

Density Functional Theory Study of Methyl Iodide and Its Oxidative Addition to Trinuclear Gold(I) Complexes

Gabby Costner '21, Brandon Lam '23
Professor Brooke M. Otten, Department of Chemistry

Introduction

Cyclic trinuclear gold(I) complexes (CTCs) have garnered attention in recent years due to their electronic and luminescent properties. These properties have led to breakthroughs in the fields of organic LEDs and thin film development for anti-corrosion materials. Previous studies show that a methyl iodide substrate is very easily polarizable, thus allowing the activation of the carbon-iodine bond. (1) The weak σ -bond in the substrate allows the oxidative addition reaction to proceed which allows the methyl and iodide to become σ -ligands attached to the gold(I) center resulting in an oxidation state of 3+.

There are more studies that show CTCs are capable of undergoing oxidative addition with dihalogens using a stepwise mechanism, resulting in mixed valent gold(I) and gold(III) centers. (3) There are currently no computational studies on the mechanism for the oxidative addition reactions of CTCs. This research can be used for to determine if these products can lead to the production of iodine and ethane gas through photoinduced reductive elimination. Gold(I) imidazolite is a prime example of a CTC that can easily undergo oxidative addition because of the electron withdrawing imidazolite groups. If the thermochemical and kinetic properties of the reactants and products shown in Figure 1 can be determined, along with their intermediates and transition state, then an accurate model of the reaction mechanism can be obtained.

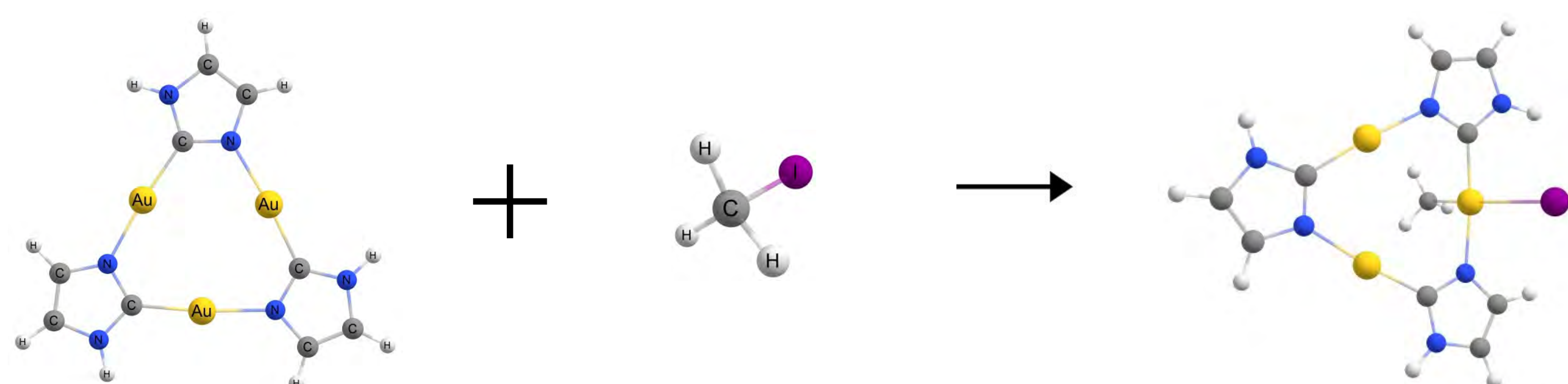


Figure 1: Overall reaction of the oxidative addition of methyl iodide to the gold (I) imidazolite trimer

Computational Results

Computational Methods

All calculations were performed using the Gaussian 09 package. All structures and orbitals were rendered using ChemCraft. Benchmarking was performed on methyl iodide using a total of 11 different functionals, including some functionals with and without Grimme's dispersion (D3). All functionals were used in combination with 6 different basis sets. A percent error analysis was performed assessing both the C-I bond length and the vibrational frequency to identify the highest performing functional and basis set combinations. It was determined that B3PW91, with and without dispersion, combined with the augmented triple- ζ basis set had the best performance.

