

Recommended reading: 22, 26 (3rd edition)

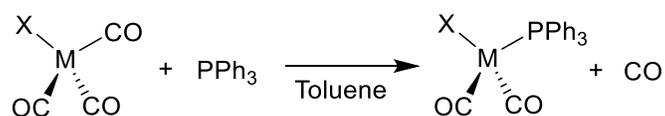
Recommended reading: 21, 26 (4th edition)

Ch 102 Problem Set 6

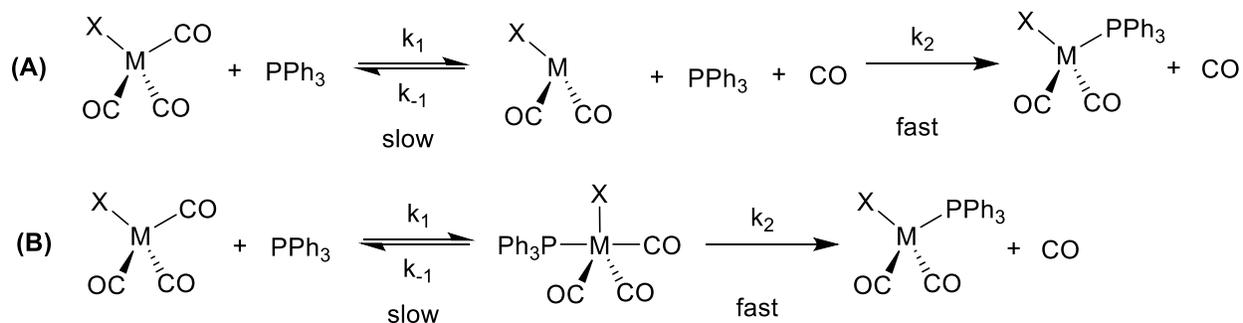
Due: Thursday, May 19, before class

Problem 1 (2 points)

The kinetics of ligand substitution between metal carbonyl complex, $\text{Co}(\text{NO})(\text{CO})_3$, and triphenylphosphine were compared to the isoelectronic metal complex $\text{Ni}(\text{CO})_4$. Both complexes have the same coordination geometry and d electron count. Below is a generalized scheme for the two substitution mechanisms for you to consider:



M = Ni, X = CO
M = Co, X = NO



a) Derive rate laws for mechanisms (A) and (B), showing your work. Assume steady-state concentrations for both intermediates.

b) The mechanisms of substitution for $\text{Ni}(\text{CO})_4$ and $\text{Co}(\text{NO})(\text{CO})_3$ with triphenylphosphine were evaluated through kinetics experiments. Data collected on the observed rate of triphenylphosphine substitution with different initial concentrations of the ligand for both metal complexes are listed below. Assuming that these were pseudo first-order conditions for this reaction, plot the k_{obs} vs. $[\text{PPh}_3]$ for both complexes.

For $\text{Ni}(\text{CO})_4$		For $\text{Co}(\text{NO})(\text{CO})_3$	
$[\text{PPh}_3], \text{M}$	$k_{\text{obs}}, \text{sec}^{-1}$	$[\text{PPh}_3], \text{M}$	$k_{\text{obs}}, \text{sec}^{-1}$
0.038	4.16×10^{-4}	0.0089	8.5×10^2
0.11	3.99×10^{-4}	0.018	1.8×10^3
0.33	4.03×10^{-4}	0.035	3.3×10^3
0.56	4.25×10^{-4}	0.101	9.3×10^3
0.74	4.30×10^{-4}	0.376	3.7×10^4
0.80	4.10×10^{-4}	0.682	7.2×10^4
0.99	4.47×10^{-4}	0.993	1.1×10^5

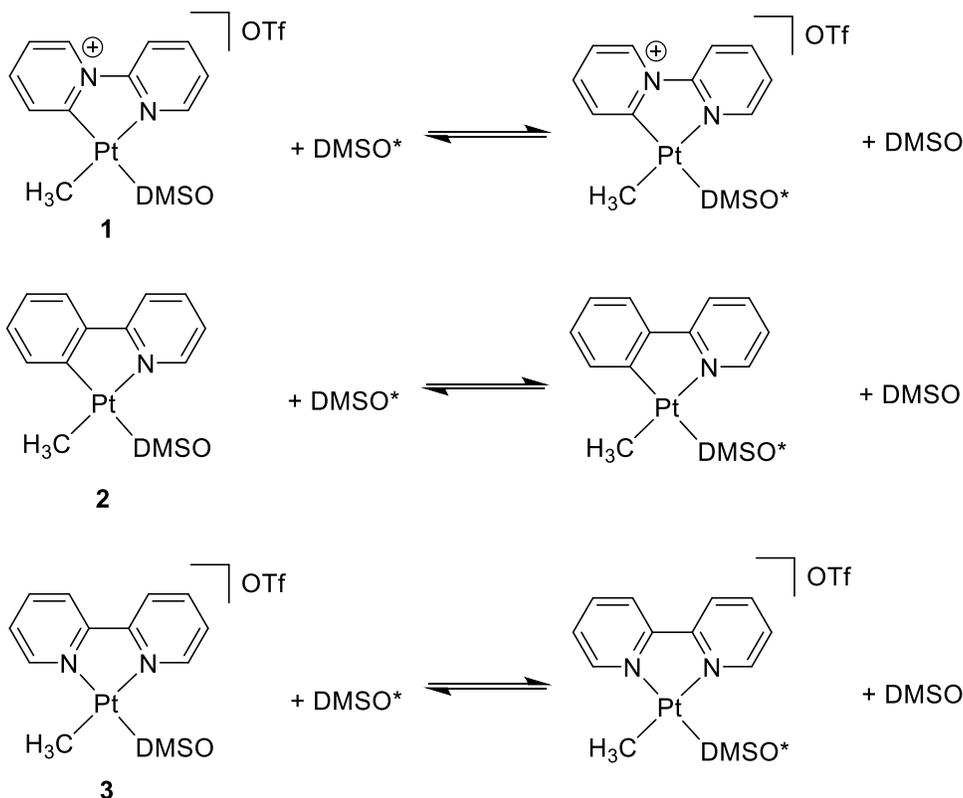
c) Based on your plots, what is the overall order of the substitution reaction for the two metal complexes? Which mechanism is operating for each metal complex? Write the rate law for the overall reactions.

