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A Density Functional Study of the Relative Stability of Intermediates in a McMurry Coupling Reaction

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A Density Functional Study of the Relative Stability of Intermediates in a McMurry Coupling Reaction

Abstract

Reductive cyclization via McMurry coupling is a common way to form pyrrolizidine rings. In this work we investigate the titanium-catalyzed McMurry coupling reaction leading to a pyrrolizidine alkaloid using density functional methods. Specifically, we compare the relative energies of all possible pinacolate intermediates at the UB3LYP/6-31G level of theory. The most stable intermediate is found to be the one resulting from C-O bond insertion in the ester group. The McMurry product is not predicted to form.

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A DENSITY FUNCTIONAL STUDY OF THE RELATIVE STABILITY OF
INTERMEDIATES IN A MCMURRY COUPLING REACTION

By

Andrew Jozef Livingston

A Senior Thesis Submitted to the

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Honors College

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with Honors in Chemistry

Approved at Ypsilanti, Michigan, on this date _____

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1. Abstract

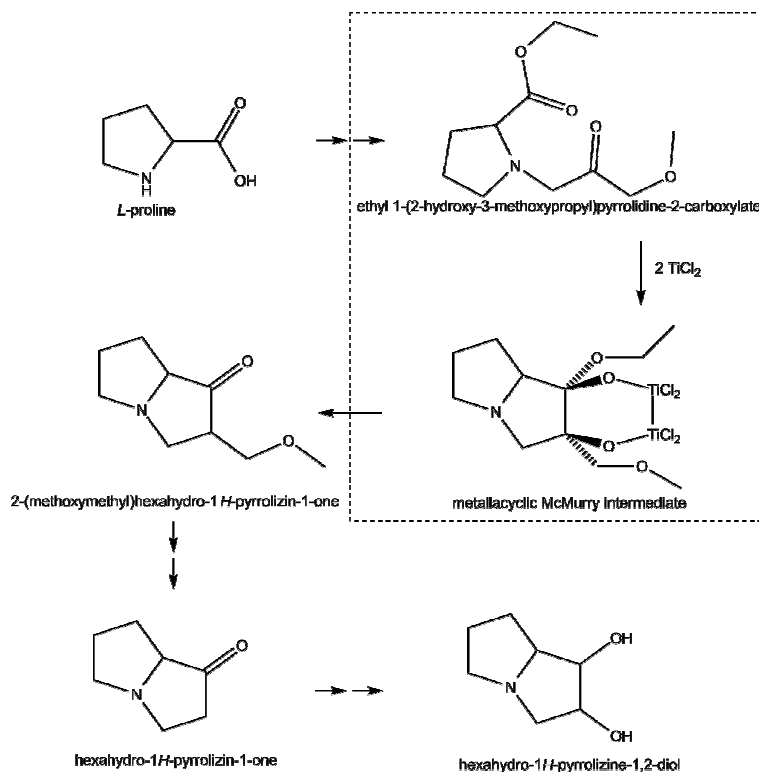
Reductive cyclization via McMurry coupling is a common way to form pyrrolizidine rings. In this work we investigate the titanium-catalyzed McMurry coupling reaction leading to a pyrrolizidine alkaloid using density functional methods. Specifically, we compare the relative energies of all possible pinacolate intermediates at the UB3LYP/6-31G level of theory. The most stable intermediate is found to be the one resulting from C-O bond insertion in the ester group. The McMurry product is not predicted to form.

2. Introduction

Scheme 1 shows a recent proposed synthesis of a pyrrolizidine alkaloid precursor from the readily available natural amino acid derivative L-proline that includes a McMurry cyclization step.^[1] Pyrrolizidine alkaloids (PAs) are a class of sugar mimics, molecules that share structural properties with sugars, that are found in some members of the Asteracea, Boraginaceae, and Fabaceae families of plants.^[2] PAs interest biochemists because certain sugar mimics inhibit glucose-metabolizing enzymes. For example, the synthetic derivative of a sugar mimic of the piperidine class (these have a secondary amine in place of an ether in the hemi-acetal ring) has been developed to treat diabetes.^[3] Although some PAs have medicinal potential, this class of sugar mimic often breaks down to more toxic compounds during biological metabolism, causing toxic responses in humans and animals.^[2] Mulberry trees use two piperidine sugar mimics to

kill herbivorous insects by disrupting their metabolic processes.^[4] Toxicologists and other chemists researching these compounds desire the ability to make new PAs in order to better understand how a sugar mimic's structure determines its biological properties. The polyhydroxylated PA that is the target in the multi-step reaction shown in Scheme 1 belongs to a class of compounds that have been shown to serve an ecological function in plant-insect relationships as well as being studied for their therapeutic potential as anticancer and antiviral agents.^[5] Because of this potent biological activity and because of the opportunity for stereochemical variation within the bicyclic framework, PA compounds have emerged as attractive targets for the development of new synthetic methodology.^[6] Scheme 1 depicts the synthetic strategy employed by Dr. Lindsay and her group at Eastern Michigan University to produce polyhydroxylated pyrrolizidine alkaloids with controlled stereochemistry.

Scheme 1



The portion of the overall synthesis that is of interest in this work is the boxed step in Scheme 1: the McMurry reaction between the keto-ester ligand and titanium(II) chloride to produce an enol ether which is converted by acid into the corresponding cyclanone in a later step.^[7] The keto-ester ligand in Scheme 1 is ethyl 1-(3-methoxy-2-oxopropyl)pyrrolidine-2-carboxylate and the cyclanone product is 2-(methoxymethyl)hexahydro-1H-pyrrolizin-1-one. When the Lindsay group attempted the reaction it yielded a mixture of products that proved difficult to characterize. The present work describes a theoretical analysis of the cyclization reaction aimed at determining the most energetically favorable pathway for the reaction between the keto-

ester ligand in Scheme 1 and titanium chloride. The goal is to delineate the preferred reaction pathway and suggest modifications to the synthesis that would improve the results. Specifically, we will focus on the intermediate of the McMurry reaction step since the subsequent deoxygenation reaction has been shown to be the rate-determining step.^[8]

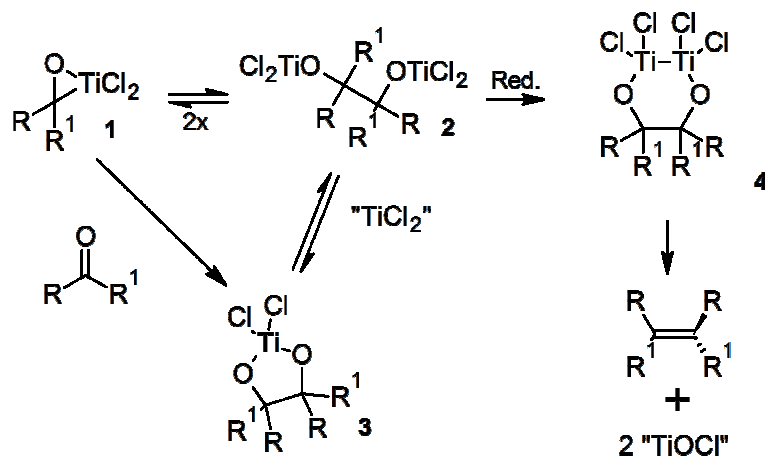
McMurry was among the scientists who, in 1983, discovered that low-valent titanium species reduce aldehydes or ketones, forming a new bond between the carbonyl carbons in the process (referred to as coupling). Intramolecular McMurry reactions in particular have become a staple of organic synthesis because they are an efficient method of generating medium-to-large sized cycloalkanes and cycloalkenes. However, not all ketones or aldehydes are suitable for reductive coupling. A carbonyl's reactivity depends on its associated functional groups and chemical environment. Usually the ability to control stereochemistry makes a reaction more useful to the synthetic chemist, but the selectivity of the McMurry reaction is not always predictable, in part because the mechanism is not fully understood.^[7] A mechanistic interpretation of low-valent titanium-mediated reductive coupling reactions such as the McMurry reaction is difficult because Ti reagents are usually generated in situ and present in heterogeneous phase, hence their oxidation state and structure are often only vaguely characterized.^[9]

The ligand of interest here represents a challenging case because of its multiple functional groups and the pronounced affinity of low-valent titanium for oxygen. For this reason, there have been few reports to date of cyclizations involving two functional groups where a third one has remain unaffected.^[10] Of particular interest to us is the nature of the possible conformations of the McMurry intermediate through which the

cyclization proceeds. Unfortunately, while several types of intermediates have been postulated, none have been characterized experimentally and the energetics of the reaction pathway are not known. The mechanistic information currently available does not support the presence of radicals as intermediates. While titanium carbenes cannot be rigorously excluded, the available information points to dianions as the reactive intermediates.^[10]

Previous theoretical work has shed some light on the nature of the intermediate species. In 1997 Frenking modeled the McMurry coupling reaction between two molecules of formaldehyde by comparing the two pathways shown in Scheme 2.^[12]

Scheme 2



This mechanism had been proposed by Furstner and Bogdanovic, and was supported by the results of the calculations. Most importantly, Frenking found that the side-on coordinated carbonyl complex (1 in Scheme 2) goes on to form the Ti(IV) pinacol complex 3 preferentially to the Ti(III) pinacol complex 2.^[7] Further

reduction leads to the Ti(II) species **4**, in which two TiCl₂ moieties are arranged in a dimer with a weak Ti-Ti bond. We use such a dimer as a starting point for the possible intermediates in our model system.

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3. Theoretical Background^[1]

3.1 *The Schrödinger Equation*

Erwin Schrödinger's wave mechanics was the first widely-accepted theory describing the physics of the subatomic world. Because of the general ignorance of linear algebra among physicists of the early twentieth century, it came to dominate Heisenberg's matrix mechanics as the preferred formulation of quantum mechanics, and is an extension of operator theory to the theory of atomic structure. It is a little-known fact that Schrödinger discovered his famous equation in its time-independent form of, the form the equation most commonly used by computational chemists, rather than the time-dependent form. We may easily derive it from the time-independent classical wave equation for a particle in 3-space:

$$\nabla^2 f(\mathbf{r}) + \frac{\omega^2}{v^2} f(\mathbf{r}) = 0. \quad (1.1)$$

where $f(\mathbf{r})$ is the function describing the amplitude of the wave for the position vector \mathbf{r} , ω is the angular frequency of the wave, and v is the speed of propagation of the wave.

Now we consider the nonrelativistic expression for the momentum vector \mathbf{p} (in Cartesian coordinates) for a particle of mass m moving in an external force field:

$$\mathbf{p} = \{2m[U - V(\mathbf{r})]\}^{1/2}. \quad (1.2)$$

where U is the particle's total energy and $V(\mathbf{r})$ is the particle's potential energy as a function of its position vector \mathbf{r} (in Cartesian coordinates) in the external field. We can

use (1.2) and the de Broglie relation $\lambda = h/\mathbf{p}$, where λ is the wavelength and h is Planck's constant, to create an expression for the wavelength of the particle:

$$\lambda = \frac{h}{\mathbf{p}} = \frac{h}{\{2m[U - V(\mathbf{r})]\}^{1/2}}. \quad (1.3)$$

We recall that $\omega = 2\pi f$ and $v = \lambda f$ and write:

$$\frac{\omega^2}{v^2} = \frac{4\pi^2}{\lambda^2} = \frac{2m}{\hbar^2}[U - V(\mathbf{r})]. \quad (1.4)$$

where \hbar is the reduced Planck constant $h/2\pi$. Inserting (1.4) into (1.1) we get the wave equation for a matter wave in 3-space:

$$\nabla^2 f(\mathbf{r}) + \frac{2m}{\hbar^2}[U - V(\mathbf{r})]f(\mathbf{r}) = 0. \quad (1.5)$$

This equation is usually written as:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = U\psi(\mathbf{r}). \quad (1.6)$$

with $\psi(\mathbf{r})$ replacing $f(\mathbf{r})$ to denote that ψ is specifically the wave function of a matter wave. Looking carefully at (1.6), we can spot that ψ is an eigenfunction, U is an eigenvalue, and the operator that acts on ψ to produce U is:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V. \quad (1.7)$$

The operator \hat{H} is called the Hamiltonian, representing the total energy of the matter wave. Using operator notation we can write (1.6) succinctly as:

$$\hat{H}\psi = U\psi. \quad (1.8)$$

We now turn to the molecular Hamiltonian, which operates on a wave function of an interacting system of N nuclei and n electrons:

$$\begin{aligned} \hat{H}(1 \dots N; 1 \dots n) &= -\frac{\hbar^2}{2} \left(\sum_A^N \frac{1}{M_A} \nabla_A^2 + \frac{1}{m_e} \sum_i^n \nabla_i^2 \right) - \sum_A^N \sum_i^n \frac{e^2 Z_A}{r_{iA}} \\ &+ \sum_j^n \sum_{i>j}^n \frac{e^2}{r_{ij}} + \sum_A^N \sum_{B>A}^N \frac{e^2 Z_A Z_B}{r_{AB}}. \end{aligned} \quad (1.9)$$

The newly introduced or redefined symbols are:

A, B, \dots, N	Nucleus A, B, \dots to nucleus N
Z_A	Atomic number of nucleus A
M_A	Mass of nucleus A
i, j, \dots, n	Electron i, j, \dots to electron n
m_e	Mass of electron: 9.109×10^{-31} kg
e	Charge of electron: 1 eV or 1.602×10^{-19} C
r	Distance between two particles (identified in subscript)

The first term, in parentheses, represents the total kinetic energy of all nuclei and electrons in the molecule. The second represents electron-nuclear electrostatic interaction for all n electrons and N nuclei, and the third the electrostatic electron-electron interaction term for all n electrons. The last term represents nuclear-nuclear electrical interaction for all N nuclei. In the future we will represent it with the notation V_{NN} . This is commonly done because V_{NN} represents the internuclear repulsion energy and is a constant for a given set of fixed atomic coordinates.

3.2 *The Born-Oppenheimer approximation*

The molecular Hamiltonian, (1.9), while complete, is cumbersome to use in calculations. We can simplify it with an efficient approximation that has little impact on the accuracy of our results.

Nuclei, because of their much higher mass, have much lower velocities than electrons. From the perspective of electrons, nuclei move relative to each other at such a slow pace that they may be regarded as standing still—just as, from the perspective of humans, continental drift occurs at such a slow pace that we regard continents as being largely static. In the Born-Oppenheimer approximation we assume that nuclei are in fact stationary and the nuclear momentum operator in the first term of (1.9) is zero.^[2] This leads to the Born-Oppenheimer Hamiltonian.

$$\hat{H}(1 \dots N: 1 \dots n) \cong -\frac{\hbar^2}{2m_e} \sum_i^n \nabla_i^2 - \sum_A^N \sum_i^n \frac{e^2 Z_A}{r_{iA}} + \sum_j^n \sum_{i>j}^n \frac{e^2}{r_{ij}} + V_{NN} \quad (2.1)$$

We recall that V_{NN} is a constant and can be calculated separately. The remainder of (2.1) is called the electronic Hamiltonian,

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i^n \nabla_i^2 - \sum_A^N \sum_i^n \frac{e^2 Z_A}{r_{iA}} + \sum_j^n \sum_{i>j}^n \frac{e^2}{r_{ij}}, \quad (2.2)$$

which operates on the electronic portion of the wave function, ψ_{el} .

$$\hat{H}_{el}\psi_{el} = E\psi_{el} \quad (2.3)$$

(2.3) is the electronic version of (1.8), where E is the electronic contribution to the molecular energy U . Since (2.3) is the form of the equation most relevant to molecular systems, for the rest of the text ψ and \hat{H} will refer to ψ_{el} and \hat{H}_{el} in (2.3).

Note that the molecular energy, U , is simply the sum of E and V_{NN} . Therefore,

$$(\hat{H} + V_{NN})\psi = (E + V_{NN})\psi = U\psi, \quad (2.4)$$

where ψ and \hat{H} are the electronic wave function and electronic Hamiltonian.

3.3 Inseparability and the Variation Principle

There is a rather nasty bogey man still lurking in (1.9) through (2.4). It is the electron-electron interaction term, which we'll denote ϵ_R , characterizing the repulsion between electrons:

$$\varepsilon_R = \sum_j^n \sum_{i>j}^n \frac{e^2}{r_{ij}}. \quad (3.1)$$

The problem with ε_R is that it makes the Schrödinger equation (a partial differential equation) inseparable for multi-electron systems. Presently there is no way to find exact solutions for the multi-electron Schrödinger equation. This is such a serious problem that much of the remainder of the Theoretical Background section will discuss various ways the brightest minds in physics and chemistry have tried to work around it using approximations and, in the case of Density Functional Theory, entirely different approaches to characterizing multi-electron systems.

