

2013

# Is Ir<sub>6</sub> a hydrocarbon cracker

Ashley Nichole Nashleanas  
Iowa State University

Follow this and additional works at: <https://lib.dr.iastate.edu/etd>

 Part of the [Physical Chemistry Commons](#)

## Recommended Citation

Nashleanas, Ashley Nichole, "Is Ir<sub>6</sub> a hydrocarbon cracker" (2013). *Graduate Theses and Dissertations*. 13471.  
<https://lib.dr.iastate.edu/etd/13471>

This Thesis is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact [digirep@iastate.edu](mailto:digirep@iastate.edu).

Is Ir<sub>6</sub> a hydrocarbon cracker?

by

**Ashley Nashleanas**

A thesis submitted to the graduate faculty  
in partial fulfillment of the requirements for the degree of

MASTER of SCIENCE

Major: Physical Chemistry

Program of Study Committee:  
Mark S. Gordon, Co-Major Professor  
Theresa Windus, Co-Major Professor  
Thomas Holme

Iowa State University  
Ames, Iowa  
2013

Copyright © Ashley Nashleanas, 2013. All rights reserved.

## TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS .....	iv
ABSTRACT .....	v
CHAPTER 1 INTRODUCTION.....	1
1.1. General Introduction .....	1
1.2. Organization .....	3
1.3. Computational Methods .....	3
1.4. Basis Sets.....	7
Chapter 1 References .....	10
CHAPTER 2 ARGUMENTS AND ENERGETICS FOR THE BARE Ir <sub>6</sub> CLUSTER .....	13
Abstract .....	13
2.1. Introduction .....	14
2.2. Arguments for Ir <sub>4</sub> and Ir <sub>6</sub> .....	15
2.3. Methods and Basis Sets for Bare Ir <sub>6</sub> .....	17
2.4. The Ir <sub>6</sub> Minima .....	18
2.5. The Energetics of Bare Ir <sub>6</sub> .....	19
2.6. Conclusions .....	22
Chapter 2 References .....	22
CHAPTER 3 HYDROCARBONS ON THE IRIDIUM CLUSTER .....	25
Abstract .....	25
3.1. Introduction .....	25
3.2. Methods and Basis Sets for Calculations .....	28
3.3. Gas Phase Mechanism of Ethylene Hydrogenation to Ethane.....	29
3.4. Binding of the Hydrocarbon Species to the Ir <sub>6</sub> Cluster.....	33
3.5. Thermodynamics and Mechanism of Ethylene Hydrogenation to Ethane on the Cluster .....	39
3.5.1. Thermodynamics.....	39
3.5.2. Mechanism on the Cluster.....	40
3.6. Conclusions .....	40
Chapter 3 References .....	41
CHAPTER 4 CONCLUSIONS.....	44

## ACKNOWLEDGEMENTS

I have always had a deep love for learning and taking on new challenges. The exploration of hydrocarbons on iridium posed many new and exciting challenges, and working under Dr. Mark Gordon and Dr. Theresa Windus has deepened my passion for learning. Working under Dr. Gordon and Dr. Windus has allowed for me to reach higher goals than I had imagined being able to reach before. Their enthusiasm and encouraging words during my time as their student will always be cherished. I would like to thank both Dr. Gordon and Dr. Windus for their support as well as the opportunity to explore an exciting branch of chemistry. I would also like to thank Dr. Thomas Holme for agreeing to serve on my Masters committee. Finally, I would like to thank the Air Force Office of Scientific Research (AFOSR) as well as the DoDSTTR for providing the necessary funding for me to pursue an enjoyable and exciting project, as well as Iowa State University for the funding that has been provided while I was a teaching assistant. This work was performed at the Ames Laboratory under contract number DE- AC02-07CH11358 with the U.S. Department of Energy. The document number assigned to this dissertation is IS-T 3107.

## ABSTRACT

Health and the economy are common topics of discussion today. Over time, emissions of harmful substances into the environment can negatively affect one's health, and rising gasoline prices are causes for concern. Hydrocarbon conversions to other hydrocarbons are among many key processes in the petrochemical industry, and small transition metal clusters can be used to catalyze reactions of hydrocarbons to other substances by significantly lowering the high energy barriers associated with these processes. In the present work, computational methods were used to investigate the hydrogenation of ethylene to ethane on an iridium cluster. Iridium resists temperature and chemical attack well, and the six atom cluster was thought to give a balance between reasonable catalytic performance and computational time. When invoking electron correlation into the calculations, the singlet state of Ir<sub>6</sub> was stabilized with respect to higher spin states, and the proper treatment for binding of the hydrocarbons to the cluster was taken into account. Ethylene and H<sub>2</sub> exhibited much stronger binding to the cluster than did ethane to the cluster. The mechanism for the hydrogenation of ethylene to ethane on Ir<sub>6</sub> is currently being explored as an addition of hydrogen to ethylene on the cluster. Since a transition state has not yet been found for ethylene hydrogenation to ethane on the cluster, the energetics of the hydrogenation of ethylene to ethane on the cluster will be compared with the energetics for the reaction in the gas phase in future work.

## CHAPTER 1. INTRODUCTION

### 1.1. General Introduction

Catalysis is a ubiquitous process that can oftentimes be taken for granted. Catalytic converters, for example, turn harmful combustion byproducts into substances that are more friendly to the environment<sup>1</sup>. A catalyst increases the rate of a reaction by lowering the barrier height, and it is regenerated at the end of the chemical reaction. Processes in which the substrate and catalyst phases differ are known as heterogeneous, and processes in which all of the species are in the same phase are referred to as homogeneous. Higher-temperatures and pressures are employed to carry out the reactions, and mechanism elucidation is more of a challenge for heterogeneous processes than for homogeneous ones<sup>2</sup>. However, catalysts are more easily recovered for heterogeneous processes since the substrate and catalyst are separated more readily when they are in different phases.

Iridium is a transition metal mainly observed as clusters or in bulk. As reported by Anderson et al.<sup>3,4</sup> and Smith and Solomon<sup>5</sup>, iridium is used in monopropellant thruster applications because of its high resistance to temperature changes and corrosion. Iridium is also of importance to the petroleum industry, as the breakdown of hydrocarbons is a means for producing gasoline products from oils, reported by Chester<sup>6</sup>. In a DFT study by Hall and Fan<sup>7</sup>, it is reported that more thermodynamically

and kinetically favorable pathways are available for alkane dehydrogenation through the use of Pincer iridium complexes. Small clusters of iridium atoms supported on alumina are used for hydrogenation of ethylene to ethane as reported by Gates et al.<sup>8</sup>. While most studies report reactions of substrates with supported metal clusters, the present work reports the details of the mechanism of hydrogenation of ethylene to ethane in the gas phase and on unsupported Ir<sub>6</sub>. Gates et al.<sup>8</sup> observed through X-ray Absorption Fine Structure and IR spectroscopy that the gamma-alumina support did not actively participate during the hydrogenation of ethene to ethane on Ir<sub>4</sub> and Ir<sub>6</sub> clusters. But there is convincing evidence by Chretien and Metiu<sup>9,10</sup> that the support does aid in the catalytic process. These latter studies present various Lewis acid-Lewis base interactions. But before beginning to understand the dehydrogenation mechanism on supported Ir<sub>6</sub>, the mechanism on the bare Ir<sub>6</sub> cluster needs to be established.

In the present work, computational studies at various levels of theory and basis sets were used to understand the hydrogenation mechanism of ethylene to ethane on bare Ir<sub>6</sub> as groundwork for the mechanism on supported Ir<sub>6</sub>. The GAMESS (General Atomic and Molecular Electronic Structure System) code described by Gordon et al.<sup>11</sup> was used for all calculations discussed herein. The following needs to be considered. What is  $\Delta E$  for the reaction of ethene and H<sub>2</sub> to produce ethane? How do these values at each level of theory compare with the experimental value? Is iridium playing the role of a catalyst? How does the barrier height in the gas phase compare with that on the cluster? What kinds of transition states and local minima will be observed once the hydrogenation

reaction is considered when placed on Ir<sub>6</sub>? Based on the computational findings reported here along with other studies, will it be wise to stick with the 6-atom iridium cluster when exploring the reaction with support added or would Ir<sub>4</sub> be a better choice?

## 1.2. Organization

The next section will give reasons for the methods and basis sets used for the calculations. Chapter 2 will first outline the reasons for choosing Ir<sub>6</sub> over Ir<sub>4</sub> for exploration of the hydrogenation mechanism. Then the energetics and spin states of the bare Ir<sub>6</sub> cluster will be reported and analyzed. Chapter 3 will first cover the findings on the reaction of ethylene and hydrogen to form ethane without the iridium cluster and in its presence. Thereafter, the findings from this study will be compared with those from outside studies. Conclusions will be made on the quality of the Ir<sub>6</sub> cluster for catalyzing the ethylene to ethane hydrogenation reaction.

## 1.3. Computational Methods

The Hartree-Fock (HF) energy is based on the variational principle and always stays above the exact energy. In the present work, the restricted Hartree-Fock (RHF) method from Roothaan<sup>12</sup> is used when referring to the closed shell singlet state of the Ir<sub>6</sub> cluster and iridium/hydrocarbon complexes. The restricted open-shell Hartree-Fock (ROHF) method from Roothaan and Bagus<sup>13</sup> is used when referring to higher spin states.



