Core Chemistry 3 (CHEM3012) - Inorganic Reaction Mechanisms

You are expected to have attempted these questions before the workshop

Substitution in Square Planar complexes.

(a) Using either $[PtCl_4]^{2-}$ or $[Pt(NH_3)_4]^{2+}$ as metal containing starting materials, outline the synthesis of *cis* and *trans* isomers of $[Pt(NH_3)(NO_2)Cl_2]^-$, given that the substituent *trans* effects are in the order $NO_2^- > Cl^- > NH_3$.

(b) Why do phosphine ligands show such a high *trans* effect? (Hint: recall the molecular orbital basis for the *trans* effect, and consider the orbital interactions when a phosphine bonds to a metal centre.) What are the products of the reaction of K_2PtCl_4 with
   (i) two moles of R_3P, and
   (ii) two moles of R_3N?

(c) Predict the products of the reaction of each of the following metal complexes with
   (i) one mole, and
   (ii) two moles of the nucleophile listed:
      (I) $[Pt(PPh_3)_4]^{2+}$ with Br^-,
      (II) $[PtBr_4]^{2-}$ with PPh_3,
      (III) $[Pt(NH_3)_4]^{2+}$ with Cl^-.

(d) Using the reagents PPh_3, NH_3 and $[PtCl_4]^{2-}$, propose efficient routes to all the possible isomers of $[PtCl_2(NH_3)(PPh_3)]$. (Shriver, Atkins and Langford, 1st edition, p474)

(e) For the reaction below, the second-order rate constants, in $dm^3\ mol^{-1}s^{-1}$, for M = Ni, Pd, Pt are 33, 0.58 and 6.7×10^{-6}, respectively. Explain.
   $$trans\text{-}[Pt(PEt_3)_2(C_6H_5)Cl] + pyridine \rightarrow trans\text{-}[Pt(PEt_3)_2(C_6H_5)(pyridine)]^+ + Cl^-$$

General Substitution reactions of Octahedral complexes.

(f) Put the following complexes in order of rate of substitution by H_2O:
   (i) $[Co(NH_3)_6]^{3+}$, (ii) $[Rh(NH_3)_6]^{3+}$, (iii) $[Ir(NH_3)_6]^{3+}$, (iv) $[Mn(H_2O)_6]^{2+}$, (v) $[Ni(H_2O)_6]^{2+}$.

(g) For the reactions: $[M(H_2O)_6]^{2+} + H_2^{17}O \rightarrow [M(H_2O)_5(H_2^{17}O)]^{2+} + H_2O$,
   the volumes of activation ($\Delta V^{\ddagger}$ in $cm^3\ mol^{-1}$) are found to be
   V^{2+} -10.1, Mn^{2+} -4.1, Fe^{2+} +3.8, Co^{2+} +6.1, and Ni^{2+} +7.2.
   Discuss these data in terms of the mechanism of these reactions.

(h) Why does $[Ga(H_2O)_6]^{3+}$ exchange coordinated water molecules faster than $[Al(H_2O)]^{3+}$? How would $[Tl(H_2O)_6]^{3+}$ compare? What about $[Tl(H_2O)_n]^+$?

Substitution reaction in Octahedral Co(III) and Rh(III) complexes.

(i) The reaction of $[Co(NH_3)_4Cl_2]^+$ with H_2O is 10^3 times faster than the reaction of $[Co(NH_3)_5Cl]^{2+}$. By considering how the charge on a complex affects bond strengths, discuss briefly whether this data is consistent with a I_d or I_a mechanism.

(j) Why is the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ in the presence of base much faster than that of $[Co(py)_5Cl]^{2+}$?

(k) The reactions of Rh(III) complexes proceed via I_d mechanisms. State the effect of the following on the rate of such reactions:

(i) an increase in the positive charge on the complex;
(ii) changing the leaving group from NO_3^- to Cl^-;
(iii) changing the entering group from Cl^- to I^-;
(iv) changing the *cis* ligands from NH_3 to H_2O.