Despite our inability to solve the multi-electron Schrödinger equation, there is a very useful property relating our approximate solution to the true eigenvalue. Commonly denoted as E_0 , the unknown exact solution represents the true energy of the system, The expectation value for the energy calculated using any approximation, commonly denoted $\langle E \rangle$, is an upper bound on E_0 . This is called the variation principle:

$$\langle E \rangle = \int \varphi^* \hat{H} \varphi d\tau \geq E_0. \quad (3.2)$$

In (3.2) φ is any well-behaved, normalized function, referred to as the trial function, which satisfies the boundary conditions of the integral and φ^* is the complex conjugate of φ . The most important consequence of (3.2) is that we can operate on different trial functions with our Hamiltonian, \hat{H} , and be assured that the one giving the lowest value of $\langle E \rangle$ is the best approximation to the true wave function, ψ . Note that if we plug enough

trial functions into (3.2), we may find the true wave function, such that $\varphi = \psi$ and $\langle E \rangle = E_0$. Of course, since we cannot solve the multi-electron Schrödinger equation analytically, we will never know what an amazing discovery we have made! For the same reason we know how much greater our lowest $\langle E \rangle$ is than E_0 and therefore how close an approximation our best φ is to ψ .

Luckily, it has been shown that $\langle E \rangle$ approaches E_0 much faster than φ approaches ψ .^[1] Therefore we need not spend an excessive amount of time searching for a good approximation to φ in order to obtain a good approximation to $\langle E \rangle$.

The variation principle is so named because in practice we choose a φ with a large number of parameters which we then vary in order to reduce our calculated value of $\langle E \rangle$.

3.4 The LCAO Approximation

The Linear Combination of Atomic Orbitals (LCAO) approximation of Molecular Orbitals (MOs), sidesteps some of the difficulty in finding appropriate trial wavefunctions φ by assuming that it takes the form shown in (4.1).

$$\phi_j = \sum_{i=1}^n c_{ij} \chi_i \quad (4.1)$$

Here each electron in a multi-electron system is assumed to occupy a volume of space spanning the entire system which is referred to as a molecular orbital (MO). Each MO function takes its shape from a linear combination of single-electron, or hydrogenic, atomic orbitals. In (4.1) ϕ_j is the j th molecular orbital, $1 \dots i \dots n$ are the 1st, i th, and last or n th atomic orbital, and χ_i is a function describing the i th atomic orbital. The coefficient c_{ij} weights the contribution of the i th atomic orbital to the j th molecular orbital. The advantage of the LCAO-MO approximation is that it defines the form of the trial wavefunction in a way that is physically meaningful: electrons in molecules occupy molecular orbitals that arise from atomic orbitals.

3.5 Basis Sets

The functions χ_i comprise what is known as a basis set. The most common form of function used for basis sets in computational chemistry is the primitive Gaussian function (PGF).^[1] In polar coordinates they have the general form:

$$G_{nlm} = N_n r^{n-1} \exp(-\alpha r^2) Y_l^m(\theta, \phi). \quad (5.1)$$

In this physical interpretation, n is the principal quantum number, which determines an orbital's radial distance (r) of maximum amplitude from a nucleus. The simple radial function $r^{n-1} \exp(-\alpha r^2)$ specifies an orbital's size and, with the parameter α , its diffuseness. The letter l represents the angular momentum or azimuthal quantum

number, which determines an orbital's shape; m is the magnetic quantum number, which determines an orbital's orientation relative to other orbitals with the same n and l . N_n is a normalization constant which forces the PGF to satisfy the constraint that the overall probability of finding an electron *somewhere* in space is unity:

$$\int_{-\infty}^{\infty} G^* G dr = 1. \quad (5.2)$$

PGFs can be linearly combined into contracted Gaussian functions (CGFs) to fit more complex curves that better represent hydrogenic functions. CGFs have the form of (4.1) with the χ_i being a set of PGFs. Since modern computers can integrate PGFs quickly, a basis set of CGFs made from multiple PGFs is often more convenient to use than a basis set where the χ_i more closely resemble hydrogenic atomic orbitals. In the present work we will use three types of CGF basis sets: the 3-21G basis, the 6-31G basis, and the LanL2DZ basis (see section 4).

The simplest of the three is the 3-21G basis set.^[3] It follows a common naming scheme for Gaussian basis sets in which the first integer is the number of PGFs used in the CGF modeling the core orbitals (which do not engage in bonding) of an atom. Each integer following the hyphen represents a valence orbital CGF and its value is the number of PGFs used to create the CGF. The “G” at the end of the name indicates that the basis set is based on Gaussian functions. Therefore we know from the name that the 3-21G basis set is comprised of functions of Gaussian type, with three-PGF CGF modeling the core orbitals, one two-PGF CGF modeling a portion of the valence orbitals, and an additional PGF modeling the remainder. Because the valence orbitals are modeled with

more than one CGF, this type of basis set is called a split-valence basis set.

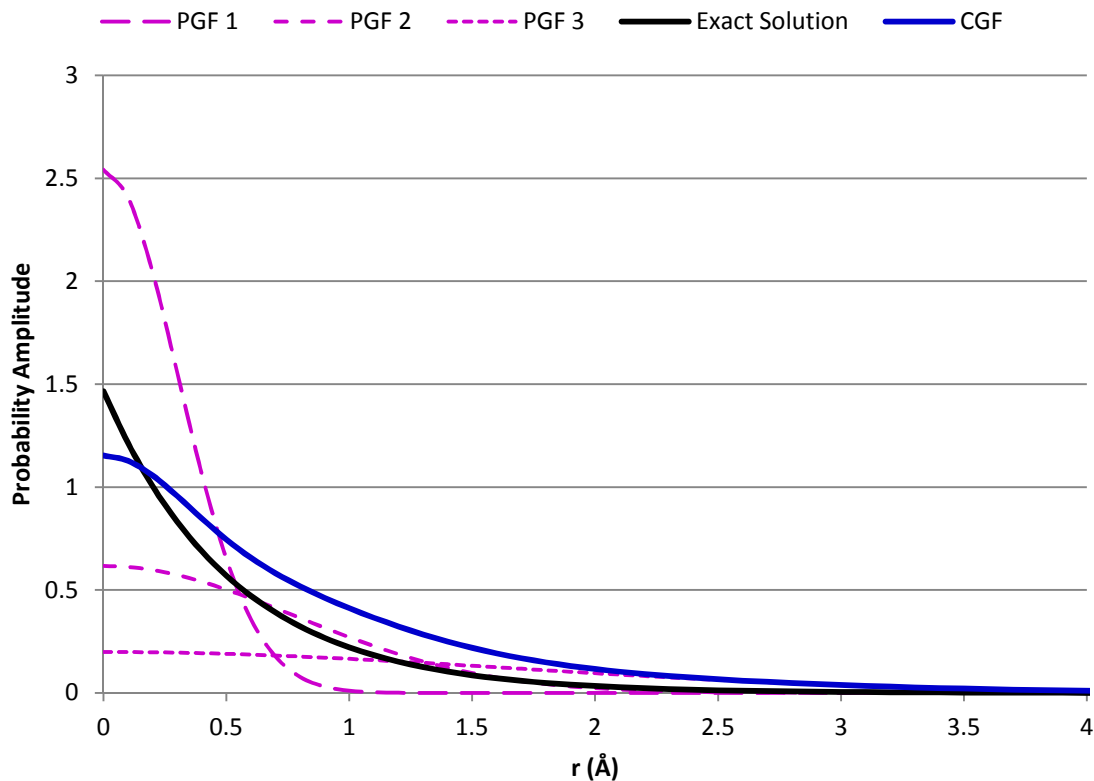


Figure 3.5.1. Probability amplitude vs. radius comparison of exact and 321-G hydrogen 1s core orbital. Data taken from the Basis Set Exchange.^{[4], [5]}

Figure 3.5.1 shows how using multiple PGFs in a CGF provides a better approximation to the probability amplitude of a core hydrogen 1s orbital. The black line shows the probability amplitude vs. radius in angstroms for the exact wave function of the single-electron hydrogen 1s orbital. The dashed purple lines show the amplitudes of the three PGFs comprising core CGF for the 1s orbital. Each of the three gives an extremely poor approximation to the exact amplitude for some interval of radial distances. The CGF gives a much better approximation over the entire range.

The 3-21G set currently provides basis functions for the elements hydrogen through xenon.

In general we obtain a better approximation by increasing either the number of CGFs we use to model the valence orbitals or the number of PGFs combined in a given CGF. The 6-31G basis takes the latter approach, doubling the number of PGFs in its core CGF and adding another PGF to its first valence CGF. Unfortunately, at this time the 6-31G basis provides functions only for hydrogen through krypton, fewer than 3-21G.^[6]

The aim of the LanL2DZ basis set is not to provide an increase in accuracy over the above split-valence basis sets; instead, it makes concessions in that regard for the sake of reducing calculation time for molecules containing large nuclei.^[7] This is accomplished by changing the way in which the repulsion between electrons in core orbitals and electrons in valence orbitals is calculated. Instead of attempting to find approximate solutions to two-electron integrals for all pairs of electrons, the core electrons are treated as an average potential centered on the nucleus, called an effective core potential (ECP). It is a parameter taken from experimental data and is unique to each element. For this reason basis sets with ECPs are called semi-empirical, as opposed to ab initio methods which use no parameters. The ECP method balances its reduced accuracy in calculating electron-electron repulsion energies with an ability to take into account relativistic effects that are too complex for ab initio methods to model in a reasonable time frame.

Einstein's theory of special relativity predicts, and experiment observes, that mass depends on velocity. The extremely high velocities of core electrons cause their mass to

exceed that of the electron rest mass, m_e . For small atoms the difference is slight. It is generally considered to become significant to chemists for systems containing third-row elements and higher. These effects must be calculated with the Dirac time-dependent relativistic Schrödinger equation, which is computationally very expensive. An advantage of ECPs is that relativistic effects can be included without affecting calculation times. However, this boon is outweighed by the basis set's approximations for very small systems containing large atoms.

3.6 The Hartree-Fock (HF) Self-Consistent Field (SCF) Method

The use of different basis sets does not address the problem of solving the multi-electron Schrödinger equation. The HF-SCF method attempted to provide an efficient and accurate approximation. It is a legacy method; it has been surpassed by more accurate or more efficient methods for most applications. But, like an old junker past its prime, new methods often ransack HF-SCF for spare parts.

The SCF in particular is part of most modern methods. It uses an arbitrary trial function φ_0 as an initial guess at the wave function for a molecular orbital. The electronic Hamiltonian is numerically integrated to obtain a set of eigenvalues. These are then used to generate a new trial function φ_1 and the process repeats iteratively. If we are very good at guessing trial functions our φ_0 may be so close to the best approximate φ that successive iterations do not produce significant change in the eigenvalues. More likely, however, we will have chosen a φ_0 that is not particularly good and must perform many iterations in order to reach the point of negligible change in eigenvalues and

eigenfunctions. At this point we have achieved self-consistency. This does not mean we can get arbitrarily close to the true wave function or energy, however. The accuracy is limited by the degree to which the form of the φ s matches the (unknown) form of the true wave function. For example, the choice of basis set is an important factor in this regard.

As elements of HF are also important to modern methods, we provide a brief description of this approach. We begin our treatment by defining a closed-shell, ground-state wave function in a form known as a Slater determinant:

$$D = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \cdots & \psi_n(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \cdots & \psi_n(2)\beta(2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_1(n)\alpha(n) & \psi_1(n)\beta(n) & \psi_2(n)\alpha(2) & \cdots & \psi_n(n)\beta(n) \end{vmatrix}, \quad (6.1)$$

where n is the number of electrons and the ψ_i are one-electron functions called spatial orbitals that depend on the position vector \mathbf{r} . The first row refers to electron 1, the second to electron 2, and so on to electron n . The functions α and β are called spin orbitals. Their only variable is the spin variable, ξ . They are equal to zero unless $\xi = \pm 1/2$. Those familiar with quantum mechanics will recognize that electrons have these and only these values for their fourth quantum number, the spin quantum number m_s .

Spin is not an easy concept to grasp since it does not correspond to any property in the macroscopic world, but is rather an angular momentum intrinsic to elementary particles which, like all the quantum numbers, may only take on a limited range of values. The Pauli Exclusion Principle states that no fermions, a class of particle to which

electrons belong, may share all four quantum numbers. However, since the special orbitals ψ_i depend only on the first three numbers, n , l , and m , electrons of opposite spin may share the same spatial orbital without violating the Pauli Principle.

The spin variable, ξ , is the sum of the electron spins in a spatial orbital. If two electrons of opposite spin share an orbital then $\xi = 0$ and the spin orbitals vanish. (6.1) is constructed so that it ensures no two electrons of like spin can share an orbital. If they did, the determinant would vanish—along with the wave function!

If we force n in (6.1) to be a multiple of two we are restricting the system to its closed-shell ground state in which all electrons occupy ψ_i in pairs. That is, electrons with spin α are forced to occupy the same spatial orbitals as electrons with spin β . This is called the restricted HF method, or RHF. If the molecular system contains one or more unpaired electrons, or is in an excited state, the model will not give an accurate result. For these systems we use the open-shell, unrestricted HF method, or UHF, in which electrons with spin α occupy an entirely separate set of spatial orbitals, than those occupied by spin β electrons. This improves the accuracy of the results for open-shell systems and for some systems where electrons in d or f shells are involved in bonding, but at a hefty cost in terms of efficiency.

Now we define an operator: the one-electron core Hamiltonian:

$$\hat{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - \sum_A^N \frac{Z_A}{r_{1A}}, \quad (6.2)$$

which represents the kinetic energy of electron 1 plus the potential energy of attraction of that electron to each of the N nuclei. The designation “electron 1” is arbitrary since electrons are indistinguishable.

By applying (6.2) to (6.1) we obtain two new terms:

$$J_{ij} = \langle \psi_i^*(1)\psi_i(1) \left| \frac{1}{r_{12}} \right| \psi_j^*(2)\psi_j(2) \rangle. \quad (6.3)$$

(6.3) is the Coloumb integral and it gives the electrostatic repulsion between electron 1 in ψ_i and electron 2 in ψ_j .

$$K_{ij} = \langle \psi_i^*(1)\psi_j^*(2) \left| \frac{1}{r_{12}} \right| \psi_i(2)\psi_j(1) \rangle \quad (6.4)$$

(6.4) is the exchange integral. It comes from terms in the expansion of the Slater determinant that differ only by exchanging electrons. It has no easy physical interpretation, but J and K together represent the average electrostatic repulsion of an electron in an orbital due to all the other electrons.

Using (6.2) through (6.4), the LCAO approximation, and a good deal of behind-the-scenes mathematics, we can write the HF equations as a system of homogenous differential equations:

$$\sum_{s=1}^m c_{si}(F_{rs} - \epsilon_i S_{rs}) = 0, \quad (6.5)$$

where m is the number of basis functions, the c_{si} are the coefficients in the LCAO linear expansion and our variational parameters, ϵ_i is the energy of the i th molecular orbital, and the F_{rs} are the elements of the Fock matrix.

$$F_{rs} = \langle \psi_r(1) | \hat{H}^{core}(1) | \psi_s(1) \rangle + \sum_{j=1}^{n/2} [2\langle \psi_r(1) | \hat{J}_j(1) | \psi_s(1) \rangle - \langle \psi_r(1) | \hat{K}_j(1) | \psi_s(1) \rangle], \quad (6.6)$$

and

$$S_{rs} = \langle \psi_r | \psi_s \rangle, \quad (6.7)$$

also called the overlap integral.

Using the SCF strategy, an initial set of trial coefficients is used in conjunction with the appropriate basis set functions to construct the Fock matrix and solve (6.5). The new set of c_{si} coefficients is then used to construct the Fock matrix again and equation (6.5) is solved again. This process continues until self-consistency is achieved, thus providing the best approximate solution.

3.7 Density Functional Theory (DFT)

The Hohenberg-Kohn theorem states that for any system with a non-degenerate ground state, all electronic properties can be determined from only the ground state electron probability density, $\rho_0(\mathbf{r})$, where \mathbf{r} is the position vector.^[8] This theorem was the birth of DFT, and it represented a break with past ab initio methods.^[1] DFT gets its

name from the fact that the electronic energy of a system, E , is a function of ρ , which is itself a function of the position vector: $E = E(\rho(\mathbf{r}))$. A function of a function is called a functional.

The density functional approach addresses a number of problems inherent to the HF-SCF method. Perhaps most importantly, in HF-SCF wave functions electrons in orbitals interact with other electrons as an average potential that is static through time, while in reality they interact instantaneously as moving particles. This phenomenon is called electron correlation, and it causes HF-SCF to overestimate the electron density between atoms.

Hohenberg and Kohn presented a density functional form of the variational theorem:

$$\begin{aligned} E_v(\varphi) &\geq E_0 \\ E_0 &= E(\rho_0) \end{aligned} \tag{7.1}$$

where $E_v(\varphi)$ is the system energy calculated from a trial density function φ . The subscript v indicates that $E_v(\varphi)$ depends on the nuclear-electron interaction potential $v(\mathbf{r}_i)$. E_0 is the true ground-state energy of the system calculated from its true ground-state electron density function ρ_0 . (7.2) gives several properties of trial density functions:

$$\int_0^\infty \varphi(\mathbf{r}) \, d\mathbf{r} = n \tag{7.2}$$

where n is the number of electrons in the system, and

$$\varphi(\mathbf{r}) \geq 0 \text{ for all } \mathbf{r}.$$

One of the most important of Hohenberg and Kohn's theorems specifies how to calculate the system energy for a given ρ_0 :

$$E_v(\rho_0) = \int_0^\infty \rho_0(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \bar{T}(\rho_0) + \bar{V}_{ee}(\rho_0). \quad (7.3)$$

The kinetic energy term $\bar{T}(\rho_0)$ and the electron-electron repulsion term $\bar{V}_{ee}(\rho_0)$ are commonly grouped together in the functional F . The theorem does not tell us how to find F , however.

