QUANTUM MECHANICAL ANALYSIS OF DONOR-ACCEPTOR INTERACTIONS IN ORGANOMETALLIC COMPLEXES AND COMPARATIVE ANALYSIS OF CLASS SIZE AND TEACHER EXPERIENCE ON STUDENT SATISFACTION AND LEARNING

BY

CHARITY FLENER

DISSERTATION

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Doctoral Committee:

Professor Gregory Girolami, Chair and Director of Research
Professor Thom Dunning, Co-Director of Research
Assistant Professor Roman Boulatov
Specialist in Education Don Decoste
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Charity Flener, PhD
Department of Chemistry
University of Illinois at Urbana-Champaign, 2009
Gregory S. Girolami Advisor
Thom H. Dunning Jr., Co-advisor

The first five chapters of this thesis use modern density functional and ab initio methods to analyze donor-acceptor complexes of transition metals. Chapter 1 gives background for the theories used in this work.

In chapter 2, density functional theory (DFT) is used to investigate the geometries and metal-ligand bonds in nickel complexes of bidentate phosphines, Ni(CO)2(R2P(CH2)nPR2) and NiH2(R2P(CH2)nPR2), where n = 1, 2, or 3; and R = H, Me, CF3, Et, i-Pr, t-Bu, Ph, OMe, or F. The net donor/acceptor properties of the phosphine ligands can be deduced from the computed frequency of the symmetric CO stretch of the Ni(CO)2(R2P(CH2)nPR2) complexes. This frequency can be estimated from the empirical expression ν(CO) = 1988 + Σ χB − 4 n, where the sum is over the four phosphorus bound substituents; χB is a substituent-dependent parameter; and n is the number of carbon atoms in the backbone (1 ≤ n ≤ 3). The deduced values of χB (in units of cm⁻¹): t-Bu (0.0), i-Pr (0.8), Et (3.0), Me (4.0), Ph (4.3), H (6.3), OMe (10.8), CF3 (17.8), and F (18.3), are generally similar to Tolman’s electronic parameter, χ derived from nickel complexes of unidentate phosphines, except that OMe is significantly less electron donating when incorporated into a bidentate phosphine vs. a unidentate phosphine. The calculated frequencies also show that the phosphine appears to be a better donor (or weaker acceptor) as the number of carbon atoms in the backbone increases. Increasing
the number of carbons by one has about the same effect as changing all four substituents from iso-propyl to tert-butyl (or changing one of the four substituents from methyl to tert-butyl). For the NiH₂(R₂P(CH₂)₆PR₂) complexes, the global minimum is a non-classical dihydrogen structure irrespective of the nature of the phosphine. For bidentate phosphines that are strongly donating, a classical cis-dihydride structure lies 2 kcal mol⁻¹ or higher in energy than the global minimum. For phosphines that are less electron donating, this structure is no longer a local minimum, but instead is an inflection point on the potential energy surface. Atoms in molecules and natural bond order analyses confirm that the Ni-H₂ interaction is a three-center two-electron bond in the dihydrogen tautomer. Energy decomposition analysis of these complexes is used to differentiate between the π and σ donor interactions in these complexes. There is a very good linear correlation between the calculated strength of the [M]←(H₂) σ donation and [M]→(H₂) π back donation which clearly shows that the π back donation has a much stronger effect on stretching the H-H distance than the σ donation.

In Chapter 3, density functional theory and ab initio methods have been used to calculate the structures and energies of minima and transition states for the reactions of methane coordinated to a transition metal. The reactions studied are reversible C-H bond activation of the coordinated methane ligand to form a transition metal methyl/hydride complex, and dissociation of the coordinated methane ligand. The reaction sequence can be summarized as L₅M(CH₃)H ⇋ L₅M(CH₄) ⇋ L₅M + CH₄, where L₅M is the osmium-containing fragment (C₂H₅)Os(R₂PCH₂PR₂)⁺ and R is H or CH₃. Three-center metal-carbon-hydrogen interactions play an important role in this system. Both basis sets and functionals have been benchmarked in this work, including new correlation consistent
basis sets for a third transition series element, osmium. Double zeta quality correlation consistent basis sets yield energies close to those from calculations with quadruple zeta basis sets, with variations that are smaller than the differences between functionals. The energies of important species on the potential energy surface, calculated by using ten DFT functionals, are compared both to experimental values and to coupled cluster CCSD(T) single point calculations. Kohn-Sham natural bond orbital descriptions were used to understand the differences between functionals. Older functionals favor electrostatic interactions over weak donor-acceptor interactions, and therefore are not particularly well suited for describing systems, such as σ-complexes, in which the latter are dominant. Newer kinetic and dispersion-corrected functionals such as MPW1K and M05-2X provide significantly better descriptions of the bonding interactions, as judged by their ability to predict energies closer to CCSD(T) values. Kohn-Sham and natural bond orbitals are used to differentiate between bonding descriptions. Our evaluations of these basis sets and DFT functionals led us to recommend the use of dispersion corrected functionals in conjunction with double zeta or larger basis sets with polarization functions for calculations involving weak interactions, such as those found in σ-complexes with transition metals.