(l) Explain the trends in the rate constants given in the table below for the following reaction:
$$Cr(CO)_5L + *CO \rightarrow Cr(CO)_4(*CO)L + CO$$
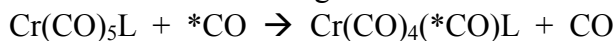
L	CO	PMe$_2$Ph	PPh$_3$	Br$^-$	Cl$^-$
k (s^{-1}, 30°C)	1.0×10^{-12}	1.5×10^{-10}	3.0×10^{-10}	2.0×10^{-5}	1.5×10^{-4}

Ligand substitution, insertion, and oxidative addition in Organometallics

(m) Indicate whether the following complexes would undergo substitution by PPh$_3$ by associative or dissociative pathways:
   $Mo(CO)_6$, $Fe(\eta\text{-}C_5H_5)(CO)(NO)$, $V(CO)_6$, $PtCl_4^{2-}$, $Co(\eta^5\text{-indenyl})(CO)_2$.

(n) The complex $Fe(\eta\text{-}C_5H_5)(CO)_2(CH_3)$ reacts with PMe$_3$ to give $Fe(\eta\ C_5H_5)(CO)(COCH_3)(PMe_3)$, in a reaction that is first order in both starting materials. Explain.

(o) The complex $[cis\text{-Pt}(PEt_3)_2H(solv)]^+$ (solv = methanol or acetone) isomerises 1-hexene to a mixture of 2-hexene and 3-hexene. Suggest a mechanism for this process.

(p) Account for the stereochemistry of the following reaction:
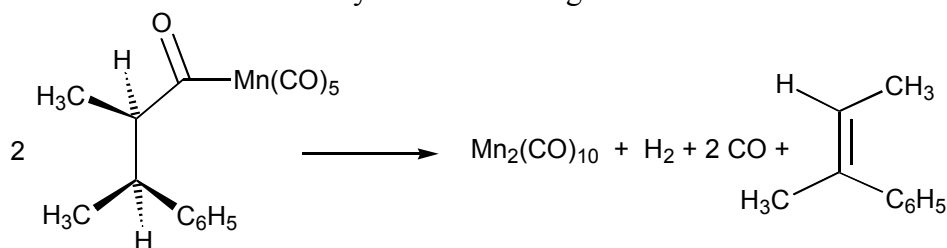
(q) The reaction of $V(CO)_5(NO)$ with PMe$_3$ to give $V(CO)_4(NO)(PMe_3)$ obeys the rate law:
$$\frac{-d[V(CO)_5(NO)]}{dt} = k_1[V(CO)_5(NO)] + k_2[PMe_3][V(CO)_5(NO)]$$
Suggest a mechanism for this reaction consistent with the rate law and the 18-electron rule.

Electron transfer reactions

(r) In the reaction of $[Co(NCS)(NH_3)_5]^{2+}$ with $[Fe(H_2O)_6]^{2+}$ in water as solvent, it is possible to identify $[Fe(NCS)(H_2O)_5]^{2+}$ as an intermediate. Explain. What are the final products of this reaction?

(s) The rate constants for the exchange reaction:
$$[Cr(H_2O)_5X]^{2+} + [*Cr(H_2O)_6]^{2+} \rightarrow [*Cr(H_2O)_5X]^{2+} + [Cr(H_2O)_6]^{2+}$$
where *Cr is ^{51}Cr, a radioactive nuclide and X is a mono-anionic ligand, are given in the table. Outline the likely mechanism and explain the difference in the rate constants.
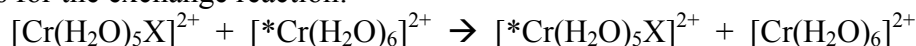
X	F$^-$	Cl$^-$	Br$^-$	N$_3^-$
k (mol^{-1} dm^3 s^{-1})	1.2×10^{-3}	11	60	>1.2

(t) Account for the relative rates of the following two reactions:

$[Fe(CN)_6]^{3-} + [*Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{4-} + [*Fe(CN)_6]^{3-}$	10^5 dm^3 mol^{-1} s^{-1}
$[Co(NH_3)_6]^{3+} + [*Co(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_6]^{2+} + [*Co(NH_3)_6]^{3+}$	10^{-4} dm^3 mol^{-1} s^{-1}