Kohn and Sham suggested a clever method for finding an approximation to F using an ideal system, s , of n non-interacting electrons in the external potential $v(\mathbf{r}_i)$.

The important consequence of this is that:

$$\rho_s(\mathbf{r}) = \rho_0(\mathbf{r}), \quad (7.4)$$

where $\rho_s(\mathbf{r})$ is the ground-state density of the reference system.^[9] The form of the Hamiltonian for the reference system is very simple because the electrons do not interact, and all parts of the energy functional can be calculated exactly except for the two in F . However, we can now represent them as differences between the real and reference systems:

$$\begin{aligned} \Delta\bar{T}(\rho_0) &= \bar{T}(\rho_0) - \bar{T}(\rho_s) \\ \Delta\bar{V}_{ee}(\rho_0) &= \bar{V}_{ee}(\rho_0) - \frac{1}{2} \iint \frac{\rho_s(\mathbf{r}_1)\rho_s(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (7.5)$$

where 1 and 2 represent a given pair of electrons. These are combined into a new functional called the exchange-correlation energy functional, E_{xc} :

$$E_{xc} = \Delta\bar{T}(\rho_0) + \Delta\bar{V}_{ee}(\rho_0). \quad (7.6)$$

Rewriting (7.3) in terms of (7.5) and (7.6), we obtain:

$$E_v(\rho_0) = \int \rho_0(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \bar{T}(\rho_s) + \frac{1}{2} \iint \frac{\rho_s(\mathbf{r}_1)\rho_s(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (7.7)$$

$$+ E_{xc}(\rho_0).$$

Now that we have isolated our unknowns into the exchange-correlation functional, it should be clear that the usefulness of a DFT method depends upon the selection of a good approximation to E_{xc} .

3.8 Hybrid Density Functionals

E_{xc} can be written as the sum of an exchange functional, E_x , and a correlation functional, E_c . The Becke88 exchange functional uses the Generalized-Gradient Approximation (GGA) which improves on pure DFT by allowing electron density to vary with position. Other methods split E_x into a portion based on the GGA method and a portion taken from the Hartree-Fock method. These can be linearly combined with weighted coefficients in the same way orbitals are in the LCAO approximation. These are called hybrid exchange functionals and generally provide better accuracy than pure DFT functionals.

Currently, a hybrid functional popular for its efficiency and accuracy is the B3LYP hybrid functional, which contains the B3 functional, a GGA exchange functional, and a correlation functional named for its creators, Lee, Yang, and Parr. The present work uses both the spin-restricted and spin-unrestricted flavors of this hybrid functional, RB3LYP and UB3LYP.

3.9 Mulliken Population Analysis

A final difficulty in characterizing molecular systems using computational methods is that of determining the strength of the bond between two atoms. A Mulliken population analysis uses the products of LCAO coefficients to apportion the electron density of the molecule.^[10]

For the purpose of determining bonding, it is the LCAO coefficients in the overlap integrals S_i which are of interest. The electron density corresponding to the bond is located in the overlap region between two atoms and it is called the overlap population. Overlap populations are calculated as follows: a single electron in molecular orbital ϕ_i between atomic centers 1 and 2 contributes $2c_{1i}c_{2i}S_{12}$ electrons to the overlap population between the atomic centers; c_{1i} and c_{2i} are the LCAO coefficients for the functions describing atomic orbitals 1 and 2 which comprise ϕ_i , while S_{12} is the value of the overlap integral between the centers.^[11] If there are n electrons in ϕ_i then they contribute $2nc_{1i}c_{2i}S_{12}$ electrons to the overlap populations.

The Mulliken population analysis can also be used to determine approximate partial charge on a given atomic center, but that aspect of the method is outside the scope of the present work.

3.10 References

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4. Details of the calculations

We used GaussView 3 and GaussView 4 to construct all structures and Gaussian 03 to perform the density functional calculations.^{[1], [2], [3]} Structures were optimized to a minimum using the Berny algorithm; force constants and resulting vibrational frequencies were computed analytically.^[4]

Geometry optimization calculations for the $(\text{TiCl}_2)_2$ dimer were carried out using B3LYP functionals and both the 3-21G and LanL2dZ basis sets.^{[6], [7], [8]}

For the capnellene system, we constructed all possible metallacyclic intermediates by attaching one of the titanium atoms in the dimer to one of the three electronegative atoms in the ligand. We ensured that the bond lengths in the metallacycle of these initial structures conformed as much as possible to those calculated by Frenking for the optimized pinacolate intermediate complex of CH_2O and TiCl_2 (vide infra).^[12] We performed the optimization and frequency calculations on the capnellene intermediates using spin-unrestricted B3LYP hybrid functionals and the 6-31G basis set.^{[6], [9]}

We followed the same procedure for the intermediates involving the pyrrolidine ligand, constructing all structures in which each titanium atom attaches to one of the five electronegative centers in the ligand. We performed two sets of optimization and frequency calculations, one using the spin-unrestricted B3LYP functionals and the 6-31G basis set and one using spin-restricted B3LYP functionals and the LanL2DZ basis set.^[8]

Analyses of the electron density distributions were done using the Mulliken approximation.^[10] We programmed a simple collection of VBA macros in Microsoft Excel 2007 to collect the off-diagonal elements of the density matrix from the Gaussian

03 output file and generate tables of Mulliken overlap populations between pairs of atoms (see section 6).

4.1 References




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5. Results and Discussion

In this section we describe all calculations and their outcomes. A note about nomenclature: we designate intermediates according to the bonding in the initial, pre-optimization structure. Intermediates are labeled [X,Y] to indicate that the two metal atoms in the titanium dimer are attached to atoms X and Y in the ligand. The ligand atoms labels are shown in Figure 5.2.1 for capnellene and in Figure 5.3.1 for the pyrrolidine. Table 5.1 shows the legend used in figures to indicate any changes in the bonding occurring during optimization.

Table 5.1. Legend for symbols indicating bonding changes.

<i>Key to symbols</i>	
	Bond broken during optimization
	Future location of bonding pair after optimization
	Bond formed during optimization

5.1 Titanium(II) Chloride Dimer

We begin by examining the bonding and structure of the $(\text{TiCl}_2)_2$ dimer by itself, before bonding to any ligand. Figure 5.1.1 shows the structure of the dimer optimized at the RB3LYP/LanL2DZ level of theory: it is highly symmetrical and the chloride ligands are staggered to accommodate the lone pairs on the metal centers. Table 5.1 shows the Mulliken overlap populations between atoms in the dimer. The cyan color of the Ti-Cl bonds in the figure corresponds to a Mulliken overlap population of $0.30 e^-$. This is roughly average for Ti-Cl bonds in the other optimized structures discussed below and it indicates a single bond. The green color of the Ti-Ti bond corresponds to a Mulliken overlap population of $0.22 e^-$. In no other optimized structure is the Ti-Ti population above $0.15 e^-$. This indicates that the Ti-Ti bond in the isolated dimer is stronger than in the metallacycles described below, as predicted by the lengthening of said bond upon complexation to the ligand.

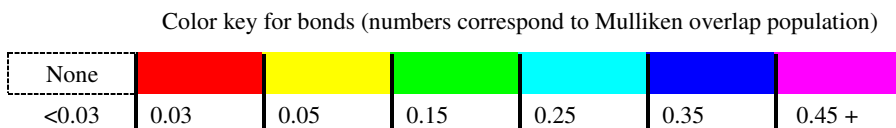
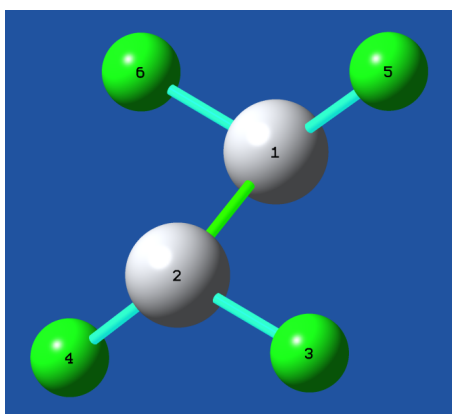


Figure 5.1.1. Optimized titanium(II) chloride dimer.

Table 5.1. Mulliken overlap populations between atoms in the titanium (II) chloride dimer optimized using the RB3LYP/LanL2DZ method. The integers correspond to the atom numbers in Figure 5.1.1 above. The colors of the atom name cells correspond to the atom colors. The decimals are the overlap population in e^- . The colors of the population cells are mixtures of the colors of the two atoms the population lies between. “-“ denotes a negative population or a positive population less than $0.03 e^-$.

		1	2	3	4	5	6
		Ti	Ti	Cl	Cl	Cl	Cl
1	Ti		0.22	-	-	0.30	0.30
2	Ti	0.22		0.30	0.30	-	-
3	Cl	-	0.30		-	-	-
4	Cl	-	0.30	-		-	-
5	Cl	0.30	-	-	-		-
6	Cl	0.30	-	-	-	-	

5.2 Capnellene

Our general approach to determining the most stable conformation of the intermediate in the McMurry cyclization step is to consider all possible intermediates and compare their relative energies. To make sure that our approach is valid, we decided to test our method by using it to determine the most favorable intermediate in the McMurry cyclization reaction that produces capnellene. This molecule is a sesquiterpene precursor that can be synthesized in high yield (72%) using a titanium-induced oxo ester cyclization.^[1] Consequently, the results of the calculations should show that the McMurry intermediate is the most energetically favorable of the possible intermediates. For the capnellene system there are three possible metallacyclic intermediates where each titanium atom in the dimer is attached to one of the three electronegative atoms in the ligand, labeled A, G, and H in Figure 5.2.1. Of these, only one resulted in the desired McMurry product ([A,G] in Figure 5.2.2) while in the other two the structure remained essentially unchanged ([G,H] and [A,H] in Figure 5.2.3).

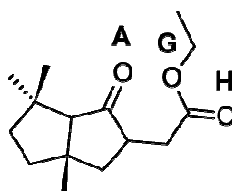


Figure 5.2.1. Capnellene precursor with electronegative atoms labeled alphabetically.

Figure 5.2.2 shows the initial and optimized structures for intermediate [A,G], wherein the titanium chloride dimer is initially, and remains, bonded to the ligand at oxygens 29 and 35 (A and G respectively). On the left is the input structure for the calculation. Note

that in the optimized structure the dimer is rearranged so that no bond exists between the two titanium atoms; instead, chlorines 48 and 50 bridge them. Other investigators have noted bridging chlorine atoms in titanium complexes. Frenking et al. found that a single chlorine atoms bridged the titanium centers in the intermediate of their model system.^[2] Titanium cluster compounds with bridging chlorine atoms have also been confirmed experimentally. Cotton et al. isolated the molecule $[\text{Ti}(\mu\text{-Cl})\text{Cl}(\text{dmpe})]_3$ in which three chlorine atoms bridge three titanium centers; polymer-like chains containing a repeated structure in which two chlorine atoms bridge two titanium atoms have also been observed.^{[3], [4]}

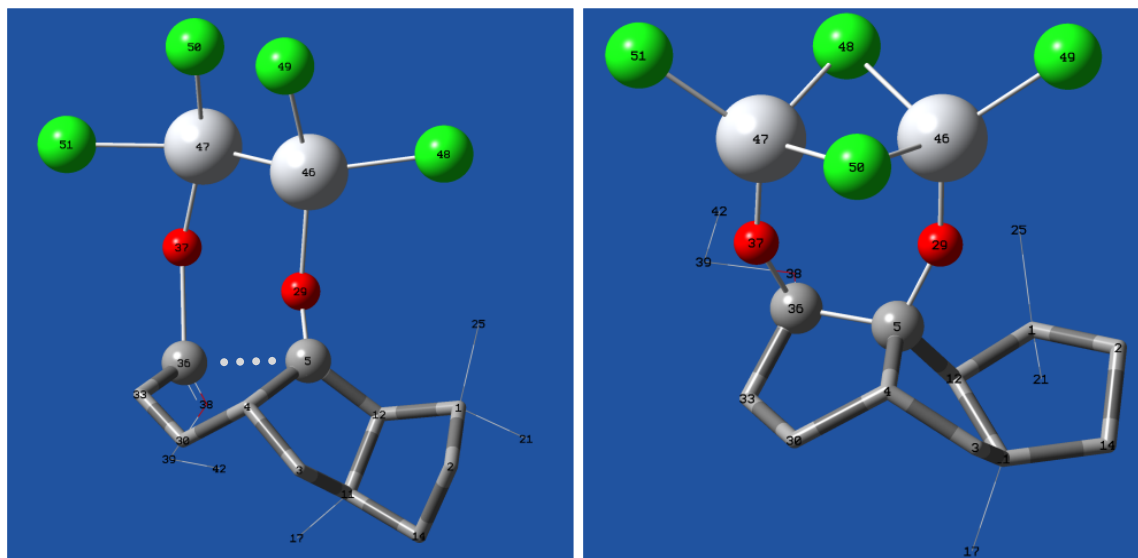


Figure 5.2.2. The [A,G] intermediate of capnellene. At left is the initial structure. At right is the structure optimized at the UB3LYP/6-31G level of theory. A gray dotted line shows where a new C-C bond will form in the optimized structure.

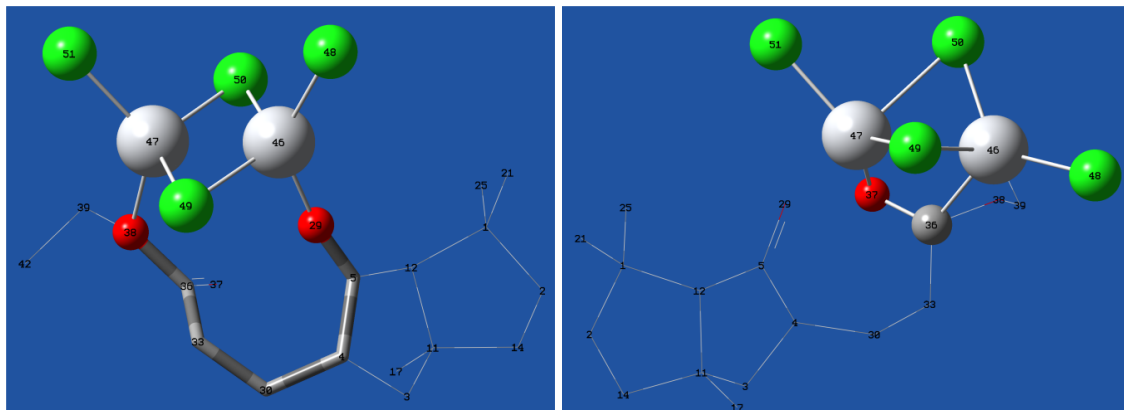


Figure 5.2.3. Optimized structure of the [A,H] intermediate (left) and [G,H] intermediate (right).

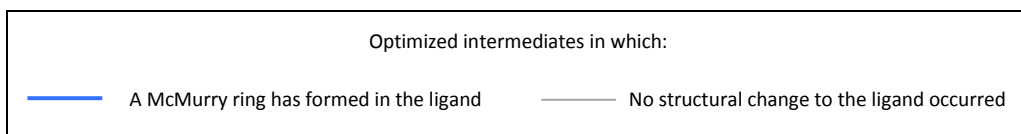
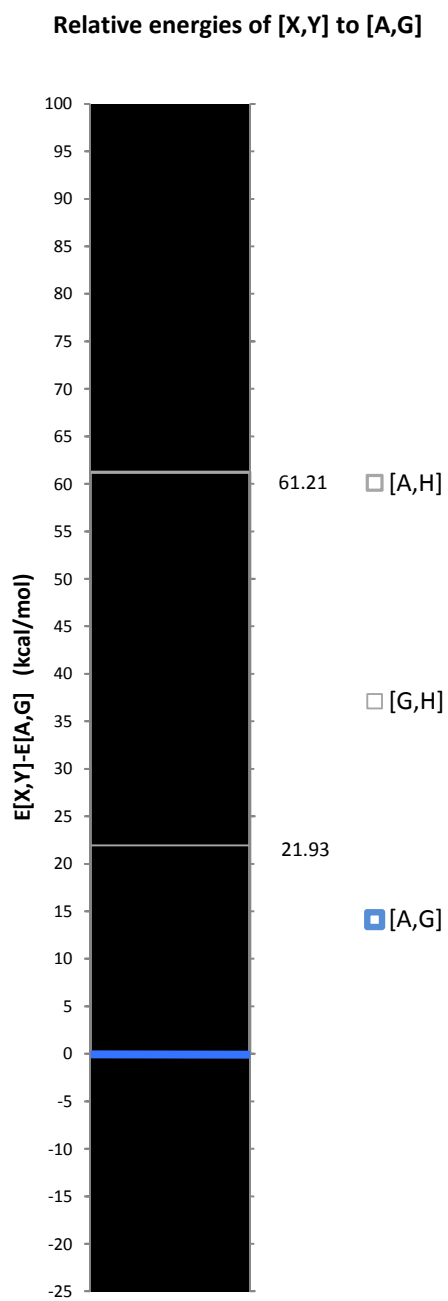


Figure 5.2.4. Energy diagram of optimized capnellene intermediates relative to [A,G].

