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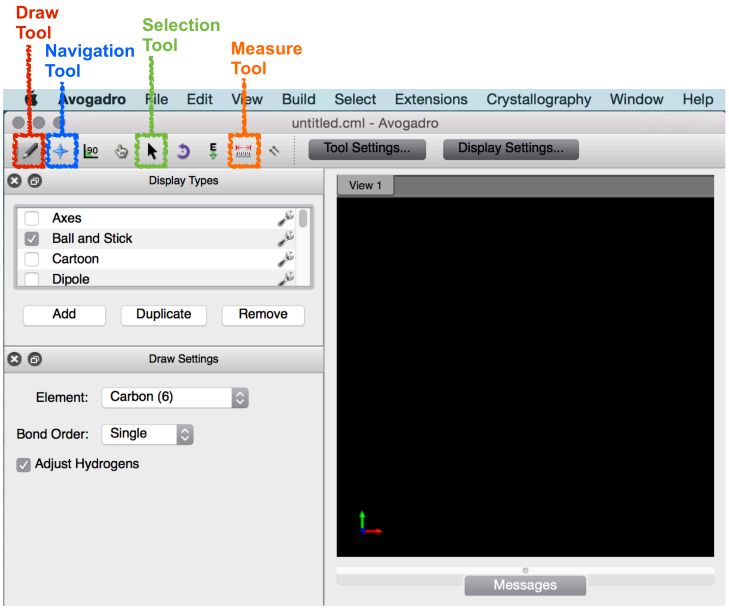
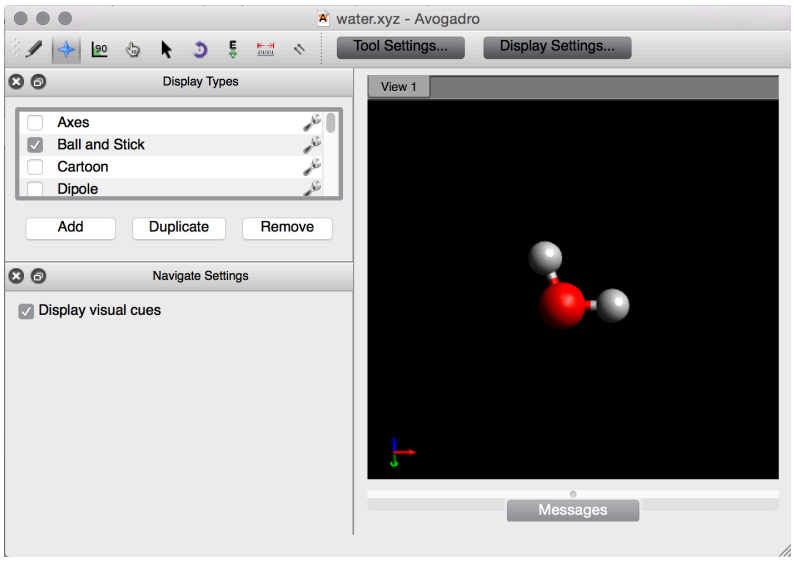
Exercise 1

Build a molecule with Avogadro

Avogadro is a free, open source molecular editor and visualization tool. When you open Avogadro, a window such as the one shown below will appear on your screen.



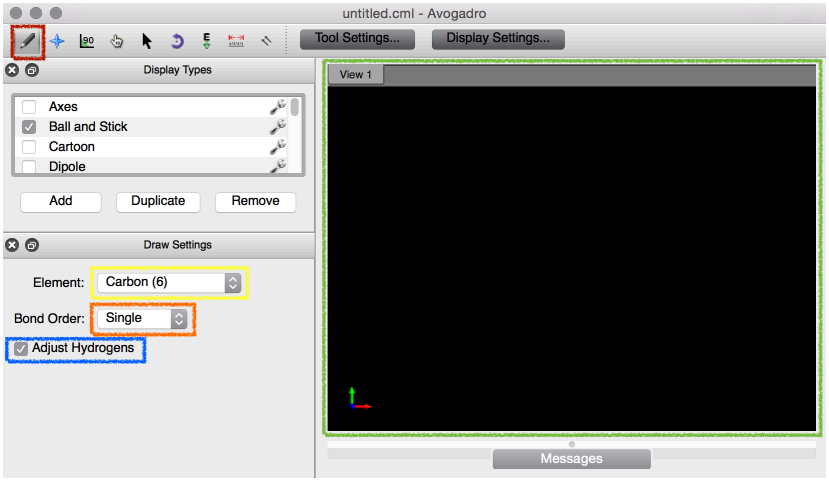
If you choose to open an existing file, go to the "File" menu, choose "Open", and select the file you wish to open. Avogadro supports a large number of file formats (cml, xyz, pdb, mol2 and other common formats). Figure below shows how a water molecule from "water.xyz" file appears in Avogadro. By default, the molecule is displayed using the "Ball and Stick" display type. You can easily choose a different display type from the "Display Types" menu.



Notice that when a new file is opened Avogadro switches from the Draw Tool to the Navigate Tool. Table below shows how to navigate in Avogadro.

zoom in/out	use the scroll wheel on your mouse or hold down the middle mouse button and move the mouse cursor up/down
rotate	hold down the left mouse button and move the mouse cursor
translate	hold down the right mouse button and move the mouse cursor

If you choose to draw a molecule in Avogadro, it can be done using the Draw tool. Click on the Draw tool, and then on the drawing area (green rectangle in the figure below).



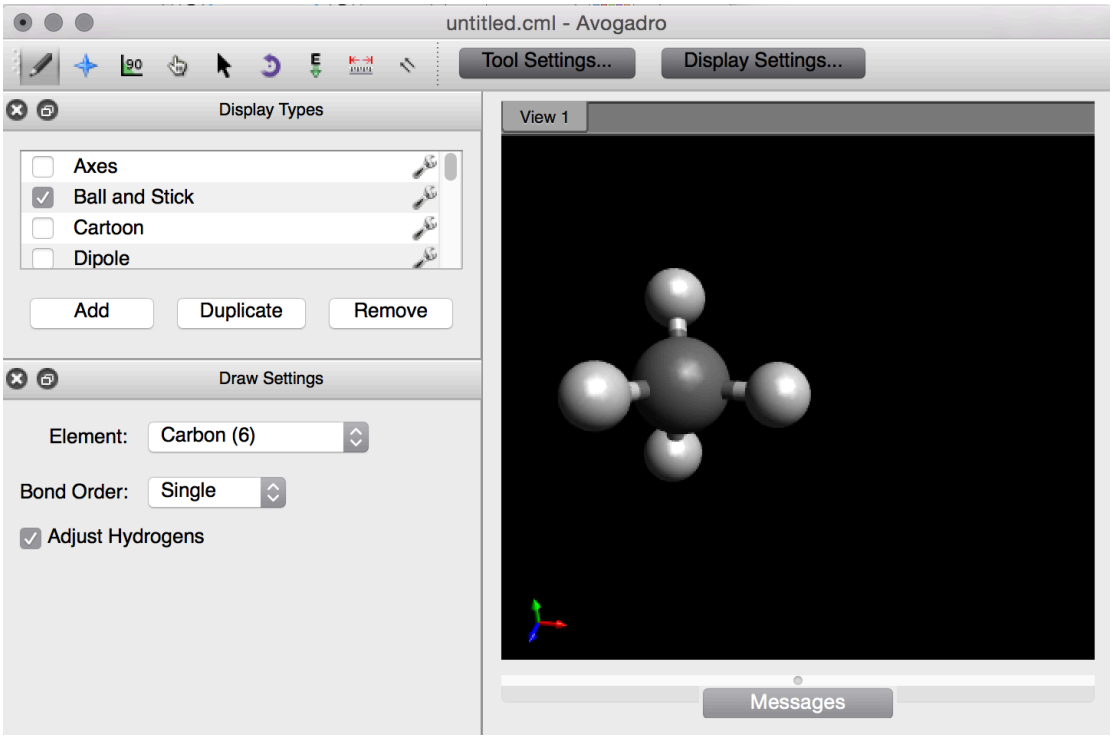
Now you may begin drawing your molecule. These are the basics:

- A left click will generate an atom.
- A right click on an atom will delete the atom.
- Left clicking on an atom and dragging the mouse will generate a bond to another atom.
- Carbon is the default element. A different element can be selected through the "Element" drop down menu (yellow rectangle).
- Left clicking on an atom that has already been generated will change the element to the currently selected element in the "Element" menu.
- If the "Adjust Hydrogens" box (blue rectangle) is checked, hydrogen atoms in the molecule will be automatically adjusted to satisfy valency.
- Bond order is changed through the "Bond Order" drop down menu (orange rectangle), or by typing the numbers "1", "2", or "3". Bonds are added by left clicking on a bond that has already been created. Right clicking on a bond deletes the bond, and the atom it's bonded to.

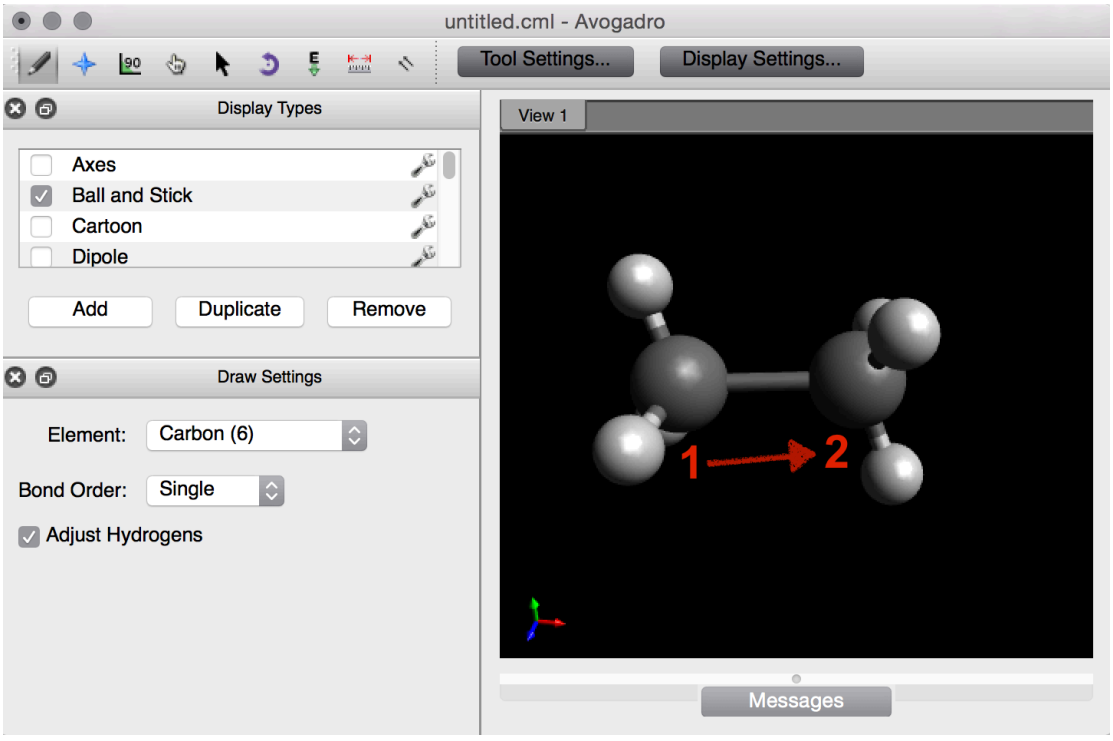
To show how this works, we will now apply the rules above to generate a series of small molecules, starting from methane and ending with methane and water:

$CH_4 \rightarrow CH_3{-}CH_3 \rightarrow CH_2{=}CH_2 \rightarrow CH{\equiv}CH \rightarrow CH_3{-}OH \rightarrow CH_4 + H_2O$

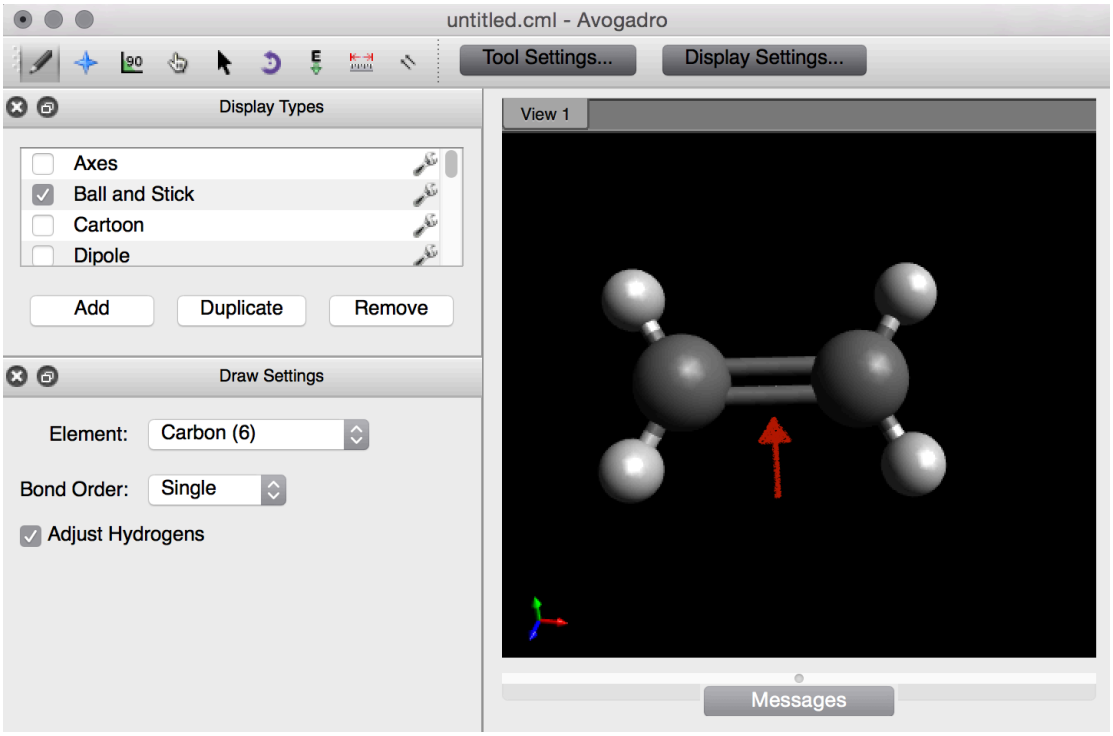
Left click on the drawing area will generate methane, CH_4, since the default element is carbon and the "Adjust Hydrogens" box is checked.



