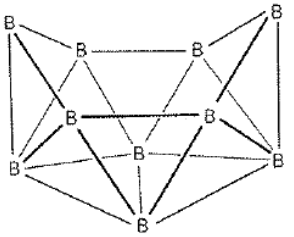
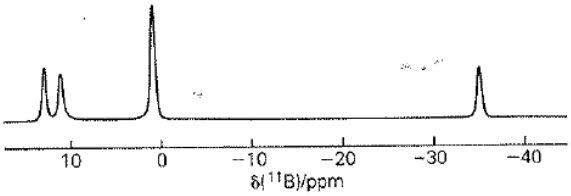
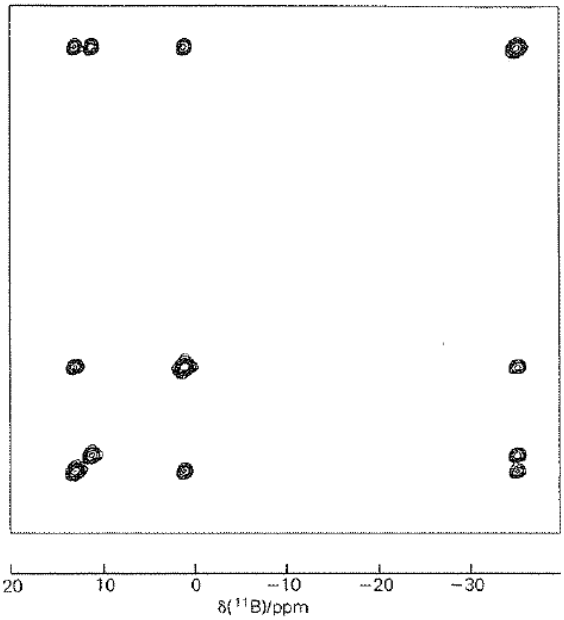
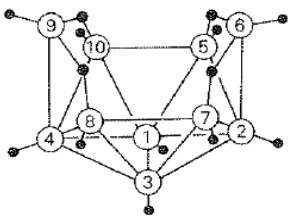
Problem Set #3

1. (10 points) The ^{11}B NMR spectrum of $B_{10}H_{14}$ (obtained with ^{1}H decoupling) and the corresponding ^{11}B COSY are shown below. If coupling is observed only between ^{11}B nuclei which are directly bonded to each other (and not via bridging hydrogen atoms), assign the observed resonances.

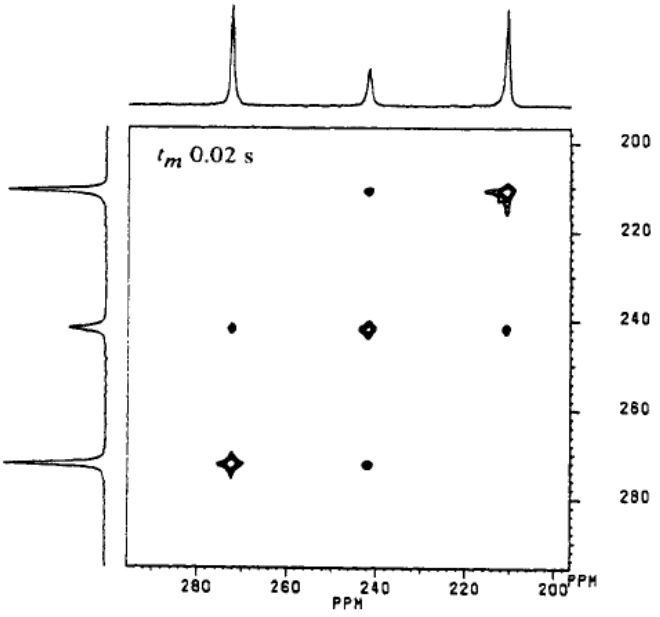


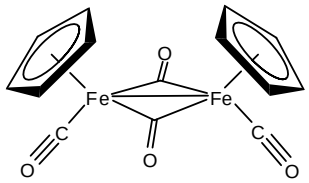




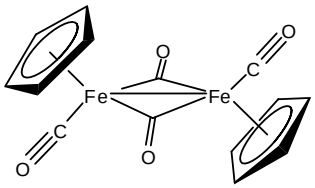


2. (20 points) The well-known organometallic complex $[CpFe(CO)_2]_2$, has been isolated in the solid-state as both a *cis* and *trans* isomer. A third minor isomer, known as *open*, has also been detected in solution (present in very small amounts under all conditions). Initial attempts to characterize $[CpFe(CO)_2]_2$ by NMR spectroscopy proved difficult. For instance, a ^1H NMR spectrum $[CpFe(CO)_2]_2$ at room temperature consists of a single peak at 5.0 ppm. However on cooling, this peak disappears into the baseline and reappears as two singlets (in a four-to-one ratio). A ^{13}C NMR spectrum of $[CpFe(CO)_2]_2$ at low temperature reveals three singlets in the carbonyl region. The singlets at 270 ppm and 210 ppm were assigned to the cis isomer while the singlet at 240 ppm was assigned to the trans isomer. In addition, a low-temperature ^{13}C EXSY spectrum of $[CpFe(CO)_2]_2$ has also been recorded to further understand this complex (see below).

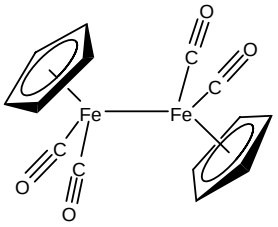




cis



trans



open

(a) Develop a model which explains the ^1H NMR spectrum of $[CpFe(CO)_2]_2$. (b) Explain why two peaks are observed (in the carbonyl region of the ^{13}C NMR spectrum) for the *cis* isomer and only one for the *trans* isomer at low temperature? (c) Account for the observed cross peaks in the ^{13}C EXSY spectrum.

3. (8 points) The ESR spectrum below was obtained from a solution containing $V(O)Cl_2$ and PEt_3. Explain the observed spectrum and predict the formula of the product.

4. (10 points) The X-band ESR spectrum of $S_2^{-\cdot}$ (enriched with 60% ^{33}S, I = 3/2) is shown below. It consists of 11 lines. Considering that $S_2^{-\cdot}$ contains one unpaired electron assign this spectrum. (Hint: the outer two peaks are separated by 30 G, while the other peak separations are all 15 G. Also for ^{32}S, I = 0)