Figure 5.2.4 shows the relative energies in kcal/mol of the three optimized capnellene intermediates. Table 5.2 shows total energies in a.u. and relative energies in kcal/mol. [A,G] is the most stable structure (represented by the blue line in Figure 5.2.4) and is also the only McMurry intermediate.

Table 5.2. Energies of optimized capnellene intermediates.

Intermediate	Total energy (a. u.)	Energy rel. to [A,G] (kcal/mol)
[A,G] •	-4390.8081	0
[G,H] •	-4390.7731	21.93
[A,H] •	-4390.7105	61.21

From the results of the calculations we conclude that the McMurry intermediate is the most stable. Additionally, Table 5.3 shows that the optimized bond lengths in the metallacycle are very similar to those found by Frenking for a similar compound, the pinacolate intermediate complex formed from two equivalents of CH₂O and two equivalents of TiCl₂.^[2] Taken together, these two pieces of evidence provide corroboration that the method we have chosen is valid and allows us to correctly predict whether a reaction will result in a McMurry cyclization product.

Table 5.3. Comparison of calculated metallacycle bond lengths in the capnellene intermediate and in a CH₂O-TiCl₂ intermediate.

Metallacycle bond type	Calc. length in capnellene intermediate [A,G] (Å)	Calc. length in CH ₂ O-TiCl ₂ complex ^[2] (Å)
Ti-Ti	2.65	2.51
Ti-O	1.78	1.80
C-O	1.46	1.41
C-C	1.57	1.54

5.3 Pyrrolidine Ligand

We first performed geometry optimization calculations on the pyrrolidine ligand using spin-restricted B3LYP functionals and the LanL2DZ basis set. We selected the latter because it is usually the basis set of choice for transition metal atoms like titanium. However it has the drawback of describing the core electrons as an average field (the effective core potential) in order to keep the basis functions to a manageable number. Since higher-level basis sets can be used with first row transition metals, we also tried the 6-31G basis which yields more accurate energies. In addition, while we started by constraining the calculations to closed-shell wavefunctions (spin restricted - R), we later realized that the nature of the transition state structures is such that open-shell wavefunctions (spin unrestricted - U) would provide a better description of the bonding. In summary, we carried out two sets of optimization calculations: the first at the RB3LYP/LanL2DZ level and the second at the UB3LYP/6-31G level. The results are somewhat different and they are compared in the analysis below.

5.3.1 Results of Geometry Optimization Calculations

We built the initial structures of the intermediates involving the pyrrolidine ligand and the titanium(II) chloride dimer following the same procedure we used for capnellene. We attached each titanium atom to one of the five electronegative centers in the ligand (labeled A, C, F, I, and J in Figure 5.3.1) and obtained ten unique initial configurations; we provide an example of one of these metallacyclic intermediates in Figure 5.3.2.

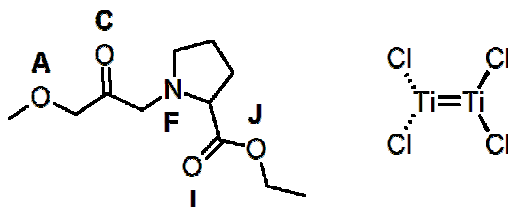


Figure 5.3.1. On the left is the ligand, ethyl 1-(3-methoxy-2-oxopropyl)pyrrolidine-2-carboxylate, with selected atoms in the ligand labeled alphabetically. On the right is the titanium(II) chloride dimer.

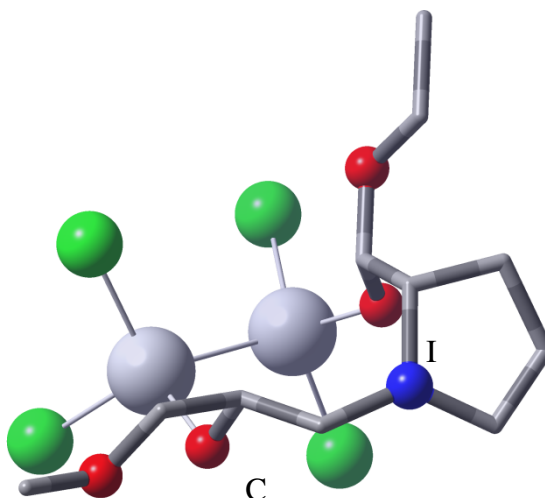
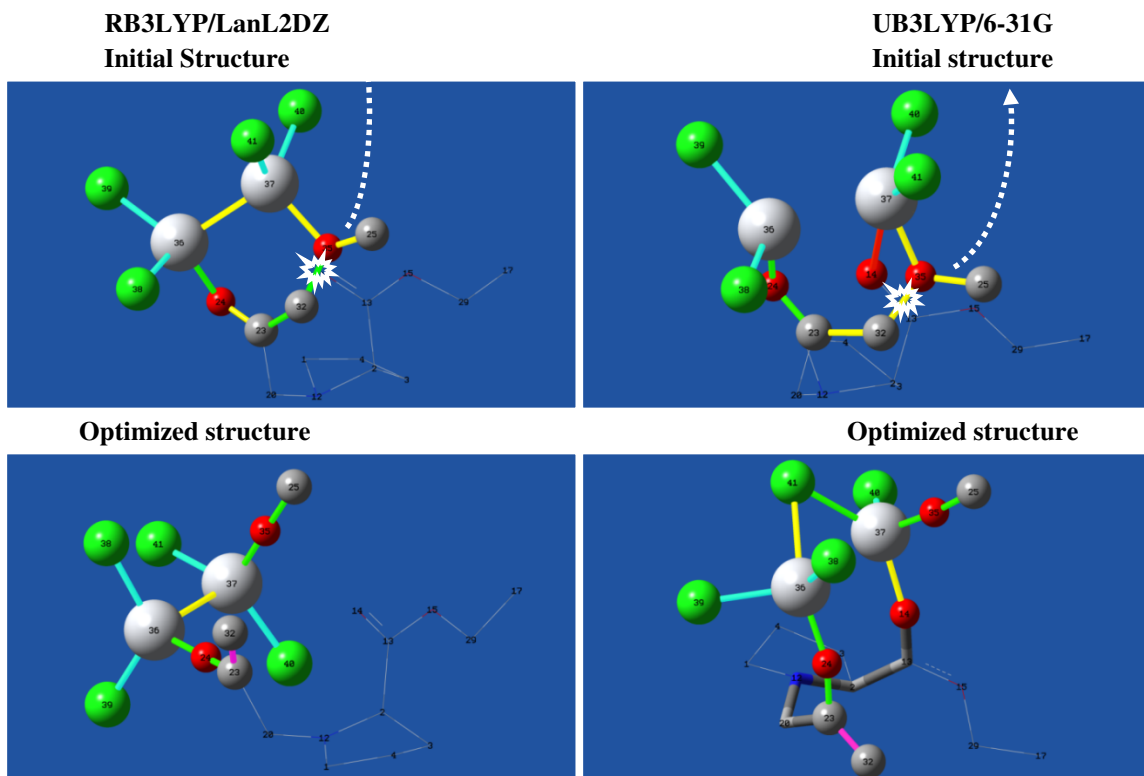


Figure 5.3.2. The initial structure of intermediate [C,I] wherein the titanium atoms (large, gray) are attached to the carbonyl oxygen (red) of the ketone (C) and the carbonyl oxygen of the ester (I). Chlorine atoms are green and the carbon backbone is shown in a tube representation. Hydrogen atoms are omitted for clarity.

Figures showing the initial and optimized structures for each configuration are shown below, in alphabetical order of ligand atom. In the following discussion, initial and optimized structures are compared using results from both RB3LYP/LanL2DZ and UB3LYP/6-31G calculations.

The initial structures for the two levels of theory for the [A,C] intermediate (see Figure 5.3.3) differ in two minor ways: the RB3LYP/LanL2DZ initial structure has a weak bond between titanium atoms that is nonexistent in the UB3LYP/6-31G structure and there is a weak Ti-O bond in the UB3LYP/6-31G structure but not in the RB3LYP/LanL2DZ structure. These differences are produced by the description of the bonding unique to each basis set.



Color key for bonds (numbers correspond to Mulliken overlap population)

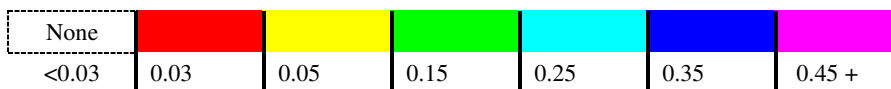
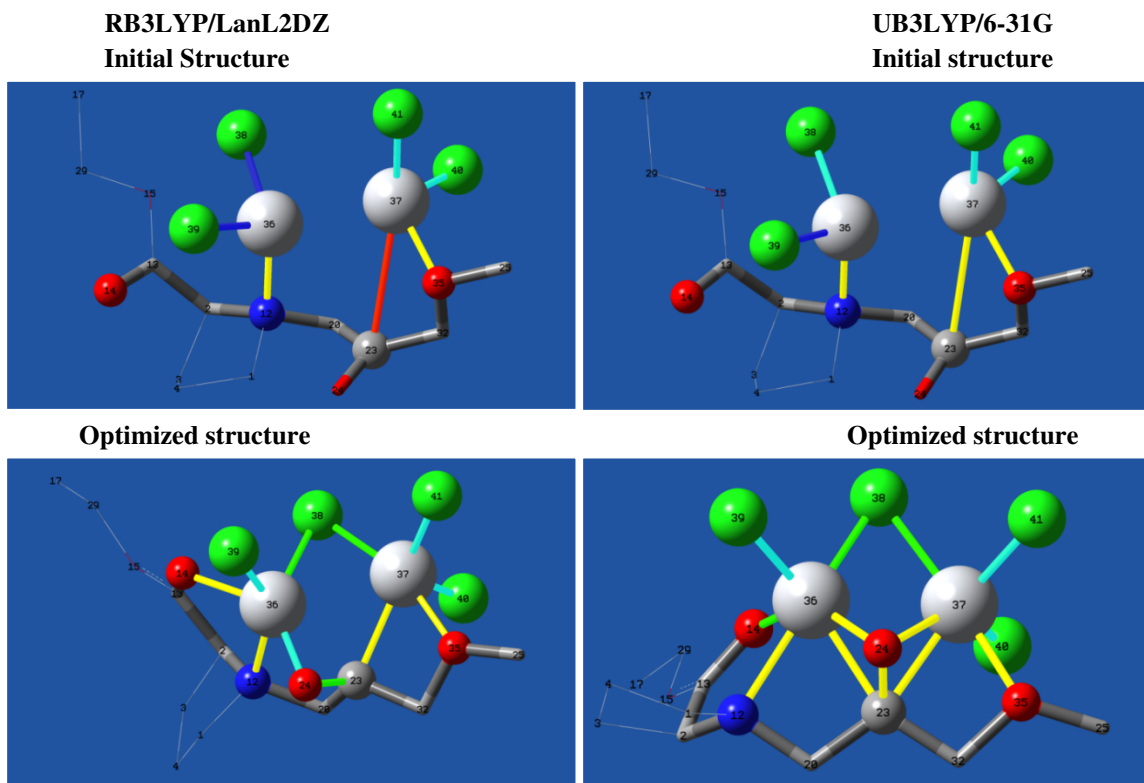


Figure 5.3.3. Initial and optimized structures for intermediate [A,C]. Note that the bond colors correspond to the Mulliken overlap population between the atoms, measured in e^- . There are full Mulliken overlap population tables for the all thepyrrolidine intermediates in section 6.

The two optimized structures are significantly different: there is a metal-metal bond in the RB3LYP/LanL2DZ structure but in the UB3LYP/6-31G structure there is an anti-bonding interaction between the two titanium atoms. The weak Ti-O bond in the UB3LYP/6-31G initial structure becomes significant in the optimized structure but it is nonexistent in the RB3LYP/LanL2DZ optimized structure.

Both optimization calculations of the [A,F] intermediate resulted in structures in which one of the chlorine atoms is bridging the titanium centers (see Figure 5.3.4). The UB3LYP/6-31G structure in particular shows evidence of the Ti dimer arranging itself into the bridged structure seen in the capnellene optimizations.



Color key for bonds (numbers correspond to Mulliken overlap population)

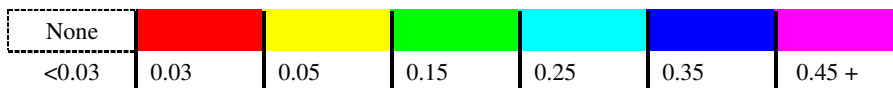


Figure 5.3.4. Initial and optimized structures for intermediate [A,F].

There are significant differences in the bonding of the two initial structures of the [A,I] intermediate (see Figure 5.3.5). The RB3LYP/LanL2DZ structure shows a Ti-Ti bond that is absent in the UB3LYP/6-31G structure, as is the case for most of the

intermediates. But, uncharacteristically, the UB3LYP/6-31G input structure shows a very weak bond between carbon 32 and oxygen 35. This is merely a minor curiosity since the two optimized structures are nearly identical. The only significant difference between them is that chlorine 41 bridges the titanium atoms in the RB3LYP/LanL2DZ structure but does not in the UB3LYP/6-31G structure.

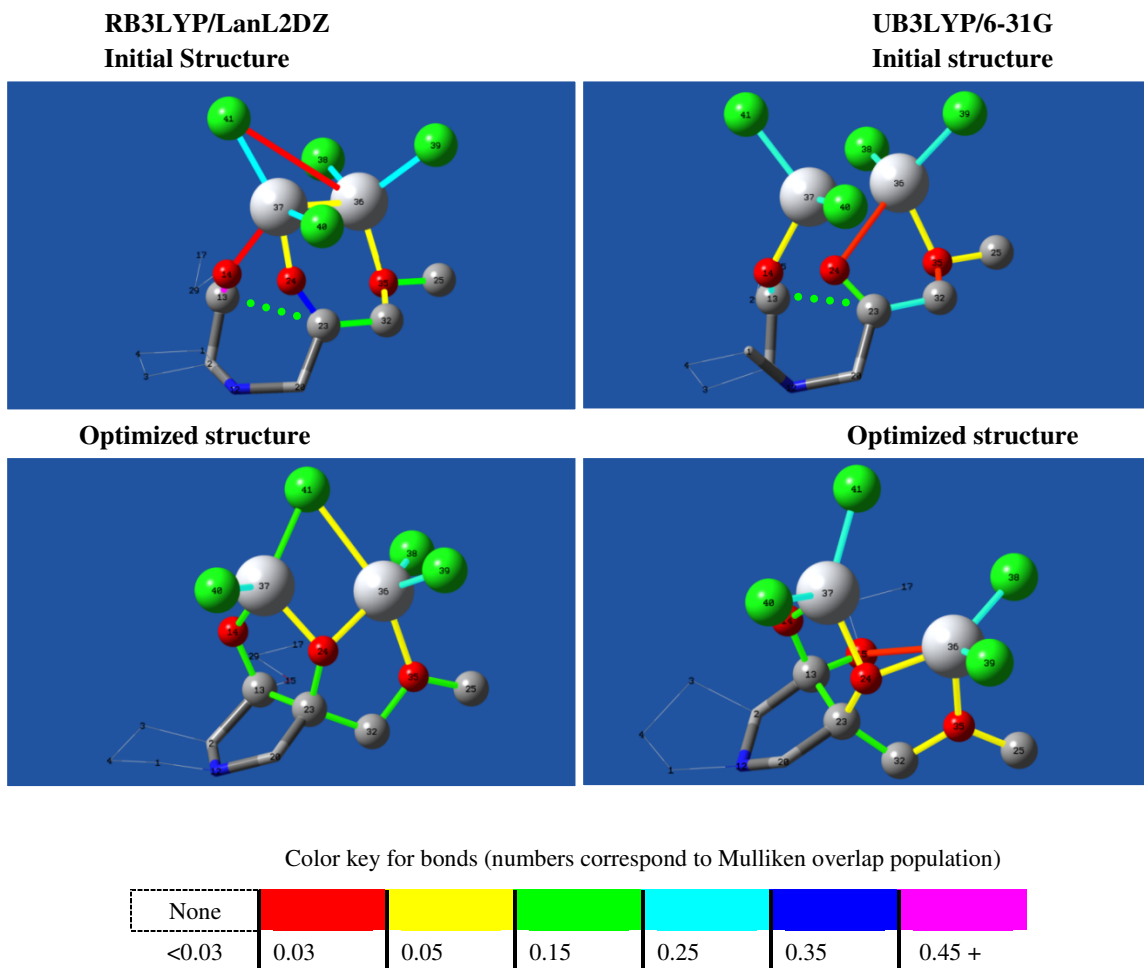


Figure 5.3.5. Initial and optimized structures for intermediate [A,I].

As with [A,I], the two optimized structures of [A,J] (see Figure 5.3.6) are nearly identical and the bonding in the initial structures is similar aside from the C25-O35 bond,

which is stronger in the UB3LYP/6-31G structure.