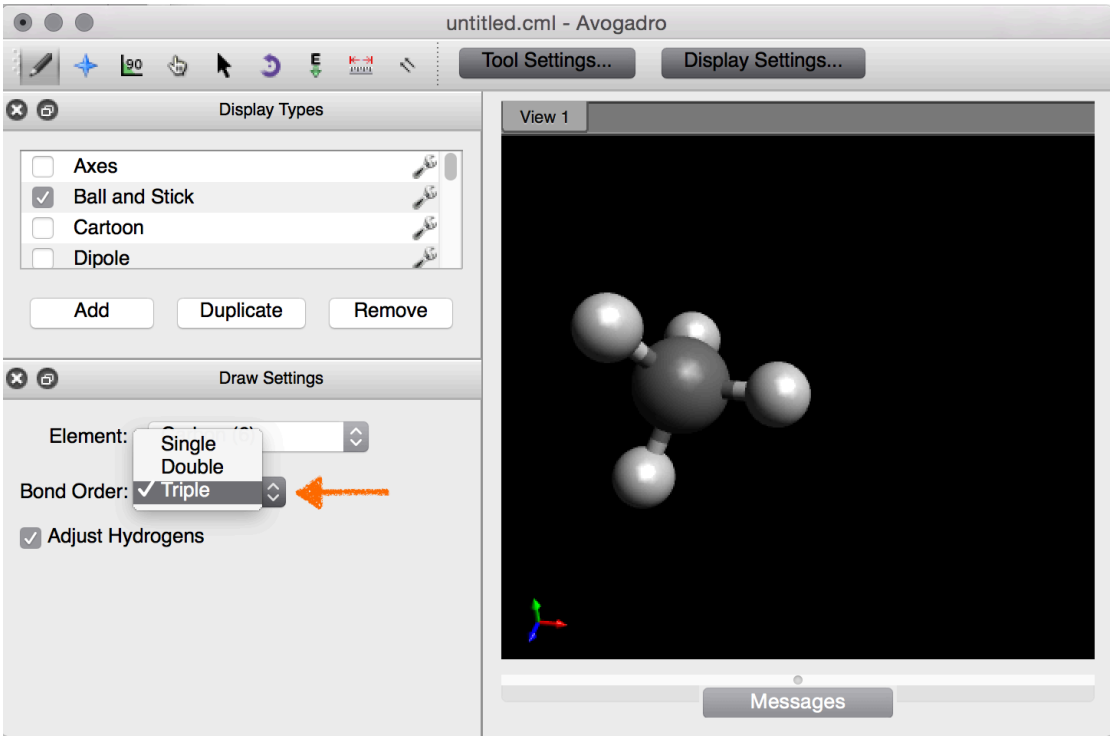
To generate ethane, $CH_3–CH_3$, left click on the carbon atom and drag the mouse to any direction to create another carbon atom bound to the first carbon atom with a single bond. The single bond is due to "Bond Order" being set to single. Note that the number of hydrogen atoms changed.

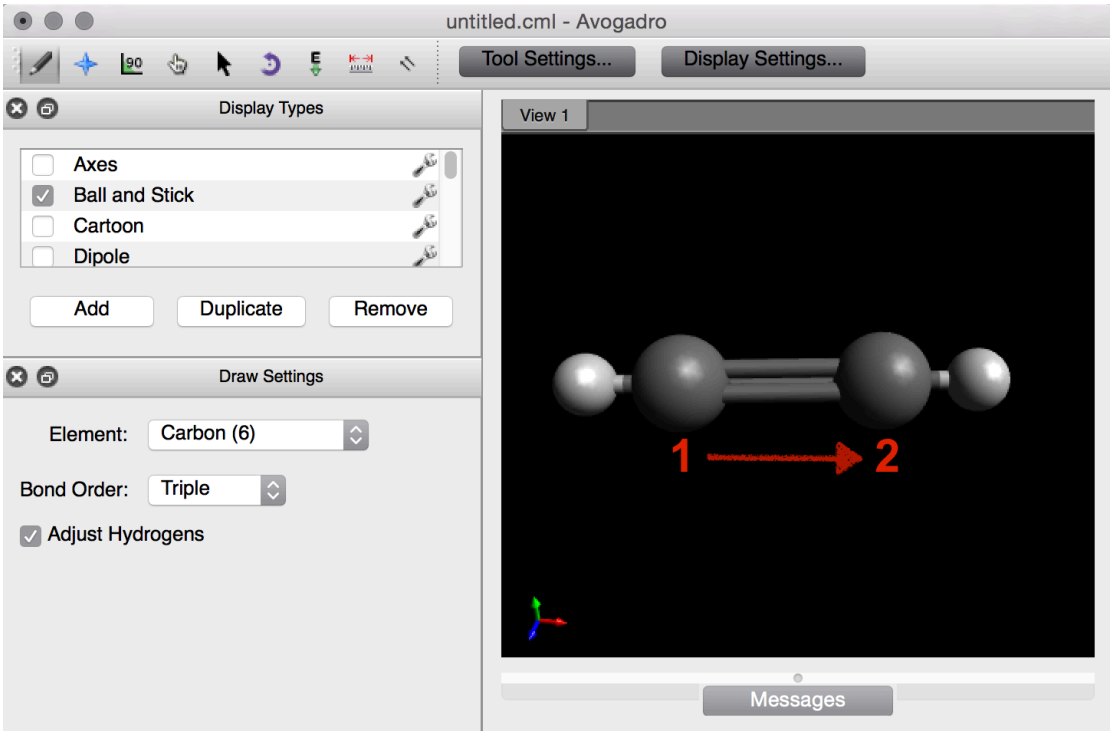


To go from ethane to ethylene, CH_2=CH_2, simply left click on the bond. This will change the bond order and adjust the number of hydrogen atoms accordingly.