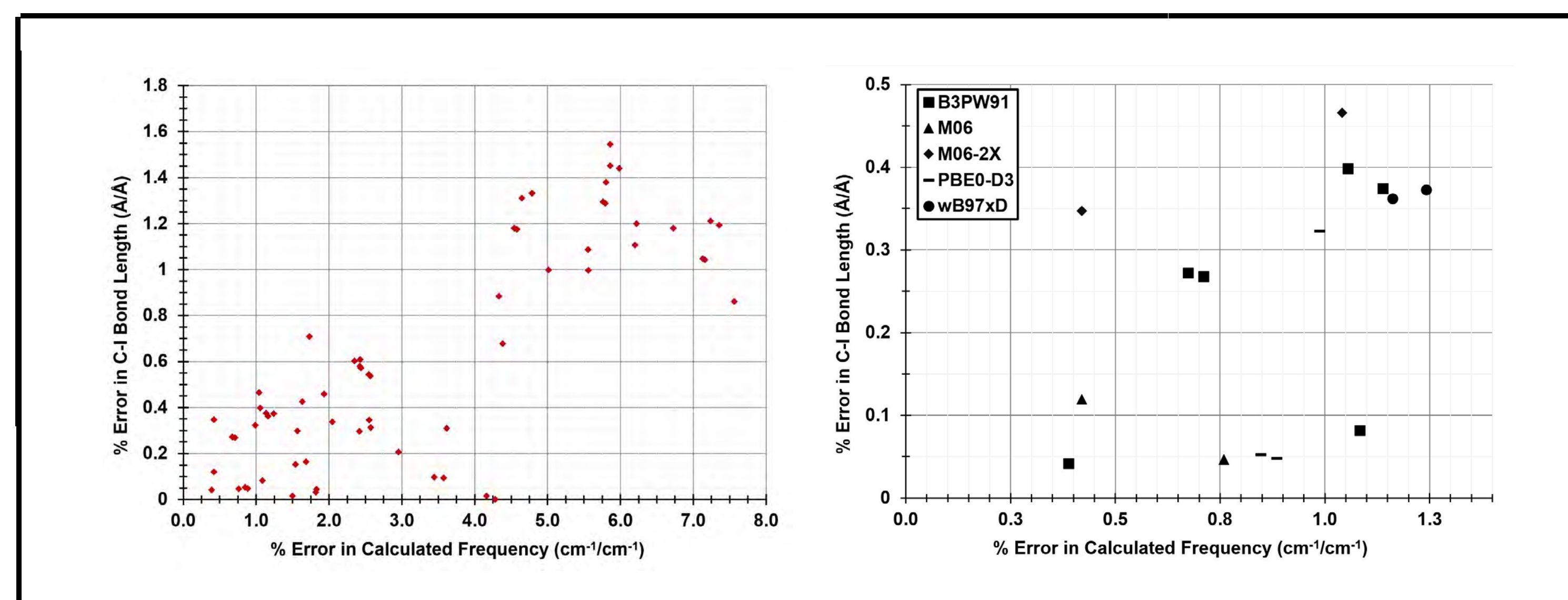


Figure 2: Graph (left) comparing the percent error of the C-I bond, and the percent error in the calculated frequency across all combinations. Graph (right) comparing the percent error of both the C-I bond and the frequency across a shortened range.

