1. From the reaction of $NiBr_2$ and Ph_2EtP, it is possible to isolate green crystals of $[Ni(Ph_2EtP)_2Br_2]$, which has a magnetic moment of 3.2 BM, and red crystals of $[Ni(Ph_2EtP)_2Br_2]$, which has zero magnetic moment. When either of these is dissolved in dichloromethane at 40 °C, the resultant solution has a magnetic moment of 2.69 BM. Suggest structures of the green and red crystals and explain the solution magnetic moment. (2+2)
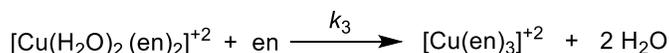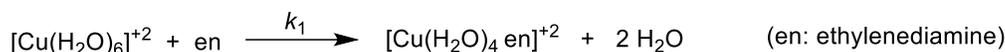

Tetrahedral, green crystal, 3.2 BM   Square planar, red crystal, 0 BM
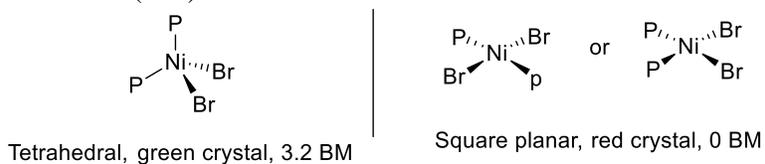
Suggest structures of the green and red crystals: 1 point for each correct structure
explain the solution magnetic moment: 2 points for correct explanation that is the equilibrium between tetrahedral and square planar complexes.

2. Determine the total number of metal-metal bonds in $[\eta^5\text{-}CpMo(CO)_2]_2$ (Group 6: Cr, Mo, W). (3)

A. Total M–M bonds = $[(18 \times n) - \text{total valence electron}]/2 = [(18 \times 2) - 30]/2 = 3$
Mo≡Mo.

One point for correct answer that is 3. One point for showing correct formula or method. One point for correct calculation.

3. In the following stepwise reactions, the order of the values of rate constants is $k_1 \approx k_2 \gg k_3$. Explain in details why? (2)
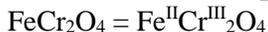
$$[Cu(H_2O)_6]^{+2} + en \xrightarrow{k_1} [Cu(H_2O)_4\,en]^{+2} + 2\,H_2O \qquad \text{(en: ethylenediamine)}$$

$$[Cu(H_2O)_4\,en]^{+2} + en \xrightarrow{k_2} [Cu(H_2O)_2\,(en)_2]^{+2} + 2\,H_2O$$

$$[Cu(H_2O)_2\,(en)_2]^{+2} + en \xrightarrow{k_3} [Cu(en)_3]^{+2} + 2\,H_2O$$

A. k_3 is smaller compared to k_1 and k_2, due to the lack of stability of $Cu(en)_3]^{+2}$. The metal in the six coordinated Cu^{+2} complex is d^9 ion and the complex undergo strong John-Teller distortion. The bis(ethylenediamine) complex can distort readily by letting the two water molecules move out from the copper, leaving the two ethylenediamine rings relatively unchanged. In contrast, the $Cu(en)_3]^{+2}$ complex cannot distort without straining at last two of the chelate rings. However, the constraint of the chelating ring system prevents distortion, but the resulting perfectly octahedral complex will lack the stabilization inherent in J-T distiortion. Therefore, $Cu(en)_3]^{+2}$ is less stable and k_3 is much smaller compared to k_1 and k_2.

4. Has $FeCr_2O_4$ normal or inverse spinel structure? Explain why? (2)

   A. **$FeCr_2O_4$ is a normal spinel** since the divalent Fe^{2+} is a high spin d^6 ion with CFSE = 4 Dq and the trivalent Cr^{3+} is a high spin d^3 ion with CFSE = 12 Dq. Hence Cr^{3+} gets more OSSE while occupying octahedral sites.

   B. $FeCr_2O_4$ has normal spinel structure
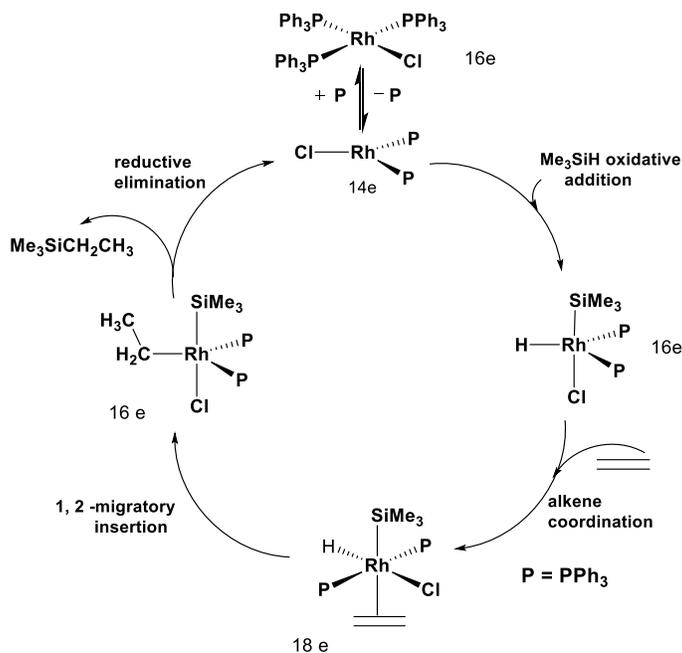 $FeCr_2O_4 = Fe^{II}Cr^{III}{}_2O_4$
   O^{2-} = a weak field ligand
   $Fe^{2+} = d^6$ HS: CFSE in octahedral field = -0.4 Δ_o
   $Cr^{3+} = d^3$ HS: CFSE in octahedral field = -1.2 Δ_o
   Since, the CFSE of Cr^{3+} in octahedral field is higher than that of Fe^{2+}, Fe^{2+} and Cr^{3+} will not interchange their position and thus give normal spinel structure.

5. Wilkinson's catalyst catalyses the reaction of trimethylsilyl hydride (Me_3SiH) with ethylene to give ethyltrimethylsilane (Me_3SiEt). Show the steps involved in the catalytic cycle and also mark the electron count and type of the reactions at each step. (2+1+1)

electron count: 0.25 for each correct electron count of each intermediate.
type of the reactions at each step: 0.25 for each correct type (oxidative addition, alkene coordination, migratory insertion and reductive elimination)