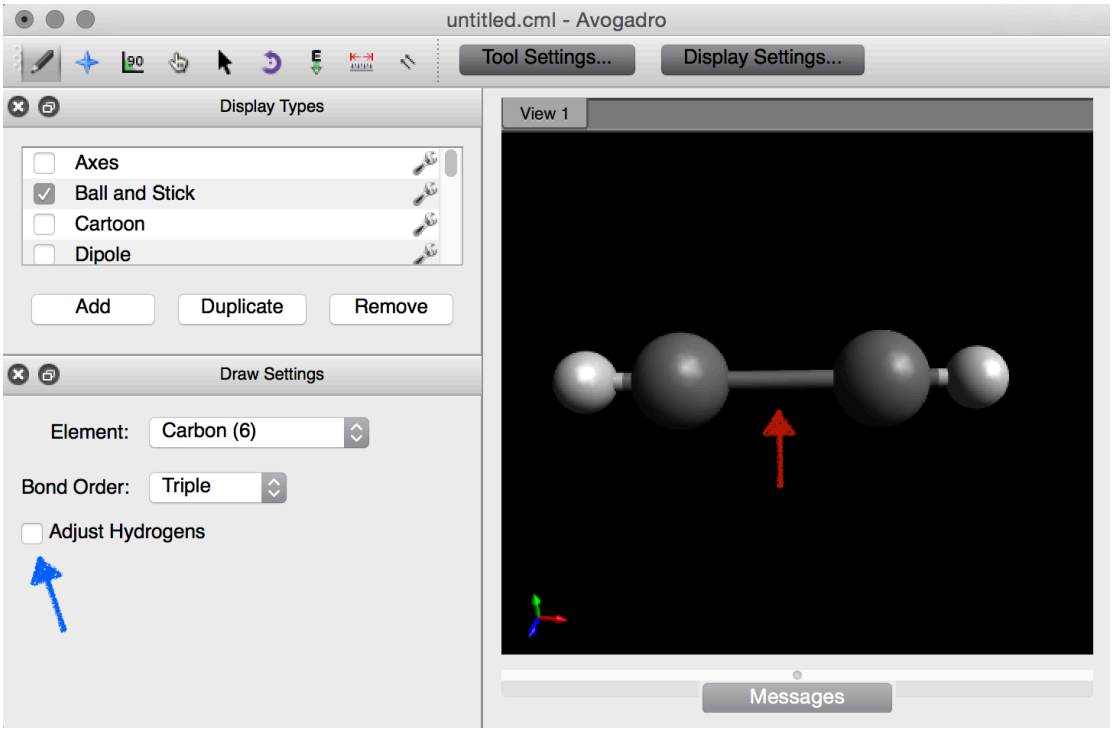


In the same way we can obtain ethyne, CH≡CH. However, in order to practice, first delete one of the carbons and the corresponding hydrogen atom by right clicking on the carbon atom. You should see methane again. Then, change the bond order to "Triple" and generate ethyne using the click and drag option again.

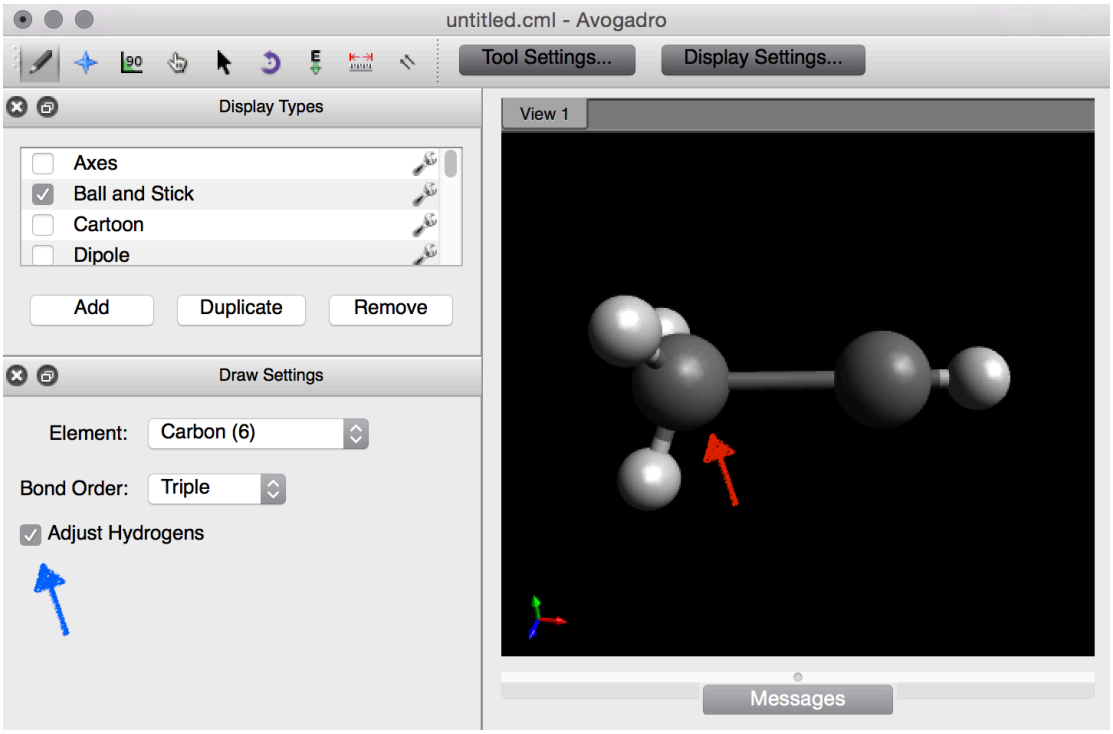




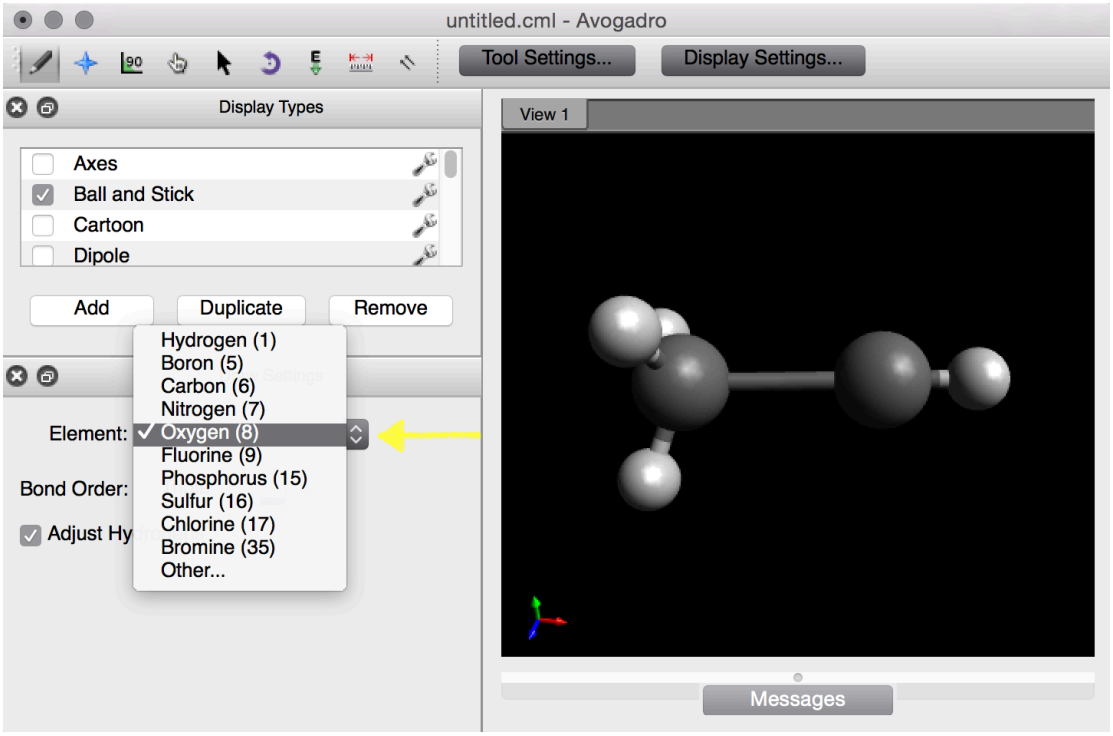
Now, uncheck the "Adjust Hydrogens" box and go back to single bond by left clicking on the C–C bond. Note that the number of hydrogen atoms did not change. You should see CH–CH on your screen.