In Chapter 4, M05-2X and BB1K were used to analyze the effect of ancillary ligands on the hydrogen exchange reaction of \((\text{C}_5\text{H}_x\text{R}_{5-x})\text{Os}(\text{Y}_2\text{PCZ}_2\text{PY}_2)(\text{CH}_3)\text{H}^+)\), where \(R = \text{Me, F, CF}_3, \text{SiH}_3, \text{SiMe}_2, \text{or H}\); \(x = 1-5\); \(Y = \text{H, Me, Ph, or F}\); and \(Z = \text{H or F}\). Three points on the potential energy surface are studied: the methyl hydride 1, the methane tautomer 2, the transition state 1\(^\dagger\) between 1 and 2, and the fragment molecule 3. We find that the steric and electronic effects of the ligands affect the relative energies of these
structures on the potential energy surface. Electron withdrawing ligands such as CF$_3$ or F decrease the energy of 1$^\dagger$ and stabilize 2 relative to 1, while electron donating ligands such as SiMe$_3$ increase the energy of 1$^\dagger$ and destabilize 2 relative to 1. The energy of 3 relative to 1 was found to be correlated to the steric bulk of R or Y.

In Chapter 5, we use M05-2X, B3LYP, and PBE0 methods to analyze a possible agostic interaction in the compound Ti$_2$Cl$_6$[N(t-Bu)$_2$]$_2$. The crystal structure of Ti$_2$Cl$_6$[N(tBu)$_2$]$_2$ shows very close contact (2.634 Angstroms) between the electron poor titanium atom and a methyl group. Short distances between an electron deficient metal center and carbon-hydrogen bonds are often assigned to be agostic, i.e., attractive interactions involving 3-center-2-electron bonds. To ascertain whether or not this close contact is due to an agostic interaction between the Ti and C-H atoms, the gas phase structure of the complex and related model compounds were optimized with dispersion corrected density functional methods, which have been shown to be capable of accurately describing agostic interactions. These calculations reveal that decreasing the steric bulk of the amido ligand (by replacing the non-interacting tert-butyl ligand with a smaller alkyl group) caused the Ti-H distances to increase significantly. Natural bond order (NBO) analysis of the gas phase structure showed that there are no bonding interactions between titanium and hydrogen. We conclude that close contacts between electron deficient metal centers and nearby C-H bonds are not always attractive, and that some agostic interactions are repulsive and are consequences of steric repulsions between the ligands in the inner coordination sphere.

Chapter 6 discusses the results of a year long research project studying student perceptions and success in two types of general chemistry courses. Studies have shown
that college students perform better in courses with 30 or fewer students, but in large public universities such as University of Illinois Urbana-Champaign (UIUC) economic and space constraints dictate larger class sizes. In an effort to provide a small, intimate classroom setting for first semester students, the department created a general chemistry course consisting of discussion classes of 30 students taught by graduate teaching assistants (TAs). The 2,000 students who enrolled in the course were given the choice to participate in a traditional lecture section of 350 students taught by teaching staff or the smaller TA-led discussion course. This study uses three ways to determine if student performance and satisfaction were different between the two types of sections: exam scores, attrition rates, and student happiness in the class (as measured by effectiveness ratings). On average, students in the small discussion performed worse on exams, left the course in higher numbers than large lecture students and rated their instructor less effective than students in the large lecture course. However, students in sections with experienced TAs performed significantly better than students in the large lecture course, suggesting that small classes with TAs can be effective provided that TAs are trained and motivated. These results show clearly that the quality of instruction matters much more than the quantity of students instructed.
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CHAPTER 1. INTRODUCTION TO COMPUTATIONAL METHODS

In 1929, Paul Dirac told the Royal Society of London,

“The general theory of quantum mechanics is now almost complete…The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved. It is therefore desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.”

For 50 years, the complex calculations required to implement these theories were limited to specialized theoretical experts with access to large computer systems. Upon the invention of affordable microprocessors and efficient algorithms in the late 1980s, accurate approximations could be implemented on personal computers, so bench chemists with some knowledge of theory could use theoretical calculations to predict and describe complex chemical phenomena. Many detailed treatments of the history and methods of chemical theory are available.\textsuperscript{2-5} This chapter seeks to provide a brief background into approximations used in modern computational theory as applied to organometallic chemistry.

Section 1.1 Computational models complement experimental data.

