

# Chapter 10

## Inorganic and Organometallic Molecules

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*This chapter illustrates applications to inorganic and organometallic molecules constructed using the inorganic builder in **Spartan's** model kit.*

Organic molecules typically comprise only a relatively few elements and obey conventional valence rules. The geometry about individual atoms is “tetrahedral” ( $sp^3$ ), “trigonal planar” ( $sp^2$ ) or “linear” ( $sp$ ). As such they are easily constructed using the organic model kit. On the other hand, construction of many inorganic and organometallic compounds in particular those involving transition metals may require the enhanced flexibility provided by the inorganic builder.

Transition-metal inorganic and organometallic compounds may also require different quantum chemical methods from those that have proven to be satisfactory for organic molecules. While there are a large number of experimental structures, almost entirely from X-ray diffraction, accurate experimental thermochemical data on molecules incorporating transition metals is virtually non-existent making assessment of the various models problematic.

The PM3 and PM6 semi-empirical models have been explicitly parameterized for most transition metals and generally (but not always) provide a reasonable account of geometries. However, they would not be expected to properly account for reaction energies as they generally perform poorly for reactions involving molecules without metals.\* Hartree-Fock and MP2 models are known to produce poor geometries where transition metals are involved and cannot be

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\* It should be noted that experimental thermochemical data for inorganic molecule especially for those incorporating transition metals is far less common (and likely less reliable) than that for organic molecules.


recommended.\* On the other hand, density functional models appear to be quite successful for calculation of geometries of molecules incorporating both transition metals and lanthanides (although their performance for energy comparisons remains to be clarified).

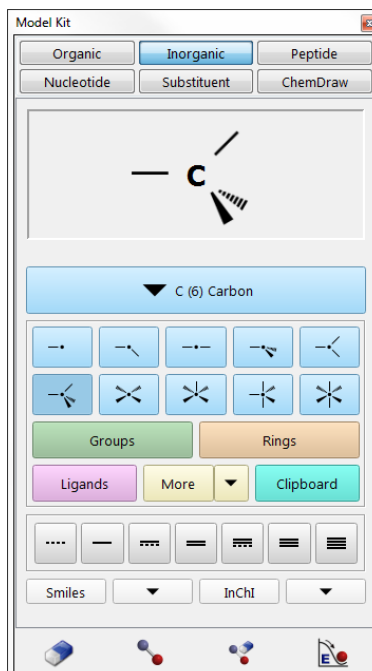
1 min

## Sulfur Tetrafluoride



Sulfur tetrafluoride cannot be constructed using *Spartan's* organic builder. This is because sulfur is not in its normal bent dicoordinate geometry, but rather in a trigonal bipyramid geometry with one of the *equatorial* positions vacant. However, the molecule can easily be made using the inorganic builder.

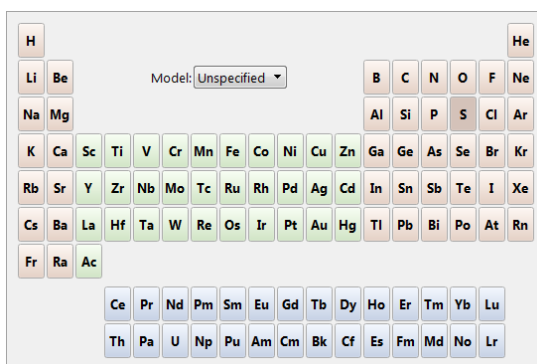
1. Bring up the inorganic builder by *clicking* on  and then *clicking* on the **Inorganic** tab at the top of the model kit.










\* The poor performance of the MP2 model is most likely a consequence on its dependence on a Hartree-Fock wave function.

The inorganic builder comprises an atom bar (*clicking* on this brings up the *Periodic Table*\*) followed by a selection of atomic hybrids. Buttons access menus of groups, rings and ligands, additional libraries (**More**) and the clipboard. Finally, a selection of bond types is provided at the bottom of the model kit.

