

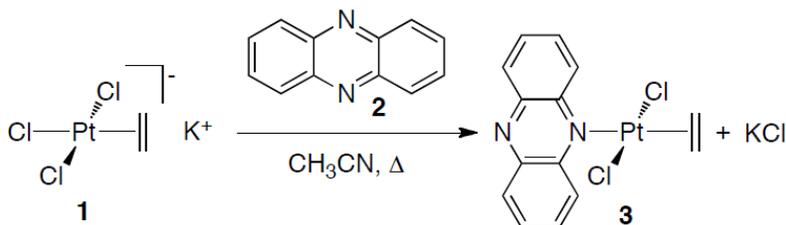
Recommended reading: 22, 26 (3rd edition); 21, 26 (4th edition)

Ch 102 – Problem Set 6

Due: Thursday, May 25 – Before Class

Problem 1 (2 points)

Zeise's salt (potassium trichloro(ethylene)platinate, **1**) undergoes ligand exchange in acetonitrile in the presence of aromatic N-donors such as phenazine (**2**) to yield platinum salt **3** exclusively as the isomer shown in the reaction scheme below. The isolation of a single isomer from the reaction below is due to the 'trans effect'. Note that in both compounds **1** and **3** ethylene is coordinated to platinum perpendicular to the Pt coordination square plane.

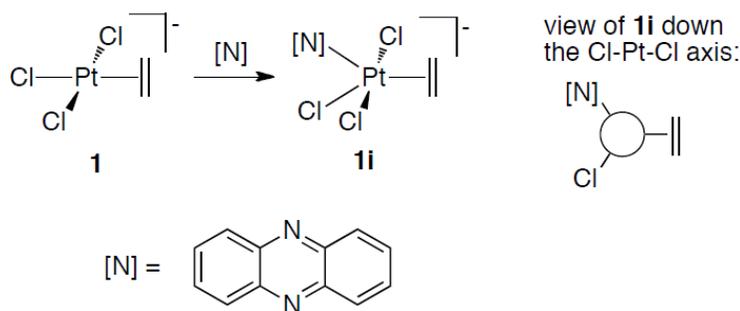


a) Consider compound **1**. Derive a full molecular orbital (MO) diagram for the σ -only framework of this complex. For simplicity, approximate complex **1** with the analogous four-coordinate platinum complex $[\text{PtH}_4]^{2-}$. For full credit make sure to include all of the following:

- Assign the point group of $[\text{PtH}_4]^{2-}$, and generate the reducible and irreducible representations for the ligand σ -bonding interactions
- Label metal orbitals with the appropriate Mulliken symbols and designate them as d, s, or p
- Label the SALCs with the appropriate Mulliken symbols
- Place the metal and ligand orbitals at the appropriate relative energies
- Label the generated molecular orbitals with Mulliken symbols and indicate whether they are σ , σ^* , or nb
- Fill in the correct number of electrons
- Circle the orbitals that have d-parentage
- Draw the molecular orbitals that correspond to the four bonding interactions in $[\text{PtH}_4]^{2-}$

b) The five molecular orbitals of d-orbital parentage make up the d splitting diagram for a σ -only general square planar molecule (such as model $[\text{PtH}_4]^{2-}$). Focus only on these d-orbitals for this part. Ethylene is a good π -acceptor due to its low-lying LUMO of π -axial symmetry (the C-C π^* orbital) and affects the d splitting. How does the d splitting diagram for the square planar geometry change by introduction of just one π -accepting ligand, as with ethylene in **1**? Derive the corresponding d splitting diagram by interacting the d-set derived in part a) with the LUMO of ethylene. Clearly label each orbital as σ , σ^* , π -backbonding, or nb. Fill with the correct number of d electrons.

c) As discussed in class, ligand exchange reactions involving square planar complexes usually proceed with an associative mechanism. Association of a fifth ligand to a square planar complex (such as attack on compound **1** above by phenazine) generates a five-coordinate, trigonal bipyramidal intermediate, as shown below.