The goal of computational chemistry is to create robust and accurate models of chemical systems that have predictive value. Experimental chemists probe molecular structure from the outside in, where accuracy and understanding is limited by the resolution of the probe used to study the molecule and limitations in the interpretation of
the data. Computational chemists work from the inside out, creating accurate models that are limited only by the accuracy of the approximations employed. In this thesis, computations have been used in three ways that complement the experimental studies: to interpret ambiguous experimental results; to assist in choosing optimal experimental parameters for an experimentally known system; and to provide reliable predictions of properties for molecules that have not been studied experimentally, perhaps because they are too difficult or dangerous to isolate.

One of the strengths of computational chemistry is the ability to determine potential energy surfaces (PES) for arbitrary arrangements of the atoms in a given molecular system. The typical features of a PES can be shown for the example of a molecule with one degree of freedom, e.g., the distance between two atoms. As illustrated in Figure 1.1, important features on the surface include global and local minima and intervening transition states, flat shoulders without a minimum, the repulsive wall at short separations, and the dissociative asymptotic limit at long separations. The relative energies between minima, transition states, and the dissociation limit can be used to predict the kinetic behavior of the system.

Figure 1.1. PES of molecule with one degree of freedom.
Most systems are composed of multiple atoms with many degrees of freedom. For a molecule of N atoms, there are $3N-6$ internal degrees of freedom ($3N-5$ for linear molecules). A triatomic system has three degrees of freedom, which can consist of various combinations of internuclear separations and bond angles. Possible choices include the three separations or two distances and one bond angle. Each of these choices can be mapped onto the others. The particular choice of degrees of freedom depends on what makes the most intuitive chemical sense for a given system.

Qualitatively, a chemical potential energy surface is analogous to what a hiker encounters on mountainous terrain, where energy is mapped into height or elevation. At a given location, the ground slopes up or down in different directions and with varying steepness, which is described mathematically by the first derivatives. The terrain may range from flat to very irregular. The change in slope is described by the second derivatives. Terrain has valleys (which often have minima) and passes (which have local maxima in one direction). A representative 3D surface is shown in Figure 1.2.

**Figure 1.2.** PES showing 2 degrees of freedom. Grid supplied by DEW.
Features on a multidimensional potential energy surface have mathematical definitions. The elements of the gradient vector are the first derivatives (the partial derivative with respect to each coordinate). The second derivatives (second partial derivatives with respect to one or two coordinates) are collectively grouped into the hessian matrix. Any point where all of the gradient vector elements are zero is a stationary point, e.g., a minimum or a transition state. To further characterize the nature of a stationary point, the hessian matrix is diagonalized to yield eigenvalues from which vibrational frequencies are derived. A stationary point is a minimum if all of the vibrational frequencies are positive, and it is a transition state if all the frequencies are positive except for one.

Guesses for possible minima can be derived from the crystal structures of similar compounds. However, sometimes the calculations will return complexes that make little chemical sense. Thus it is important to remember that the structure obtained from the computations is not always the correct structure chemically, the approximations made in the calculations may be invalid or the calculations may have converged on a local minimum. Evaluation of the surface must always be accompanied by chemical intuition.

It is important to note that most programs calculate one local minima at a time, which corresponds to one structure. Experimental measurements often reflect a distribution of various structures and thus the computed properties may not agree with the experimental measurements. In an ideal world with infinite computer time, a chemist would calculate the structures of all of the low-lying conformers (indeed this approach is used in predicting solubility and thermal properties of drug candidates) but this approach
is time consuming and single structures often provide the insight necessary to complement most experimental data.

**Classes of computational models.** In this thesis, most of the computer models are derived from quantum mechanical approaches. Quantum mechanical (QM) models can be divided into two classes, one which seeks wavefunction solutions to the Schroedinger equation and another which uses electron density derived from solving the Kohn-Sham equations, the density functional theory (DFT) methods. Both approaches may incorporate some experimental data and be termed semiempirical methods, but both approaches (at least in principle) can produce predictions *ab initio* (from first principles), without any experimental parameters. However, while most wavefunction-based methods are *ab initio* methods, all of the DFT methods in common use today employ empirical parameters in the functionals they use. Although the application of quantum mechanics to molecular problems is mathematically intensive, for the purpose of this thesis we will focus primarily on the qualitative aspects of the postulates and the approximations that are necessary to use the methods. For more detailed mathematical derivations, refer to McQuarrie-Simon\(^9\) or Szabo-Ostlund\(^10\) for *ab initio* methods and Koch-Holthausen\(^2\) for DFT methods.

**Section 1.2. Wavefunction based methods.**

Most wavefunction-based quantum chemical models involve approximate solutions of the time-independent Schroedinger equation, an eigenvalue equation of the form.