For ROHF, the spatial functions need to stay the same for paired electrons, but the spins can differ. The unrestricted Hartree-Fock (UHF) method from Pople and Nesbet<sup>14</sup> can also be used for higher spin states but was not chosen for the calculations described herein. The UHF method takes greater advantage of the variational principle by allowing the spatial functions to differ as well as the spin functions. Although allowing the spatial function flexibility can give lower energies, spin contamination becomes a problem, as higher spin states are included along with the desired spin state.

Although HF does not give reliable relative energies for chemical processes, the converged orbitals generated from an HF calculation are used for calculations with better levels of theory, and reasonable geometries can be produced using basis sets such as the 6-31G(d) basis from Hariharan, Lathan and Pople<sup>15</sup> and Francl et al.<sup>16</sup> and the 6-31G basis described by Hehre, Ditchfield and Pople<sup>17</sup>. Basis sets from references 15-17 will be described further in Section 1.4. Hartree-Fock does not include explicit electron correlation since each electron is assumed to be interacting in the average field of all other electrons in the system. The correlation energy is given by  $E_{\text{HF}} - E_{\text{exact}}$  and is recovered by allowing excitations of electrons from occupied to virtual orbitals. Correlation is necessary when comparing the potential energy surfaces for different spin states of the iridium cluster, which will be discussed in more detail in chapter 2. It is also necessary when considering the proper treatment for binding of one species to another, as well as reaction paths, which will be discussed further in chapter 3. Correlation is recovered at different levels depending on the theory used. The next two levels of theory

include correlation and will be discussed below.

The Second Order Moller-Plesset perturbation theory (MP2)<sup>18</sup>, is an expansion beyond the Hartree-Fock energy and recovers a majority of the correlation upon double excitations of electrons from occupied molecular orbitals to virtual molecular orbitals. The HF ground state energy is written as (using the Dirac notation for two-electron integrals)

$$\text{Equation 1. } E_0 = E_0^0 + E_0^1 = \sum_a \varepsilon_a - \sum_{a<b} \langle ab||ab \rangle.$$

The index  $\varepsilon_a$  represents the energy of molecular orbital a.

$$\text{Equation 2. } \langle ab||ab \rangle = \langle ab|ab \rangle - \langle ab|ba \rangle.$$

Indices a and b correspond to molecular orbitals. The Coulomb term is defined as  $\langle ab|ab \rangle$  and the exchange term is defined as  $\langle ab|ba \rangle$ .

The Hartree-Fock energy consists of  $E_0^0 + E_0^1$ , so  $E_0^2$  is the first real correction to the HF energy. The expression for the second-order energy correction in the molecular orbital basis is written as

$$\text{Equation 3. } E_0^2 = \sum_{a<b, r<s} \frac{|\langle ab||rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}.$$

The indices a and b are associated with occupied molecular orbitals, while indices r and s correspond to unoccupied molecular orbitals.

The transformation from the atomic orbital basis to the molecular orbital basis is the time-consuming piece when running a calculation using MP2. N is the number of basis functions, and MP2 scales in computational time as  $N^5$ . The transformation from atomic orbitals to molecular orbitals is the multiplication of four linear combination of atomic orbital (LCAO) coefficients with the electron repulsion integral and is expressed as

$$\text{Equation 4. } \langle ab||rs \rangle = \sum_{\mu} c_{\mu,i} * \sum_{\nu} c_{\nu,j} * \sum_{\lambda} c_{\lambda,k} \sum_{\sigma} c_{\sigma,l} \langle \mu\nu||\lambda\sigma \rangle$$

The completely renormalized coupled cluster with iterative singles and doubles and perturbative triples (CR-CC(2,3)) method from Piecuch et al.<sup>19</sup> and Piecuch and Wloch<sup>20</sup> recovers more of the electron correlation than MP2 and was the final method used in the present work. The general coupled cluster wave function is expressed as

$$\text{Equation 5. } \Psi = e^{\hat{T}} \Psi_{\text{HF}}$$

$$\text{Equation 6. } \hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n.$$

$\hat{T}$  is the cluster operator and is the sum from one particle to N particles in the system.  $\hat{T}_1$  operates on one particle,  $\hat{T}_2$  operates on two particles, and  $\hat{T}_n$  operates on N particles. The  $N^7$  scaling for CR-CC(2,3) implies more time-consuming calculations but often provides more accurate energies.

CR-CC(2,3) is specific to GAMESS and is an improvement to the coupled cluster with singles, doubles and perturbative triples (CCSD(T)) method used by other software packages. Although CCSD(T) and CR-CC(2,3) scale similarly, the CCSD(T) method cannot be applied to the breaking of single bonds due to its single reference character<sup>21</sup>. However, CR-CC(2,3) is a good compromise between accuracy and cost in that it generates energies of comparable quality to those given by coupled cluster with singles, doubles and triples (CCSDT) which scales as  $N^8$ . Furthermore, the energies from the CR-CC(2,3) method at equilibrium geometries for closed shell systems can be more accurate than energies given by CCSD(T). With that in mind, it makes sense to consider the basis sets used at each level of theory.

#### 1.4. Basis Sets

A basis set is a set of orbitals spanning a space. Slater type orbitals (STOs), introduced by Slater<sup>22</sup>, are of the form

Equation 7.  $\phi_{abc}^{STO(x,y,z)} = N x^a y^b z^c e^{-\zeta r}$ .

N is the normalization constant, a, b, and c determine the directionality of the orbital from the angular momentum, expressed as

$$\text{Equation 8. } l = a + b + c.$$

The parameter  $\zeta$  determines the size of the orbital, and

$$\text{Equation 9. } r = (x^2 + y^2 + z^2)^{1/2}.$$

is the electron-nucleus distance. The cusp at the origin and the exponential tail show the correct behavior for atoms at short and long distances from the nucleus. However, STOs do not have a closed form for the integrals in systems where more than two atoms are present. Gaussian type orbitals (GTOs), introduced by Boys<sup>23</sup>, are more easily integrable and take the form

$$\text{Equation 10. } \phi_{abc}^{\text{GTO}(x,y,z)} = Nx^a y^b z^c e^{-\zeta r^2} = Nx^a e^{-\zeta x^2} y^b e^{-\zeta y^2} z^c e^{-\zeta z^2}$$

since

$$\text{Equation 11. } r^2 = x^2 + y^2 + z^2$$

Also, GTOs are more easily integrable since the multiplication of one Gaussian with a second Gaussian results in a third Gaussian.

Effective core potentials (ECPs), introduced by Melius and Goddard<sup>24</sup> and model core potentials (MCPs), introduced by Huzinaga<sup>25</sup>, were developed to reduce the cost of calculations for many-electron systems while modeling the relevant chemistry. In both cases, the valence basis set and potential are jointly optimized. Radial nodes are absent in the ECPs that are available in GAMESS. Radial nodes are present in MCPs since orthogonality of the valence orbitals is maintained with respect to the core orbitals. Each core potential needs to be matched with a different basis set and level of theory.

Basis sets fit for core potentials were used for the Ir<sub>6</sub> cluster, and all-electron basis sets were used for the hydrocarbons. During HF optimization runs on the bare Ir<sub>6</sub> cluster, the ECP/SBKJC basis set from Stevens et al.<sup>26</sup> was used to match the double  $\zeta$  quality of the 6-31G basis from reference 17. The Pople sets were used in conjunction with SBKJC for HF optimizations on the hydrocarbon/iridium complexes. For the Pople sets, six Gaussians are fitted to the core, three are fitted to one part of the valence region and one is used to model the rest of the valence for carbon while only the valence region was modeled for hydrogen. The 6-31G(d) set was used on ethylene and ethane and the 6-31G set was used on H<sub>2</sub>. For ethylene and ethane, d functions were included on the carbon p orbitals.

After obtaining optimized geometries with the combined SBKJC and Pople basis sets at the HF level, single-point energy calculations were performed on the optimized geometries with MP2 and CR-CC(2,3) levels of theory. For calculations on bare Ir<sub>6</sub>, the model core potential basis set with triple  $\zeta$  polarization from Osanai et al.<sup>27</sup> was used for each atom. The Dunning type correlation consistent polarized valence triple  $\zeta$  (cc-pVTZ) basis set described by Dunning<sup>28</sup> was used for each atom when considering all of the hydrocarbons with a correlated method. Both of these basis sets are optimized to perform well with correlated methods and were combined such that the MCP basis represented the Ir and the cc-pVTZ basis represented the hydrocarbons when considering the complexes. Now that the levels of theory and basis sets have been outlined, the results and analysis will be discussed in the following chapters.

#### References

- [1]. INTERNATIONAL PLATINUM GROUP METALS ASSOCIATION. Catalytic Converters. {<http://www.ipa-news.com/en/89-0-Catalytic-Converters.htm>}. Accessed Jan 7, 2013.
- [2]. B.R.Jagirdar. Resonance 4, 9, 63 (1999).
- [3]. S.Lee, C.Fan, T.Wu and S.L.Anderson. J.Phys.Chem. B 109, 381 (2005).
- [4]. C.Fan, T.Wu, W.E.Kaden and S.L.Anderson. Surf.Sci 600, 461 (2006).
- [5]. O.I.Smith and W.C.Solomon. Ind.Eng.Chem.Fundam 21, 374 (1982).
- [6]. A.W.Chester. Process for Cracking Hydrocarbons US 4107032 A.

Published August 15, 1978.

{<http://www.google.com/patents/US4107032>}.

Accessed May 18, 2013.

[7]. M.B.Hall and H.Fan.

Adv.Inorg.Chem 54, 321 (2003).

[8]. A.M.Argo, J.F.Odzak and B.C.Gates.

