EHMO study of the charge distribution in [AuL]3NNR2^{+} as a function of the N-N-Au angle

"The Hueckelberries"
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Introduction -

It was once thought that gold was essentially and inert metal because it's elemental form was found in nature. Only recently has gold been found to interact with other compounds. One possible application of gold/non-metal interactions is the fixation of nitrogen[1]. It is therefore essential that we understand the nature of the interaction between nitrgen and gold.

The [AuL]3NNR2^{+} structure has been previously studied by Paul Sharp and Yi Yang (Figure 1)[2,3] . This compound undergoes decomposition by dimerization, and then electron tansfer to yield [(LAu)6]2^{+} and R2NN=NNR2. The kinetics of this decomposition appear to be related to the nature of the ligands attached to the gold. Using EHMO theory, we plan to gain some information as to where the charges in this structure are being distributed as it decomposes and how this is related to the nature of the ligands.

Goals and Objectives -

It is presumed that electron density in [AuL]3NNR2^{+} is being transfered from the nitrogen to the golds, causing the nitrogen-gold bond to separate. The degree of this charge transfer seems to relate to the size of the ligand (L). It been observed in Paul Sharp's research group that as the ligand becomes larger, the kinetic stability becomes greater. This increase in ligand size causes the gold atoms to be pulled further apart and increases the Au-N-Au angle. Because of the nature of the z-matrix for this structure, we find it more convenient to look at the N-N-Au angle. Using EHMO theory, we plan to construct a Walsh diagram of the atomic charge (on nitrogen and gold) as a function of the N-N-Au angle being varied from 110^{o} to 130^{o}. We hypothesize, based on experimental observation, that increasing the N-N-Au angle (ϕ) will

increase the charge on the nitrogen, and simulatenously decrease the charge on the golds.

Computational approaches would be better than experimental approaches because of time and costs. These compounds are difficult to make and difficult to study because they decompose in about one hour or less depending on the ligand. Gold is also very expensive to work with.

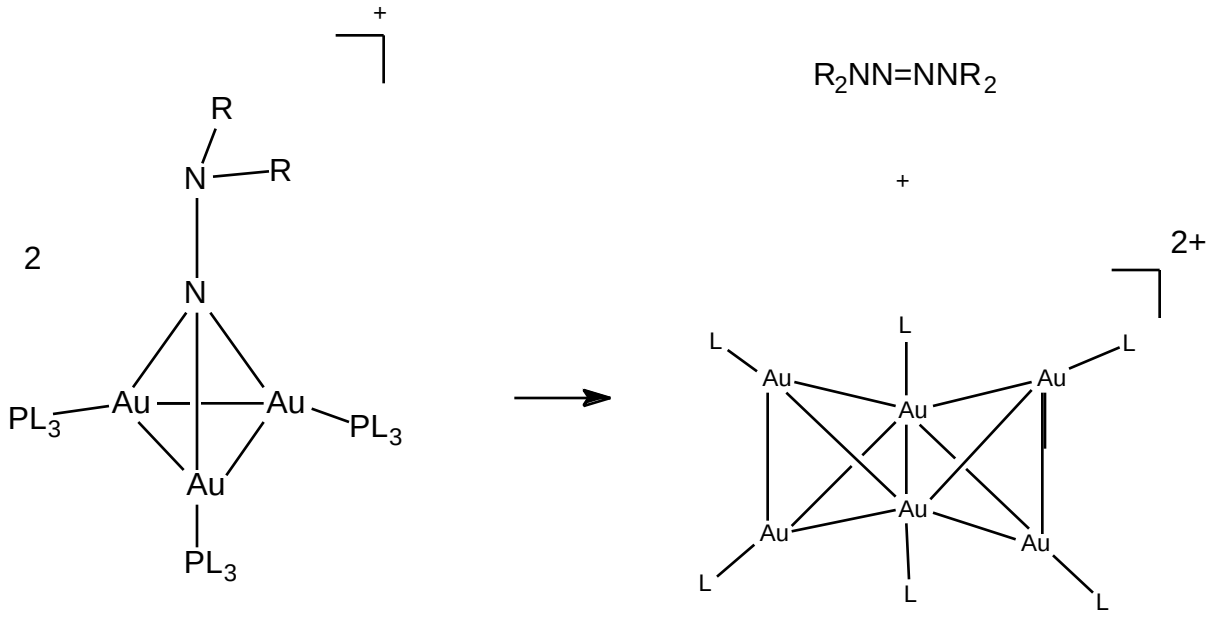

Figure 1

Proposed research

a) Choice of Methodology - We are using EHMO primarily because of the gold atoms. They have not been parameterized for semi-empirical methods and the structure is complicated for ab initio methods. Because the valence electrons of Au are located in 6s, 5d, and 4f, it requires higher basis set and the large number of parameters would require far too much computation time. HMO ignores the overlap between atoms next to each other. Since we are looking at the electron transter process and HMO does not consider the bond distance, HMO will not give a proper result. Since Komiya and Dong report the extended Hueckel parameters for gold [4,5], EHMO appears to be the most reasonable method.

b) Scope of Project - To simplify this problem, we will start with the most simple model we can construct, by replacing the R with

hydrogens, and L with PH3. Bond distances and bond angles will be taken from x-ray crystal data in Yi Yang's thesis [1]. We will vary the N-N-Au angle and compute the charge density on the nitrogen and gold atoms. Next, will will plot the charges of each of these as a function of the N-N-Au angle.

c) Interpretation- We are assuming that as the ligand increases in size, the Au-N-Au angle will increase and thus, the N-N-Au angle will decrease. Exactly how the size of the ligand relates to this angle cannot be easily determined by computation. The point is to determine how the N-N-Au angle affects the decomposition. If our hypothesis is correct, then we will expect to see electron density being transfered from the nitrogen to the gold as the N-N-Au angle increases. Another assumption that we are making the N-N-Au angle can vary from 110 to 130 degrees in reality. This was the range we chose from x-ray crystal data.

d) Facilities and Feasibility- This problem should be easy enough to perform on a PC workstation. We plan to use the CACAO program in Sharp's group office.

e) Timeline- Since all we are doing is varying the N-N-Au angle, each calculation should not take more than a couple of minutes based on Dr. Sharp's group's past experience with CACAO. The tedious part will be changing the angle in the z-matrix for each calculation one degree at a time. Most of our time will be spent in collection and organization of the data. This project should take no more than a week.

Group Actions and Dynamics -

Sang and I spent a lot of time on this project! I (Bruce) was excited about this project because I could relate it to my research. At our first meeting, I gave Sang all the background information to look over and he agreed this would be an interesting project. We spent four hours on Friday, six hours on Saturday, and all of thursday working on the project. We did a CAS search and found exteded Huekel parameters for gold. We feel we learned a lot about how to plan a computational problem and how to approach it, as well as what the limitations are and what factors are involved.

References

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