**Equation 1.1.** \( \hat{H} \Psi = E \Psi \)
where \( \hat{H} \) represents the Hamiltonian operator, \( \Psi \) is the wavefunction and \( E \) is a scalar quantity called an eigenvalue which corresponds to the total energy. The wavefunction, \( \Psi \), is a function of the spatial coordinates of the electrons and nuclei of an atom or molecule. Once \( \Psi \) and \( E \) are found, other observable properties can be obtained by application of the appropriate operators to the wavefunction. This is the first postulate of quantum mechanics (Equation. 1.2(1)).

**Equation 1.2.**

1) \( \Psi(x) = \text{eigenfunctions} \)
2) \( \Psi^*(x) \Psi(x) dx = |\Psi(x)|^2 dx = \text{probability} \)
3) \( \int_{\text{all space}} |\Psi(x)|^2 dx = 1 \)

A quantum mechanical wavefunction has two other properties. The second postulate states that the square of the wavefunction, \( |\Psi|^2 \), is the probability density, and \( |\Psi|^2 \) \( dx \) is the probability of locating a particle in an incremental volume of space, \( dx \). The third postulate states that when the wavefunction is integrated over all space, it yields a finite value (subject to normalization), since the probability of finding the particle must be 100%.

The molecular Hamiltonian is (Equation 1.3)

**Equation 1.3.** \( \hat{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 - \sum_i \sum_k e^2 Z_k \frac{1}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{R_{KL}} \)

This Hamiltonian accounts for contributions to the total energy of a molecule from the kinetic energy of the electrons (first term) and nuclei (second term), the attractive potential energy due to the interaction of the electrons and the nuclei (third term), the repulsive potential energy due to interactions between electrons (fourth term) and nuclei
(last term). Once $\Psi$ is known, other properties of the molecule can be determined as the expectation values of the relevant operator. Thus all physical observables for which operators exist can be obtained from the wavefunction. However, exact solutions of the Schrödinger equation are limited to one-electron systems, such as the hydrogen atom or one-electron ions. To solve the equation for other molecular systems, approximations must be made.

One of the first approximations is the Born-Oppenheimer approximation, which provides a way to simplify the Schrödinger equation by separating nuclear and electronic motion, leaving only the electronic terms in the Hamiltonian. The electronic Hamiltonian is:

\[
H_{\text{elec}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \sum_K e^2 Z_K \frac{1}{r_{ik}} + \sum_{i<j} e^2 \frac{1}{r_{ij}} + \sum_K \sum_L e^2 Z_K Z_L \frac{1}{R_{KL}}
\]

**Equation 1.4.**

In this approximation the wavefunction is only a function of the electron coordinates, with the solution depending parametrically on the nuclear coordinates. Under the BO approximation, one obtains the potential energy surface by calculating the electronic energies for various positions of the nuclei.\(^{11}\) This yields the potential energy surface.

The Hamiltonian operator acts on the wavefunction to yield discrete or quantized solutions with definite eigenvalues, $E$. When the electronic Hamiltonian is applied to a wavefunction of the electronic coordinates, the eigenvalues give the energy levels of the electronic states for a specific geometric arrangement of the nuclei. The electronic energies depend parametrically on the positions of the nuclei, so by varying the positions of nuclei, one can obtain a smooth potential energy surface. Each potential energy surface corresponds to one electronic state.\(^{12}\)
**Variational Principle.** Although the BO approximation simplifies the Schroedinger equation, it still can not be solved exactly. Instead, an approximate solution is obtained through use of the variational principle. The variational principle states that the energy \( E_i \) of any approximate trial wavefunction \( \Phi \) is higher than the energy \( E_0 \) for the exact wavefunction \( \Psi \).

\[
\text{Equation 1.5.} \quad \hat{H} \Phi = \tilde{E}_0 \Phi
\]

\[
\text{Equation 1.6.} \quad E_0 \leq \tilde{E}_0
\]

Thus, the energy for the trial wavefunction provides an upper bound to the exact energy of the system. If a new trial wavefunction yields a lower energy, then it is considered to be more accurate than other wavefunctions with higher energies. (for proof, see Szabo-Ostlund\textsuperscript{10} and McQuarrie-Simon\textsuperscript{9}). Most approaches to solving the Schroedinger equation utilize the variational principle.