Draw a σ -only d-orbital splitting diagram for a general trigonal bipyramidal complex ($[\text{PtH}_5]^{3-}$). Do not derive an entire MO diagram; only show the five d orbitals. Fill in the correct number of d electrons.

d) Include now a π -accepting ligand (ethylene) in the equatorial plane of this trigonal bipyramid (i.e. the plane perpendicular to the C_3 axis) in complex **1i**. How does the π -accepting ability of the single ethylene ligand affect the d orbital splitting diagram? Draw the corresponding d splitting diagram, clearly labeling each orbital as σ , σ^* , π -backbonding, or nb (again, you don't have to derive a full MO diagram, just focus on the d-parentage orbitals). Fill with the correct number of d electrons.

e) For candy (no points): Compare the π -interactions you described in part (b) and part (d). Which interaction do you expect to have a larger effect on the d-parentage orbitals? (Hint: remember that the LUMO of ethylene is higher in energy than the Pt d-orbitals).

Problem 2 (2 point)

a) For the following set of complexes, predict the order of **decreasing** Δ_o values and explain your prediction (please be brief!).



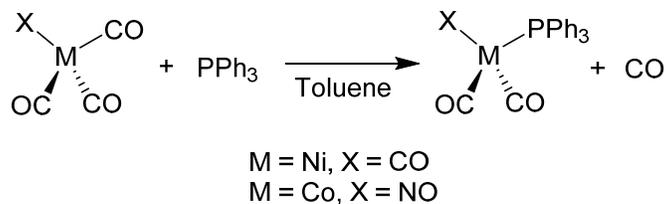
b) For CoCl_4^{2-} and $[\text{Co}(\text{CNPh})_5(\text{OH}_2)]^{2+}$, draw d-orbital splitting diagrams, label the d-orbital parentage, and populate with electrons (CNPh is a strong π -accepting ligand). Predict the spin only magnetic moment for these complexes.

c) Which complex do you expect to have faster degenerate water exchange (exchange of a water ligand with a water molecule from solution) kinetics, $[\text{Cr}(\text{OH}_2)_6]^{3+}$ or $[\text{Co}(\text{CNPh})_5(\text{OH}_2)]^{2+}$? Explain in terms of d-electron configuration.

d) For the following reactions, provide the structure of the products and compare their rates.

- $[\text{PtCl}_3(\text{CO})]^- + \text{NH}_3 \rightarrow$
- $[\text{PtCl}_3(\text{PH}_3)]^- + \text{NH}_3 \rightarrow$
- $[\text{PtCl}_3(\text{NH}_3)]^- + \text{NH}_3 \rightarrow$

e) Consider potential mechanisms of ligand substitution of one CO ligand from isoelectronic metal carbonyl complexes, $\text{Co}(\text{NO})(\text{CO})_3$ and $\text{Ni}(\text{CO})_4$, with triphenylphosphine (see below). Both complexes have similar pseudo-tetrahedral geometry. Which complex is more likely to undergo ligand substitution via an associative mechanism? Provide an explanation. Draw the five-coordinate intermediate and provide valence electron count, metal oxidation state, and d-electron count for the starting material and intermediate. Clearly distinguish linear and bent NO coordination.



Problem 3 (2 Points)

The following ligand substitution reaction is known to occur rapidly even at -70 °C in hexane.



You are tasked with determining whether the mechanism is associative or dissociative and have obtained the following data (the units of concentration are molar):

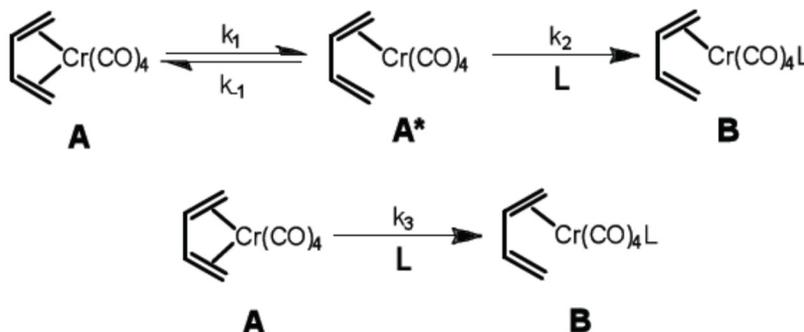
Table V. Observed Rate Constants as a Function of Ligand Concentration and Temperature for Carbon Monoxide Substitution of V(CO)_6 in Hexane Solution