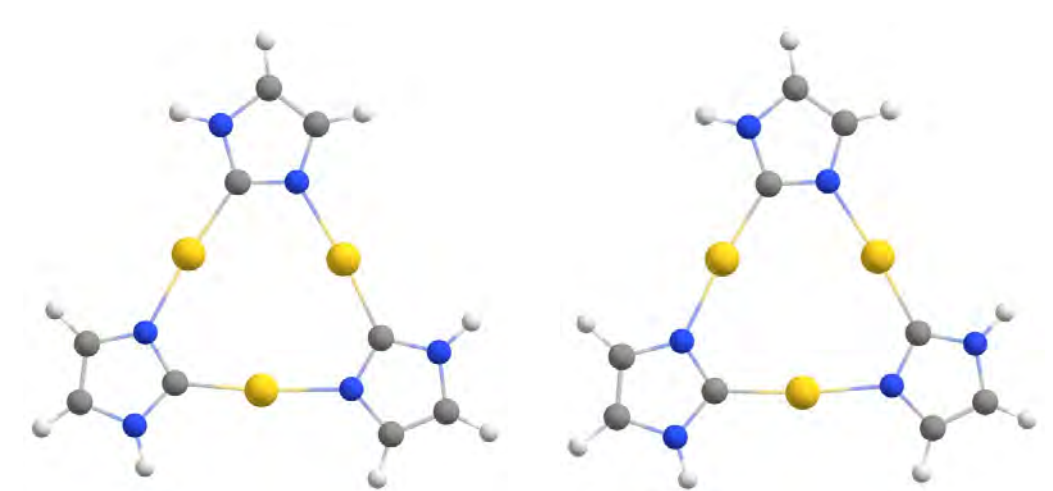


Figure 3: Monomer structures using the B3PW91 (left), and the B3PW91-D3 (right) functional.

Figure 4: Comparing Computational and Experimental Data

	B3PW91	B3PW91-D3	Experimental
Au-Au (Å)	3.53475	3.53479	3.488
	3.53468	3.53483	3.438
	3.53475	3.53472	3.479
C-Au-N (°)	174.413	174.414	173.7
	174.412	174.413	175.4
	174.411	174.408	175.9

Figure 4 is a comparison between computational data and experimental data for the cyclic trinuclear gold(I) complex using imidazolite. The structural data for the functional B3PW91 (with and without dispersion) with the augmented triple- ζ basis is compared to the structural data of the same complex synthesized experimentally (4). The mostly linear C-Au-N angle indicated weak Au-Au interaction.