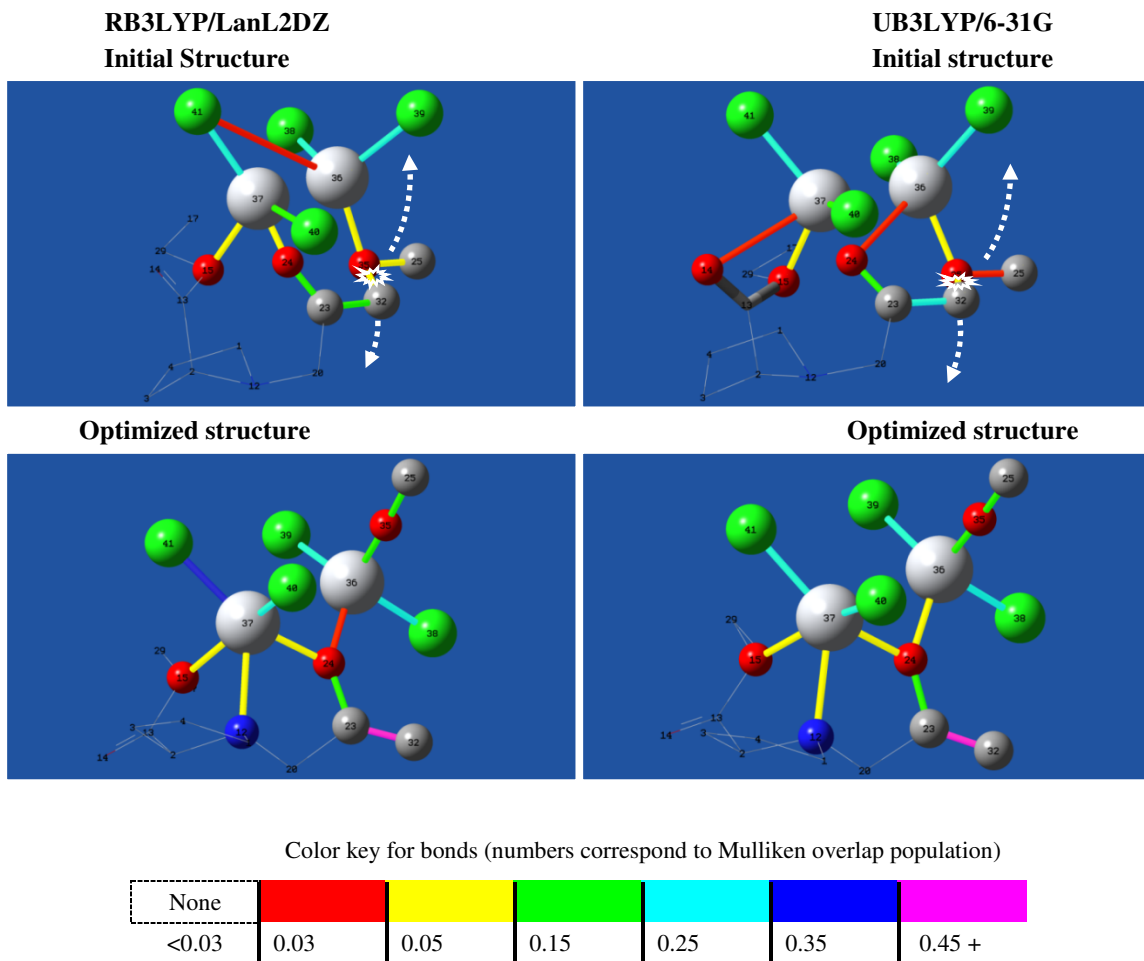
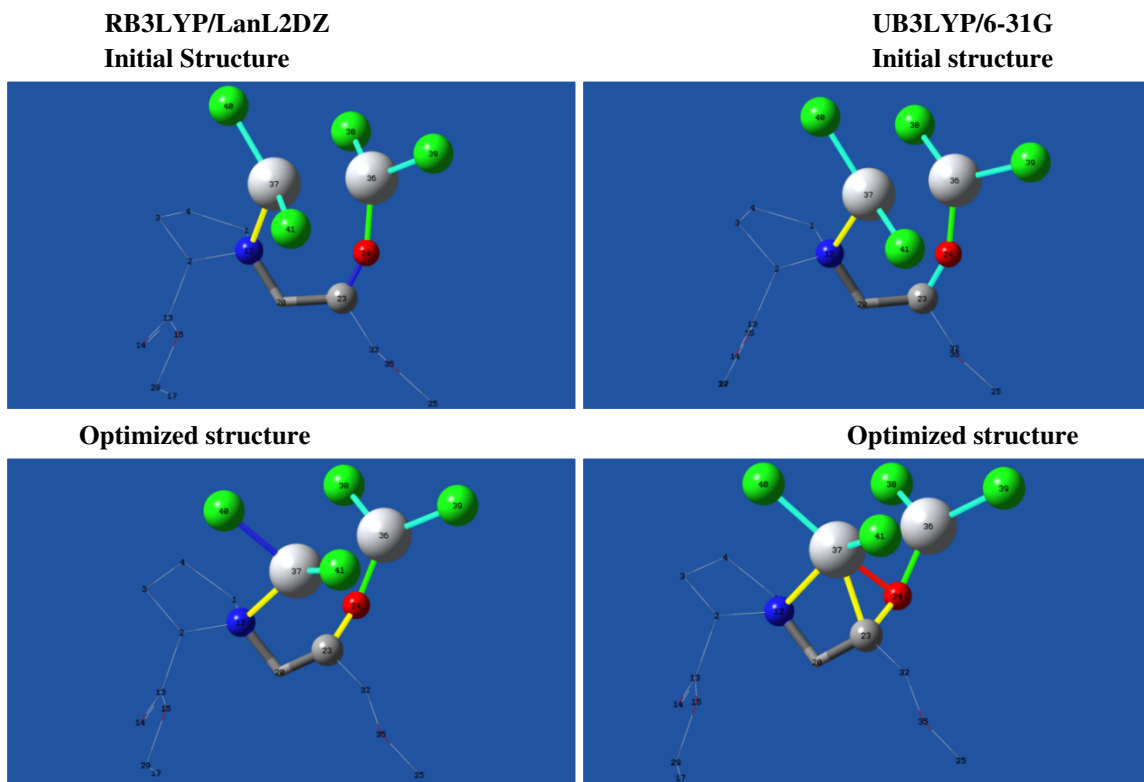


Figure 5.3.6. Initial and optimized structures for intermediate [A,J].

For [C,F] the initial and optimized structures are nearly identical under RB3LYP/LanL2DZ and UB3LYP/6-31G conditions (see Figure 5.3.7).



Color key for bonds (numbers correspond to Mulliken overlap population)

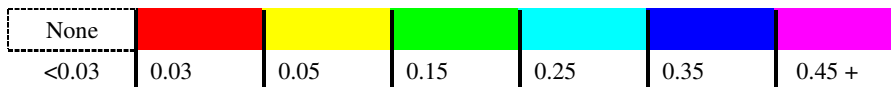
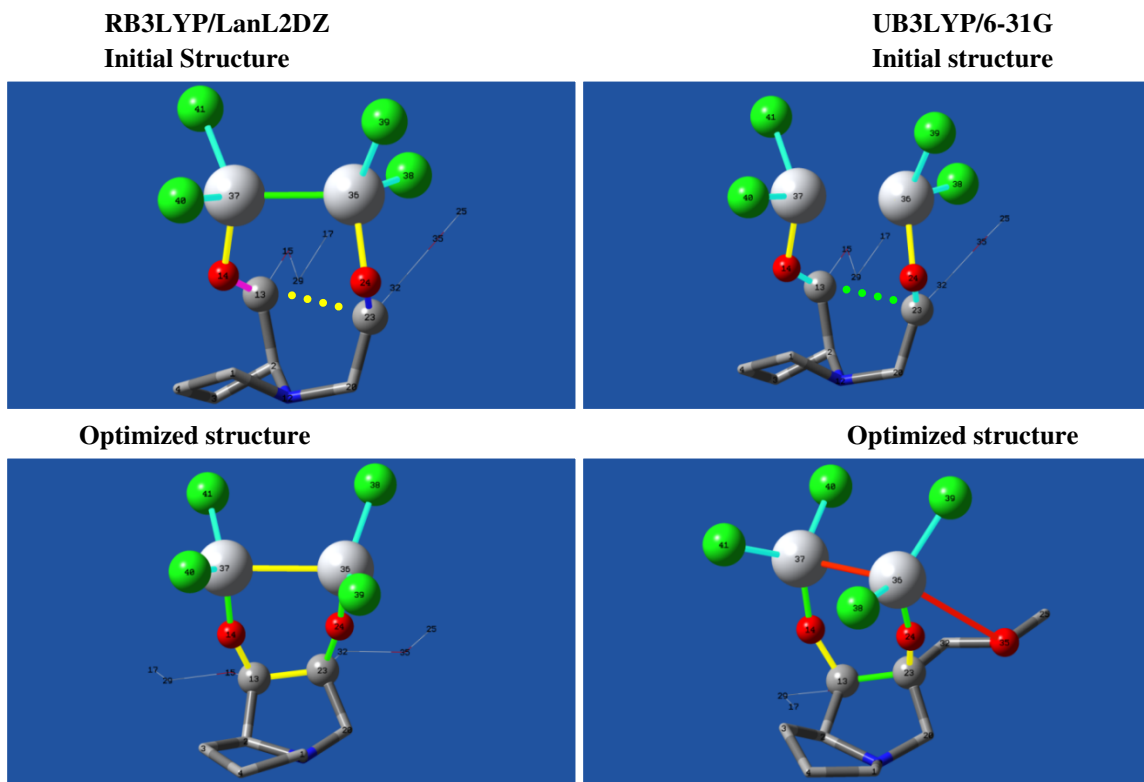


Figure 5.3.7. Initial and optimized structures for intermediate [C,F].

For [C,I] the bonding in the initial structures (see Figure 5.3.8) is very similar aside from the rather strong bond between the titanium atoms under RB3LYP/LanL2DZ conditions that is an anti-bonding interaction under UB3LYP/6-31G conditions. The dimer is twisted slightly relative to the ligand in the UB3LYP/6-31G optimized structure but no such change occurs in the RB3LYP/LanL2DZ optimized structure. This may have something to do with the bond between titanium 36 and oxygen 35. The weakness of the bond, however, seems to argue that the bond is a symptom of the different geometry rather than its cause.



Color key for bonds (numbers correspond to Mulliken overlap population)

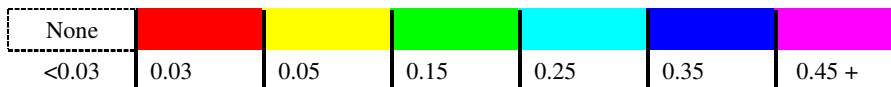
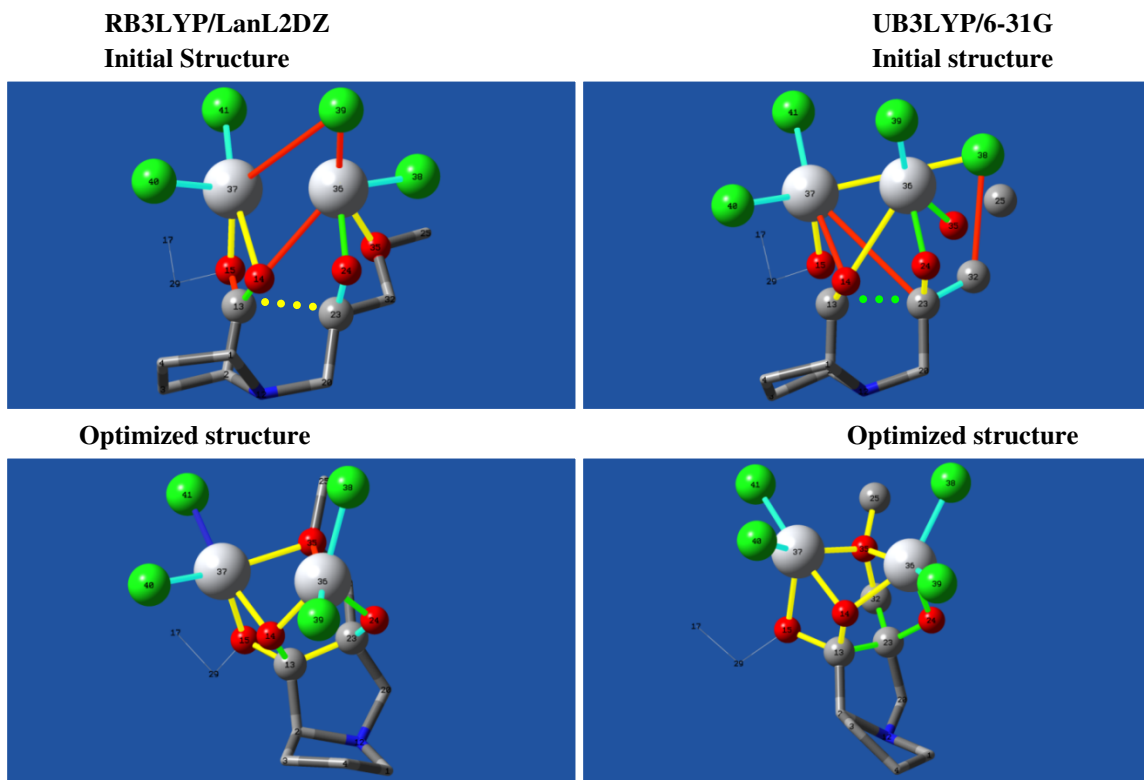


Figure 5.3.8. Initial and optimized structures for intermediate [C,I].

The [C,J] structure is highly problematic for any discussion of bonding in the initial structures based on Mulliken overlap populations. Interpreting these values as an indication of bonding yields the completely nonsensical structure seen in the UB3LYP/6-31G initial structure (see Figure 5.3.9), where the ligand appears to be highly fragmented. However Mulliken overlap populations in the optimized [C,J] structures are not unusual and are very similar under RB3LYP/LanL2DZ and UB3LYP/6-31G conditions.



Color key for bonds (numbers correspond to Mulliken overlap population)

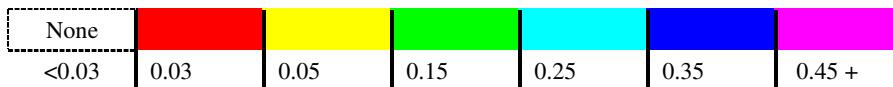
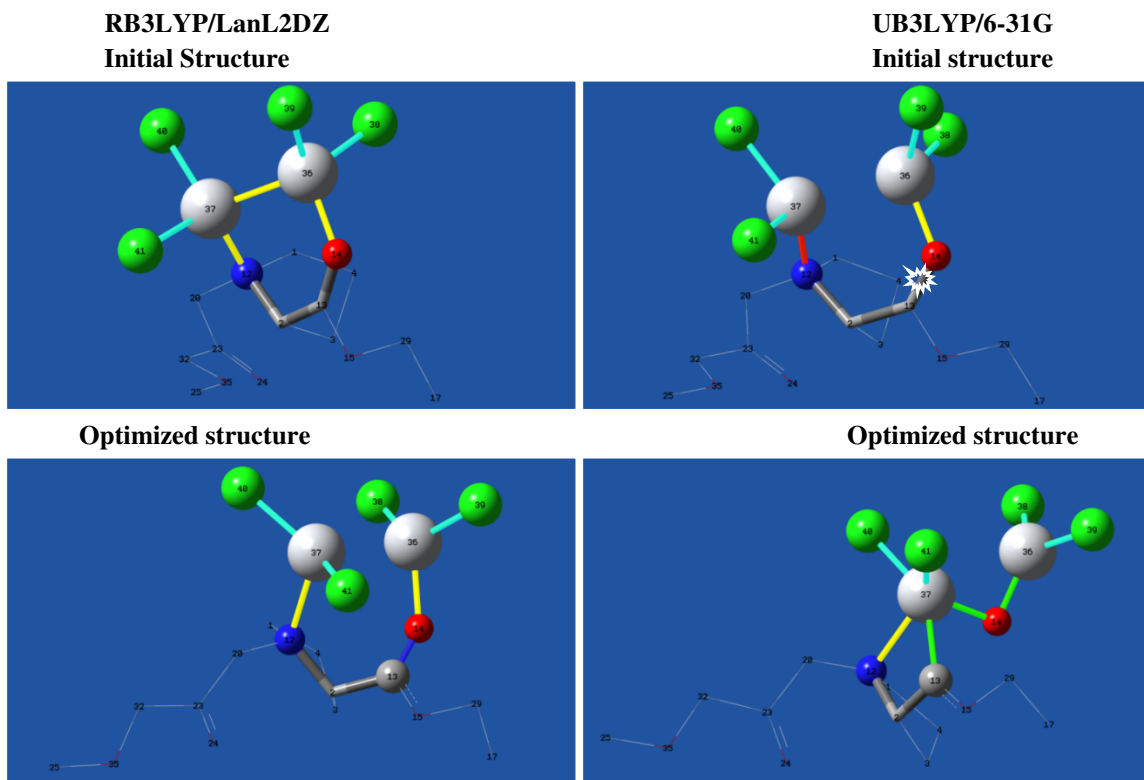


Figure 5.3.9. Initial and optimized structures for intermediate [C,J].