J.Am.Chem.Soc 125 23, 7107 (2003).

[9]. S.Chrétien and H.Metiu.

J.Chem.Phys 128, 044714 (2008).

[10]. S.Chretien and H.Metiu.

J.Chem.Phys 127, 084704 (2007).

[11]. A. M.W.Schmidt, K.K.Baldrige, J.A.Boatz, S.T. Elbert, M.S.Gordon, J.J.Jensen, S.Koseki, N.Matsunaga, K.A.Nguyen, S.Su, T.L.Windus, M.Dupuis and J.A.Montgomery.

J.Comput.Chem. 14, 1347 (1993).

B. M.S.Gordon and M.W.Schmidt. in "Theory and Applications of Computational Chemistry, the first forty years"

C. E.Dykstra, G.E.Frenking, K.S.Kim, G.E.Scuseria, (editors), Elsevier, Amsterdam, 2005.

[12]. C.C.J.Roothan.

Rev.Mod.Phys 23, 69 (1951).

[13]. C.C.J.Roothan and P.S.Bagus.

Meth.Comput.Phys 2 (1963).

[14]. J.A.Pople and R.K.Nesbet.

J.Chem.Phys 22, 573 (1954).

[15]. P.C.Hariharan, W.A.Lathan and J.A.Pople.

Chem.Phys.Lett 14, 385 (1972).

[16]. M.M.Francl, W.J.Pietro, W.J.Hehre, J.S.Binkley, M.S.Gordon, D.J.DeFrees and J.A.Pople.

J.Chem.Phys 77, 3654 (1982).

[17]. W.J.Hehre, R.Ditchfield and J.A.Pople.

J.Chem.Phys 56, 2257 (1972).



- [18]. C.Moller and M.S.Plesset.  
Phys.Rev 46, 618 (1934).
- [19]. P.Piecuch, S.A.Kucharski, K.Kowalski and M.Musial.  
Comp.Phys.Commun 149, 71 (2002).
- [20]. P.Piecuch and M.Wloch.  
J.Chem.Phys 123, 224105-1 (2005).
- [21]. A.J.Taube and R.J.Bartlett.  
J.Chem.Phys 128, 044110 (2008).
- [22]. J.C.Slater.  
Phys.Rev 36, 57 (1930).
- [23]. S.F.Boys.  
Proc.Roy.Soc A200, 542 (1950).
- [24]. C.F.Melius and W.A.Goddard.  
Phys.Rev A10, 1528-1540 (1974).
- [25]. S.Huzinaga.  
Can.J.Chem 73, 619 (1995).
- [26]. W.J.Stevens, M.R.Krauss, H.Basch and P.G.Jasien.  
Can.J.Chem 70, 612 (1992).
- [27]. Y.Osanai, T.Noro, E.Miyoshi, M.Sekiya and T.Koga.  
J.Chem.Phys 120, 6408 (2004).
- [28]. T.H.Dunning Jr.  
J.Chem.Phys 90, 1007 (1989).

CHAPTER 2. ARGUMENTS AND ENERGETICS FOR THE Ir<sub>6</sub> CLUSTER

## Abstract

Catalysts aid in a significant lowering of the energy barriers associated with many reactions. Various studies show that cluster size has an effect on catalysis. While some studies claim that smaller clusters of atoms are better than larger clusters at enhancing reaction rates, other studies claim that catalytic activity increases as cluster size increases, and larger clusters do not degrade as easily as smaller clusters during the reaction. In the present work, previous studies which use cluster size as a gauge for catalytic activity are reported, and the choice to explore Ir<sub>6</sub> rather than Ir<sub>4</sub> as a potential catalyst was based on the findings from these previous studies. The findings on the Ir<sub>6</sub> minimum from the present work are compared with findings from previous theoretical studies. The results obtained from the calculations reported herein show that the C<sub>2</sub> isomer in the quintet state is the minimum energy structure when explicit electron correlation is not taken into account. The introduction of electron correlation stabilizes the singlet state of the cluster with respect to the triplet and quintet states, and the singlet triangular prism with D<sub>3h</sub> symmetry is found to be the minimum energy structure. The choice to explore the hydrogenation of ethylene to ethane on the singlet state of the Ir<sub>6</sub> cluster was based on the results obtained with correlated methods.

## 2.1. Introduction

The catalytic activity of supported metal clusters has been explored for many chemical processes. Iridium withstands extreme pressures and temperatures well. Small iridium clusters have been used by Gates et al.<sup>1</sup> and Tsyshevsky et al.<sup>2</sup> for hydrogenation reactions which are important in the petrochemical industry. Iridium clusters have also been used for the decomposition of hydrazine for rocket thruster applications in experiments by Anderson et al.<sup>3,4</sup>. In this chapter, the symmetries and multiplicities of Ir<sub>6</sub> are explored at various levels of theory, discussed below.

Chapter 2 is organized as follows. The reason for choosing Ir<sub>6</sub> over Ir<sub>4</sub> as a potential catalyst for hydrogenation of ethene to ethane is outlined. Kinetic arguments point to Ir<sub>4</sub> as the better choice, while thermodynamic arguments point to Ir<sub>6</sub>. The methods and basis sets pertaining to the bare iridium cluster will briefly be discussed. Then findings on energetics and spin states of the Ir<sub>6</sub> cluster from outside studies will be reported, and the energetics obtained from the calculations herein will be discussed.

## 2.2. Arguments for Ir<sub>4</sub> and Ir<sub>6</sub>

Kinetic arguments suggest that the rate for the hydrogenation reaction of ethylene to ethane is enhanced with smaller iridium clusters. X-ray absorption fine structure (XAFS) and IR spectroscopy experiments by Gates et al.<sup>1</sup> suggest that tetrahedral Ir<sub>4</sub> reacts with ethene more readily than octahedral Ir<sub>6</sub> does. It is suggested in reference 1 that the adsorbates interact more strongly with Ir<sub>4</sub> than Ir<sub>6</sub> upon an increase in H<sub>2</sub> pressure. However, other factors aside from the increase in H<sub>2</sub> pressure may be responsible for greater enhancement of the rate of ethylene hydrogenation to ethane with Ir<sub>4</sub> relative to Ir<sub>6</sub>. A study by Feng, Huang and Li employing restricted and unrestricted Hartree-Fock (HF)<sup>5</sup> also suggests that reaction rates are more strongly enhanced with tetrahedral Ir<sub>4</sub> than they are with octahedral Ir<sub>6</sub>. The suggestion in reference 5 for Ir<sub>4</sub> as the better catalyst is attributed to the smaller gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for Ir<sub>4</sub> than for Ir<sub>6</sub>. However, the claim that the difference between the HOMO and LUMO determines the quality of a catalyst is based on Huckel theory, discussed further in reference 6. When using Huckel theory, the total energy of a system is given by the sum of all of the orbital energies. Therefore, the electron repulsion and exchange included in the expression for the HF energy are not correctly taken into account when considering this argument. Since the calculations in reference 5 are performed with HF, the claim that a smaller energy gap results in improved catalytic activity is not valid. The claim that the HOMO-LUMO difference is a gauge for determining catalytic activity is not the

only faulty argument. One needs to take into account that Hessian calculations are not mentioned in reference 5. Therefore, it is not known whether any of the structures reported therein are minima on the potential energy surface. The background work claiming that larger clusters make for higher quality catalysts will be discussed next.

The experiments by the Anderson group motivated the exploration of Ir<sub>6</sub> as the catalyst model for hydrazine decomposition in the computational study by Schmidt and Gordon<sup>7</sup> and hydrocarbon reactions described in the present work. Sputtering experiments reported in references 3,4 and 8 show that cluster size is a gauge for determining catalytic activity, and larger clusters make for better catalysts. As reported by Anderson et al. in reference 3, activity increases about two fold per atom towards hydrazine decomposition for samples containing Ir<sub>5</sub>, Ir<sub>7</sub> and Ir<sub>10</sub>. Also reported by Anderson et al. in reference 4, there is no significant activity for hydrazine decomposition for clusters with less than seven iridium atoms, and catalytic activity increases as cluster size increases. Additionally, Aizawa, Lee and Anderson show in reference 8 that oxygen isotope exchange in carbon monoxide was observed for clusters with five or more iridium atoms. The computational study by Schmidt and Gordon employing HF optimizations and MP2 single point energies shows that deformation is more likely for the Ir<sub>4</sub>/alumina model than Ir<sub>6</sub>/alumina, and more coordination sites are available for hydrazine when considering Ir<sub>6</sub>. For the present work, the choice to explore Ir<sub>6</sub> as a potential catalyst rather than Ir<sub>4</sub> was based on the results from references 3,4,7,8. It is anticipated that the cluster frame will be better maintained during the hydrogenation

reaction of ethylene to ethane on Ir<sub>6</sub>. However, the hydrogenation reaction will need to be explored on Ir<sub>4</sub> as well as Ir<sub>6</sub> to determine which cluster is the better catalyst. Also considered was the smaller computational cost for Ir<sub>6</sub> than for larger clusters. The methods and basis sets used for the present work will be discussed next.