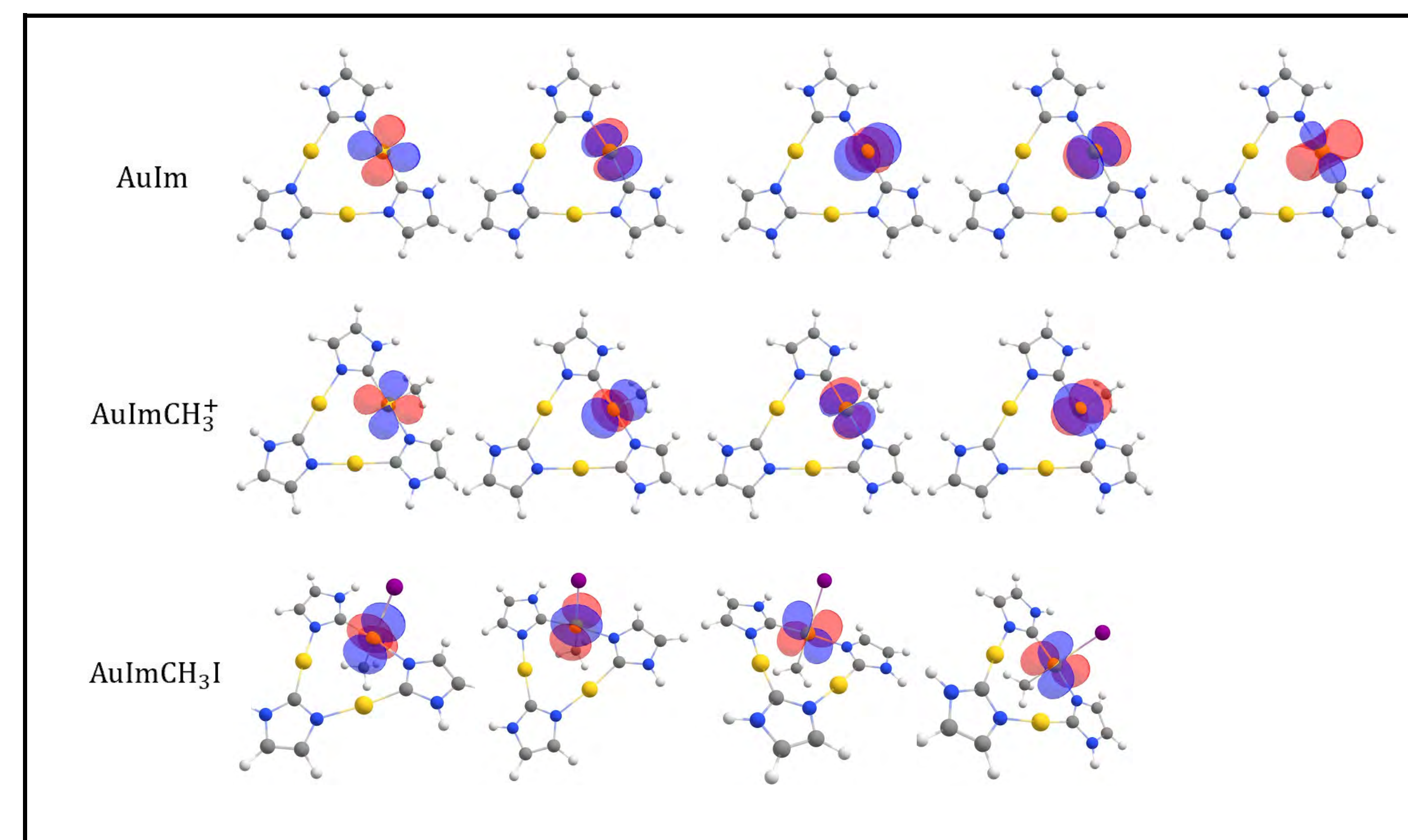


Figure 5: Chemcraft-rendered d-orbitals for the reactant (top), intermediate (middle), and product (bottom).