2. Click on the atom bar to bring up the *Periodic Table*.



Select (*click* on) **S** in the *Periodic Table* and the five coordinate trigonal bipyramid structure  from the list of atomic hybrids. *Double click* on screen. A trigonal bipyramid sulfur will appear at the top of the model kit.

3. Again, *click* on the atom bar, select **F** in the *Periodic Table* and the one-coordinate entry  from the list of atomic hybrids. Alternatively switch to the organic builder (*click* on the **Organic** tab) and select  icon. One after another, *click* on both *axial* free valences of sulfur, and two of the three *equatorial* free valences.
4. It is necessary to delete the remaining free valence (on an *equatorial* position); otherwise it will become a hydrogen. *Click* on  and then *click* on the remaining *equatorial* free valence.
5. *Click* on . *Click* on .
6. Select **Calculations...** from the **Setup** menu (). Specify

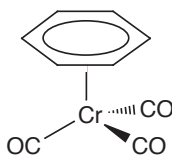
\* Not all methods are available for all elements listed. Elements for which a specific method (selected in the **Calculations** dialog) are available will be highlighted following selection of a theoretical model or basis set from the **Model** menu that appears in the center of the *Periodic Table*. Note the availability of some heavier elements (>Kr) assumes use of the LANL2DZ basis set which *Spartan* will employ automatically when required.

calculation of equilibrium geometry\* using the  $\omega$ B97X-D/6-31G\* density functional model and *click* on **OK**.

7. Select **Surfaces** from the **Setup** menu, *click* on **Add** and select **HOMO** from the menu that results. Leave the dialog on screen.
8. Submit the job. Accept the name *sulfur tetrafluoride*. When completed, select **Properties** from the **Display** menu ( ⓘ ) and *click* on an atom, for example, sulfur. Three different atomic charges will appear in the (**Atom Properties**) dialog (corresponding to different methods for establishing atomic charge). Of these, the procedure based on fitting the electrostatic potential is generally considered to be the best. Are the electrostatic charges consistent with covalent or ionic bonding?
9. *Check* the box to the left of **HOMO** inside the **Surfaces** dialog. The HOMO is largely concentrated along the *axial* direction which lacks a fluorine, consistent with the notion that sulfur is surrounded by six electron pairs (five involved in SF bonds and one a “lone pair”).
10. Close *sulfur tetrafluoride* and any open dialogs.

no calculations



## Benzene Chromium Tricarbonyl

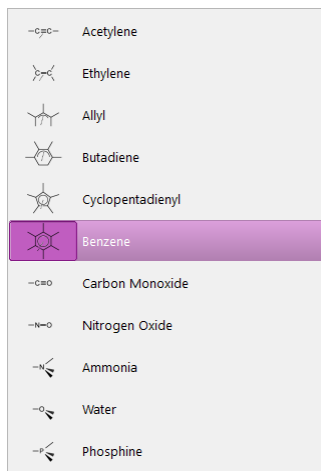



benzene chromium tricarbonyl



Comparison of electrostatic potential maps for benzene chromium tricarbonyl and free benzene will allow you to classify  $\text{Cr}(\text{CO})_3$  as an electron-donor or an electron-acceptor substituent.






\* It should be noted that were an incorrect geometry specified at the outset, optimization would lead to the correct structure, as long as the starting geometry possessed no symmetry ( $C_1$  point group). Thus, square planar  $\text{SF}_4$  in  $D_{4h}$  symmetry would remain square planar, while an “almost” square planar structure (distorted only slightly from  $D_{4h}$  symmetry to  $C_1$  symmetry) would collapse to the proper structure upon geometry optimization.

1. Select **New Build** from the **File** menu () and *click* on the **Inorganic** tab at the top of the model kit. *Click* on the atom bar and select **Cr** from the *Periodic Table*. Select the four-coordinate tetrahedral structure  from the list of atomic hybrids. *Double click* anywhere on screen.
2. *Click* on **Ligands** in the model kit and select **Benzene** from the menu of available ligands.



