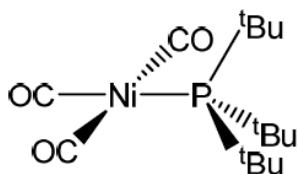


Tutorial 3

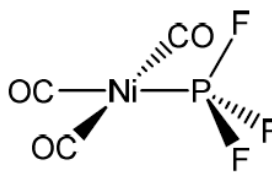
Q1. Using the 18 electron rule, determine whether the following complexes are electron precise or not.

- 1) $\text{Cr}(\text{CO})_6$
 Total charge on ligands = 0, so charge on Cr = 0, so Cr = d^6
 6 CO ligands x 2 electrons each = 12 electrons
 Total of 18 electrons
- 2) $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$
 Total charge on ligands = 2^- , so $\text{Fe}^{2+} = d^6$
 $(\eta^5\text{-C}_5\text{H}_5 = 6) + (2\text{CO} \times 2 = 4) + (\text{Cl}^- = 2) = 12$ electrons
 Total of 18 electrons
- 3) Charged complex: $[\text{Mn}(\text{CO})_6]^+$
 Total ligand charge = 0, so $\text{Mn}^+ = d^6$
 12 electrons from 6 CO ligands gives a total of 18 electrons
- 4) M—M Bond: $(\text{CO})_5\text{Mn—Mn}(\text{CO})_5$
 Each bond between metals counts 1 electron per metal: $\text{Mn—Mn} = 1 \text{ e-}$
 Total ligand charge = 0, so $\text{Mn}^0 = d^7$
 5 CO ligands per metal = 10 electrons for a total of 18 electrons per Mn

Q2. Using the bonding schemes for metal carbonyl and metal phosphine complexes explain the difference observed in $\nu(\text{CO})$ by FTIR spectroscopy for the trans-CO ligand of the following complexes.



$$\nu(\text{CO})_{\text{trans}} = 2056 \text{ cm}^{-1}$$



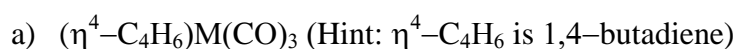
$$\nu(\text{CO})_{\text{trans}} = 2111 \text{ cm}^{-1}$$

Due to the greater electronegativity of F vs. C., the PF_3 ligand is a better p-acceptor than the $\text{P}(\text{tBu})_3$ ligand. As a result of this, the PF_3 ligand has a greater back-donation from the Ni metal than the $\text{P}(\text{tBu})_3$ ligand and thus decreases the back-donation to the trans CO ligand relative to the analogous $\text{P}(\text{tBu})_3$ complex. This decreased back-donation to the trans CO ligand in the PF_3 complex results in a stronger C=O bond and a higher energy stretching frequency in the IR spectrum.

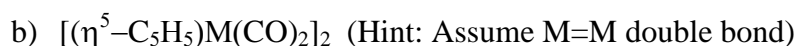
Q3. The carbon-carbon bond distance in ethylene is 133.7 pm compared to 137.5 pm in $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ and 143 pm in $[\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4]$. Explain this observation.

A3. The carbon-carbon bond length in ethylene increases on coordinating to platinum due to backbonding. Platinum is in the +2 oxidation state in $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ and in zero oxidation state in $[\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4]$. Hence the extent of backbonding will be greater on the Pt(0) complex leading to more donation of electrons from Pt to the π^* of ethylene and causing the C-C bond length to increase.

Q4. Assuming that the following complexes are electron precise (the 18 electron rule is obeyed), determine the identity of the transition metal M.



Answer: The metal M is in zero oxidation state. We know that all three CO's will give 6 electrons and that butadiene will give 4. Since the 18 electron rule is followed, the number of electrons donated by M = $18 - (6 \times 3 + 4) = 8$. Hence the metal M is Fe.



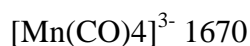
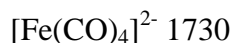
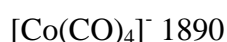
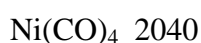
Answer: There is one charged ligand per metal, the oxidation state of metal is +1. We know that $(\eta^5\text{-C}_5\text{H}_5)$ is a 6 electron donor and the two CO's will donate 4 electrons. Also, in a M=M double bond, each metal atom contributes two electrons.

Therefore, the electrons contributed by the metal M comes to $18 - 12 = 6$.

Therefore, M(I) with a d6 configuration, i.e, Mn is the metal.

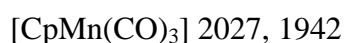
Q5. Rationalize the trend in each of the following sets of IR-active CO stretching frequencies (cm^{-1}):

(a)



Answer: These isoelectronic complexes have increasing negative charges to delocalize in the order $\text{Ni}(\text{CO})_4 < [\text{Co}(\text{CO})_4]^- < [\text{Fe}(\text{CO})_4]^{2-} < [\text{Mn}(\text{CO})_4]^{3-}$. Delocalization via back donation into the π^* orbitals of the CO ligands causes a decrease in the CO bond order and thus a shift of the CO stretching frequencies (ν_{CO}) to progressively lower energies in the order given.

(b)



Answer: Mn(I) has higher effective nuclear charge than Cr(0). Hence it attracts the electrons more strongly and less charge is back-donated into the π^* orbitals of the CO ligands. The CO bond in the manganese compound is therefore weakened to a lesser extent and ν_{CO} is higher.

Q6. Consider the complex ions $[\text{Fe}(\text{NH}_3)_6]^{3+}$, $[\text{Ru}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Ir}(\text{NH}_3)_6]^{2+}$. Which **ONE** of these complexes will definitely **NOT** show a **Jahn-Teller distortion**? Explain why.

[**HINT:** the magnetic moments of the Fe and Co complexes are *considerably* higher than those of their heavier congeners, Ru and Ir, respectively.]

Answer:

In order to answer this question, one must first decide on the electron configurations for the d orbitals. Fe^{3+} and Ru^{3+} are both d^5 while Co^{2+} and Ir^{2+} are both d^7 . The heavier members of a group are always low spin (because Δ_o increases substantially from the 3d to 4d or 5d sets) while the first row elements can be either high or low spin. The higher magnetic moment clearly establishes that the lighter group members (Fe, Co) are high spin while the heavier members (Ru, Ir) are low spin.

A Jahn-Teller distortion can theoretically occur if there is a partially occupied degenerate set of orbitals. This is true in all of these cases **EXCEPT high spin d^5 Fe^{3+}** so it is the only one that definitely will not show a Jahn-Teller distortion.

Q7. Explain why $[\text{FeF}_6]^{3-}$ is colourless while $[\text{CoF}_6]^{3-}$ is coloured.

Answer:

High spin Fe^{3+} is likely with a weak field ligand like F^- so this is a high spin d^5 ion and no $d \rightarrow d$ transitions are possible (Laporte forbidden as well as spin forbidden). In the case of Co^{3+} , this is a high spin d^6 ion for which spin-allowed $d-d$ transitions can occur leading to colour.