### 2.3. Methods and Basis Sets for Bare Ir<sub>6</sub>

All computations reported herein were performed with the General Atomic and Molecular Electronic Structure System (GAMESS) code<sup>9</sup>. The MacMolPlt graphics package<sup>10</sup> was used for all structure visualizations. Geometry optimizations on the singlet, triplet and quintet states of the D<sub>3h</sub>, C<sub>s</sub> and C<sub>2</sub> isomers of Ir<sub>6</sub> were performed. Restricted Hartree-Fock theory<sup>11</sup> was used for calculations on the structures in the singlet state, and Restricted Open Shell Hartree-Fock theory from Roothaan and Bagus<sup>12</sup> was used for the structures in the triplet and quintet states. After considering the relative energies of the HF-optimized geometries, HF Hessian calculations were performed on the D<sub>3h</sub> isomer in the singlet state, C<sub>s</sub> in the triplet state, and C<sub>2</sub> in the quintet state to confirm that the structures were minima. Second-order Moller-Plesset (MP2) theory<sup>13</sup> energies were obtained at the HF geometries for the singlet D<sub>3h</sub>, triplet C<sub>s</sub> and quintet C<sub>2</sub> structures after they had been confirmed as minima with the Hessians. The orbitals generated for the structures from the HF optimizations were used to obtain the MP2 energies to reduce computational cost and improve convergence of the HF iterations. The ECP/SBKJC basis set from Stevens et al.<sup>14</sup> was used for the HF optimizations and

Hessians as well as the MP2 energies on bare Ir<sub>6</sub>. Zero point energy corrections from the HF Hessians were added to all energies reported herein. The model core potential basis set of triple zeta quality from Osanai et al.<sup>15</sup> was not chosen for the calculations on bare Ir<sub>6</sub> since the SBKJC basis set is computationally less expensive than the MCP-TZP basis set. However, the MCP-TZP basis set from reference 15 was used to obtain more accurate energetics for iridium/hydrocarbon binding and will be discussed in more detail in Chapter 3. Next will come a discussion of the minima of Ir<sub>6</sub> reported by outside studies along with the findings of the Ir<sub>6</sub> minima reported for the present work.

#### 2.4. The Ir<sub>6</sub> Minima

A discussion of the findings for the Ir<sub>6</sub> minima from other studies will precede the discussion of the Ir<sub>6</sub> minima from the present work. Different arguments exist for which Ir<sub>6</sub> isomer is the minimum. Symmetry and multiplicity are taken into account. The bond lengths from UHF calculations in reference 5 were compared with experiments that used XAFS to claim that the minimum for Ir<sub>6</sub> is a distorted octahedron with D<sub>4h</sub> symmetry in the singlet state. A DFT/B3LYP study by Dixon and Chen<sup>16</sup> finds the minimum to be a distorted octahedron with D<sub>4h</sub> symmetry as the 15-tet instead of the singlet. In contrast, a DFT/BPW91 study by Du et al.<sup>17</sup> suggests the Ir<sub>6</sub> minimum to be a triangular prism with D<sub>3h</sub> symmetry in the singlet state. The study by Schmidt and Gordon<sup>7</sup> also finds the triangular prism in the singlet state as the minimum. However, the findings reported in reference 7 were based on restricted and restricted open-shell HF

optimizations followed by MP2 single point energy calculations.

The HF and MP2 methods were also employed in the present work. MP2 is an ab initio method and is therefore more reliable than the semi-empirical B3LYP<sup>18,19</sup> and BPW91<sup>18,20</sup> methods. In addition to the faulty arguments in reference 5 mentioned previously, the results from the current work are also more reliable than the results presented there due to the spin contamination that arises from UHF.<sup>21</sup> While higher spin states were explored in references 5, 16, 17, the general trend of the present work observed with MP2 single point energies show that the singlet is the lowest energy minimum and higher energies were obtained for the cluster in the triplet and quintet states. This trend led to the decision to ignore spin states beyond the quintet.

## 2.5. The Energetics of Bare Ir<sub>6</sub>

The isomers of the Ir<sub>6</sub> cluster and energetics at each level of theory are shown in Figure 1 and Table 1. The energies with zero point energy corrections added are shown in parentheses.



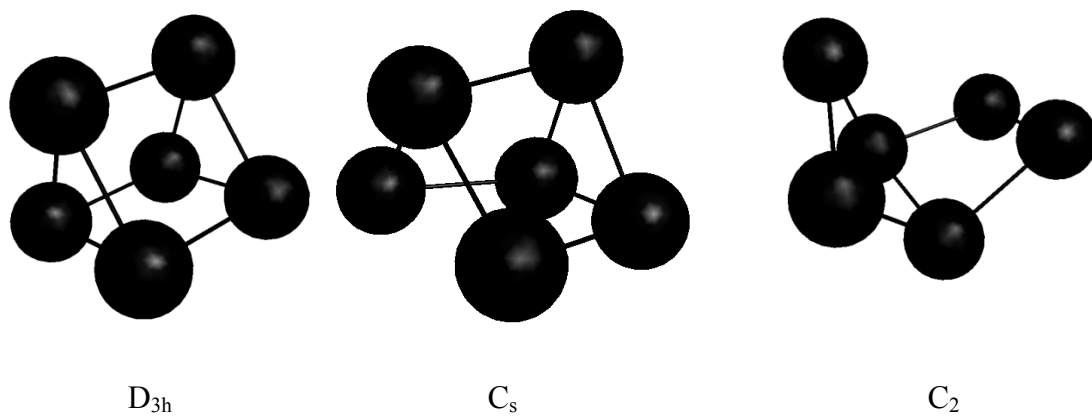


Figure 1. The  $D_{3h}$  isomer is on the far left with the label  $D_{3h}$ , the  $C_s$  isomer is in the middle with the label  $C_s$ , and the  $C_2$  isomer is on the far right with the label  $C_2$ .

Table 1. Spin states and relative energies of Ir<sub>6</sub> with zero-point energy corrections shown in parentheses (kcal/mol).

	Singlet	Triplet	Quintet
HF/SBKJC	0.0 (0.0)	-20.5 (-20.8)	-45.4 (-46.0)
MP2/SBKJC	0.0 (0.0)	52.7 (52.4)	101.1 (100.5)

In Figure 1 are the Ir<sub>6</sub> isomers in the singlet, triplet and quintet states. At the HF level, the singlet lies highest in energy. The C<sub>s</sub> triplet lies 20.8 kcal/mol below the singlet and the C<sub>2</sub> quintet lies 46.0 kcal/mol below the singlet. At the MP2 level of theory, the energies are reordered. The singlet is the lowest in energy, the triplet lies 52.4 kcal/mol above the singlet and the quintet lies 100.5 kcal/mol above the singlet.

The largest amount of energy due to correlation was recovered for the singlet with smaller amounts recovered for higher multiplicities. As the multiplicity increases, so does the number of electrons residing in different spatial orbitals with parallel spins. Described further by Slater in reference 22, the probability of finding electrons near each other decreases. Since the MP2 calculations show that the singlet is much lower in energy than the triplet and quintet, the interactions of the Ir<sub>6</sub> cluster with the hydrocarbons, discussed in the following chapter, will be considered only in the singlet state.

## 2.6. Conclusions

The choice to explore Ir<sub>6</sub> as a potential catalyst for the hydrogenation of ethylene to ethane was based on the observation that less distortion in the cluster frame occurred for Ir<sub>6</sub> than for Ir<sub>4</sub> for hydrazine decomposition<sup>7</sup>, as well as the observation that catalytic activity for hydrazine decomposition increased with increasing cluster size.<sup>3-4,8</sup> The introduction of electron correlation to the system with MP2 stabilized the singlet state of the Ir<sub>6</sub> cluster with respect to higher spin states, with the singlet lying 52.4 kcal/mol lower in energy than the triplet state and 100.5 kcal/mol lower in energy than the quintet state. The stabilization of the singlet state with respect to higher spin states motivated the choice to explore the hydrogenation of ethylene to ethane on Ir<sub>6</sub> in the singlet state. The binding of the substrates to the Ir<sub>6</sub> cluster and the mechanism of ethylene hydrogenation to ethane will be discussed further in Chapter 3.

## References

- [1]. A.M.Argo, J.F.Odzak and B.C.Gates.  
J.Am.Chem.Soc 125, 7107 (2003).
- [2]. R.V.Tsyshevsky, G.G.Garifzianova, I.V.Aristov, A.G.Shamov, and G.M.Khrapkovskii.  
Int.J.Quantum.Chem 111, 11, 2663 (2011).
- [3]. S.Lee, C.Fan, T.Wu and S.L. Anderson.  
J.Phys.Chem. B 109, 381 (2005).
- [4]. C.Fan, T.Wu, W.E.Kaden and S.L.Anderson.  
Surf.Sci 600, 461 (2006).
- [5]. J.Feng, X.Huang and Z.Li.  
Chem.Phys.Lett 206, 334 (1997).

- [6]. E.Huckel.  
Z.Phys 70, 204 (1931).
- [7]. M.W.Schmidt and M.S.Gordon.  
Z.Phys.Chem. In Press.
- [8]. M.Aizawa, S.Lee and S.L.Anderson.  
Surf.Sci 542, 253 (2003).
- [9]. A. M.W.Schmidt, K.K.Baldrige, J.A.Boatz, S.T. Elbert, M.S. Gordon, J.J.Jensen, S.Koseki, N.Matsunaga, K.A. Nguyen, S.Su, T.L.Windus, M.Dupuis, J.A.Montgomery.  
J.Comput.Chem. 14, 1347-1363 (1993).
- B. M.S.Gordon and M.W.Schmidt. in "Theory and Applications of Computational Chemistry, The First Forty Years." C. E. Dykstra, G.E.Frenking, K.S.Kim, G.E.Scuseria, (editors), Elsevier, Amsterdam, 2005.
- [10]. B.M.Bode and M.S.Gordon.  
J.Mol.Graphics Mod. 16, 133 (1998).
- [11]. C.C.J.Roothaan.  
Rev.Mod.Phys 23, 69 (1951).
- [12]. C.C.J. Roothan and Paul Bagus.  
in Methods of Computational Physics 2, 1963.
- [13]. C.Moller and M.S.Plesset.  
Phys.Rev 46, 618 (1934).
- [14]. W.J.Stevens, M.R.Krauss, H.Basch and P.G.Jasien.  
Can.J.Chem 70, 612 (1992).
- [15]. Y.Osanai, T.Noro, E.Miyoshi, M.Sekiya and T.Koga.  
J.Chem.Phys 120, 6408 (2004).
- [16]. M.Chen and D.A.Dixon.  
J.Phys.Chem. A, 117, 17, 3676 (2013).
- [17]. J.Du, X.Sun, J.Chen and G.Jiang.  
J.Phys.Chem. A 114, 12825 (2010).
- [18]. A.D.Becke.  
Phys.Rev. A38, 3098 (1988).

