Chemistry 605 (Reich)

THIRD HOUR EXAM

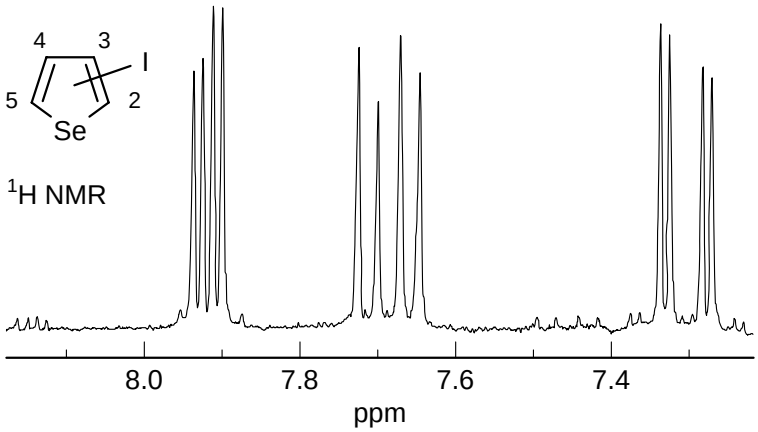
Wed. May 15, 2013

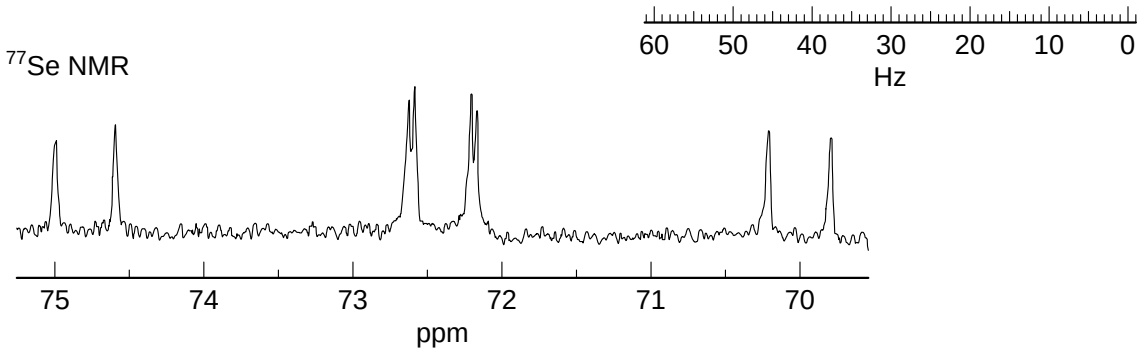
Question	Points
R-12L	/20
R-12M	/15
R-12N	/25
R-12O	/10
R-12P	/20
Total	/90

Name_____

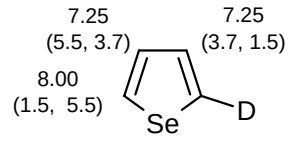
If you place answers anywhere else except in the spaces provided, (e.g. on the spectra or on extra pages) clearly indicate this on the answer sheets.

Problem R-12L. The 100 MHz ^{1}H and 19.15 MHz ^{77}Se NMR spectra of a mono-iodo selenophene are shown below. Both spectra are at the same Hz scale.





Note: there is an error in the H-DATA entry under Selenophene:



JOMC-74(67)-327

(a) Interpret the ^{1}H NMR spectrum, including the various small peaks (e.g., those at 7.45 and 8.15 δ). Report δ and all coupling constants in the standard format.