d) For the mechanism of substitution of $\text{Co}(\text{NO})(\text{CO})_3$, give the valence electron count, metal oxidation state, and d-electron count for the starting material, intermediate, and product of the reaction. Clearly distinguish linear and bent NO coordination.

e) Explain the difference in substitution mechanisms of $\text{Ni}(\text{CO})_4$ of $\text{Co}(\text{NO})(\text{CO})_3$. Base your explanation off of the relative stability of each intermediate for the two metal complexes.

Problem 2 (3 points)

A series of Pt(II) complexes bound by bidentate ligands containing different kinds of N- or C-donors was investigated for their ligand substitution kinetics. Specifically, the exchange of coordinated DMSO at the coordination site trans to the different binding moiety was measured:



a) For complexes **1-3**, give the valence electron count and describe the nature of the ligand trans to DMSO (σ base, π base, π acid, etc).

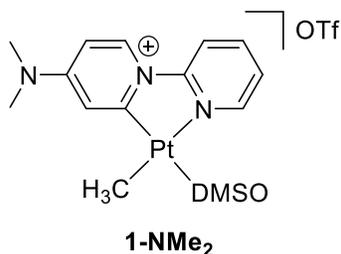
b) The rate of DMSO exchange was measured at various temperatures for **1**. Using the data shown below, plot the temperature-dependent kinetics with the Eyring equation to calculate ΔH^\ddagger and ΔS^\ddagger .

Temp. (K)	k_{obs} (s^{-1})
256.4	5.9
265.3	14.6
274.0	47.6
285.7	95.1
294.1	108.2
298.5	141.0
303.0	183.8

c) Based on your answers from part a) and b), what is the likely mechanism of DMSO exchange for complex **1**?

d) Calculate the overall rate constant for complexes **1**, **2**, and **1-NMe₂** (complex **1** with a NMe₂ substituent on the pyridinium ring, making the π -system more electron rich) from the data below. **3** is given because it had to be measured a different way.

1		2		1-NMe₂		3
[DMSO], M	k_{obs} (s ⁻¹)	[DMSO], M	k_{obs} (s ⁻¹)	[DMSO], M	k_{obs} (s ⁻¹)	k_{overall} (M ⁻¹ s ⁻¹)
0.0197	20.5	1.240	0.236	0.0530	0.340	0.16
0.0504	36.3	2.063	0.419	0.1610	1.000	
0.0738	40.8	3.094	0.692	0.1365	0.940	

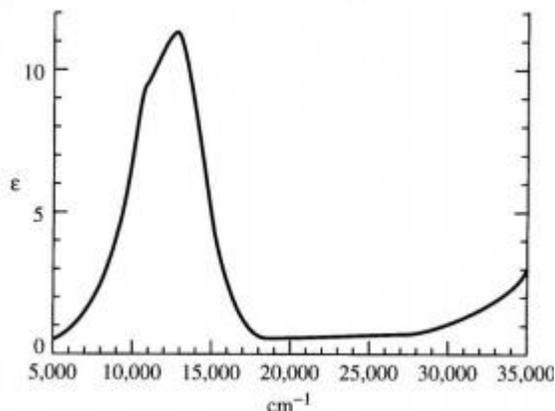


e) Based on the substitution rates of DMSO trans to the binding atom, rank the relative trans effect of the different ligands of **1-3** and **1-NMe₂**. Note that in the solid state, all of these complexes have comparable Pt–S_{DMSO} distances, so no trans influence is observed.

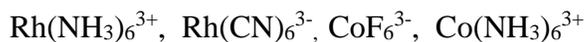
f) Rationalize the faster substitution of **1** in terms of the different trans effect exerted by the pyridinium-derived N-heterocyclic carbene bond. In your answer, make sure to rationalize the differences in DMSO exchange rate between **1** and **1-NMe₂**. (Consider the relative π accepting abilities of the supporting ligands). It will be helpful to sketch relevant metal-ligand bonding interactions.

