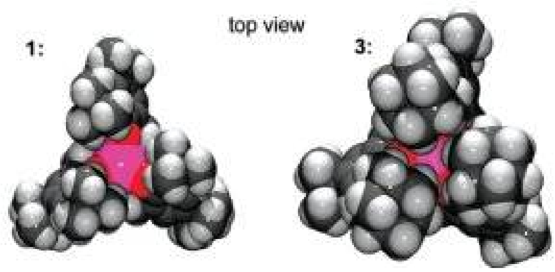
March 2008

Controlling uranium reactivity

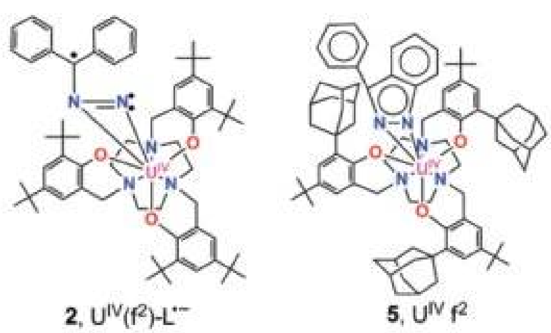
March 18, 2008

Uranium is an often misunderstood metal. Many people envision mushroom clouds and the ugly results of radiation poisoning when they think about uranium research. In reality, uranium presents a wealth of possibilities for fundamental chemistry. Many research groups have been involved in utilizing the large size and unique reactivity of the uranium atom for the last decade. Most of their work involves depleted uranium, a more common form of uranium that is not weapons-grade.

Among the techniques developed are methods to restrict access to the reactive surface of the uranium atom by attaching different ligands to the uranium atom. The ligands they employ are easily synthesized molecules that are known for their ability to bind metals; they act as bulky shields around the uranium atom core. Depending on the type of ligand used, the shape and size of available space to the uranium atom can be altered. By controlling the depth and width of the reactive pocket, novel chemistry can occur.



A recent publication in *JACS* illustrates the importance of ligand size in uranium reactivity. As you can see from the figure, the smaller ligand (uranium complex 1) leaves a wide, bowl-shaped opening to the uranium center, while the larger ligand (uranium complex 3) creates a narrow, cylindrical channel. The disparity in size of the reactive sites leads to the formation of different products when the uranium complexes were reacted with a chemical compound, diphenyldiazomethane, under identical conditions.



The smaller ligand system led to the creation of uranium complex 2; the larger ligand system produced uranium complex 5. While both complexes are new discoveries, complex 5 is truly unique. The force exerted by the colossal structure surrounding the reactive site caused a nitrogen atom to be inserted into a carbon and hydrogen bond. Such an insertion is extraordinary because it is extremely energetically unfavorable—this is only the second time in history that such a transformation has been shown to occur with these chemicals.

Using clever ligand designs, uranium can be used to make useful metal complexes that lead to rare transformations in chemistry. This sort of fundamental chemical research is necessary to stretch the limitations of our synthetic abilities, and the knowledge gained from studying uranium can be applied to other metals with similar atomic structures. With a significant portion of the periodic table untouched by synthetic chemists, the possibilities seem limitless.

Images courtesy of the Meyer research group.

JACS, 2008. DOI: 10.1021/ja0766472