[19]. C.Lee, W.Yang and R.G.Parr.  
Phys.Rev. B37, 785 (1988).

[20]. J.P.Perdew and Y.Wang.  
Phys.Rev. B45, 13244 (1992).

[21]. J.A.Pople and R.K.Nesbet.  
J.Chem.Phys 2, 573 (1954).

[22]. J.C.Slater.  
Phys.Rev 81, 385 (1951).

## CHAPTER 3. HYDROCARBONS ON THE IRIDIUM CLUSTER

## Abstract

The demands to improve the quality and lower the cost of available fuel resources have been growing for quite some time, and those same demands continue to grow today. Gasoline prices and emissions of harmful substances into the environment are causes for concern. Hydrogenation and dehydrogenation reactions, with the help of catalysts, are two key processes involved in the production of fuels which are more friendly to health and pocket books. At each level of theory used in the present work, the thermodynamics were compared with the experimental  $\Delta E$  value, and the values obtained with correlated methods and larger basis sets agree well with experiment. The binding of the substrates to the cluster was also explored. Ethylene and  $H_2$  bind much more strongly to the cluster than ethane binds to the cluster. The mechanism of ethylene hydrogenation to ethane on the cluster is currently being investigated by addition of hydrogen to ethylene on  $Ir_6$ . The energetics of the gas phase mechanism of ethylene hydrogenation to ethane are reported in the present work and will be compared with the energetics of the mechanism on the cluster in future work.

## 3.1. Introduction

Hydrogenation and dehydrogenation reactions are important processes which are

involved in the production of high quality fuels. For example, hydrogenation of acetic acid to ethanol on a Pt-Sn catalyst was investigated by Zhang et al.<sup>1</sup> as a means for reducing toxin emissions to the environment. Wang, Froment and Goodman<sup>2</sup> investigated dehydrogenation of jet fuel as a means for hydrogen storage in low temperature fuel cells. In the present work, the hydrogenation of ethylene to ethane in the gas phase and on the Ir<sub>6</sub> cluster was investigated. Hydrocarbon cracking on iridium clusters is of interest to the petroleum industry<sup>3,4</sup>. Iridium is also important in catalyzing the decomposition of hydrazine for rocket thrusters<sup>5-8</sup>.

Very high energy transition states are associated with decompositions of hydrocarbons or hydrazine when a catalyst is not present. A study by Irle and Morokuma<sup>9</sup> employing DFT/B3LYP and the 6-31G(d) basis set for optimizations, followed by second-order Moller-Plesset (MP2) single point energies using the G2MS scheme<sup>9</sup>, found a barrier of 105.6 kcal/mol and 114.0 kcal/mol at the MP2/G2MS level for 1,1 and 1,2 H<sub>2</sub> eliminations from ethane in the gas phase, respectively. The addition of a catalyst can drastically decrease the heights of reaction barriers associated with hydrocarbon or hydrazine cracking. For example, the study in reference 5, employing HF optimizations with MP2 single point energies using the SBKJC/6-31G(d) basis, reports the marked decreases in transition state energies for hydrazine decomposition upon the addition of an iridium/alumina model. A study by Hall and Fan<sup>10</sup> employing a double  $\zeta$  quality basis set with DFT/B3LYP optimizations and MP2 single point energy calculations reports that much lower energy barriers are found for alkane

dehydrogenation with Pincer iridium complexes than are found for alkane dehydrogenation in the gas phase.

Many studies report reactions of substrates on supported metal clusters. In reference 3, the presence of a magnesium oxide support for tetrahedral Ir<sub>4</sub> resulted in less distortion of the cluster frame and more favorable reaction channels for ethylene hydrogenation. Studies by Chretien and Metiu employing DFT/BPW91 and pseudo potentials on gold clusters supported on titanium oxide<sup>11,12</sup> show that the support aids in catalytic activity by participating in various Lewis acid-Lewis base interactions. While the support is shown to boost catalytic activity, the work herein reports results of hydrocarbon reactions on unsupported Ir<sub>6</sub>. Comparing the barrier heights of the hydrogenation of ethylene on unsupported Ir<sub>6</sub> to the bare hydrogenation of ethylene is a reasonable step in beginning to evaluate the quality of Ir<sub>6</sub> as a catalyst. If significantly lower reaction barriers are found for ethylene hydrogenation on the cluster, then Ir<sub>6</sub> is deemed a high quality catalyst.

The rest of this chapter is organized into the following sections. First is an overview of the methods and basis sets used for calculations on the bare species and complexes. Then the results and analysis on the mechanism of ethylene hydrogenation to ethane in the gas phase are presented. Following the gas phase mechanism is an analysis of the binding of ethylene, hydrogen and ethane to the Ir<sub>6</sub> cluster using the methods discussed below. Then, there will be a discussion of the thermodynamics and mechanism



of ethylene hydrogenation on the Ir<sub>6</sub> cluster.

### 3.2. Methods and Basis Sets for Calculations

All computations were performed with the General Atomic and Molecular Electronic Structure System (GAMESS) package<sup>13</sup>. All structures were visualized with the MacMolPlt graphics package<sup>14</sup>. For the gas phase chemistry, optimizations, Hessians, transition state searches, and intrinsic reaction coordinate (IRC) runs were performed with Restricted Hartree-Fock theory<sup>15</sup>. The 6-31G(d) basis<sup>16-17</sup> was used for ethylene and ethane. Polarization d functions were added on the carbon p orbitals. After obtaining the minima and transition states associated with the hydrogenation mechanism using Hartree-Fock (HF) with the 6-31G(d) (HF/6-31G(d)) basis set, single point energies were obtained with correlated methods and larger basis sets for more accurate energetics. Single-point energy calculations on the minima and transition states were first obtained with second-order Moller-Plesset perturbation theory (MP2)<sup>18</sup>, along with the correlation consistent polarization triple  $\zeta$  valence (cc-pVTZ) basis set<sup>19</sup>. Single point energy calculations with the completely renormalized coupled cluster for singles, doubles and perturbative triples (CR-CC(2,3))<sup>20-21</sup> were performed with the cc-pVTZ basis set as well.

The same basis sets associated with the hydrocarbons in the gas phase were used for the hydrocarbons when placed on Ir<sub>6</sub>. HF was used for optimizations and Hessians on

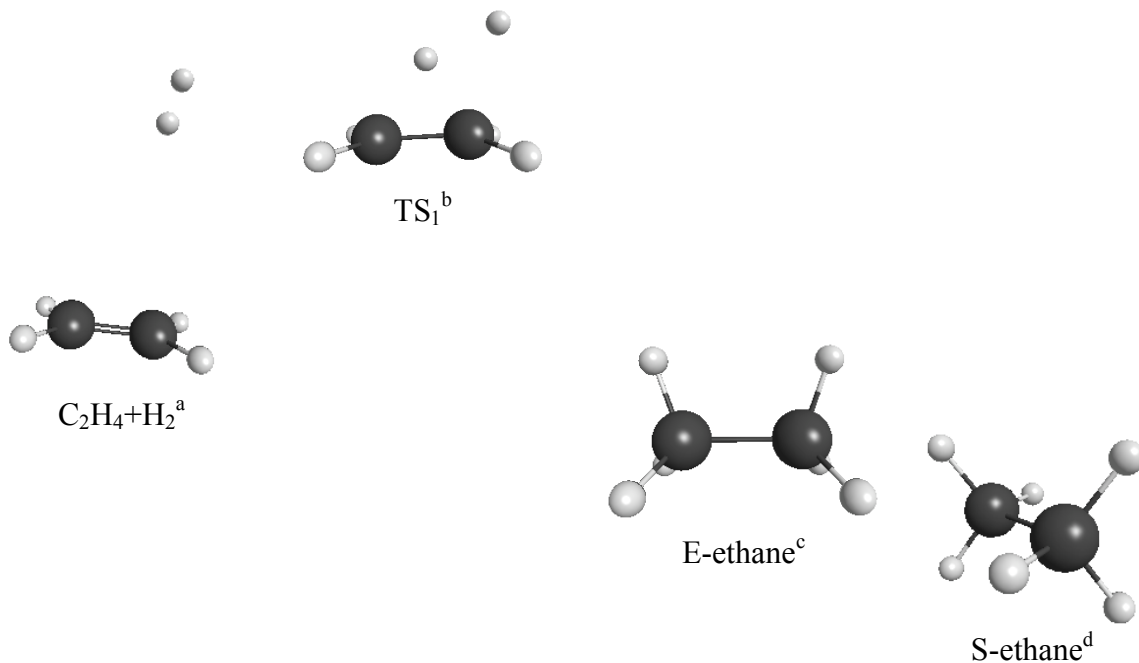
the hydrocarbon/iridium complexes, and single point energy calculations were performed using the HF optimized structures with MP2 and CR-CC(2,3). During HF optimizations, the effective core potential (ECP) and SBKJC basis set<sup>22</sup> were used for Ir<sub>6</sub>. This valence basis set is of comparable quality to the 6-31G basis set<sup>23</sup> for carbon and hydrogen. The model core potential basis of triple  $\zeta$  quality<sup>24</sup> is suited for Ir along with other fifth row d block elements and was used for Ir<sub>6</sub> during single-point energy runs with the correlated methods. Zero point energy corrections taken from the HF Hessians were added to all absolute energies at each level of theory. The electronic energies are listed in Tables 1-3 as well as the energies with added zero point energy (ZPE) corrections in parentheses. The energies with added ZPE corrections are used to compare with experiment and are referred to in the body of the text. In Table 1, the basis sets employed in the present work are represented by B1 and B2. The 6-31G(d)/6-31G basis is represented by B1, and the cc-pVTZ basis is represented by B2. In Tables 2 and 3, B3 represents the combined SBKJC/6-31G(d)/6-31G basis set and B4 represents the combined MCP-TZP/cc-pVTZ basis set. Now that the background information and methods have been outlined, the mechanism for the hydrogenation of ethylene to ethane in the gas phase will be discussed.