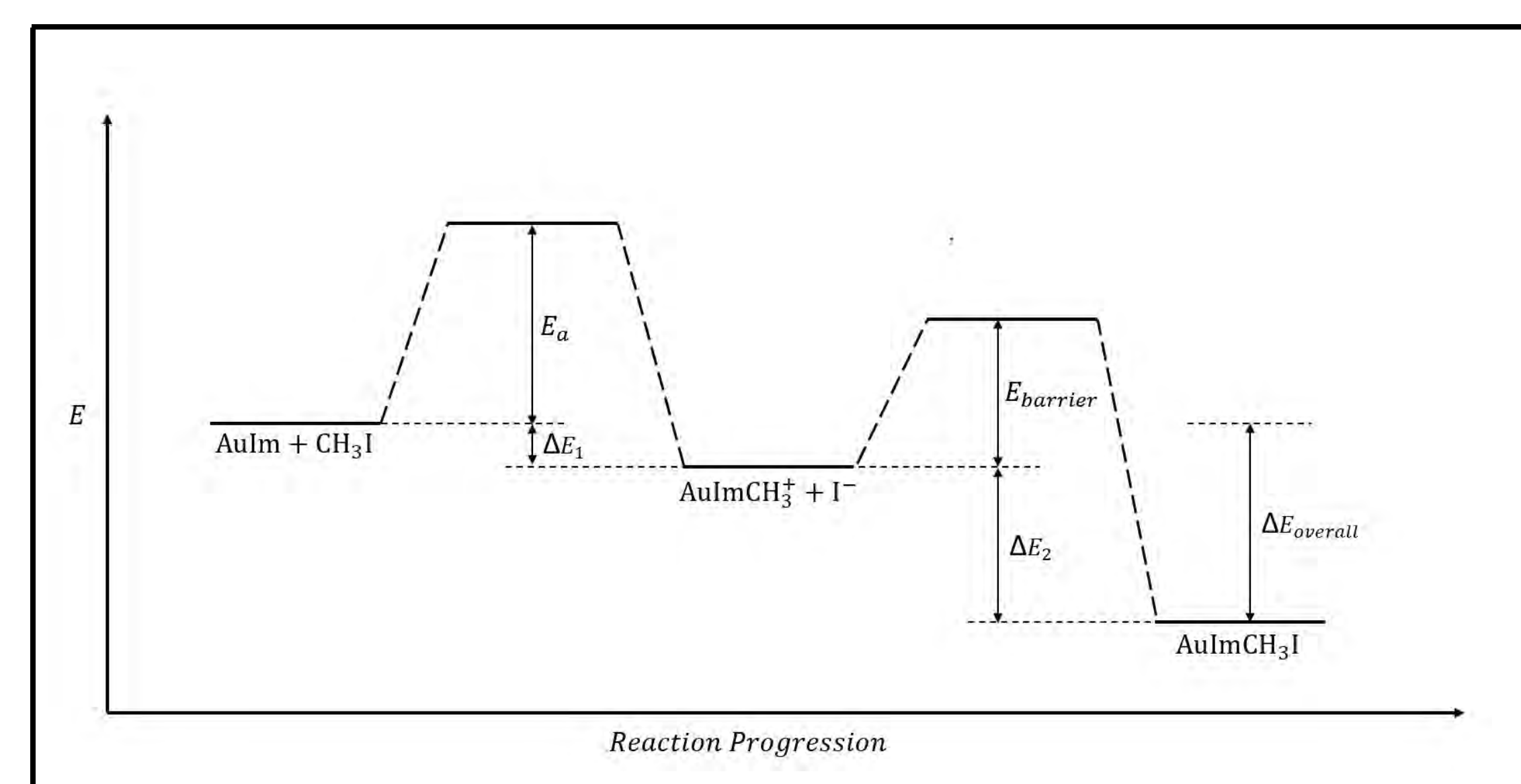


Figure 6: Reaction diagram of the overall reaction.

Figure 7: Reaction Energetics Data

	Reaction Energetics ($kcal\ mol^{-1}$)			
	ΔE_1	ΔE_2	$\Delta E_{overall}$	$\Delta H_{overall}$
B3PW91	$\Delta E_1 = -22.59$ $\Delta E_2 = -109.97$ $\Delta E_{overall} = -132.56$	$\Delta G_1 = -12.06$ $\Delta G_2 = -102.31$ $\Delta G_{overall} = -114.37$	$\Delta H_1 = -14.82$ $\Delta H_2 = -110.31$ $\Delta H_{overall} = -125.13$	
B3PW91-D3	$\Delta E_1 = -25.34$ $\Delta E_2 = -119.61$ $\Delta E_{overall} = -144.95$	$\Delta G_1 = -14.66$ $\Delta G_2 = -61.98$ $\Delta G_{overall} = -76.64$	$\Delta H_1 = -17.58$ $\Delta H_2 = -169.61$ $\Delta H_{overall} = -187.19$	

Conclusions

The methyl iodide benchmarking results show that the basis sets with diffuse functions performed the best and accurately described the energy needed to break the carbon-iodide bond. The functionals that performed best was a hybrid functionals with dispersion corrections. These combinations were able to produce an accurate representation of the linearity of the C-Au-N angle. For the mechanism, the computational results were able to confirm that the gold(I) center acts as a nucleophile that attacks the carbon center in the methyl iodide, creating an intermediate with a gold(III) center. The center remains gold(III) for the product, which is consistent with results in the literature. The energetics of the reaction are not exactly what we expected - there was not much consideration for the solvation of the complex, which will be addressed in future work. Exploring the energetics of the dimer in a chair conformation can also give vital information on the mechanism of this reaction.

References

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Explanation