**One-electron orbital expansion of the wavefunction.** To this point, the form of the wavefunction has not been specified beyond the fact that it is a function of the electronic \((x_i)\) and nuclear \((X_i)\) coordinates,

\[
\text{Equation 1.7.} \quad \Psi = \Psi(x_1, x_2, \ldots, x_i, \ldots, x_n; X_1, X_2, \ldots, X_i, \ldots, X_N)
\]

Since the nuclei are fixed for a given determination of the electronic energy under the BO approximation, the nuclear coordinates can be treated implicitly, leaving only the electron wavefunction. A conceptually simple approach to solve for the electronic wavefunction is to expand \( \Psi \) in terms of functions of one electron, \( \tilde{\phi}_i(x_i) \), which are commonly known as orbitals:

\[
\text{Equation 1.8.} \quad \Psi = \Psi[\tilde{\phi}_1(x_1), \tilde{\phi}_2(x_2), \ldots, \tilde{\phi}_n(x_n)]
\]

This form of the wavefunction leads to separation of variables and the solution of \( n \)
equations, one for each electron, rather that one equation for all \( n \) electrons. The Hartree product function is an appealing first choice for such an orbital wavefunction:

**Equation 1.9.** \[ \Psi_{Hartree} = \bar{\Phi}_1(x_1)\bar{\Phi}_2(x_2)\cdots\bar{\Phi}_n(x_n) \]

Unfortunately, the Hartree wavefunction fails to meet a critical condition that any quantum chemical wavefunction must satisfy: since electrons are fermions, the wavefunction must be antisymmetric, i.e., it must change sign whenever the coordinates of any two electrons are interchanged.

**Equation 1.10.** \[ \Phi(x_1,\ldots,x_j,\ldots,x_n) = -\Phi(x_1,\ldots,x_j,\ldots,x_n) \]

This is the basis of the Pauli exclusion principle.

The Hartree product function can be transformed into an acceptable wavefunction by a suitable expansion that includes all of the terms that are needed to make the wavefunction antisymmetric. The mathematical form of such a product function is a determinant.

\[ \Psi(x_1,x_2) = \frac{1}{\sqrt{2}} \left( \bar{\Phi}_1(x_1)\bar{\Phi}_2(x_2) - \bar{\Phi}_1(x_2)\bar{\Phi}_2(x_1) \right) = \frac{1}{\sqrt{2}} \begin{vmatrix} \bar{\Phi}_1(x_1) & \bar{\Phi}_1(x_2) \\ \bar{\Phi}_2(x_1) & \bar{\Phi}_2(x_2) \end{vmatrix} \]

**Equation 1.11.**

\[ = \frac{1}{\sqrt{2}} \det[\bar{\Phi}_1(x_1)\bar{\Phi}_2(x_2)] \]

The determinant is known as a Slater determinant of one-electron spin orbitals. With a wavefunction in the form of a Slater determinant, the wavefunction is naturally antisymmetric and the Pauli Principle is satisfied (the probability is zero that electrons of the same spin will be found in the same position in space). Thus, Slater determinants provide a physically correct mathematical representation of the anti-symmetry of the wavefunction.
If one starts with a set of one-electron orbitals, one can optimize the functional form of the orbitals to obtain the lowest energy state (lowest energy Slater determinant). The lowest energy configuration of spin orbitals corresponds to the ground state with energy, $\tilde{E}_0$.

The orbitals in the Slater determinant have four coordinates associated with them, the three spatial coordinates for the position of the electron and one coordinate for the spin state of the electron, which has quantum numbers $m_s = \pm 1/2$ (usually represented by $\alpha$ and $\beta$). Thus the one-electron orbitals can be written in terms of four component spin orbitals.

Equation 1.12. $\bar{\phi}_i(x, y, z) = \phi(x, y, z) \alpha \text{ or } \phi(x, y, z) \beta$

The form of the wavefunction. If we assume that the wavefunction describing an $n$-electron molecule places each of the electrons in a one-electron orbital, the wavefunction for all $n$ electrons is simply:

Equation 1.13. $\Psi(x_1, x_2, ... , x_n) = \frac{1}{\sqrt{n}} \det [\bar{\phi}_1(x_1)\bar{\phi}_2(x_2) \beta ... \bar{\phi}_n(x_n)]$

The form of orbitals. The one-electron functions describing the distribution of the electrons around the nuclei are called orbitals. These orbitals, $\{\bar{\phi}_i\}$, are a function of the coordinates of only one electron (it can be any of the electrons since the electrons are indistinguishable but it is usually selected to be electron 1 or electron $i$, depending on the situation). The equations that determine the orbitals can be derived from the Schroedinger equation using the variational principle. The resulting orbitals are the solutions to the Hartree-Fock (HF) equation:
**Hartree-Fock approximation.** The Hartree-Fock wavefunction is a Slater determinant of the orbitals. The orbitals in the HF wavefunction are the solutions to the HF equations:

\[
\hat{f}_i \Phi_i = \varepsilon_i \Phi_i \\
\hat{f}_i = -\frac{1}{2} \nabla_i^2 - \sum_{\text{nuclei}} \frac{Z_k}{r_{ik}} + \sum_{\text{orbitals}} (\hat{J}_k - \hat{K}_k)
\]

(Equation 1.14.)