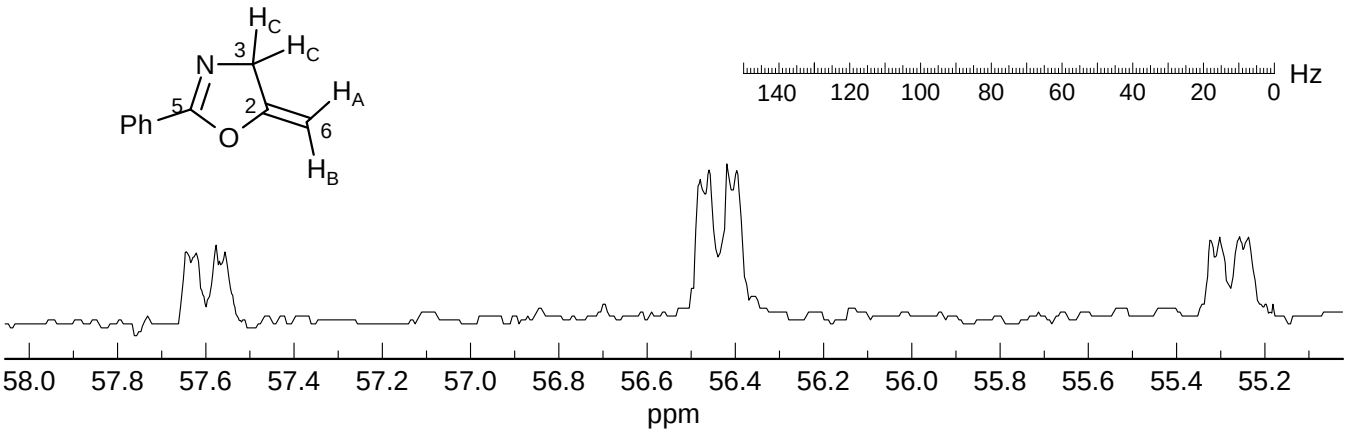
(b) Interpret the ^{77}Se NMR spectrum. Report all coupling constants. Draw a "coupling tree" on the spectrum.

(c) Draw the structure of **R-12L** below, briefly give your reasoning.

15

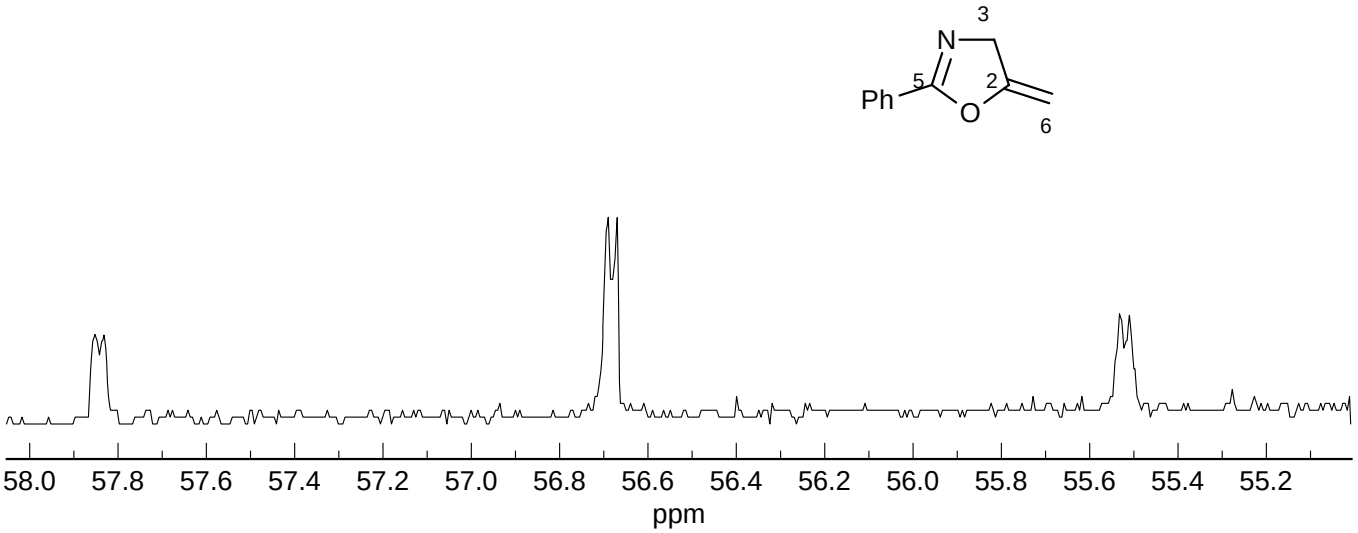
Problem R-12M. You are asked to interpret the coupled ^{13}C NMR spectrum of an oxazoline.

