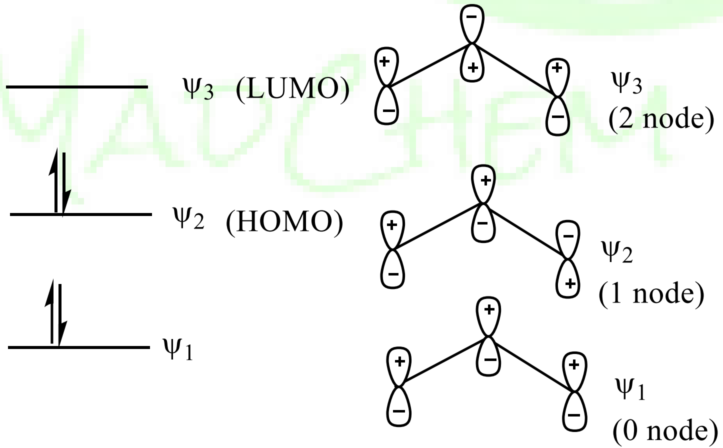
162.

Ans. **(b)**

Sol. methyl Azide



4 electrons are involved in conjugation between 3p orbitals.



$\psi_2 \longrightarrow$ (HOMO)

163.

Ans. **(a)**

Sol. ion pair $\frac{1}{r}$ E = $k_1 \frac{q_1 q_2}{r}$

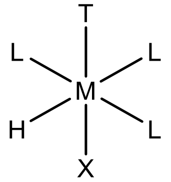
ion – dipole $\frac{1}{r^2}$ E = $\frac{k_1 qu}{r^2}$

dipole $\frac{1}{r^3}$ E = $\frac{Cl_1 qu_2}{r^3}$

164.

Ans. **(b)**

Sol. Dissociation substitution for octahedral complex



(A) High steric hindrance between ligand courses repulsion and favours dissociation.

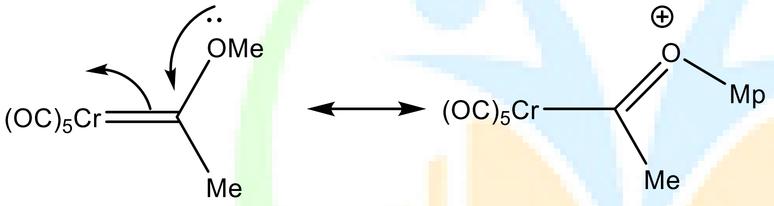
(C) PentaCoordinated intermediate is observed as complex loses one ligand.

a and c is correct

165.

Ans. **(a) & (c)**

Sol.



Carbene donate two electron Fischer carbene is electrophilic As them is nesonance the double bond conversion barrier is low.

166.

Ans. **(b)**

Sol. $[(\eta^5\text{–}C_5H_5)\,Fe(\mu_2\text{–}CO)\,(NO)]_2$

Fe→8 electron Linear NO → 3

Cp→ 5 Bent NO → 1

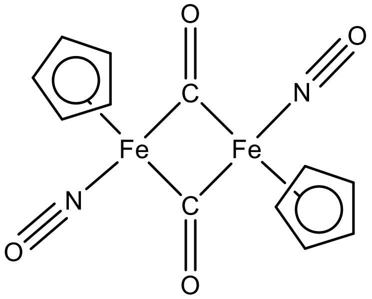
C = θ → 2

Metal Metal bonds (8 + 5 + 3 + 2) × 2

= 18

$\frac{36-36}{2} = 0$

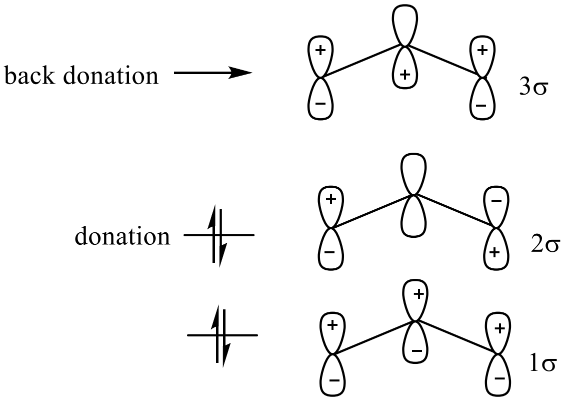
Correct structure



167.

Ans. **(a)**

Sol. Moluecular orbital of $[CH_2 = CH\text{–}CH_2]^-$

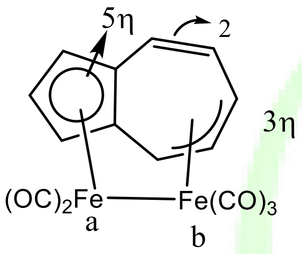


So 2σ and 3σ

168.