(in atomic units). The Fock operator, \(\hat{f}_i\), treats each electron as if it is moving in a static potential field defined by the nuclei and the \((n-1)\) other electrons. The eigenvalues to these equations, \(\varepsilon_i\), give the energies of the \(i\)-th spin orbital. In effect, the Hartree-Fock approximation replaces a many electron equation with \(n\) single electron equations that averages the effect of the other electrons through the coulomb, \(\sum \hat{J}_k\), and exchange, \(\sum \hat{K}_k\), operators in the last term in the Hamiltonian.

**Self-consistent field solution of the HF equations.** In the self-consistent field approach, a trial HF wavefunction is constructed by guessing the forms of the orbitals. Then the orbitals in the trial wave function, \(\Phi\), are used to construct the \(V_i^{HF}\) term in the Hamiltonian \(\hat{f}^{(0)}\). Equation 1.14 is then solved to obtain a new set of orbitals and wavefunction. These orbitals are then used to construct a new Fock operator, \(\hat{f}^{(1)}\), and the equations are again solved. This process continues until the orbitals do not change, or vary little between cycles according to specified convergence criteria. When the orbitals become self-consistent, the calculation is said to have converged and the calculation is complete. An added bonus of the HF approach is that the wavefunction includes the concept of exchange correlation, through the exchange operator, where electrons with the same spin are correlated.
Atomic orbitals. If we solve the HF equation for an atom, the optimum orbitals are the familiar 1s, 2s, 2p, … atomic orbitals discussed in chemistry courses and the wavefunction is a determinant of these atomic orbitals, e.g., for the neon atom, the wavefunction is:

Equation 1.15. $\Psi = \frac{1}{\sqrt{10}} \det \begin{bmatrix} \alpha \phi_1 \beta \phi_2, \alpha \phi_2 \beta \phi_2, \alpha \phi_2 \beta \phi_2, \alpha \phi_2 \beta \phi_2 \beta \phi_3 \end{bmatrix}$

Note that the orbitals are different for each atom, that is, $\phi_2s(C) \neq \phi_2s(\text{Ne})$.

Molecular orbitals. If we solve the HF equations for a molecule, the orbitals are distributed over the entire molecule, although some orbitals may be concentrated in certain regions of the molecule. Most computational chemistry programs, like Gaussian, solve the molecular HF equation by expanding the spatial part of the molecular orbitals in terms of a basis set, $\{\chi_i\}$, that is:

Equation 1.16. $\phi_i = \sum_{j=1}^{N_B} c_{ij} \chi_j$

In the simplest case, the basis set, $\{\chi_i\}$, is just the set of atomic orbitals on each of the atoms. More accurate solutions of the HF equations can be obtained by allowing additional flexibility in the basis set. For additional information on basis sets, see section 1.3.

Exchange and correlation. The difference between exchange correlation and electron correlation can be confusing. Exchange correlation refers to the fact that, for a properly antisymmetric wavefunction, the wavefunction vanishes if electrons with the same spin occupy the same point in space. Electron correlation refers to correlation as a whole, including the instantaneous correlations of the electrons as a result of their repulsive Coulombic interactions. Because exchange correlation between electrons with
the same spin is naturally built into antisymmetric wavefunctions, instantaneous

correlation between electrons with opposite spin tend to dominate the total correlation

energy. A brief qualitative description of these concepts will be given.\textsuperscript{13}

Since electrons are fermions, electrons of the same spin can not be found in the

same spatial location as the wavefunction will be identically zero when that happens.

Consider a two-electron system with $S = 1$ (i.e., both electrons have the same spin).

When the first electron is located at $(x_1,y_1,z_1)$, it creates exchange hole, or an area of much

reduced probability density, around $(x_1,y_1,z_1)$, so that the second electron will not be

likely to be found there [and it cannot be exactly at $(x_1,y_1,z_1)$]. This hole is called the

exchange hole or Fermi hole. No matter where electron 1 is in a given volume element,

the second spin up electron can not be found there and will be found somewhere else.

In the second type of correlation interaction, electrons of opposite spins could be

found in the exact same spatial location since the electrons are distinguished by their spin

(three coordinates would be the same, but the last coordinate, the spin coordinate, would

be different). However, since both electrons are negatively charged, they are unlikely to

be located in the same position, but at times may be close. For electrons of different

spins, the correlation hole is dynamic, meaning that it changes according to the location

of the first electron. This interaction, often referred to as dynamic correlation, is much

more difficult to model. In fact, besides a full CI calculation, no mathematical model yet

exists that can exactly describe correlation interactions, although wavefunctions such as

those in coupled cluster theory can provide very accurate approximations. Hartree-Fock

theory describes exchange correlation exactly, but it completely neglects dynamic

correlation interactions.
For this reason, the amount of (dynamic) electron correlation in a system is defined as the difference between the energy calculated by the given method (e.g., MP2 or CCSD) and the Hartree-Fock energy.