(a) Which carbon are we looking at? _____



(b) Analyze the spectrum, report all coupling constants in the standard format ($^{n}J_{X\text{-}Y}$ = 00.0 Hz).

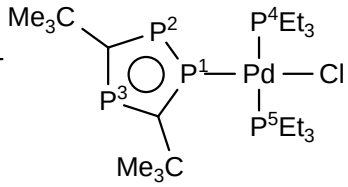
(c) The spectrum below is of the same compound with one H replaced by D. Where is the deuterium? Place it on the structure, and explain briefly.



(d) What is the proton NMR frequency of the spectrometer they were using?_____

Problem R-12N. Analyze the ^{1}H decoupled 32.4 MHz ^{31}P NMR spectra of a palladium-phosphine complex shown on the next page (Bartsch, R.; Carmichael, D.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F.; Sillett, G. J. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1615).

(a) Identify all signals in the low temperature spectrum (-75 °C), and report approximate coupling constants using the form: δ ____, $^{X}J_{1\text{-}2}$ =____ Hz. Use the numberings shown on the structure. For each signal briefly give your reasoning for the assignment.



P^1 _____

P^2 _____

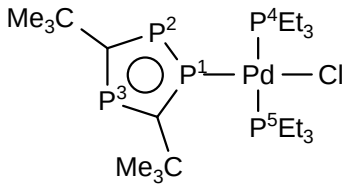
P^3 _____

P^4, P^5 _____

(b) Identify the process which is responsible for the changes in the NMR spectrum at the higher temperatures (-30 °C and +50 °C). The signal at -122 ppm in the +50 °C spectrum is a triplet. Draw a structure or an equation.

(c) What is the proton frequency (MHz) of the spectrometer which was used for these spectra?

Problem R-12N. 32.4 MHz ^{31}P-{^{1}H} NMR spectra.
Solvent toluene-d_8
(Source: *Chem. Commun.* **1988**, 1615)