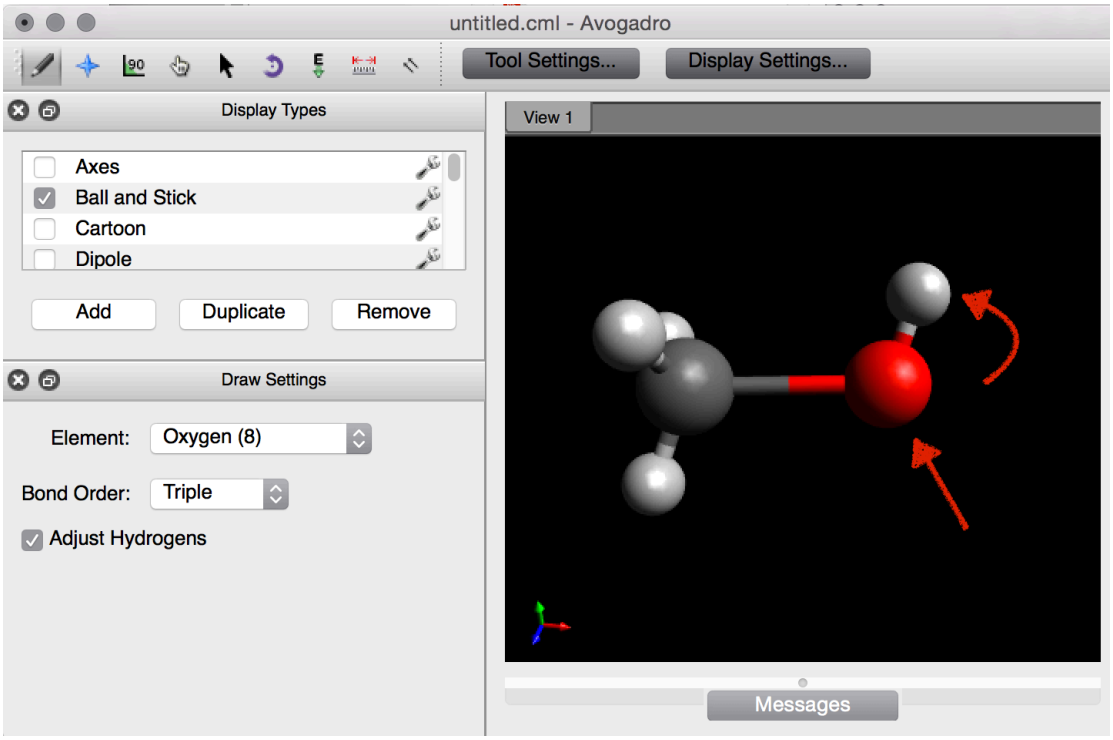


Check the "Adjust Hydrogens" box back again and click on one of the two carbon atoms to add the missing hydrogen atoms.

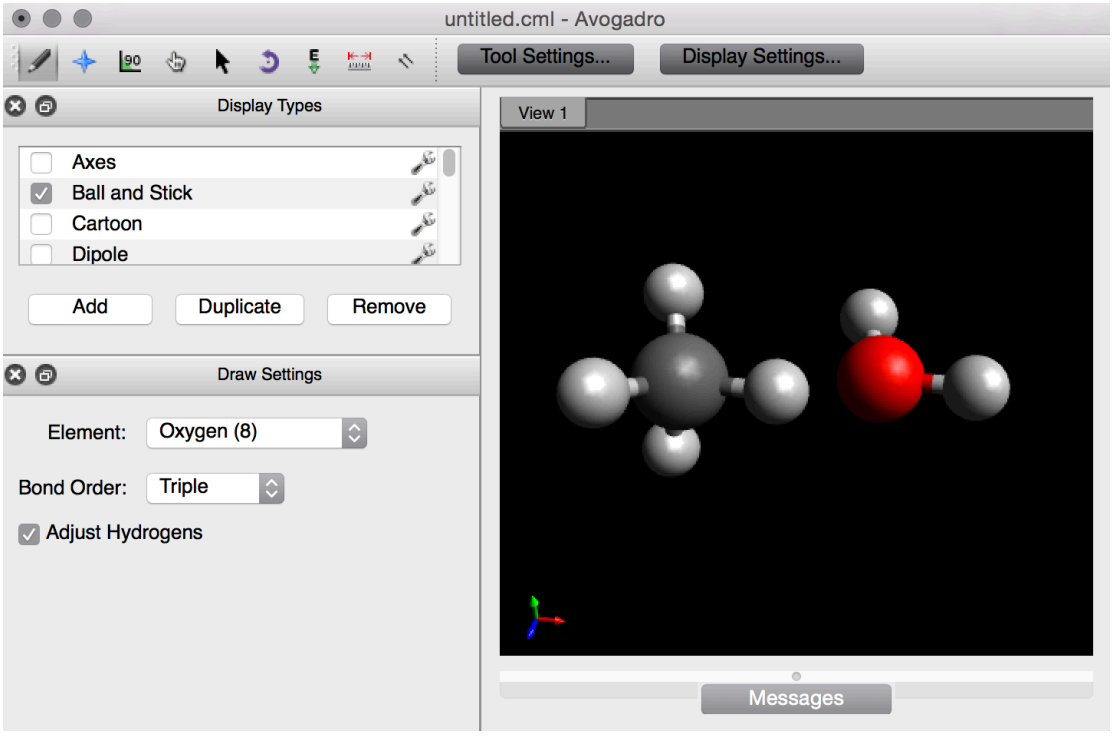


In the "Element" menu select "Oxygen" and click on the second carbon atom (the one with only one bound hydrogen). This will generate methanol, CH_3–OH. Note that the position of the hydrogen atom bound to now oxygen changed.