The optimized [F,I] structures at the RB3LYP/LanL2DZ and UB3LYP/6-31G levels of theory are quite different (see Figure 5.3.10). In the RB3LYP/LanL2DZ optimized structure there is a strong bond between oxygen 14 and carbon 13. There is no such bond in the UB3LYP/6-31G structure. Furthermore, in the UB3LYP/6-31G optimized structure the dimer appears to have plucked oxygen 14 from the ligand and forced it into the bridging position we often see chlorines assuming in these optimizations (see Figure 5.2.2).



Color key for bonds (numbers correspond to Mulliken overlap population)

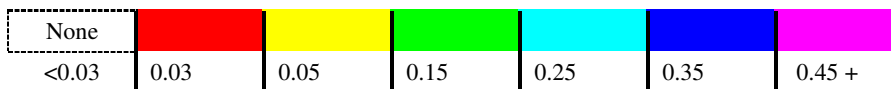
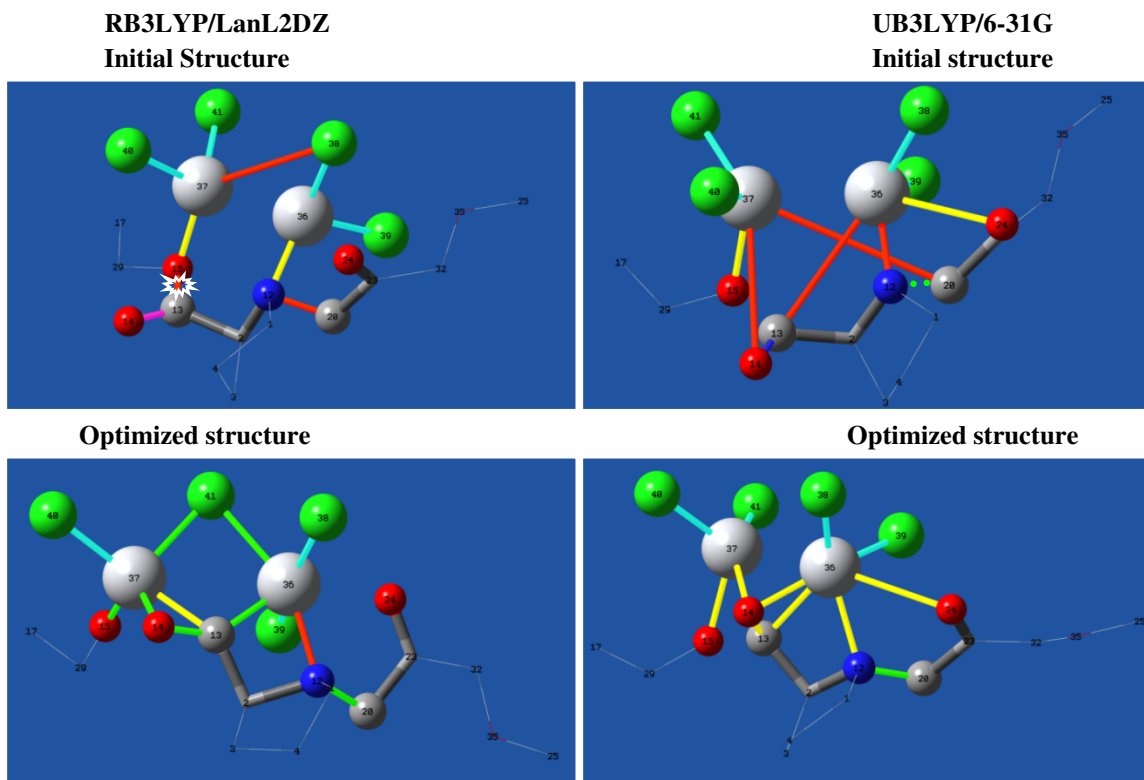


Figure 5.3.10. Initial and optimized structures for intermediate [F,I].

In the [F,I] structures the two conditions yielded significant differences in the optimized geometry and bonding and a corresponding lowering of molecular energy relative to the [A,I] intermediate. In the [F,J] intermediate there is little to differentiate the two optimized structures in terms of Mulliken overlap populations or geometry (see Figure 5.3.11), yet the relative energy ordering of the intermediates is quite different, as discussed below. It appears that, at least in this case, the more accurate UB3LYP/6-31G level of theory yields very different results from the RB3LYP/LanL2DZ method.



Color key for bonds (numbers correspond to Mulliken overlap population)

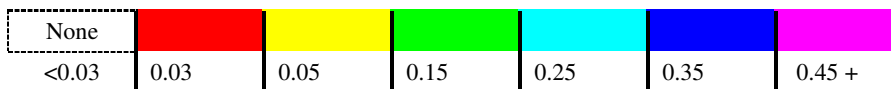
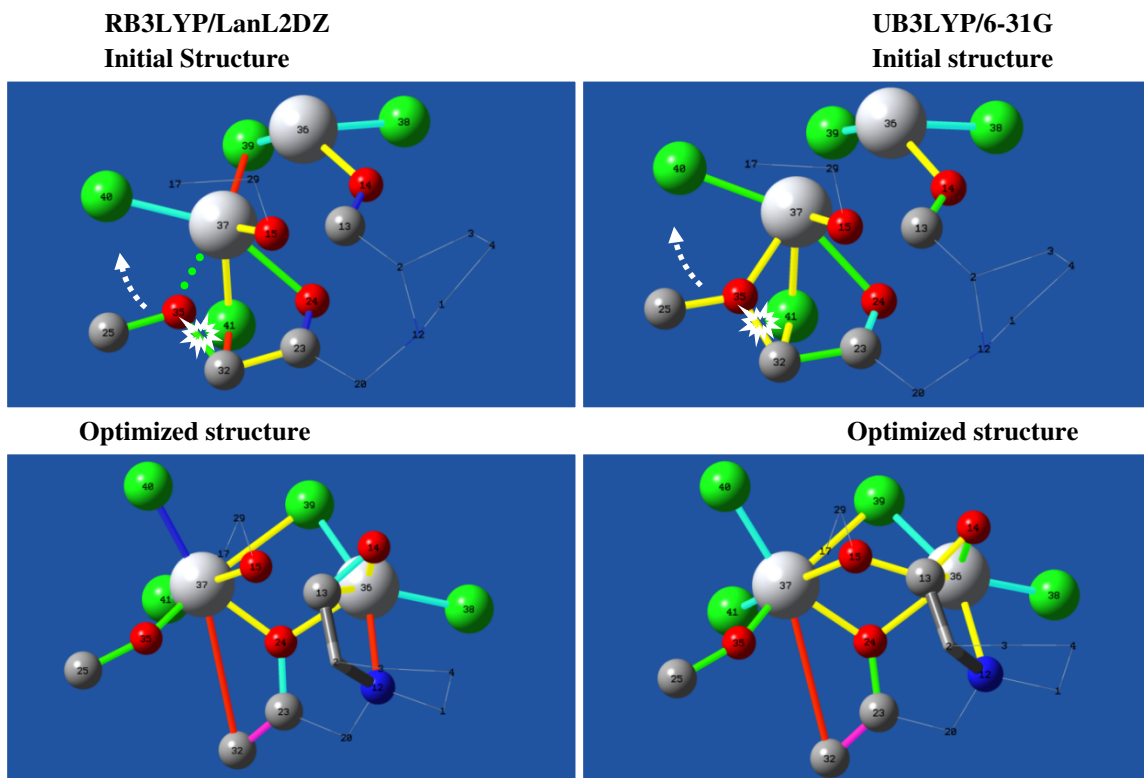


Figure 5.3.11. Initial and optimized structures for intermediate [F,J].

As in [F,J] above, in [I,J] the bonding according to the Mulliken overlap populations is nearly identical in both optimized structures (see Figure 5.3.12), perhaps more so than in any other intermediate, despite the fact that the relative energy ordering is quite different. It is interesting to note that in both this and the [A,J] intermediates the dimer interacts with the ligand to produce bridging bonds between the two titanium atoms, as we see in the capnellene optimizations. However, this similarity to the bonding and geometry of the dimer in the capnellene optimizations does not directly correlate with lower molecular energy (see the discussion of intermediate [A,F]).



Color key for bonds (numbers correspond to Mulliken overlap population)

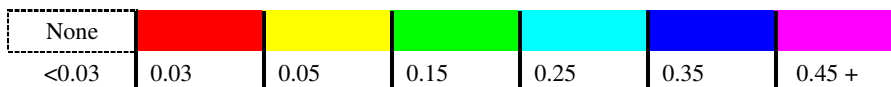
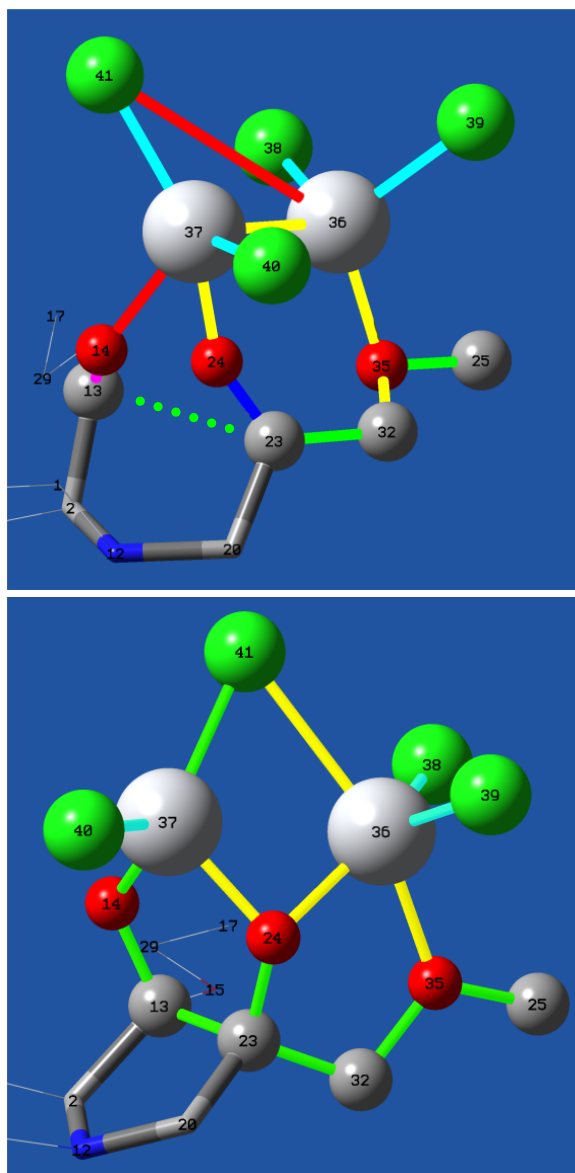


Figure 5.3.12. Initial and optimized structures for intermediate [I,J].

5.3.2 Summary

The two levels of calculations yielded similar optimized structures for all intermediates but [A,C], [F,I] and, to a lesser extent [C,I]. As for the capnellene system, optimization calculations resulted in three kinds of structures: 1) McMurry intermediates ([A,I], [C,J], [C,I]), in which a new C-C formed during optimization; 2) intermediates in which a ligand bond was eliminated during optimization due to bond insertion ([A,J], [I,J], [F,J], [A,C]); and 3) and intermediates in which no significant change to the ligand

structure occurred during optimization ([A,F], [C,F], [F,I]). Examples from categories 1) and 2), are shown in Figure 5.3.13 and Figure 5.3.14 below. For an example from category 3), see intermediate [C,F], Figure 5.3.7.



Color key for bonds (numbers correspond to Mulliken overlap population)

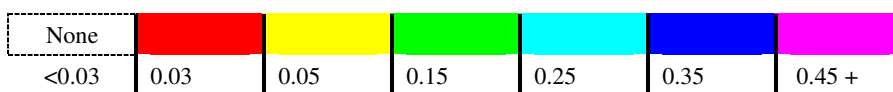
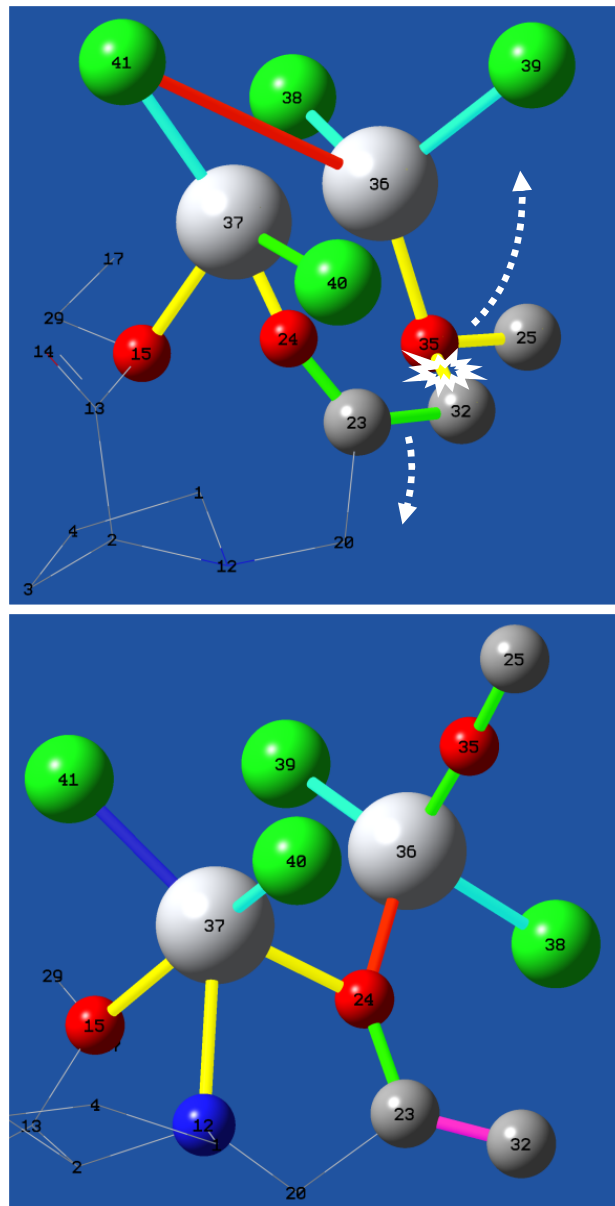


Figure 5.3.13. Structure of the [A,I] intermediate. On top is the initial structure. On bottom is the structure optimized at the RB3LYP/LanL2DZ level of theory. Bonds are color-coded according to the size of the Mulliken overlap population between atoms (see legend below the figures). A green dotted line shows where a new C-C bond (Mulliken overlap population $0.15 e^-$) will form in the optimized structure.



Color key for bonds (numbers correspond to Mulliken overlap population)

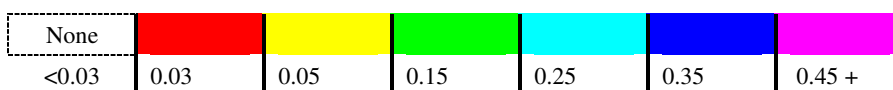


Figure 5.3.14. Structure of the [A,J] intermediate. On top is the initial structure. On bottom is the optimized structure at the RB3LYP/LanL2DZ level of theory. A white starburst in the initial structure shows where the bond between O 35 and C 32 will be eliminated and Ti 36 will insert itself between the two atoms in the optimized structure.

It is interesting to note that, as for the capnellene McMurry product [A,G], the structures of McMurry products [A,I] and [C,I] are very similar to that of Frenking's Ti(II) intermediate.^[2] Relevant bond lengths are compared in Table 5.4 below. In addition, crystallographic data of another titanapinacolate complex shows a similarly long pinacolic C-C distance of 1.610Å.^[5]

Table 5.4. Comparison of Optimized Bond Distances. All values in Å. Pyrrolidine values are for the structures optimized at the UB3LYP/6-31G level of theory.

Metallacycle bond type	Calc. length in pyrrolidine intermediate [A,I] (Å)	Calc. length in pyrrolidine intermediate [C,I] (Å)	Calc. length in CH ₂ O-TiCl ₂ complex ^[2] (Å)
Ti-Ti	2.83	2.83	2.51
Ti-O	1.86, 1.95	1.77, 1.75	1.80
C-O	1.44	1.43	1.41
C-C	1.57	1.58	1.54

The relative energy ordering of all intermediates is discussed in the next section.

5.3.3 Relative Energies

Table 5.5 and Table 5.6 show total energies in a.u. and relative energies in kcal/mol of all intermediates at the RB3LYP/LanL2DZ and UB3LYP/6-31G levels of theory, respectively. We calculated the energies in kcal/mol relative to the energy of the lowest-energy McMurry intermediate, [A,I]. Figure 5.3.15 below shows this information

in the form of an energy diagram. The structures in the tables and in the figure are colored-coded to indicate the type of optimized structure: red represents those structures in which optimization resulted in bond insertion, blue represents those structures in which optimization resulted in the formation of the McMurry intermediate, and grey represents those structures in which optimization did not change the structure of the ligand.