### 3.3. Gas Phase Mechanism of Ethylene Hydrogenation to Ethane

Hessian guesses at the HF level from reference 15 were performed to search for a species that contained one imaginary frequency. Then a transition state search was

performed to follow the imaginary mode until a set of coordinates was found with a zero gradient and that geometry is considered to be a saddle point. After the saddle point search had been completed, a second Hessian was performed to confirm that the said geometry was a saddle point with one imaginary frequency of  $2566 \text{ i cm}^{-1}$  ( $\text{TS}_1$ ). To show that this geometry was the transition state that leads to the desired reactants and products, an intrinsic reaction coordinate (IRC) calculation was performed. After the IRC calculation had completed, Hessians at the endpoints showed that the separated ethylene+ $\text{H}_2$  species was a minimum and eclipsed ethane (E-ethane) was a saddle point with an imaginary frequency of  $314.9 \text{ i cm}^{-1}$ . Rotation about the C-C bond to form the lower energy staggered ethane (S-ethane) requires reduction of symmetry to  $\text{D}_3$ . Eclipsed ethane can then be optimized to form staggered ethane. Single point energy calculations were performed with the  $\text{MP2}^{18}$  and  $\text{CR-CC}(2,3)^{20-21}$  methods. Figure 1 displays all of the stationary points described above, and Table 1 displays their relative energies.

Figure 1. Reaction path from intrinsic reaction coordinate with  $C_2H_4+H_2$ ,  $TS_1$ , E-ethane and S-ethane.



<sup>a</sup>Separated ethylene and  $H_2$

<sup>b</sup>Transition state

<sup>c</sup>Eclipsed ethane

<sup>d</sup>Staggered ethane

Table 1. Gas phase reaction path energies for  $C_2H_4+H_2$ ,  $TS_1$ , E-ethane and S-ethane at HF/B1, MP2/B2 and CR-CC(2,3)/B2 with ZPE corrections in parentheses, (kcal/mol).

	$C_2H_4+H_2^a$	$TS_1^b$	E-ethane <sup>c</sup>	S-ethane <sup>d</sup>
HF/B1 <sup>e</sup>	0(0)	106.4(107.1)	-40.7(-32.8)	-43.4(-35.3)
MP2/B2 <sup>f</sup>	0(0)	87.9(88.6)	-39.6(-31.7)	-41.2(-33.0)
CR-CC(2,3)/B2	0(0)	86.4(87.1)	-38.2(-30.3)	-39.8(-31.7)

<sup>a</sup>Separated ethylene and  $H_2$

<sup>b</sup>Transition state

<sup>c</sup>Eclipsed ethane

<sup>d</sup>Staggered ethane

<sup>e</sup>6-31G(d)/6-31G basis set

<sup>f</sup>cc-pVTZ basis set

Table 1 displays the relative energies of the reaction mechanism at the HF, MP2 and CR-CC(2,3) levels of theory, where the separated ethylene+H<sub>2</sub> is always the zero of the energy. TS<sub>1</sub> lies 107.1 kcal/mol higher in energy relative to separated ethylene and H<sub>2</sub> with HF. The energy of the barrier drops from 107.1 kcal/mol with HF to 88.6 kcal/mol with MP2 and 87.1 kcal/mol with CR-CC(2,3) due to the electron correlation energy that is recovered when using the MP2 and CR-CC(2,3) methods.

The mechanism described in the present work can be thought of as a 1,2 addition of H<sub>2</sub> to ethylene to produce ethane or a 1,2 elimination of H<sub>2</sub> from ethane to produce separated ethylene and H<sub>2</sub>. The energetics of the 1,2 elimination process were reported in reference 9 with DFT/B3LYP optimizations followed by MP2 single-point energy runs. The work therein reports the 1,2 elimination pathway as well as a 1,1 elimination pathway and shows that the 1,1 dehydrogenation is about 8 kcal/mol more favorable in energy than the 1,2 dehydrogenation. In the 1,1 elimination process, H<sub>2</sub> dissociates from one of the carbon atoms with ethylidene as the first transition state with an imaginary frequency of 59 i cm<sup>-1</sup>, and the second reported transition state is a 1,2 hydrogen transfer from the methyl carbon to the carbene carbon with an imaginary frequency of 923 i cm<sup>-1</sup>. For the present work, attempts to find these transition states were made using the coordinates provided by the authors as well as the DFT/B3LYPV1R functional<sup>25-26</sup>, but neither transition state reported in reference 9 was located. Therefore, the mechanism discussed here will be the 1,2 elimination of ethane to ethylene and hydrogen, the reverse of the 1,2 hydrogen addition to ethylene to produce ethane.

In the present work, separated ethylene and H<sub>2</sub>, TS<sub>1</sub> and eclipsed ethane are restricted to be in C<sub>s</sub> symmetry based on the rules relating to orbital symmetries discussed in the work of Woodward and Hoffmann<sup>27</sup>. H<sub>2</sub> approaches the π-bond of ethylene in a side-on manner and the H-H bond is aimed at one of the carbon atoms. The breaking of the H-H bond and the ethylene π-bond occurs along with the formation of C-H single bonds, and the molecule conforms to staggered ethane. Now that the mechanism in the gas phase has been outlined, the binding of the substrates to the cluster will be discussed as part of the ground work for outlining the thermodynamics and mechanism on Ir<sub>6</sub>.

#### 3.4. Binding of the Hydrocarbon Species to the Ir<sub>6</sub> Cluster

In order to understand the thermodynamics and the mechanism on Ir<sub>6</sub>, substrate binding to the cluster will be analyzed. The general expression for the binding energy of any of the substrates to the cluster to give a complex is given by

$$\text{Equation 1. } E_b = E_{\text{COM}} - \{E_{\text{Ir}_6} + E_{\text{ADS}}\}$$

$E_b$  is the energy for binding of the adsorbate to the cluster,  $E_{\text{COM}}$  is the energy for the complex,  $E_{\text{Ir}_6}$  is the energy of the bare Ir<sub>6</sub> cluster, and  $E_{\text{ADS}}$  is the energy of the free adsorbate. Figure 2 displays the geometries of the iridium/hydrocarbon complexes after

the optimizations were completed, and Table 2 displays the binding of ethylene, H<sub>2</sub> and ethane to the Ir<sub>6</sub> cluster.

Table 2. Binding Energies for Ir/ethylene-1, Ir/ethylene-2, Ir/H<sub>2</sub>-1, Ir/H<sub>2</sub>-2 and Ir/ethane at HF/B3, MP2/B4 and CR-CC(2,3)/B4 with ZPE corrections in parentheses (kcal/mol)<sup>a</sup>.

	Ir/ethylene-1 <sup>d</sup>	Ir/ethylene-2 <sup>d</sup>	Ir/H <sub>2</sub> -1 <sup>e</sup>	Ir/H <sub>2</sub> -2 <sup>e</sup>	Ir/ethane
HF/B3 <sup>b</sup>	-20.7(-19.5)	-17.3(-15.6)	-8.2(-5.5)	-6.6(-3.8)	-0.3(-0.2)
MP2/B4 <sup>c</sup>	-126.1(-124.5)	-126.5(-124.8)	-91.8(-89.1)	-94.4(-91.6)	-38.7(-38.6)
CR-CC(2,3)/B4 <sup>f</sup>	-127.4(-125.9)	-127.7(-126.0)	-107.3(-101.9)	-107.0(-101.5)	RUNNING