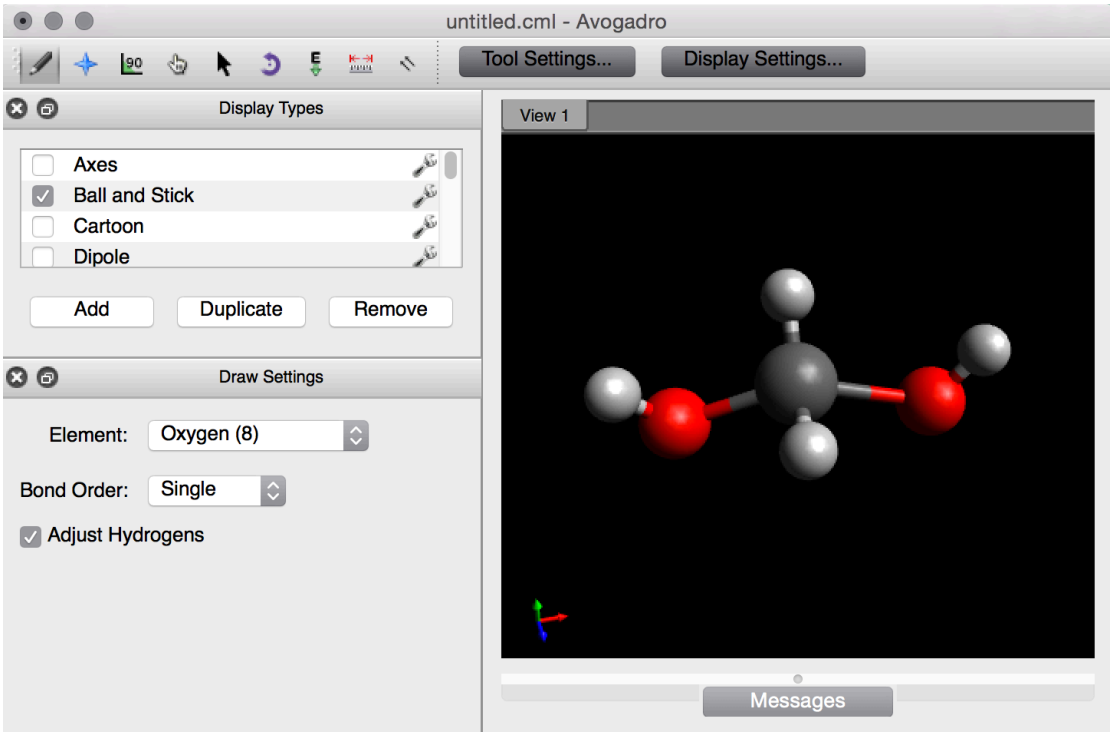




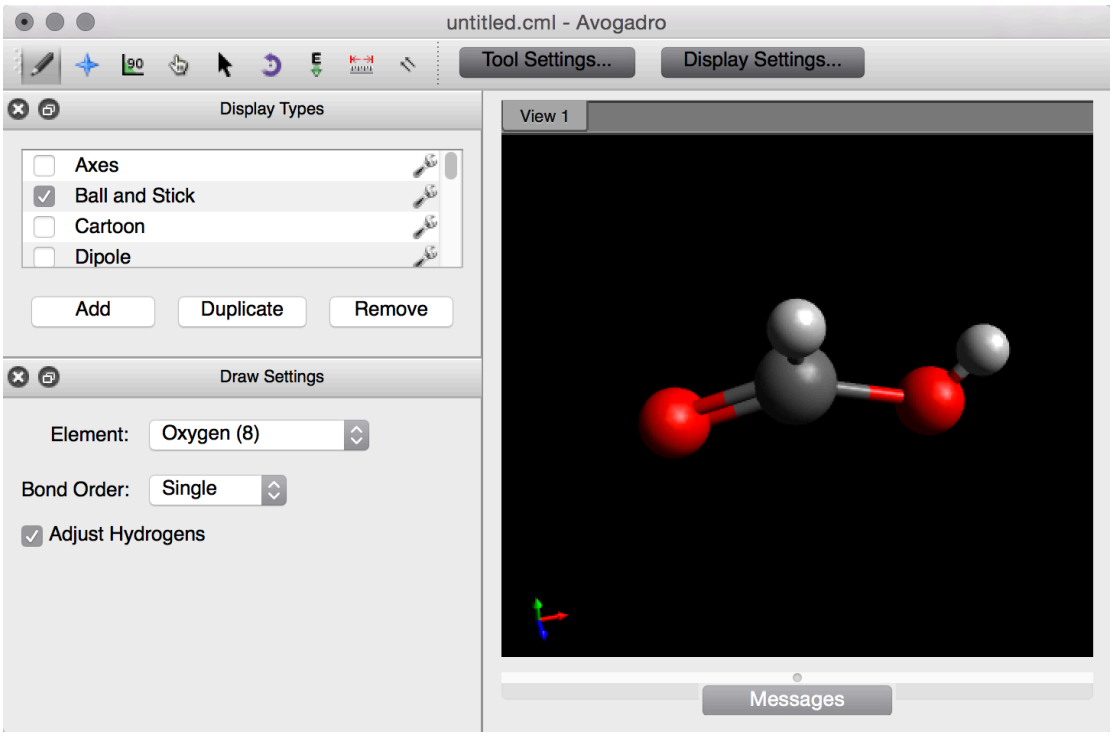
To go back to methane, simply delete the OH group by right clicking on the oxygen atom. If you try to delete the C–O bond, you will end up with methane and a water molecule next to it.

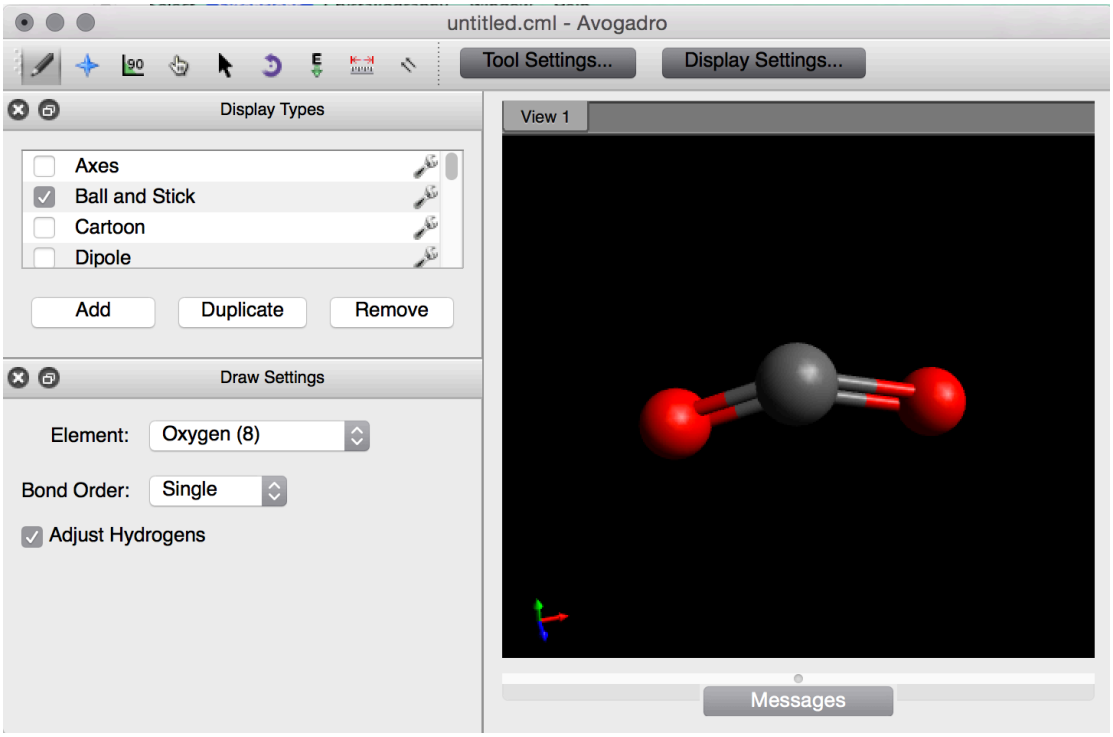


Another useful example is carbon dioxide molecule, CO_2. Begin by drawing the "O-C-O" structure.