Table 5.5. Energies of pyrrolizidine intermediates optimized at RB3LYP/LanL2DZ level of theory. Color coding is the same as that used in Figure 5.3.15.

Intermediate	Total energy (a. u.)	Energy relative to [A,I] (kcal/mol)
[A,J] •	-962.5566	-22.36
[I,J] •	-962.5559	-0.052
[A,I] •	-962.5210	0
[C,J] •	-962.5039	10.77
[F,J] •	-962.4981	14.37
[A,C] •	-962.4840	23.22
[A,F] •	-962.4807	25.31
[C,I] •	-962.4806	25.33
[C,F] •	-962.4386	51.77
[F,I] •	-962.3699	94.86

Table 5.6. Energies of pyrrolizidine intermediates optimized at RB3LYP/LanL2DZ level of theory. Color coding is the same as that used in Figure 5.3.15

Intermediate		Total energy (a. u.)	Energy relative to [A,I] (kcal/mol)
[I,J]	•	-4326.0571	-20.72
[A,J]	•	-4326.0541	-18.82
[A,I]	•	-4326.0241	0
[A,C]	•	-4326.0206	2.169
[C,J]	•	-4326.0063	11.16
[A,F]	•	-4325.9864	23.65
[C,I]	•	-4325.9770	29.52
[C,F]	•	-4325.9363	55.06
[F,I]	•	-4325.9291	59.58
[F,J]	•	-4325.9175	66.87

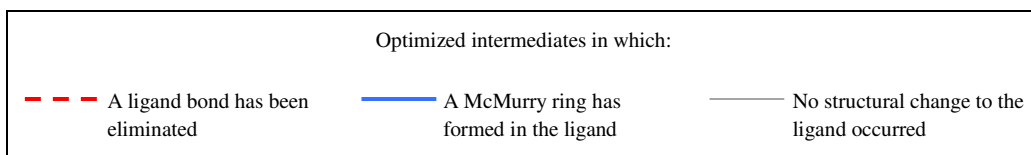
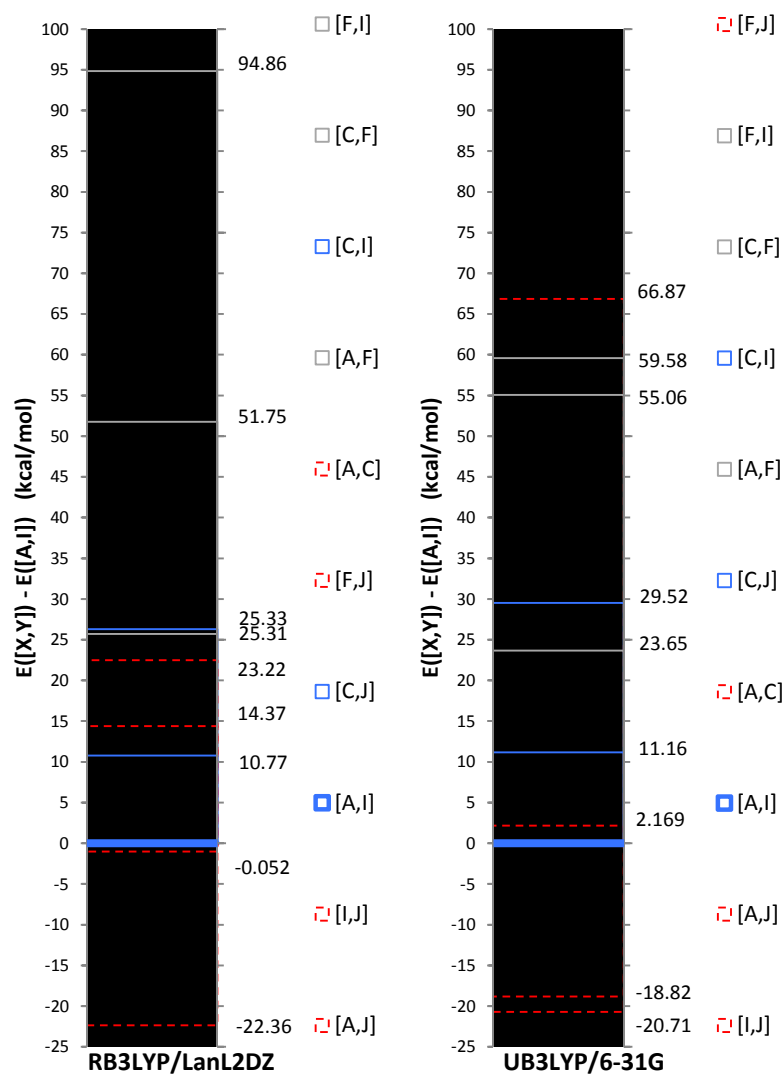
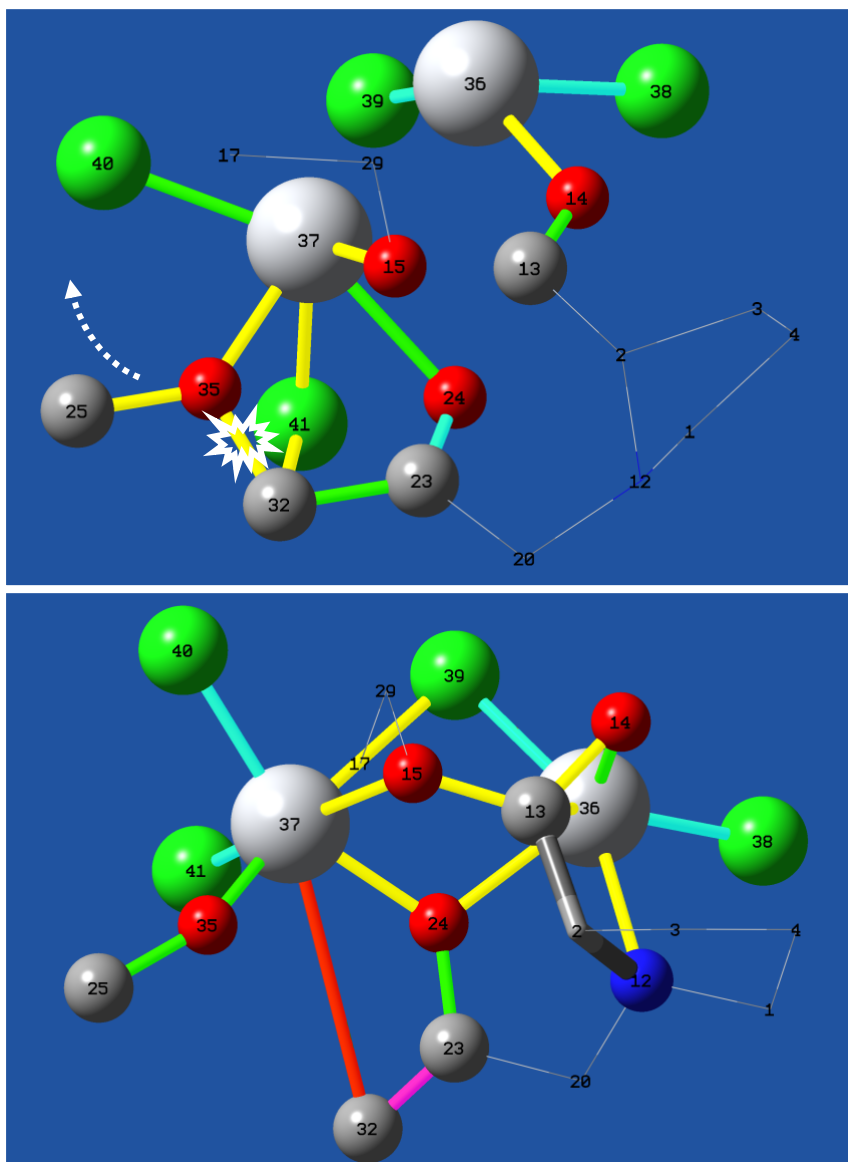


Figure 5.3.15. Energy of optimized intermediates in kcal/mol relative to the lowest-energy McMurry Intermediate, [A,I]. At left are the results of the RB3LYP/LanL2DZ calculations and at right are the results of the UB3LYP/6-31G calculations.

Our results indicate that those structures in which no significant change to the ligand occurred during the optimization process (category 3) tend to have a higher energy than structures in categories 1 or 2. The latter vary widely in relative energy. More importantly, both sets of calculations show that the most stable optimized structure contains bond insertions—although nearly identical optimized structures featuring a bond insertion are far higher in energy. Neither set of calculations predicts the McMurry product to be the thermodynamically preferred product. The analysis below focuses mostly on the UB3LYP/6-31G results, which are likely more accurate than the RB3LYP/LanL2DZ results.^[6]

Figure 5.3.16 shows the results of the UB3LYP/6-31G optimization of structure [I,J]. In Figure 5.3.15 above, [I,J] and [A,J] occupy the two lowest energy levels among the intermediates whether we use the RB3LYP/LanL2DZ method or the UB3LYP/6-31G method in our optimizations. Note, however, that [I,J], which in the RB3LYP/LanL2DZ diagram has nearly the same energy as [A,I], in the UB3LYP/6-31G diagram leapfrogs [A,J] to become the lowest energy intermediate. It is certainly interesting to note that in [I,J] the ligand and dimer have rearranged in such a way that oxygen 15 and chlorine 39 bridge the titanium atoms, similar to the conformations formed in the capnellene optimizations. However, this similarity does not directly correlate with lower molecular energy. Chlorine bridging occurs in [A,F], which is more than 40 kcal/mol higher in energy than [I,J] (see in Table 5.6).



Color key for bonds (numbers correspond to Mulliken overlap population)

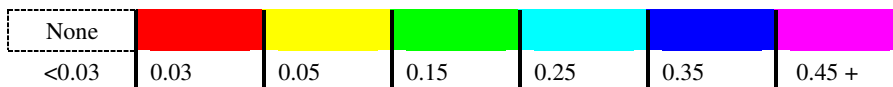


Figure 5.3.16. Structure of the [1,2] intermediate. On top is the initial structure. On bottom is the optimized structure at the UB3LYP/6-31G level of theory. A white starburst in the initial structure shows where the C-C bond between O 36 and C 32 will break in the optimized structure. Bond color indicates Mulliken overlap population between bonded atoms.

Now we turn to possible steric factors affecting the relative stability of the intermediates. The two most stable structures, [A,J] and [I,J], are also the two in which the dimer started out bonded to the oxygen atoms furthest out on the ligand's "arms." This is corroborated by experimental evidence indicating that the yield of ketone-ester cyclization is strongly influenced by the 'chain length' of the ligand.^[7] Next lowest in energy are [A,I] and [A,C], also structures containing dimer-ligand bonds relatively far out on the arms. The structures higher in energy than these four begin with one of the titanium atoms attached to atom F, the nitrogen atom—with one significant exception. Given the location of atom F in the ligand, it would be reasonable to expect a fair amount of steric strain in the formation of a bond between one of the titanium centers and its associated chlorine atoms and the ligand nitrogen. The exception mentioned above is structure [C,I], a McMurry intermediate at 29.53 kcal/mol higher energy than [A,I]. Noting that in this structure the dimer is attached to the two most internal electronegative atoms on the arms, and using the steric reasoning applied to the energies of the other structures, we would expect its energy to fall in between those of the nitrogen-bonded structures and those of the structures bonded to arm atoms. However, one nitrogen-bonded structure, [A,F], that lies in the middle of the range of relative energies, has an energy approximately 6 kcal/mol lower than that of [C,I]. We can't account for this discrepancy between calculation and chemical intuition—unless the donation of a chlorine from titanium 2 to titanium 1 in [A,F] confers some extraordinary stability upon the structure.

5.4 Conclusions

In this work we investigated the McMurry cyclization reaction of a pyrrolidine ligand by predicting the most stable conformation of the relevant intermediate. We used the results of geometry optimization calculations at the UB3LYP/6-31G level of theory and Mulliken population analyses to determine the structure and bonding of the preferred intermediate.

We initially performed an analogous set of calculations on the known capnellene sesquiterpene and the results correctly predicted the formation of the observed McMurry product. In addition, the optimized structures we obtained for the McMurry intermediates of capnellene and pyrrolidine match the results of another computational study on a similar molecule, further validating our methodology.

As for the proposed pyrrolidine cyclization we investigated, we can conclude that ethyl 1-(3-methoxy-2-oxopropyl)pyrrolidine-2-carboxylate will not undergo a McMurry cyclization reaction with titanium(II) chloride. The desired McMurry intermediate structure is much higher in energy than other configurations resulting from bond insertion. Specifically, one of the titanium atoms preferentially inserts itself into the C-O bond in the ester group. In fact, this phenomenon of formal insertion into the *endo*-Ti-C bond in the reaction of aliphatic ketones is well documented and we expect that these are the products obtained by Dr. Lindsay's group.^[8]

5.5 References

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6. Mulliken Overlap Populations for Pyrrolizidine Intermediates

Key

Intermediate and method

Atom #

Specifies initial or optimized structures

Atom type and color

Optimized Structures

[A,I]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C	-	-	0.31	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	C	-	0.27	-	0.36	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	C	-	0.27	0.29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	C	0.31	-	0.29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12	N	0.30	0.36	-	-	-	-	-	0.29	-	-	-	-	-	-	-	-	-	-	-	-	-
13	C	-	0.12	-	-	-	0.21	0.26	-	-	0.15	-	-	-	-	-	-	-	-	-	-	-
14	O	-	-	-	-	-	0.21	-	-	-	-	-	-	-	-	-	-	0.23	-	-	-	-
15	O	-	-	-	-	-	0.26	-	-	-	-	-	-	0.25	-	-	-	-	-	-	-	-
17	C	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-	-	-	-	-
20	C	-	-	-	0.29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
23	C	-	-	-	-	0.15	-	-	-	0.14	-	-	-	-	0.17	-	-	-	-	-	-	-
24	O	-	-	-	-	-	-	-	-	-	0.16	-	-	-	-	-	0.07	0.08	-	-	-	-
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.16	-	-	-	-	-	-
29	C	-	-	-	-	-	-	0.25	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-
32	C	-	-	-	-	-	-	-	-	0.17	-	-	-	-	-	0.21	-	-	-	-	-	-
35	O	-	-	-	-	-	-	-	-	-	-	-	0.16	-	0.21	-	0.09	-	-	-	-	-
36	Ti	-	-	-	-	-	-	-	-	-	-	0.07	-	-	-	0.09	-	-	0.31	0.31	-	0.14
37	Ti	-	-	-	-	-	-	0.23	-	-	-	0.08	-	-	-	-	-	-	-	-	0.30	0.20
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-	-
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-	-
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.14	0.20	-	-	-	-

Overlap populations $\leq 0.03 e^-$ not displayed

Overlap population between atoms in e^- . Colors taken from both atoms

Mulliken overlap populations for [A,F].

		Initial structures																				Optimized Structures																									
[A,F]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[A,F]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C	-	-	-	0.15	0.17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.33	-	0.18	0.10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.33	-	0.23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.15	-	0.23	-	-	-	-	-	-	-	0.04	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.17	0.18	-	-	-	-	-	-	-	0.18	-	-	-	-	-	0.11	-	-	-	-	-	-																								
13	C	-	0.10	-	-	-	0.61	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	0.61	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	0.19	-	-	-	-	-	-	0.21	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	0.32	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.18	-	-	-	-	-	0.13	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	0.13	0.61	-	0.08	-	-	0.04	-	-	-	-	-	-																								
24	O	-	-	0.04	-	-	-	-	-	-	0.61	-	-	-	-	-	-	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.13	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	0.21	0.32	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	0.08	-	-	-	-	0.18	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	0.13	0.18	-	-	0.10	-	-	-	-	-	-																								
36	Ti	-	-	-	0.11	-	-	-	-	-	-	-	-	-	-	-	-	0.35	0.35	-	-	-	-																								
37	Ti	-	-	-	-	-	-	-	-	-	0.04	-	-	-	-	0.10	-	-	-	0.32	0.29	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.35	-	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.35	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.32	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.29	-	-	-	-	-																								
1	C	-	-	-	0.20	0.10	-	-	-	-	-	-	-	-	-	-	0.32	0.19	-	-	-	-	-																								
2	C	-	-	0.34	-	0.05	0.14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.34	-	0.23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.20	-	0.23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.10	0.05	-	-	-	-	-	-	-	0.10	-	-	-	-	-	0.07	-	-	-	-	-	-																								
13	C	-	0.14	-	-	-	0.36	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	0.36	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	0.12	-	-	-	-	-	-	0.12	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	-	0.33	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.10	-	-	-	-	-	0.19	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	0.19	0.37	-	0.19	-	-	0.07	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	0.37	-	-	-	-	-	-	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.09	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	0.12	0.33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	O	-	-	-	-	-	-	-	-	-	0.19	-	-	-	-	0.12	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	0.09	0.12	-	-	-	-	0.09	-	-	-	-	-	-																								
36	Ti	-	-	-	0.07	-	-	-	-	-	-	-	-	-	-	-	-	0.30	0.35	-	-	-	-																								
37	Ti	-	-	-	-	-	-	-	-	-	0.07	-	-	-	-	0.09	-	-	0.30	0.35	-	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.35	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.29	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-	-																								
1	C	-	-	-	0.32	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.30	-	0.20	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.30	-	0.32	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.32	-	0.32	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.19	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	0.20	-	-	-	0.30	0.22	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	0.22	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	0.19	0.28	-	-	-	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	0.07	0.07	-	-	-	-	-	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	0.08	-	0.16	-	-	-	0.08	0.13	-	-	-	-	-	-	-	-	-	-	-																								
37	Ti	-	-	-	-	-	-	-	-	-	0.05	0.10	-	-	-	-	-	-	-	-	-	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								

Mulliken overlap populations for [A,I].