+50 °C

Hz scale for main spectra

2000 1800 1600 1400 1200 1000 800 600 400 200 0 Hz

-30 °C

-120 -125 -130

Hz scale for expansions

2000 1800 1600 1400 1200 1000 800 600 400 200 0 Hz

115 110

40 30 20 10 ppm 0 -10 -20 -30

-75 °C

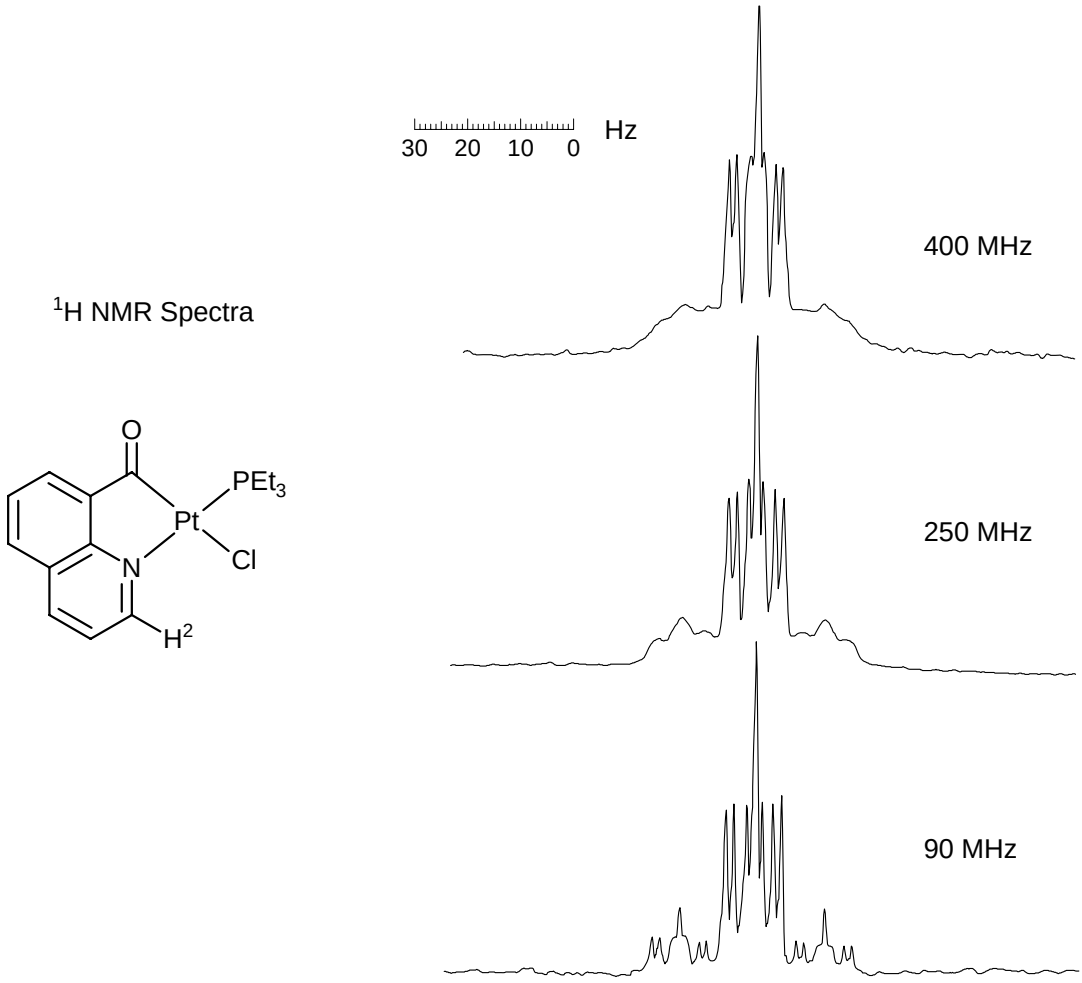
0.88 0.96 0.97 2.00

-120-125

120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140
ppm

15

Problem R-12O ($C_{16}H_{21}ClNOPPt$). Shown below are partial ^1H NMR spectra of a platinum complex at several field strengths. All three spectra are at the same Hz scale. Only the signal for H^2 is shown (source: *Magn. Res. Chem.* **1985**, *23*, 671).



(a) Explain the small outer peaks of the multiplet.

(b) Analyze the multiplet. Give approximate coupling constants, report them in the form $^nJ_{XY}$ = __ Hz. Assign the couplings.

(c) Why do the small outer peaks become broad at higher field strength? This is not a fluxional molecule, and there is no ligand exchange under these conditions.

Problem R-12P. This question requires you to assign the protons of compound **R-12P** using the 300 MHz proton NMR spectra given. The spectrum shows the normal ^{1}H NMR, and two inserts which are difference spectra resulting from subtraction of the normal spectrum from one in which the large signal at δ 0.95 or at δ 1.4 was irradiated for a second or so, and then the decoupler was turned off during acquisition of the FID. The assignment of these signals is shown on the structures. The integration of the insets has been expanded five times (5x) compared to the normal spectrum

(a) What kind of experiment is being performed here? What information does this experiment provide?

(b) For the NMR signals below assign each to one of the protons labeled H_a to H_f. Briefly summarize the evidence you used in making each assignment. Each of the signals corresponds to a single proton. The signals marked with an x are impurities.

δ 1.43_____

δ 2.08_____

δ 2.28_____

δ 2.43_____

δ 2.55_____

δ 2.60_____

Are there any ambiguities in the assignments you have made?

(c) Comment on the chemical shift difference between the two methyl signals, as well as the protons He and Hf.

Problem R-12P ($C_8H_{12}O$)

300 MHZ ^1H NMR Spectrum

Source: The XL Series NMR Spectra Collection Vol 1

Varian Associates 12/19