**Equation 1.17.** \[ E_{\text{corr}} = E_{\text{method}} - E_{\text{HF}} \]

**Correlated wavefunction methods.** Electron correlation can be accounted for by expanding the wavefunction to include configurations beyond the HF configuration and using the variational principle to calculate the expansion coefficients in the wavefunction. Thus, correlated methods are methods that use multiple Slater determinants to account for electron correlation. The SCF solution to the Hartree-Fock equations produces a set of one electron spin orbitals that provide a good approximation to the ground state but this configuration is only one of many orbital occupations that could represent this state (it is, of course, the one that gives the lowest energy and, thus, is the best single configuration description). Multi-reference or correlated theories include more than one Hartree-Fock determinant.

**Configuration Interaction.** The configuration interaction (CI) method is an approach that represents the wavefunction as a sum over all possible determinants that can be constructed from the orbitals obtained by solving the HF equations (in addition to the orbitals that are occupied in the ground state wavefunction, a set of unoccupied, or virtual, orbitals are obtained). Discussion of the CI method will be brief because current computational limitations prevent them from being applied to anything other than the smallest of organometallic complexes.
A singly excited determinant, $\Psi_i^a$, is one where one electron is excited from an occupied spin orbital in the Hartree-Fock ground state wavefunction, $\bar{\phi}_i$, to a virtual spin orbital, $\bar{\phi}_a$, $(i \rightarrow a)$:

$$\Psi_0^{HF} = \frac{1}{\sqrt{N}} \det \begin{bmatrix} \bar{\phi}_1 \bar{\phi}_2 \cdots \bar{\phi}_j \cdots \bar{\phi}_N \end{bmatrix}$$

**Equation 1.18.**

$$\Psi_i^a = \frac{1}{\sqrt{N}} \det \begin{bmatrix} \bar{\phi}_1 \bar{\phi}_2 \cdots \bar{\phi}_j \cdots \bar{\phi}_N \end{bmatrix}$$

A doubly excited determinant is one in which two electrons are excited to virtual orbitals, $(i \rightarrow a, j \rightarrow b)$:

$$\Psi_{ij}^{ab} = \frac{1}{\sqrt{N}} \det \begin{bmatrix} \bar{\phi}_1 \bar{\phi}_2 \cdots \bar{\phi}_a \bar{\phi}_b \cdots \bar{\phi}_N \end{bmatrix}$$

**Equation 1.19.**

The determinant labeled as $\Psi_0^{HF}$ refers to the Hartree-Fock wavefunction. A determinant from $\Psi_n$ refers to the $n^{th}$ configuration.

$$\Psi = \sum_{i=1}^{2N} c_i \Psi_i = c_0 \Psi_0^{HF} + \sum_{ia} c_i^a \Psi_i^a + \sum_{ia} \sum_{jb} c_{ij}^{ab} \Psi_{ij}^{ab} \cdots$$

**Equation 1.20.**

Where the $\{\Psi_i^a\}$ are all possible singly excited determinants, the $\{\Psi_{ij}^{ab}\}$ all possible doubly excited determinants and so on to all possibly N-electron excited determinants. A full CI calculation is extremely resource intensive and too complex to be applied to most real systems. The expense of this approach can be reduced by restricting the number of determinants, which is called truncating the configuration space. If one limits the configuration space to only singly excited determinants where only one spin orbital differs, the calculation is restricted to single excitations (CIS). A calculation where two spin orbitals differ is called a configuration interaction double excitation, (CID or DCI). A calculation that accounts for both single and double excitations is called CISD.

Truncating the configuration space saves time but CI solutions are not size consistent,
which means the energy of two atoms at infinite separation is not the sum of the two atomic energies calculated using the same type of wavefunction. Size inconsistency prevents the method from producing correct dissociation curves.

Another approach to CI is to use a restricted active space where only excitations to certain orbitals are considered and to optimize the orbitals self-consistently for this wavefunction. These calculations are called multi-configuration self-consistent field approaches (MCSCF). The complete active space SCF (CASSCF) and the generalized valence bond (GVB) methods use these restricted active spaces to solve for the lowest energy solution for the selected set of orbital excitations included in the wavefunction. These approaches are rigorous but require careful selection of the restricted active spaces. Application of these methods to transition metal complexes requires expertise inaccessible to the casual user.