Initial structures																					Optimized Structures																								
[A,I]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[A,I]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C			0.22	0.25																																								
2	C		0.24		0.24	0.21																																							
3	C		0.24	0.30																																									
4	C	0.22		0.30			0.04																																						
12	N	0.25	0.24				0.03			0.33																																			
13	C		0.21				0.49	0.25		0.03																																			
14	O			0.04	0.03	0.49											0.04																												
15	O					0.25								0.24																															
17	C												0.32																																
20	C				0.33	0.03					0.21																																		
23	C									0.21		0.36			0.15																														
24	O										0.36						0.08																												
25	C															0.15																													
29	C						0.24	0.32																																					
32	C									0.15							0.13																												
35	O												0.15		0.13		0.11																												
36	Ti															0.11	0.05	0.05	0.29	0.30		0.04																							
37	Ti						0.04										0.05				0.31	0.32																							
38	Cl																0.29																												
39	Cl																0.30																												
40	Cl																	0.31																											
41	Cl																0.04	0.32																											
1	C				0.30	0.17																																							
2	C		0.29		0.23	0.19																																							
3	C		0.29	0.33																																									
4	C	0.30		0.33																																									
12	N	0.17	0.23				0.03			0.26																																			
13	C		0.19				0.26	0.15																																					
14	O				0.03	0.26											0.06																												
15	O					0.15								0.15																															
17	C													0.33																															
20	C				0.26						0.32																																		
23	C									0.32		0.18			0.31																														
24	O										0.18					0.04																													
25	C															0.10																													
29	C						0.15	0.33																																					
32	O									0.31							0.04																												
35	O										0.10		0.04			0.10																													
36	Ti										0.04				0.10		0.30	0.31																											
37	Ti					0.06													0.30	0.31																									
38	Cl															0.30																													
39	Cl															0.31																													
40	Cl																																												
41	Cl																																												
1	C				0.33	0.26																																							
2	C		0.29		0.25	0.17																																							
3	C		0.29	0.32																																									
4	C	0.33		0.32																																									
12	N	0.26	0.25												0.23																														
13	C		0.17														0.16	0.16			0.23																								
14	O																0.16	0.16																											
15	O																0.16																												
17	C																				0.18																								
20	C																				0.33																								
23	C																																												
24	O																																												
25	C																																												
29	C																																												
32	C																																												
35	O																																												
36	Ti																																												
37	Ti																																												
38	Cl																																												
39	Cl																																												
40	Cl																																												
41	Cl																																												
1	C				0.33	0.26																																							
2	C		0.29		0.25	0.17																																							
3	C		0.29	0.32																																									
4	C	0.33		0.32																																									
12	N	0.26	0.25																																										
13	C		0.17																																										
14	O																																												
15	O																																												
17	C																																												
20	C																																												
23	C																																												
24	O																																												
25	C																																												
29	C																																												
32	C																																												
35	O																																												
36	Ti																																												
37	Ti																																												
38	Cl																																												
39	Cl																																												
40	Cl																																												
41	Cl																																												

Mulliken overlap populations for [A,J].

Initial structures																					Optimized Structures																								
[A,J]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[A,J]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C			0.24	0.28																																								
2	C			0.29	0.27	0.07																																							
3	C		0.29	0.28																																									
4	C	0.24		0.28																																									
12	N	0.28	0.27						0.32																																				
13	C		0.07				0.63																																						
14	O						0.63																																						
15	O												0.21				0.07																												
17	C												0.25																																
20	C				0.32					0.19																																			
23	C									0.19		0.21			0.21																														
24	O										0.21						0.11																												
25	C															0.15																													
29	C						0.21	0.25																																					
32	C								0.21								0.11																												
35	O											0.15					0.11																												
36	Ti																0.11		0.31	0.31		0.03																							
37	Ti						0.07					0.11									0.20	0.34																							
38	Cl																	0.31																											
39	Cl																	0.31																											
40	Cl																		0.20																										
41	Cl																	0.03	0.34																										
1	C																																												
2	C				0.32	0.22	0.09																																						
3	C		0.32		0.33																																								
4	C	0.31		0.33																																									
12	N	0.21	0.22						0.27																																				
13	C		0.09																																										
14	O						0.38											0.04																											
15	O												0.10				0.08																												
17	C												0.27																																
20	C				0.27																																								
23	C									0.30		0.21			0.35																														
24	O										0.21						0.04																												
25	C															0.10																													
29	C						0.10	0.27																																					
32	C										0.35																																		
35	O											0.10																																	
36	Ti										0.04						0.12		0.29	0.31																									
37	Ti						0.04	0.08													0.18	0.29																							
38	Cl																	0.29																											
39	Cl																		0.31																										
40	Cl																																												
41	Cl																			0.18																									
																				0.29																									
1	C																																												
2	C																																												
3	C																																												
4	C	0.32		0.32																																									
12	N	0.19	0.12																																										
13	C		0.19																																										
14	O																																												
15	O																																												
17	C																																												
20	C																																												
23	C																																												
24	O																																												
25	C																																												
29	C																																												
32	C																																												
35	O																																												
36	Ti																																												
37	Ti																																												
38	Cl																																												
39	Cl																																												
40	Cl																																												
41	Cl																																												
1	C																																												
2	C																																												
3	C																																												
4	C	0.32		0.32																																									
12	N	0.19	0.12																																										
13	C		0.19																																										
14	O																																												
15	O																																												
17	C																																												
20	C																																												
23	C																																												
24	O																																												
25	C																																												
29	C																																												
32	C																																												
35	O																																												
36	Ti																																												
37	Ti																																												
38	Cl																																												
39	Cl																																												
40	Cl																																												
41	Cl																																												

Mulliken overlap populations for [C,F].

		Initial structures																				Optimized Structures																									
[C,F]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[C,F]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C	-	-	-	0.23	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.27	-	0.17	0.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.27	-	0.25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.23	-	0.25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.20	0.17	-	-	-	-	-	-	-	0.20	-	-	-	-	-	-	-	0.11	-	-	-	-																								
13	C	-	0.09	-	-	-	-	0.65	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.65	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	-	0.20	-	-	-	-	-	0.21	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	0.32	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.20	-	-	-	-	-	0.18	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	0.18	0.40	-	-	0.20	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	0.40	-	-	-	-	-	0.16	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.24	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	0.21	0.32	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	0.20	-	-	-	-	-	0.28	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	0.24	-	0.28	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	-	-	-	0.16	-	-	-	-	-	-	-	0.28	0.29	-	-	-																								
37	Ti	-	-	-	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	0.31	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.28	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.29	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-																								
1	C	-	-	-	0.31	0.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.28	-	0.10	0.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.28	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.31	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.16	0.10	-	-	-	-	-	-	-	0.16	-	-	-	-	-	-	-	0.14	-	-	-	-																								
13	C	-	0.16	-	-	-	-	0.49	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.49	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	-	0.11	-	-	-	-	-	0.15	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	0.32	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	0.25	-	0.31	-	-	0.33	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-	-	0.17	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	0.15	0.32	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	0.33	-	-	-	-	-	0.18	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	0.20	-	0.18	-	-	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	-	-	0.17	-	-	-	-	-	-	-	-	0.27	0.30	-	-	-																								
37	Ti	-	-	-	0.14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	0.31	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.27	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-																								
1	C	-	-	-	0.32	0.17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.28	-	0.17	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.28	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.32	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.17	0.17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.47	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	-	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	0.24	-	0.06	-	-	0.33	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	0.06	-	-	-	-	-	-	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	0.15	0.32	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	0.33	-	-	-	-	-	-	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	0.21	-	0.20	-	-	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	-	-	-	0.18	-	-	-	-	-	-	-	-	-	0.29	0.32	-																								
37	Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								

Mulliken overlap populations for [C,I].

		Initial structures																				Optimized Structures																									
[C,I]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[C,I]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C	-	-	-	0.25	0.25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.21	-	0.21	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.21	-	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.25	-	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.25	0.21	-	-	-	-	-	-	-	0.29	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	0.19	-	-	-	-	0.49	0.13	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.49	-	-	-	-	-	-	-	-	-	0.06	-	-	-	-	-																								
15	O	-	-	-	-	-	-	0.13	-	-	-	-	-	0.22	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	0.32	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.29	-	-	-	-	-	0.19	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	0.19	0.37	-	-	0.20	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	-	0.37	-	-	-	-	0.12	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.25	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	0.22	0.32	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	0.20	-	-	-	-	0.26	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	0.25	-	0.26	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	-	-	-	-	0.12	-	-	-	-	0.17	0.31	0.27	-	-	-	-																								
37	Ti	-	-	-	-	-	-	0.06	-	-	-	-	-	-	-	-	0.17	-	-	0.33	0.30	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.27	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.33	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-	-																								
1	C	-	-	-	0.32	0.15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.29	-	0.23	0.13	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.29	-	0.34	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.32	-	0.34	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.15	0.23	-	-	-	-	-	-	-	0.24	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	0.13	-	-	-	-	0.34	0.08	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.34	-	-	-	-	-	-	-	-	-	0.07	-	-	-	-	-																								
15	O	-	-	-	-	-	-	0.08	-	-	-	-	-	0.12	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	0.33	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	0.23	0.30	-	-	0.25	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-	0.14	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.21	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	0.12	0.33	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	0.25	-	-	-	-	0.19	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	0.21	-	0.19	-	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	-	-	-	-	0.14	-	-	-	-	-	0.28	0.28	-	-	-	-																								
37	Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.28	0.28	-	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.28	-	-	-	0.25	0.25	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.28	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.25	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.25	-	-	-	-	-																								
1	C	-	-	-	0.33	0.27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.27	-	0.28	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.27	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.33	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.27	0.28	-	-	-	-	-	-	-	0.26	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	0.20	-	-	-	-	0.08	0.18	-	-	-	-	0.23	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.08	-	-	-	-	-	-	-	-	-	0.18	-	-	-	-	-																								
15	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.18	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.33	-	-	-																								
20	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	0.23	-	-	-	0.25	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	-	0.30	-	-	0.12	-	-	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
37	Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								

Mulliken overlap populations for [C,J].

		Initial structures																				Optimized Structures																									
[C,J]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[C,J]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C	-	-	-	0.23	0.26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.27	-	0.30	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.27	-	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.23	-	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.26	0.30	-	-	-	-	-	-	-	0.30	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	0.20	-	-	-	-	0.23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.23	-	-	-	-	-	-	-	-	-	0.04	0.08	-	-	-	-																								
15	O	-	-	-	-	-	-	-	-	-	-	-	-	0.16	-	-	0.15	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	-	0.29	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.30	-	-	-	-	-	0.14	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	0.14	0.31	-	-	0.07	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-	-	0.22	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.10	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	0.16	0.29	-	-	-	-	-	-	-	0.09	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	0.07	-	-	-	-	-	-	0.09	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.10	0.13	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	0.04	-	-	-	0.22	-	-	-	-	0.13	-	0.04	0.30	-	-	-																								
37	Ti	-	-	-	-	-	-	0.08	0.15	-	-	-	-	-	-	-	-	-	0.04	0.31	0.32	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.04	0.04	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.32	-	-	-																								
1	C	-	-	-	0.33	0.26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.29	-	0.27	0.15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.28	-	0.33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.30	-	0.33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.18	0.26	-	-	-	-	-	-	-	0.25	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	0.15	-	-	-	-	0.14	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.14	-	-	-	-	-	-	-	-	0.06	0.04	-	-	-	-	-																								
15	O	-	-	-	-	-	-	-	-	-	-	-	-	0.07	-	-	0.11	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	0.25	-	-	-	-	-	0.23	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	0.05	-	-	-	-	0.23	0.13	-	-	0.25	-	-	0.04	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	0.13	-	-	-	-	-	0.21	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	0.07	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	0.25	-	-	-	-	-	-	-	0.08	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.16	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	0.06	-	-	0.21	-	-	-	-	-	0.16	-	-	0.29	-	-	-																								
37	Ti	-	-	-	-	-	-	0.04	0.11	-	0.04	-	-	-	-	-	-	-	0.07	0.30	0.29	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	0.08	-	-	-	0.29	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.32	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-																								

Mulliken overlap populations for [F,I].

Initial structures																					Optimized Structures																								
[F,I]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[F,I]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C			0.27	0.24																																								
2	C			0.29	0.21	0.12																																							
3	C		0.29		0.21																																								
4	C	0.27		0.21																																									
12	N	0.24	0.21							0.13								0.09																											
13	C		0.12				0.38	0.27																																					
14	O						0.38										0.12																												
15	O						0.27							0.23																															
17	C												0.32																																
20	C				0.13																																								
23	C											0.62		0.09																															
24	O										0.62																																		
25	C														0.25																														
29	C						0.23	0.32																																					
32	C								0.09						0.29																														
35	O											0.25	0.29																																
36	Ti					0.12											0.08	0.31	0.28																										
37	Ti				0.09												0.08			0.32	0.32																								
38	Cl																0.31																												
39	Cl																0.28																												
40	Cl																	0.32																											
41	Cl																	0.32																											
1	C				0.31	0.16																																							
2	C			0.29		0.14	0.24																																						
3	C		0.29		0.25																																								
4	C	0.31		0.25																																									
12	N	0.16	0.14							0.09								0.04																											
13	C		0.24																																										
14	O						0.22	0.20										0.13																											
15	O						0.20							0.15																															
17	C												0.32																																
20	C				0.09																																								
23	C								0.10	0.10	0.43			0.18																															
24	O									0.43																																			
25	C														0.21																														
29	C						0.15	0.32																																					
32	C								0.18						0.22																														
35	O									0.21	0.22																																		
36	Ti					0.13												0.28	0.29																										
37	Ti				0.04															0.31	0.30																								
38	Cl																0.28																												
39	Cl																0.29																												
40	Cl																	0.31																											
41	Cl																	0.30																											
1	C				0.32	0.19																																							
2	C			0.30		0.16	0.21																																						
3	C		0.30		0.32																																								
4	C	0.32		0.32																																									
12	N	0.19	0.16												0.18																														
13	C		0.21																																										
14	O													0.20																															
15	O													0.20																															
17	C																																												
20	C																																												
23	C									0.11	0.53			0.11																															
24	O										0.53																																		
25	C																			0.21																									
29	C													0.13	0.31																														
32	C														0.11					0.20																									
35	O																			0.21	0.20																								
36	Ti																				0.30	0.29																							
37	Ti																					0.28	0.31																						
38	Cl																				0.30																								
39	Cl																				0.29																								
40	Cl																					0.28																							
41	Cl																					0.31																							

Mulliken overlap populations for [F,J].

		Initial structures																				Optimized Structures																									
[F,J]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[F,J]		1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ		C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C	-	-	-	0.23	0.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	0.25	-	0.26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.25	-	0.29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.23	-	0.29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.16	0.26	-	-	-	-	-	-	-	0.03	-	-	-	-	-	-	0.05	-	-	-	-	-																								
13	C	-	-	-	-	-	-	0.65	0.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	0.65	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	-	0.05	-	-	-	-	-	0.15	-	-	-	0.15	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	-	0.03	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	-	-	0.63	-	0.06	-	-	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	0.63	-	-	-	-	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	0.15	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	0.06	-	-	-	-	-	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	-	0.25	-	0.28	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	0.05	-	-	-	-	-	-	-	-	-	-	-	-	-	0.32	0.31	-	-																								
37	Ti	-	-	-	-	-	-	0.15	-	-	-	-	-	-	-	-	-	-	0.03	-	0.34	0.30	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.32	0.03	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.31	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.34	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.30	-	-	-																								
1	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.28	-	0.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.22	0.20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
37	Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
1	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
2	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
3	C	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
4	C	0.31	-	0.31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
12	N	0.17	0.15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
13	C	-	0.15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
14	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
15	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
17	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
20	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
23	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
24	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
25	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
29	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
32	C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
35	O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
36	Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
37	Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
38	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
39	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
40	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								
41	Cl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-																								

Mulliken overlap populations for [I,J].

Initial structures																					Optimized Structures																								
[I,J]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41	[I,J]	1	2	3	4	12	13	14	15	17	20	23	24	25	29	32	35	36	37	38	39	40	41
LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl	LanL2DZ	C	C	C	C	N	C	O	O	C	C	C	O	C	C	C	O	Ti	Ti	Cl	Cl	Cl	Cl
1	C			0.24	0.28																																								
2	C			0.29	0.12																																								
3	C			0.30																																									
4	C			0.24	0.30																																								
12	N			0.28	0.29																																								
13	C			0.12																																									
14	O																																												
15	O																																												
17	C																																												
20	C																																												
23	C																																												
24	O																																												
25	C																																												
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