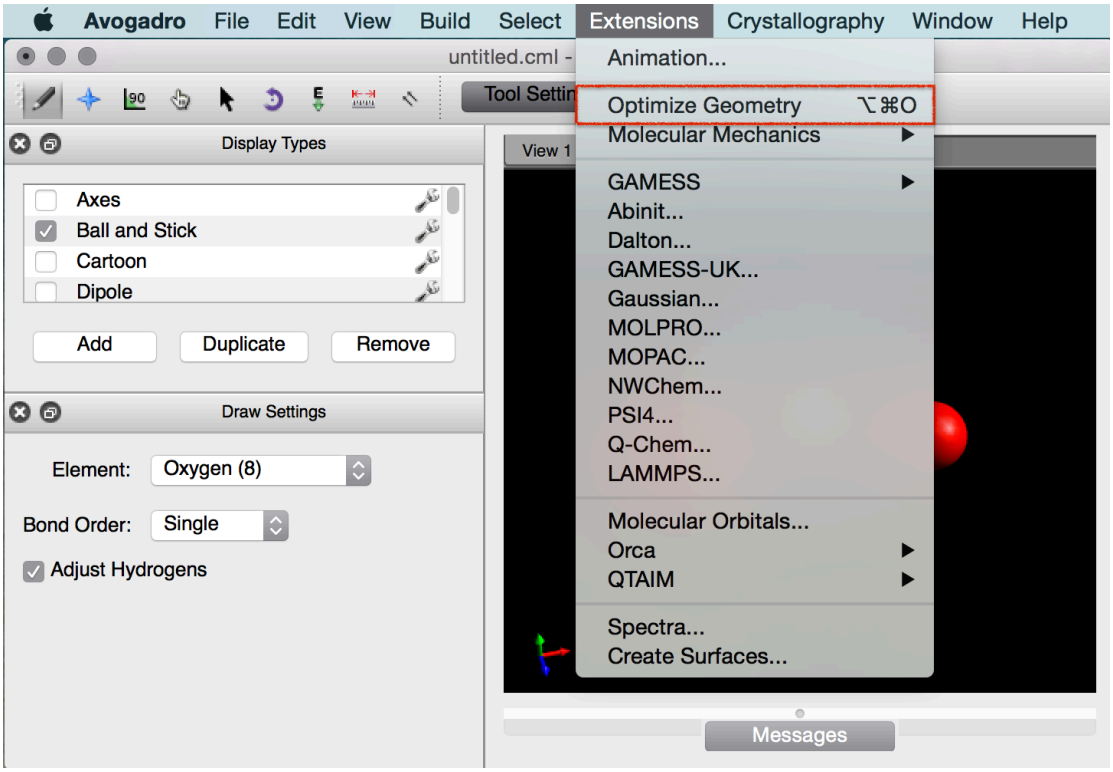


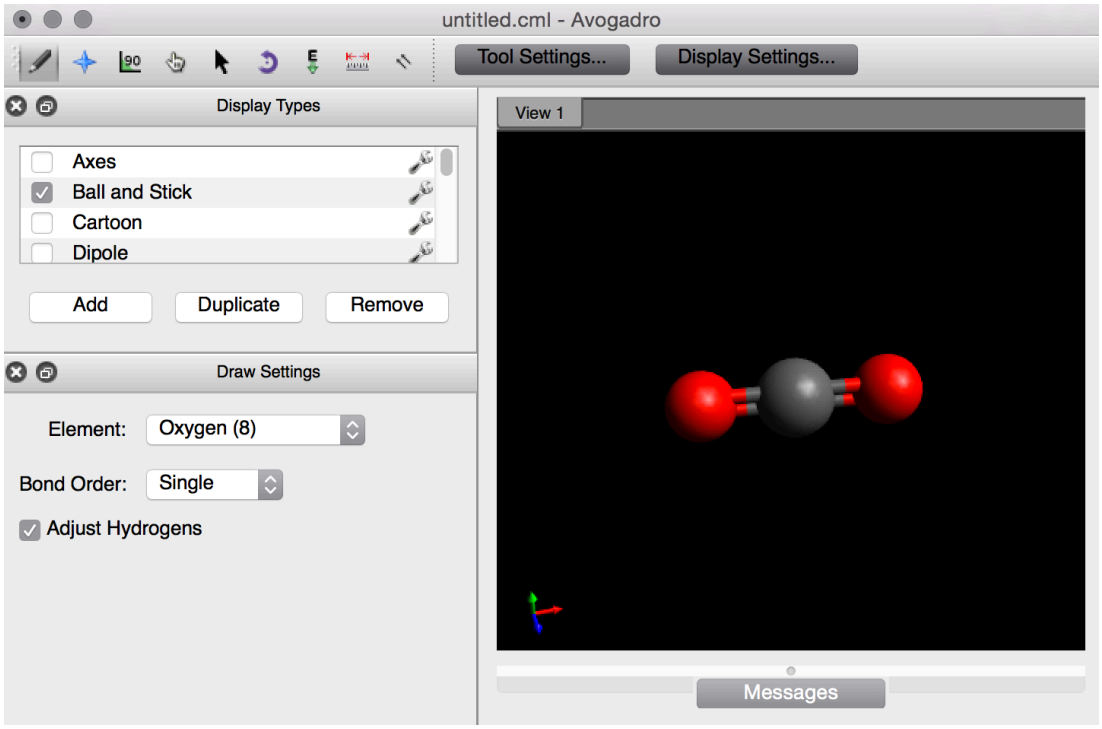
After the structure is drawn, left click on the two C–O bonds, which will create double bonds and delete the unnecessary hydrogen atoms.