Problem 3 (2 points)

a) The absorption spectrum for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is shown below. The spectrum shows two absorption peaks around $11,000\text{ cm}^{-1}$ and $13,000\text{ cm}^{-1}$ (overlapping). Given the extinction coefficients of each peaks, what do these two transitions correspond to (spin-forbidden, spin-allowed / Laporte forbidden, or fully allowed)?



b) For the following set of complexes, predict the order of *increasing* Δ_o values and briefly explain your prediction:



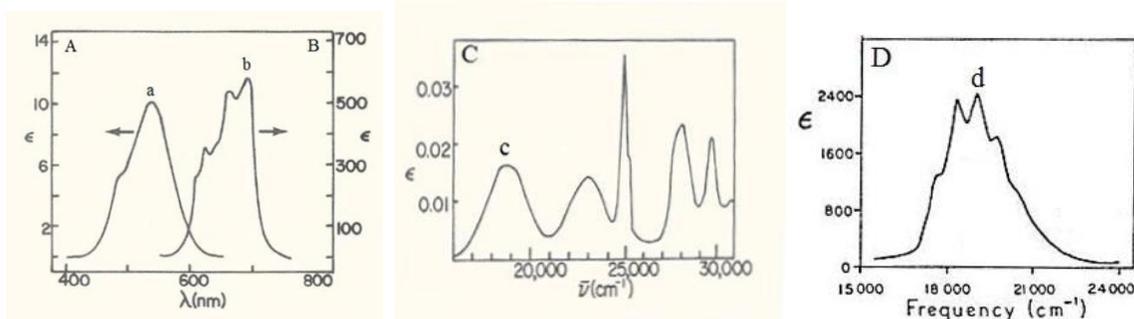
c) For $[\text{CoCl}_4]^{2-}$ and $[\text{Co}(\text{CNPh})_5(\text{OH}_2)]^{2+}$, draw d-orbital splitting diagrams, label the d-orbital parentage, and populate with electrons (CNPh is a strong π -accepting ligand). Predict the spin only magnetic moment for these complexes.

d) 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.

e) For each of the following spectra (A-D), match the spectrum to its corresponding metal complex and briefly explain your assignment. As well, label which transitions are spin-forbidden, spin-allowed and Laporte forbidden, or fully allowed transitions:



Two things to note: A and B have different scales for ϵ . Also note that the x-axis for A and B is in λ (wavelength) and for C and D is in wavenumber (energy).



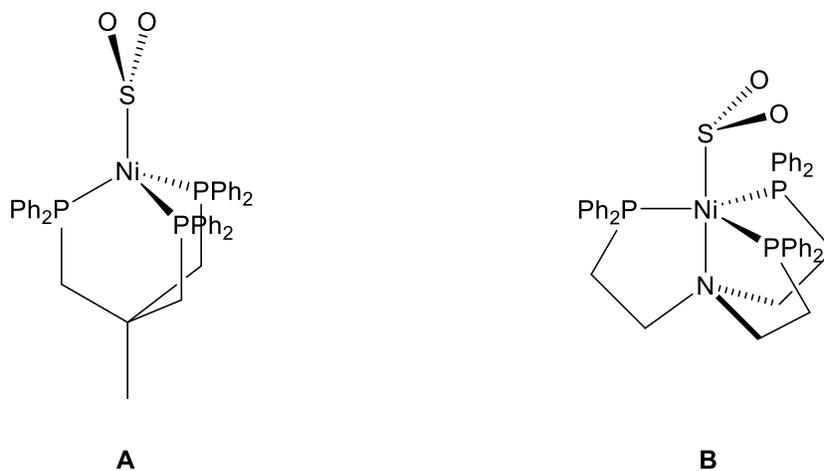
Problem 4 (1 point)

Sulfur dioxide (SO_2) has been found to bind to transition metals in a variety of ways, revealing rich coordination chemistry.

a) Draw the Lewis dot structure for SO_2 and predict its VSEPR geometry.

b) Derive and draw the frontier orbitals (HOMO and LUMO) of SO_2 . *Hint: recall the derivation in-class of the frontier orbitals of N-heterocyclic carbenes.*

Shown below are two nickel- SO_2 complexes **A** and **B**, demonstrating markedly different binding geometries at the sulfur. In **A**, the Ni- SO_2 moiety is planar, whereas in **B** the SO_2 moiety is bent into a pyramidal shape.



c) Given the frontier orbitals you derived in part *b* and the different geometries at sulfur, propose which frontier orbital is mostly involved in the Ni-S bonding interaction in **A** versus **B**. Propose an explanation as to why the tridentate phosphine ligand on Ni in **A** would promote one Ni-SO₂ binding mode versus the tetradentate ligand in **B**.

d) Assign the oxidation states, d-electron counts, and overall valence electron counts for Ni in both **A** and **B**.

e) Which complex, **A** or **B**, would you expect to exhibit a lower S-O stretching frequency? Briefly explain your reasoning.

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. Additionally, submit slides to the TAs via email by Thursday at noon, as pdf attachments.