- Click* on one of the free valences on the four-coordinate chromium center.
3. Select **Carbon Monoxide** from the **Ligands** menu, and *click* on the remaining (three) free valences on chromium. *Click* on  to produce a refined structure.

Benzene chromium tricarbonyl among many organometallics may easily be constructed using the 2D sketcher. Inside the sketch pad, *double click* on the wild card icon, select the **Periodic Table** tab and *click* on **Cr**. *Double click* inside the sketch. *Double click* a second time on the wild card icon (which will now read **Cr**), select the **Ligands** tab and *click* on benzene ligand. Draw a line upward from **Cr**. *Double click* on the wild card icon a third time (which will now display benzene ligand), select the **Ligands** tab and *click* on carbon monoxide ligand. Draw three lines down from **Cr**. Clean up the sketch () and *click* on ().

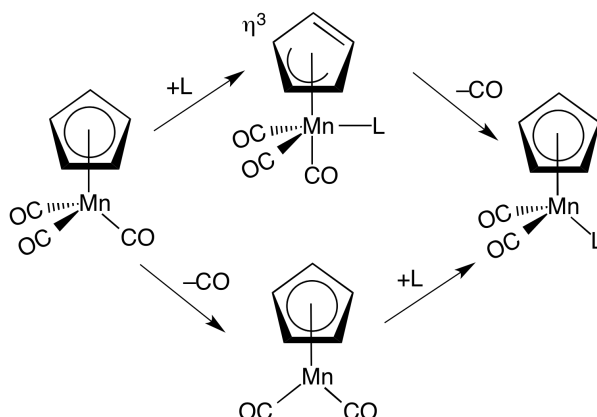
4. Select **Build New Molecule** from the **File** menu (). Click on **Rings**, select **Benzene** and click on the screen. Click on  and then on . The document now contains both benzene chromium tricarbonyl and benzene.
5. Both benzene and benzene chromium tricarbonyl are available in the Spartan Spectra and Properties Database (SSPD). Click on the name of whichever molecule is selected at the bottom of the screen, make certain that **ωB97X-D/6-31G\*** is selected and click on **Replace**. Click on **All** in the dialog that results.
6. Select **Surfaces** from the **Display** menu (). Click on **Add** and choose **electrostatic potential map** from the menu. Make certain that **Global Surfaces** is checked. Do not close the **Surfaces** dialog.
7. You don't need to submit, as graphics calculations will be performed "on-the-fly". When completed select **Spreadsheet** from the **Display** menu (), and check the box to the left of the label for both entries. This allows both molecules to be displayed simultaneously on screen. By default, the motions of the two molecules are coupled. To uncouple their motions allowing the two molecules to be moved independently, select (turn off) **Coupled** from the **Model** menu. Orient each molecule so that you can clearly see the benzene face (exposed face in the case of the organometallic).
8. Check **electrostatic potential map** in the **Surfaces** dialog. Compare electrostatic potential maps for both free and complexed benzene, with attention to the exposed benzene face.\* Does the  $\text{Cr}(\text{CO})_3$  group donate or withdraw electrons from the ring? Would you expect the aromatic ring in benzene chromium tricarbonyl to be more or less susceptible to electrophilic attack than free benzene? More or less susceptible to nucleophilic attack?
9. Close all documents and any open dialogs.

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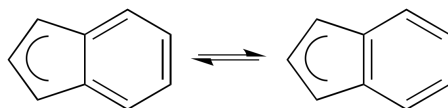
\* Electrostatic potential maps (as well as other maps) for molecules in a single *Spartan* document will be put onto the same (color) scale. This allows comparisons to be made among different members.