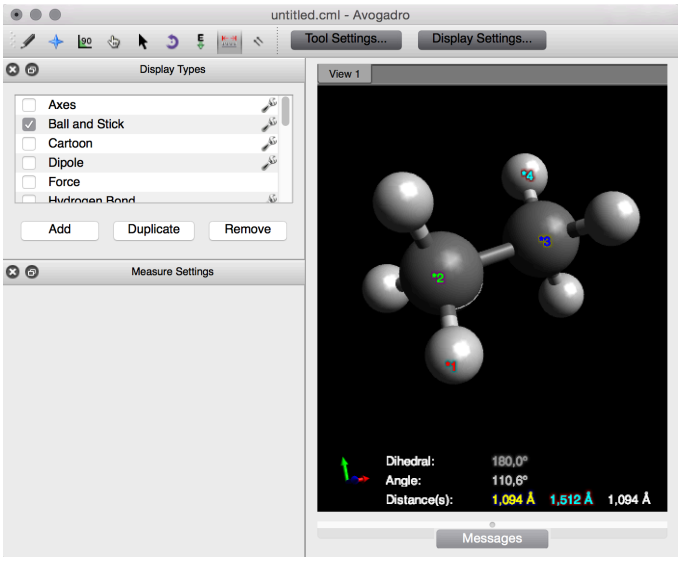
Once you've created your molecule, you can optimize its geometry through the extensions menu. Selecting the "Extensions" menu, and clicking "Optimize Geometry" will provide your molecule with proper bond lengths and angles.





In order to make building larger structures easy, Avogadro includes over 300 common molecules and molecular fragments, which can be found under the "Build" menu. Go to "Build", hold your cursor over "Insert", and then select "Fragment…". A database of fragments will then pop up. Choose the fragment you wish to insert and click "Insert".

To measure bond distances, angles and dihedrals in Avogadro, use the "Measure" tool. This tool allows you to select and assess up to four atoms. As you click on atoms Avogadro will automatically calculate the distances between atoms in a respective order. Avogadro will also determine the angle between atoms, if at least three atoms have been selected, where the second atom is used as the vertex. If four atoms are selected, a dihedral angle is determined. Right clicking the display will reset the atoms previously selected.



To save a molecule, go to "File" → "Save" and choose the format and the location where you want to save the file.

Task: Build the following molecules in Avogadro: ammonia, nitrogen, hydrogen, benzene and 1,3–butadiene. Optimize the geometries and save the molecules as xyz files (NH3.xyz for ammonia etc.). You will use the first three molecules in the following exercise, so add them to the folder Day1_Ex2.

Question 1: Note down the energy of the three molecules.

Optional: Download and install Avogadro on your own computer

To download Avogadro, visit this webpage. From there, Avogadro is automatically downloaded for the platform you are using.

For macOS users, you will find a file named "Avogadro-1.2.0.dmg" in your Downloads folder. Double-click the file and it will open a new Finder window. Drag the application's icon to your Applications folder. The software is now installed. Go to your Launchpad and open Avogadro, or open it from your Terminal application by running:

```
/Applications/Avogadro.app/Contents/MacOS/Avogadro
```

For Windows users, go to your Downloads folder and open Avogadro-1.2.0n-win32.exe file. It will launch the Avogadro Setup Wizard. Follow the instructions. For "Install Options", choose "Add Avogadro to the system PATH for current user" and, if you wish, tick the box with "Create Avogadro desktop icon". Once you are done with the installation, open Avogadro by double-clicking on the desktop icon, or type the following in your Command Prompt:

```
\Program Files\Avogadro\bin\avogadro
```

Exercise 2

Run a calculation with ORCA – Reaction energy

Learning objectives:

- **Run a calculation.**
- **Hartree Fock theory: Expected accuracy.**

Task: Calculate the energy of the reaction (use HF/STO-3G level of theory):

$$N_2 + 3H_2 \rightarrow 2NH_3$$

This reaction represents a nitrogen fixation. Industrially, the reaction is known as the Haber-Bosch process, named after two German chemists, Fritz Haber and Carl Bosch, who developed the method in the beginning of the 20th century. The method combines nitrogen gas from the air and hydrogen gas under extremely high pressures and moderately high temperatures to create ammonia. The method also uses a catalyst made mostly from iron that enables the reaction to be carried out at a lower temperature. The Haber-Bosch process remains an important industrial procedure today because it is the main source of ammonia that is used as fertilizer, which helps to feed about 40% of the world's population.

Instructions: Reaction energy is calculated as a difference between energy of the products and energy of the reactants. To calculate energy of the reaction above, you need to optimize the geometries of the three molecules at the HF/STO-3G level. For that, you will use ORCA software. ORCA is an ab initio, DFT, and semi-empirical SCF-MO package developed by Frank Neese et al. To access it, login to garm. Open your web browser and visit the following address:

garm.teokem.lu.se:8000/

Log in with your username and password. Enter the "kemm30" folder and then "Day1_Ex2" folder.

In the "Day1_Ex2" folder, you will find input files needed to run the calculations with ORCA. There are three input files, one for each molecule, named "ammonia.inp", "nitrogen.inp" and "hydrogen.inp". Each input file contains information needed to run the program and all three files have the same structure. An example input file is shown below:

```
### ammonia.inp ###
! HF STO-3G Opt
*xyzfile 0 1 NH3.xyz
### ammonia.inp ###
```

This input file instructs ORCA program to do a geometry optimization ("`Opt`" keyword) at the Hartree Fock level with a STO-3G basis set ("`HF STO-3G`"). It tells the program to read the coordinates from a xyz file named "`NH3.xyz`". The

first number in the second line is the total charge of the molecule and the second number is the multiplicity.

You can look at each of the three input files by simply clicking on them, which opens a selected file in a new tab, where you can edit the file, if needed.

The xyz files are missing from the "Day1_Ex2" folder. Therefore, you need to upload three xyz files you created in the first exercise. Make sure you name them "`NH3.xyz`", "`N2.xyz`" and "`H2.xyz`".

Once you have all the files ready, you can execute ORCA. Click on "New" and then "Terminal". This will open a Terminal window. Here, you first need to enter the "Day1_Ex2" directory. Type:

```
cd kemm30/Day1_Ex2
```

Then, you can run geometry optimizations with ORCA. To optimize ammonia, type:

```
orca ammonia.inp > ammonia.out
```

This executes ORCA, so that all information needed to run the program is read from "`ammonia.inp`" file, and all output produced by the program is printed into "`ammonia.out`" file.

To run the other two optimizations, type:

```
orca nitrogen.inp > nitrogen.out
orca hydrogen.inp > hydrogen.out
```

Apart from the "`.out`" files, ORCA produces other output files, all of them having the same prefix as the corresponding "`.inp`" file.

Read through and get familiar with the output files. For final energies, look for "TOTAL SCF ENERGY".

Question 1: Note down the energies in Table 1 and calculate the reaction energy. Compare the results you obtained to the experimental results (ΔH = –92,4 kJ/mol)?

Question 2: What happens if you replace STO-3G with the larger def2-SV(P) basis set? Edit the input files, and rerun the calculations with a different basis set.

Question 3: Why does the Haber-Bosch process require a catalyst? Is there something we have not accounted for?

NOTE: We do not exactly calculate the thermodynamic quantity ΔH. We actually calculate the reaction energy of single molecules in gas phase at 0 K, but it still

works reasonably well. We will discuss the calculation of thermochemistry in one of the future exercises.

Table 1. Calculated and experimental energies.

	Ammonia (kJ/mol)	Nitrogen (kJ/mol)	Hydrogen (kJ/mol)	Reaction E (kJ/mol)
HF/STO–3G				
HF/ def2-SV(P)				
Exp. ΔH				–92.4