Ligand	Temperature (°K)	10^2 [L]	10^2 k_{obs} (s^{-1})
PPh ₃	299	1.50	0.417
		1.52	0.430
		2.76	0.731
		4.16	1.12
		4.87	1.34
	293	1.15	0.245
		3.44	0.669
		4.10	0.773
		6.15	1.17
		6.55	1.29
	288	1.91	0.260
		4.15	0.578
		7.35	1.02
		12.2	1.70
	282	2.64	0.246
5.41		0.508	
7.35		0.676	
273	2.70	0.139	
	5.10	0.255	
	8.00	0.400	

- b) For both vanadium containing complexes give the total electron count, vanadium oxidation state, and d electron count.
- c) Assuming pseudo-first-order conditions, use the data provided to determine reaction order in phosphine.
- d) Using the observed rate constant data provided at different temperatures construct an Eyring plot and determine the enthalpy and entropy of activation for the reaction.
- e) Based upon your answers to parts b) and c) decide if the reaction is occurring by an associative or dissociative process. Explain.
- f) Given your answer to part d) and assuming the reaction is irreversible, do you expect running the reaction under an atmosphere of carbon monoxide to alter the reaction rates?
- g) The analogous substitution reaction of $V(CO)_6^-$ does not proceed even in molten PPh_3 (m.p. $80\text{ }^\circ\text{C}$). Furthermore, $Cr(CO)_6$ was found to react about 10^{10} slower than $V(CO)_6$ under comparable pseudo-first-order conditions and the reaction shows significantly slower rates under an atmosphere of carbon monoxide. Based on electron counting arguments and the aforementioned data, do you expect ligand substitution with $Cr(CO)_6$ to be associative or dissociative? Explain why ligand substitution with $Cr(CO)_6$ is far slower than with $V(CO)_6$.
- h) Studies of the ligand substitution reactions above can be complicated by the formation of disubstituted products $M(CO)_4(PPh_3)_2$. Two isomers are possible. Draw them, indicate which one is more likely to be formed in the substitution reaction and provide an explanation.

Problem 4 (2 pts)

Consider complex $Cr(CO)_4(C_4H_6)$ (**A**) described above. Reaction with a ligand L results in complete displacement of the diene ligand to generate $Cr(CO)_4L_2$; the plausible intermediate (**B**) where a single L has been added and only one of the diene double bonds remains coordinated reacts much too rapidly with additional L to be isolated or observed and this subsequent step does not affect the overall rate of the reaction. Formation of that intermediate (**B**) could proceed via either a dissociative mechanism or an interchange mechanism (shown below). Assuming that BOTH mechanisms operate, use the steady state approximation to derive the general rate law for the reaction and the expression for k_{obs} as a function of L . Sketch what a plot of k_{obs} vs. $[L]$ would look like. Indicate on this plot how some of the elementary rate constants could be determined. Then show how the rate law would simplify if only one of the two alternative mechanisms were significant, and sketch the corresponding k_{obs} vs. $[L]$ plots for each of those cases.



Problem 5. (2 points)

Pick a topic of interest from the recommended reading (descriptive chemistry) in bold at the beginning of this problem set. Prepare two power point slides including relevant *descriptive chemistry* (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (oxidation states, electron count, symmetry, MO theory, vibrational spectroscopy, etc.) and some application of the provided software (since MO theory and vibrational spectroscopy were covered in class, you are now expected to include some molecular orbital pictures / MO diagram analysis / IR/Raman analysis). Attach a printout of the slides to your solution of the problem set, and email the TAs the slides in pdf format by 12:00 noon on the due date. Please format file names as “FirstName_LastName_PSET#” and include your name on the first slide.