<sup>a</sup>For all complexes, Ir refers to Ir<sub>6</sub>

<sup>b</sup>Combined SBKJC/6-31G(d)/6-31G basis set

<sup>c</sup>Combined MCP-TZP/cc-pVTZ basis set

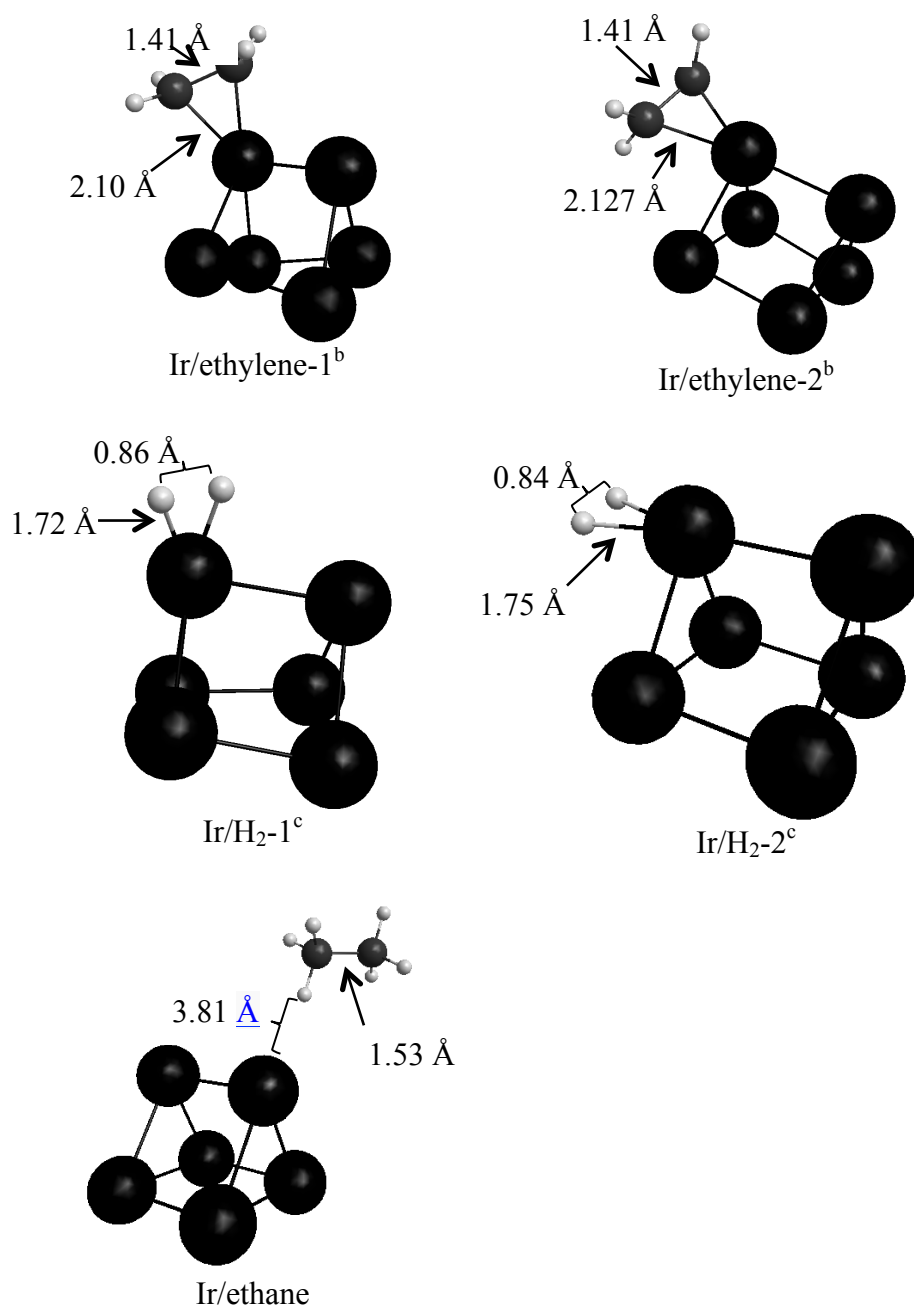
<sup>d</sup>Ir/ethylene-1 and Ir/ethylene-2 distinguish the two Ir/ethylene complexes.

<sup>e</sup>Ir/H<sub>2</sub>-1 and Ir/H<sub>2</sub>-2 distinguish the two Ir/H<sub>2</sub> complexes.

<sup>f</sup>CR-CC(2,3) single point energy calculation for Ir/ethane in progress



Figure 2. The HF Minima for Ir/ethylene-1, Ir/ethylene-2, Ir/H<sub>2</sub>-1, Ir/H<sub>2</sub>-2 and Ir/ethane in C<sub>1</sub> symmetry<sup>a</sup>.



<sup>a</sup>For each complex, Ir represents Ir<sub>6</sub>.

<sup>b</sup>Ir/ethylene-1 and Ir/ethylene-2 distinguish the optimized geometries found for the Ir/ethylene complexes

<sup>c</sup>Ir/H<sub>2</sub>-1 and Ir/H<sub>2</sub>-2 distinguish the optimized geometries found for the Ir/H<sub>2</sub> complexes.

Before all starting guesses, the xyztools package developed by Manrique<sup>28</sup> was employed to orient the adsorbates to surfaces of the cluster. Hessians were done on the optimized structures to confirm that they were minima on the potential energy surfaces. Nine starting guesses were considered for the Ir/ethylene complexes, but only two distinct structures were observed. In Ir/ethylene-1, the total Mulliken charge for the six iridium atoms is 0.07, and the total Mulliken charge for the six iridium atoms is 0.04 for Ir/ethylene-2. In both complexes, a small amount of charge was transferred from the cluster to ethylene. At all levels of theory employed in the present work, the cluster is more deformed from the binding of ethylene than from either H<sub>2</sub> or ethane to the cluster. The strong binding of ethylene to the cluster is due to the weakening of the  $\pi$ -bond. For all complexes discussed in the present work, calculations using the correlated methods result in much larger binding energies than those obtained using HF. This is in part because HF does not include dispersion as MP2 and CR-CC(2,3) do, and dispersion is likely to be important for the ethane complex. The binding of H<sub>2</sub> to the cluster will be discussed next.

Seven starting arrangements were considered when placing H<sub>2</sub> on iridium, but only two distinct structures were observed. The H-H distance is about 0.86 angstroms in Ir/H<sub>2</sub>-1 and about 0.84 angstroms in Ir/H<sub>2</sub>-2. The strong Ir/H<sub>2</sub> binding is due to the partial dissociation of H<sub>2</sub> onto the cluster. The total Mulliken charge for the six iridium atoms is -0.08 for Ir/H<sub>2</sub>-1 and -0.05 for Ir/H<sub>2</sub>-2. For each complex, a small amount of charge was transferred from H<sub>2</sub> to the cluster. The H atomic radius allows for H<sub>2</sub> to come

closer to the cluster than would be allowed for ethylene or ethane to come to the cluster.

Two starting arrangements were explored for ethane on iridium, one in which ethane was oriented to a diatomic site of Ir<sub>6</sub> and the other in which ethane was oriented to a triatomic site of Ir<sub>6</sub>. At the HF and MP2 levels of theory, ethane binds much more weakly to the cluster than does ethylene or H<sub>2</sub> to the cluster. No CR-CC(2,3) binding energies are reported for ethane on iridium with CR-CC(2,3) since the CR-CC(2,3) energy calculation is still in progress. Based on the relative binding observed with HF and MP2, it is assumed that ethane will also bind much more weakly than ethylene and H<sub>2</sub> at the CR-CC(2,3) level of theory. The cluster was not deformed after the optimizations completed, and the nearest Ir-H distance is about 3.8 angstroms. No charge was transferred between ethane and iridium in Ir/ethane. The single bond between the carbon atoms and bonding of each carbon with three other hydrogen atoms does not allow for ethane to move closer to the cluster. Now that the binding of ethylene, H<sub>2</sub> and ethane to the cluster has been analyzed, the thermodynamics of the reaction and the mechanism of ethylene hydrogenation on the cluster will be discussed next.

### 3.5. Thermodynamics and Mechanism of Ethylene Hydrogenation to Ethane on the Cluster

#### 3.5.1. Thermodynamics

The current subsection analyzes the thermodynamics of the hydrogenation reaction. The binding energies analyzed above are taken into account when considering  $\Delta E$ . The experimental  $\Delta E$  value was obtained from the National Institute of Standards and Technology in units of kcal/mol<sup>29</sup> and will be compared with the  $\Delta E$  values at each level of theory employed in the present work. The  $\Delta E$  value is given in Equation 2 as

Equation 2.  $\Delta E$

$$= \{E_{\text{Ir/ethane}} - E_{b1}\} - \{E_{\text{Ir/ethylene-1}} + E_{b2}\} - \{E_{\text{Ir/H}_2-1} + E_{b3}\} + E_{\text{Ir}}$$

Ir represents Ir<sub>6</sub>. Ir/ethylene-1, Ir/H<sub>2</sub>-1 and Ir/ethane denote the Ir/hydrocarbon complexes.  $E_{\text{Ir/ethane}}$  is the energy of the Ir/ethane complex,  $E_{b1}$  is the energy for binding of ethane to the cluster in Ir/ethane,  $E_{\text{Ir/ethylene-1}}$  is the energy of Ir/ethylene-1,  $E_{b2}$  is the energy for binding of ethylene to Ir in Ir/ethylene-1,  $E_{\text{Ir/H}_2-1}$  is the energy of Ir/H<sub>2</sub>-1, and  $E_{b3}$  is the energy for binding of H<sub>2</sub> to Ir in Ir/H<sub>2</sub>-1. Subtracting out the substrate-adsorbate binding energies implies desorbing the substrates from the cluster. Table 3 below displays the  $\Delta E$  values for ethylene hydrogenation.

Table 3.  $\Delta E$  Values for Hydrogenation of Ethylene to Ethane at HF/B3, MP2/B4 and CR-CC(2,3)/B4 with ZPE corrections in parentheses (kcal/mol).