## Indenyl Effect

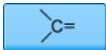

Substitution of one of the carbonyl ligands in cyclopentadienyl manganese tricarbonyl by another two-electron donor ligand may either proceed via an associative or dissociative mechanism. At first glance both mechanisms would seem to be unfavorable, the dissociative pathway because it involves a 16-electron intermediate and the associative pathway because it passes through a 20-electron intermediate. However, the associative mechanism may not be as bad as it first appears as it might be possible to reduce the coordination of the cyclopentadienyl ring from  $\eta^5$  to  $\eta^3$  giving rise to an 18-electron association intermediate.



Such a possibility is supported by the observation that substitution of cyclopentadienyl by an indenyl ligand leads to increased association rates. The indenyl effect as it is known, is attributed to the possibility of enhanced aromaticity of  $\eta^3$  coordinated indenyl relative to  $\eta^5$  indenyl.



In this tutorial, you will use the PM3 model to calculate geometries for the reactants, intermediates and products for associative ligand exchange by trimethylphosphine of cyclopentadienyl and indenyl manganese tricarbonyl complexes, and then the  $\omega\text{B97X-D/6-31G}^*$  model to calculate energies.

1. Build all eight molecules (the two reactant complexes, the two intermediates and the two product complexes as well as trimethylphosphine and carbon monoxide), and put into a single **Spartan** document. Assume  $\eta^5$  coordination of cyclopentadienyl and indenyl ligands in reactants and products and  $\eta^3$  coordination for the two intermediates.  $\eta^5$  cyclopentadienyl is available from the **Ligands** menu, and  $\eta^5$  indenyl is in the ligands document accessed by *clicking* on (▼) to the right of **More**.  $\eta^3$  cyclopentadienyl and  $\eta^3$  indenyl ligands are not available from menus and need to be built. To build  $\eta^3$  cyclopentadienyl, first complex an ( $\eta^3$ ) allyl ligand to manganese, move to the organic builder, add  $sp^2$  carbons (  ) to both inward pointing allyl free valences, *click* on **Make Bond** (  ) and then on the double free valences on the two fragments that you have just added. To build the  $\eta^3$  indenyl complex, start with the  $\eta^3$  cyclopentadienyl complex, select **Benzene** from the **Rings** menu (in the **Organic** builder) and *double click* on the “double bond” in the allyl ligand. Make certain that you minimize the energy of each of the eight structures before proceeding to the next step.
2. Select **Calculations** from the **Setup** menu and specify calculation of equilibrium geometry using the semi-empirical PM3 model. Make certain the **Global Calculations** at the bottom of the dialog is checked. Submit the job with the name *indenyl effect*.
3. When completed (a few minutes at most), compare the structure of the two reactants (or products) with those of the corresponding intermediates. Verify that the cyclopentadienyl and indenyl ligands have shifted from  $\eta^5$  to  $\eta^3$  coordination.
4. Reenter the **Calculations** dialog (**Calculations** under the **Setup** menu), and specify calculation of energy using the  $\omega$ B97X-D/6-31G\* density functional model. Resubmit the job. The eight calculations will require several minutes to complete.\*

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\* You could do the geometry and energy calculations in a single step. Inside the **Calculations** dialog, specify energy with the  $\omega$ B97X-D/6-31G\* density functional model and set the menus to the right of **Start From** to **Equilibrium Geometry**, **Semi-Empirical**, and **PM3**. Of course, this does not allow you to examine the geometries before doing the density functional calculations.



5. Use the reaction energy calculator (**Reactions** from the **Display** menu) to calculate the energy of ligand substitution in both complexes. Is trimethylphosphine a “better” or “worse” ligand than carbon monoxide? Is the difference diminished or exaggerated in the indenyl complex relative to that in the cyclopentadienyl complex? Next calculate the energy of the two intermediates. Relative to reactants, which is more stable, trimethylphosphine cyclopentadienyl manganese tricarbonyl or trimethylphosphine indenyl manganese tricarbonyl?
6. Close *indenyl effect* and any open dialogs.