Ans. **(a)**

Sol. 18 e rule must be followed



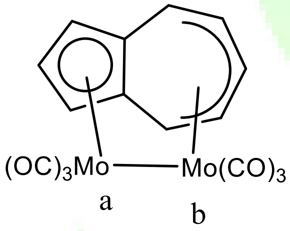
Fe——Fe bond

1 electron

$CO \rightarrow 2$ $Fe \rightarrow 8$

$Fe_a \rightarrow 8 + 4 + 5 + 1 = 18$

$Fe_b \rightarrow 8 + 6 + 3 + 1 = 18$



$Mo_a = 6 + 6 + 5 + 1 = 18$

$Mo_b = 6 + 6 + 5 + 1 = 18$

MO → 6 electron

169.

Ans. **(c)**

Sol. $[Ru_6(CO)_{17}B]^-$

$(8\times6) + (7\times2) + 3 + 1 = 86 \rightarrow$ octahedral

$[OS_6(CO)_{18}P]^-$

$(8\times6) + (18\times2) + 5 + 1 = 90 \rightarrow$ trigonal prism

$[IS_4(CO)_{16}]$

$(8\times6) + (16 \times 2) = 80 \rightarrow$ Square

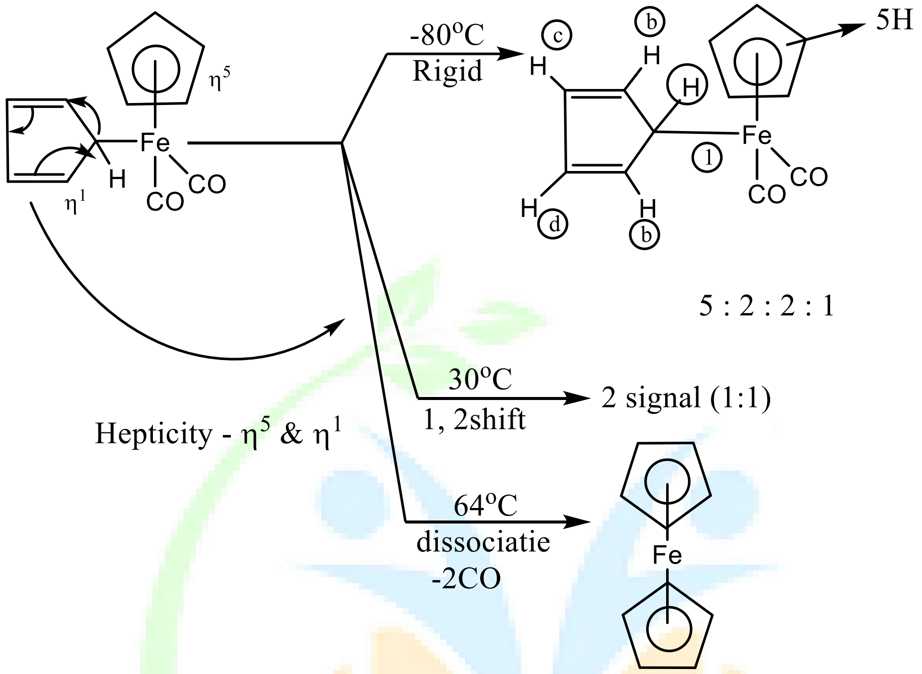
Correction option (4) A : octahedral
B: trigonal prism
C : Square

170.

Ans. **(a)**

Sol. $[(C_5H_5)= Fe(CO)_2]$

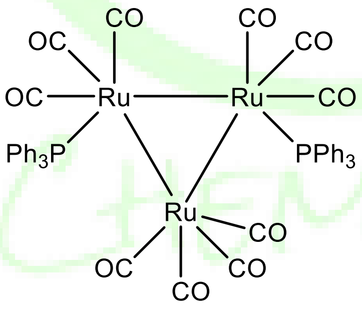
$= 5 \times 2 + 8 + 4$
$= 10 + 8 + 4$
$= 22\ e^-$ (If we take η^5)
$[\eta5\text{–}Cp\eta^1\text{– }cpFe(CO)_2] = 18e^-$



171.
Ans. **(a)**
Sol. $[Ru_3(CO)_{10}(PPh_3)_2]$

$= 8 \times 3 + 20 + 4$
$= 24 + 20 + 4 = 48$

$M - M = \frac{18 \times 3 - 48}{2}$
$= \frac{54 - 48}{2}$
$= 6/2 = 3$



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