HF/B3 <sup>a</sup>	MP2/B4 <sup>b</sup>	CR-CC(2,3)/B4 <sup>c</sup>	EXP <sup>d</sup>
-43.9(-34.9)	-41.6(-32.6)	RUNNING	-32.6

<sup>a</sup>Combined SBKJC/6-31G(d)/6-31G basis

<sup>b</sup>Combined MCP-TZP/cc-pVTZ basis.

<sup>c</sup>Experimental Value

<sup>d</sup>CR-CC(2,3) single point energy calculation for Ir/ethane in progress

As seen in Table 3, the HF/B3  $\Delta E$  value at -34.9 kcal/mol is in error by about 2 kcal/mol, while the MP2/B4 value agrees with experiment. The agreement of the MP2/B4  $\Delta E$  value to the experimental  $\Delta E$  value is due to a fortunate cancellation of errors that comes about when combining MP2 with a double or triple  $\zeta$  quality basis set, discussed further by Helgaker et al.<sup>30</sup>. The mechanism of hydrogenation of ethylene to ethane is considered on Ir<sub>6</sub>.

### 3.5.2. Mechanism on the Cluster

Showing that Ir<sub>6</sub> is a catalyst requires a significant lowering of the energy barrier in its presence. The mechanism for ethylene hydrogenation is being explored as an addition of H<sub>2</sub> to ethylene on the cluster. However, no information exists regarding a transition state for the hydrogenation reaction on Ir<sub>6</sub> since a transition states have not yet been identified. Therefore, a mechanism for the hydrogenation on the cluster is difficult to elucidate and will be reported in future work.

### 3.6. Conclusions

The computational results obtained herein show that correlated methods with larger basis sets give more accurate energetics for the thermodynamics of hydrogenation of ethylene to ethane than do uncorrelated methods, as well as the transition states found for the mechanism in the gas phase. The binding of the substrates to the cluster was explored as a means for beginning to understand the hydrogenation mechanism on Ir<sub>6</sub>. Correlated methods are more accurate, and therefore, much larger binding energies were obtained with MP2 and CR-CC(2,3) than with HF. The addition of hydrogen to ethylene on Ir<sub>6</sub> is currently being explored as a potential mechanism for hydrogenation of ethylene to ethane on the unsupported cluster. The next task at hand will be to gauge the catalyst quality of Ir<sub>6</sub> by comparing the energetics of the hydrogenation mechanism on unsupported Ir<sub>6</sub> to the energetics found for the mechanism in the gas phase at the same levels of theory and basis sets used in the present work. Future work will involve investigation of the interactions of Ir<sub>6</sub> with various supports and the hydrogenation mechanism on supported Ir<sub>6</sub>.

### References

- [1]. S.Zhang, X.Duan, L.Ye, H.Lin, Z.Xie. Catalysis today. In Press.
- [2]. B.Wang, G.F.Froment and D.W.Goodman. J.Catal 253, 239 (2008).
- [3]. R.V.Tsyshevsky, G.G.Garifzianova, I.V.Aristov, A.G.Shamov, and G.M.Khrapkovskii. Int.J.Quantum.Chem 111, 11, 2663 (2011).

- [4]. A.W. Chester.  
Process for Cracking Hydrocarbons US 4107032 A.  
Published August 15, 1978.  
Accessed May 18, 2013.  
{<http://www.google.com/patents/US4107032>}.
- [5]. M.W.Schmidt and M.S.Gordon.  
Z.Phys.Chem. In press.
- [6]. S.Lee, C.Fan, T.Wu and S.L.Anderson.  
J.Phys.Chem.B 109, 381 (2005).
- [7]. C.Fan, T.Wu, W.E.Kaden and S.L.Anderson.  
Surf.Sci 600, 461 (2006).
- [8]. O.I.Smith and W.C.Solomon.  
Ind.Eng.Chem.Fundam 21, 374 (1982).
- [9]. S.Irle and K.Morokuma.  
J.Chem.Phys 113, 6139 (2000).
- [10]. M.B.Hall and H.Fan.  
Adv.Inorg.Chem 54, 321 (2003).
- [11]. S.Chretien and H.Metiu.  
J.Chem.Phys 128 (4), 044714 (2008).
- [12]. S.Chretien and H.Metiu.  
J.Chem.Phys 127 (8), 084704 (2007).
- [13]. A. M.W.Schmidt, K.K.Baldrige, J.A.Boatz, S.T. Elbert, M.S. Gordon, J.J.Jensen, S.Koseki, N.Matsunaga, K.A. Nguyen, S.Su, T.L.Windus, M.Dupuis, J.A.Montgomery.  
J.Comput.Chem. 14, 1347-1363 (1993).
- B. M.S.Gordon and M.W.Schmidt. in "Theory and Applications of Computational Chemistry, The First Forty Years." C. E. Dykstra, G.E.Frenking, K.S.Kim, G.E.Scuseria, (editors), Elsevier, Amsterdam, 2005.
- [14]. B.M.Bode and M.S.Gordon.  
J.Mol.Graphics Mod. 16, 133 (1998).
- [15]. C.C.J.Roothan.  
Rev. Mod. Phys. 23, 69 (1951).

- [16]. P.C.Hariharan, W.A.Lathan and J.A.Pople.  
Chem. Phys. Lett 14, 385 (1972).
- [17]. M.M. Francl, W. J. Pietro, W.J. Hehre, J.S. Binkley, M. S. Gordon, D. J. DeFrees  
and J. A. Pople.  
J.Chem.Phys 77, 3654 (1982).
- [18]. C.Moller and M.S.Plesset.  
Phys.Rev 46, 618 (1934).
- [19]. T.H.Dunning Jr.  
J.Chem.PHys 90, 1007 (1989).
- [20]. P.Piecuch, S.A. Kucharski, K.Kowalski and M.Musial.  
Comp. Phys. Commun 149, 71 (2002).
- [21]. P.Piecuch and M.Wloch.  
J.Chem.Phys 123, 224105-1 (2005).
- [22]. W.J.Stevens, M.R.Krauss, H.Basch and P.G.Jasien.  
Can.J.Chem 70, 612 (1992).
- [23]. W.J.Hehre, R.Ditchfield and J.A.Pople.  
J.Chem.Phys 56, 2257 (1972).
- [24]. Y.Osanai, T.Noro, E.Miyoshi, M.Sekiya and T.Koga.  
J.Chem.Phys 120, 6408 (2004).
- [25]. A. D. Becke.  
Phys. Rev. A38, 3098 (1983).
- [26]. C.Lee, W.Yang and R.G.Parr.  
Phys.Rev. B37, 785 (1988).
- [27]. R.B.Woodward and R.Hoffmann.  
Angew.Chem. International Edition in English. 8, 11, 781 (1969).
- [28]. David Zsolt Manrique.  
Guide to xyztools 0.9B.  
May 2010.  
Accessed June 27, 2013.  
{<http://code.google.com/p/xyztools/>}.



- [29]. National Institute of Standards and Technology.  
Accessed July 10, 2013.  
{<http://webbook.nist.gov/cgi/cbook.cgi?ID=C1333740%2BC74851%3DC74840&IDType=Reac&Units=CAL&Mask=8#Thermo-React>}.
- [30]. T.Helgaker, J.Gauss, P.Jorgensen and J.Olsen.  
J.Chem.Phys 106, 6430 (1997).

## CHAPTER 4. CONCLUSIONS

This chapter gives a brief synopsis of the results obtained from the calculations, as well as the work that has yet to be done. While some studies suggest that smaller clusters are more likely to enhance reaction rates, the Ir<sub>6</sub> cluster was chosen over the Ir<sub>4</sub> cluster as the species on which to explore the hydrogenation of ethylene to ethane for the present study. The reason for choosing to explore the hydrogenation reaction on Ir<sub>6</sub> rather than Ir<sub>4</sub> was based on experimental studies which showed that catalytic activity increases with cluster size, as well as theoretical studies which showed that the cluster frame was better maintained with Ir<sub>6</sub> than with Ir<sub>4</sub>. Since it is anticipated that Ir<sub>6</sub> will be the better catalyst, the present work focused solely on Ir<sub>6</sub> as a potential catalyst for the hydrogenation mechanism. In future work, the relative energies found for the mechanism of ethylene hydrogenation on Ir<sub>4</sub> will be compared with the relative energies of the mechanism for the reaction on Ir<sub>6</sub>.

While previous computational studies claim that the Ir<sub>6</sub> lowest energy structure exists in higher spin states than the singlet, the present calculations show that the singlet state is stabilized with respect to the triplet and quintet states when correlated methods are employed. The stabilization of the singlet state with respect to higher spin states motivated the choice to explore the interactions of the hydrocarbons on Ir<sub>6</sub> solely in the singlet state.

The thermodynamics obtained for the reaction at each level of theory were compared with experiment. A fortunate cancellation of errors results in agreement of the  $\Delta E$  value obtained with correlated methods to the experimental  $\Delta E$  value. The binding of ethylene,  $H_2$  and ethane to the cluster was analyzed. In all cases, the binding of ethane to the cluster became much stronger at higher levels of theory due to the inclusion of dispersion in the calculations.

The mechanism for ethylene hydrogenation to ethane is being explored as an addition of hydrogen to ethylene on the cluster. Since a transition state has not yet been identified, the mechanism for ethylene hydrogenation on the cluster has not yet been determined and is a work in progress. After having elucidated the mechanism for the hydrogenation of ethylene to ethane on unsupported  $Ir_6$ , determining the substrate binding and mechanism on supported  $Ir_6$  will be the next set of tasks at hand.