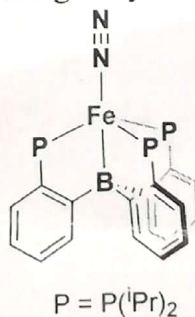
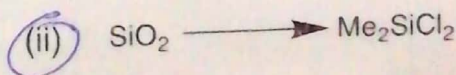
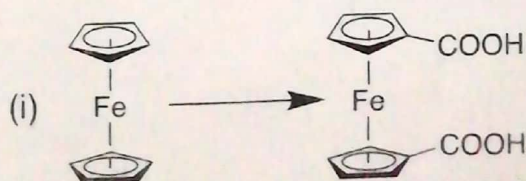


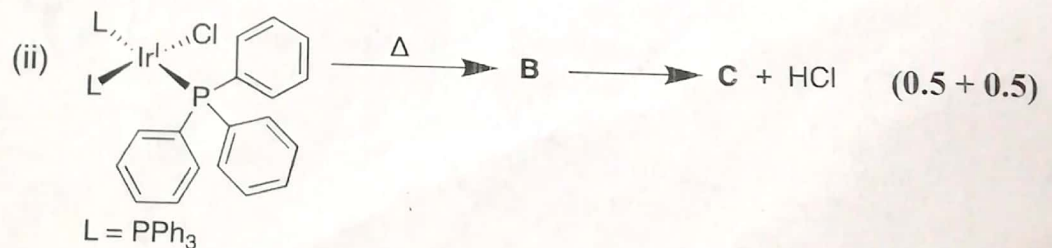
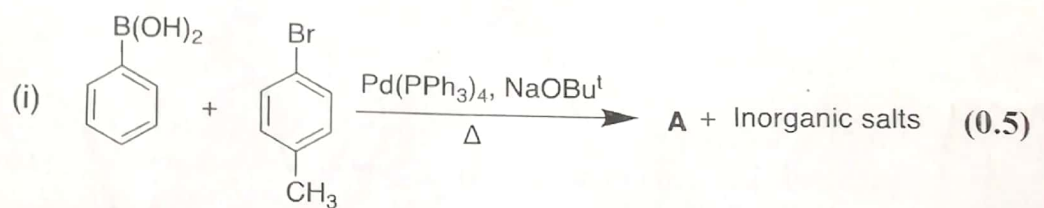
1. (a) Draw a crystal field splitting diagram for $[\text{Ni}(\text{CN})_4]^{2-}$ and show orbital occupancies. (0.5 + 0.5)
 (b) Sketch a curve that you would predict from crystal-field theory for the variation of ionic radii of the first transition series octahedral trivalent metal ions (from Ti^{3+} to Cu^{3+}) in a strong ligand field. (1.5)
2. (a) Calculate the CFSE values for $[\text{Fe}(\text{bipyridine})_3]^{2+}$ and $[\text{CuCl}_4]^{2-}$. (0.5 + 0.5)
 (b) Predict whether MnCr_2O_4 and Co_3O_4 would adopt a normal spinel or an inverse spinel structure. Explain your reasoning. (1 + 1)
3. (a) Explain on the observations that tetrahedral Ni(II) complexes have magnetic moments in the range of $3.5\text{--}4.1 \mu_B$, much higher than $\mu_{\text{spin-only}}$ value. (1)
 (b) An aqueous solution of a 0.5 M solution of manganese chloride is very weakly colored, although an aqueous solution of potassium permanganate of same concentration exhibits very intense color. Explain. (1)
 (c) Red crystalline $[\text{NiCl}_2(\text{PPh}_2\text{CH}_2\text{Ph})_2]$ is diamagnetic at 295 K. On heating to 387 K for 2 hours, a blue-green form of the complex is obtained, which has a magnetic moment of $3.18 \mu_B$ at 295 K. Suggest an explanation for these observations and draw structures for the complexes. (1)
4. (a) Construct a molecular orbital diagram for CO and show orbital occupancies. (1 + 0.5)
 (b) In your opinion which oxidation state of iron (-I to +VI) would stabilize most the complex pictured below? Give reasoning for your choice. (0.5 + 0.5)



5. (a) Consider the 18-electron rule as a guide and determine the value of x and y in the following complexes.
 (i) $[\text{MnBr}(\text{CO})_x]$, (ii) $[\text{Ni}(\text{CO})_3(\text{NO})]^y$ (consider M-NO linear coordination, y is the charge of the complex) (0.5 + 0.5)
 (b) A ruthenium complex, $[\text{Ru}(\text{PPh}_3)_2\text{Cl}(\text{NO})_2]^+$ shows $\nu_{\text{N-O}}$ values at 1845 cm^{-1} and 1687 cm^{-1} . Why are the N-O band frequencies so much farther apart? (1)
6. (a) Give an appropriate synthetic route for the following conversions. (1 + 1)



7. Predict the products (A, B, & C) in the following reactions.



Give a suitable mechanism for the formation of A and mention the oxidation state of the metal complexes involved at each step. (1 + 0.5)

8. (a) Why is the change from deoxyhemoglobin to the oxyhemoglobin accompanied by a decrease in the observed magnetic moment? (1)
- (b) Draw a plot of % O₂ saturation of hemoglobin vs pO₂ (kPa), if a drop in the pH of blood plasma from 7.4 to 7.2 occurs. (1)