Spartan tutorial – Adapted from p.158 of Spartan 06 Tutorial & User Guide

Consider this reaction: Cr(CO)3 + benzene ------> Cr(CO)3Ph
We are going to look at whether this is an endothermic or exothermic reaction, whether the Cr(CO)3 is an elector donor or electron acceptor, how complexation affects the chemical shift of the phenyl protons, and many other chemical properties. The goal of this exercise is to get you to be able to build molecules, calculate and export data, and interpret results.

Type **spartan** to start the program. Click on the **New Spreadsheet** Icon  . This will put you in Build mode. Choose the **Inorganic** Tab from the Model Kit on the right. Look for the periodic table pulldown marked with **C(6) Carbon**. Select **Cr(24) Cromium**. Now select the icon to specify that you want a 4 coordinate center  . Click anywhere in the green space to drop your fragment. Now click on the **Ligands** button and then choose **benzene** from the pulldown adjacent to the Ligands button. It is important to choose the benzene from Ligands rather than the benzene from Rings because the two versions of benzene specify different attachment points. Click on one of the yellow sticks attached to Cr. These yellow sticks are valence place holders but become H atoms when the builder is exited. You should see one now replaced with your benzene ring. Now choose **carbon monoxide** from the pulldown adjacent to the Ligands button. Click on each of the three remaining yellow sticks attached to Cr. Click on the energy icon  to do a quick geometry cleanup

Now that we have 1 molecule built and 1 spreadsheet to hold it, we will build our other molecules and include them in the same spreadsheet. Look under the **File** menu, there is a **New** option and also a **New Molecule** option. Select **New Molecule**. The other would create a new spreadsheet. Now build Cr(CO)3 using the trigonal icon  . Then use the energy icon for a cleanup. Use the **New Molecule** option again, and click on the **Organic** Tab, then click on **Rings**, and select **Benzene** from the Rings pulldown. Then use the energy icon for a cleanup.

Click on the view icon  to close the builder. Choose **Spreadsheet** from the **Display** menu. You should see three entries, M0001, M0002, M0003. Rename these as complex, Cr(CO)3 and benzene, by double clicking on the text.

Choose **Calculations** from the **Setup** menu. Calculate: **Equilibrium Geometry** at **Ground** state, change Hartree-Fock to **Semi-Empirical** and then change AM1 to **PM3**. This is a simplified quantum mechanical method and is often useful for initial geometry optimizations and first approximations at energy calculations. We would make other choices if we were in need of higher quality data. Check the box for Print: **Orbitals & Energies**. Check the box next to **Converge**. Make sure **Global Calculations** is also checked. Click **OK**.

Choose **Surfaces** from the **Setup** menu. Click **Add**. Surface: **density**, Property: **potential**. Click **Apply**. Surface: **HOMO**, Property: **none**. Click **Apply**. Surface: **LUMO**, Property: **none**. Click **OK**.

Click **Submit** under the **Setup** menu to start the calculation. When prompted for a filename, type "Cr_reaction". You should be notified when the calculations start and when they finish.

If you get a message that the calculation failed, this is probably due to the Cr(CO)3 moiety which is quite unstable. The program may struggle to find a good MO arrangement (this is called a failure in SCF). Highlight this molecule in the spreadsheet and choose **Output** from the **Display** menu. Examination of this output should help verify if this molecule is the one with the error. Then, make sure the Cr(CO)3 moiety is still highlighted in the spreadsheet, and choose **Calculations** from the **Setup** menu. Check all of the same boxes as before and make all of the same settings except this time you will uncheck **Global Calculations**. By unchecking that box, you are telling the program to run a calculation only on the selected molecule and not to rerun all three. Click **Submit**.

Once the calculations have finished, go to the spreadsheet and highlight one of the molecules. Choose **Properties** from the **Display** menu. Make a note of the Energy (this is a Heat of Formation). Repeat this for the other 2 molecules. You now have enough data to calculate the Heat of Reaction for the formation of the complex from the 2 starting materials. Choose **Surfaces** from the **Display** menu. Visualize the electron density surfaces along with the HOMO and LUMO surfaces. Which is the electron donor and which is the electron acceptor?

Now we are going to do a higher level calculation. Go back to the **Calculations** window under the **Setup** menu. Change the calculation to **Hartree-Fock 3-21G**. Check all of the boxes (UV/Vis, IR, NMR, Orbitals&Energies, Thermodynamics, Vibrational Modes, Atomic Charges, Converge, Global Calculations) but leave Pseudopotential unchecked. Click **OK**. Choose **Surfaces** from the **Setup** menu. **Delete** all of the surfaces. Click **OK**. Choose **Submit** from the **Setup** menu. This calculation will take about 10 minutes. Once the calculations are complete, you can visualize the calculated spectra by choosing **Spectra** from the **Display** menu. Then choose a spectrum and **Draw Calculated**. There is a button to **Draw Experimental** but that data is not loaded so don't bother. One of the most interesting comparisons is the proton NMR data for benzene versus the complex.

Check the energy numbers again under Display/Properties and recalculate your Heat of Reaction.

Notes: If you want to use the structural coordinate data from Spartan in other programs, use **Save As** from the **File** menu and choose pdb or mol2 formats. Many other programs can read those file types. You can also do image captures with Save As. Png and jpg are suitable for that. You can then use an image editing program on those. [On a command line, type **display** to open the image editor called ImageMagick. Open your image file and click anywhere in the image to get the control menu.]