**Perturbation Methods.** Møller-Plesset perturbation theory approaches the correlation problem by splitting the Hamiltonian into a zero-th order term, \( \hat{H}_0 \), the Hartree-Fock Hamiltonian, and then treating the difference between the full Hamiltonian and the HF Hamiltonian, \( \hat{H} - \hat{H}_0 \), as a perturbation.

**Equation 1.21.**

\[
\hat{H} = \hat{H}_0 + \lambda(\hat{H} - \hat{H}_0)
\]

where the perturbation term, \( \lambda(\hat{H} - \hat{H}_0) \), represents the effects of electron correlation and yields the exact Hamiltonian when \( \lambda = 1.10 \). Substituting the expansion in Eq. 1.21 into the Schroedinger equation, the wavefunction and energy become:

**Equation 1.22.**

\[
\Psi = \Psi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + ...
\]

\[
E = E_0 + \lambda E_1 + \lambda^2 E_2 + ...
\]
In this equation $\Psi_0$ is the HF wavefunction and $E_0$ is the HF energy. $E_1$ is identically zero for the Hartree-Fock wavefunction and, thus, $E_2$ is the first correction to the HF energy.

Perturbation theories are called MP2, MP3, MPn, etc. where the number n is the highest order contribution to the energy computed, $E_n$:

\[
E_{\text{MP2}} = E_0 + E_2
\]

\[
E_{\text{MP3}} = E_0 + E_2 + E_3
\]

\[
E_{\text{MP4}} = E_0 + E_2 + E_3 + E_4
\]

**Equation 1.23.**

MP4 describes electron correlation effects to higher order than MP3, which, in turn, describes correlation effects to higher order than MP2. Although perturbation theory can sometimes overcorrect for electron correlation, the exact energy for a molecule can sometimes be extrapolated from the results of a series of MPn calculations. As shown in Figure 1.3a, when MP2 overcorrects for electron correlation, MP3 will undercorrect, MP4 will overcorrect but to a lesser extent than MP2, etc. Sometimes, however, the perturbation models do not converge, as shown in Figure 1.3b. In these cases, another approach must be used.\(^{14}\)

Perturbation theory works very nicely for molecules with a large gap between the HOMO and the LUMO (methane) but fails spectacularly and becomes less efficient when used with systems that have a large number of low-lying virtual orbitals (which is common in transition metal complexes). In contrast to truncated CI, Møller-Plesset perturbation theory is size consistent. However, MPn is not a variational method and the energy obtained can actually be lower than the true energy of the system due to overcorrections for electron correlation. Perturbation theory can also be combined with the complete active space approach in the CASSPT2 method.\(^ {15} \)
**Coupled cluster approximation.** Another approach to solving the correlation problem is to represent the higher order determinants as cluster expansions. In this approach, the wavefunction is described as a series of exponential expansions where the Hartree-Fock wavefunction is multiplied by the exponential of a cluster operator $\hat{T}$.

(Equation 1.24)

**Equation 1.24.** $\Psi = e^{\hat{T}}\Psi_0$

The cluster operator, $\hat{T}$, is

**Equation 1.25.** $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots + \hat{T}_N$

where $\hat{T}_i$ operating on the wavefunction $\Psi_0$ produces all possible single excitations,

**Equation 1.26.** $\hat{T}_i\Psi_0 = \sum_{\alpha} c_i^\alpha \Psi_\alpha$;
\( \hat{T} \) produces all possible double excitations,

**Equation 1.27.**  
\[
\hat{T}_2 \Psi_0 = \sum_{ij} \sum_{ab} c_{ij}^{ab} \Psi_{ij}^{ab}
\]

and so on (\( N \) is the total number of electrons). Because the exponential of the operator \( \hat{T} \) is used, when \( \hat{T} \) is truncated, say at \( \hat{T}_2 \), the wavefunction will be size consistent. Thus, solutions to the coupled cluster approximation using only single and double excitations (CCSD), will be size consistent while CISD solutions will not.

CCSD calculations scale as \( N^6 \) (where \( N \) refers to the number of electrons) and thus are computationally intensive. Calculations with triplet and quadruple excitations are labeled CCSDT and CCSDTQ and scale as \( N^8 \) and \( N^{10} \) respectively. The coupled cluster approach can be improved upon by using perturbation theory to estimate the effect of higher excitations as done in the CCSD(T) method.\(^{16}\)

**Summary of wavefunction based methods.** The wavefunction is very complex and relies upon \( 4N \) variables (\( N \) = number of electrons) for the location and spin of each electron. CCSDT is the most reliable method for molecules that are reasonably well described by the HF wavefunction, but it can only be used for geometry optimizations of molecules up to 12 atoms, since it scales as \( N^8 \). As the number of electrons increases, the calculations become intractable. For larger molecules, only HF or MP2 methods are feasible. However, HF and MP2 energies have been shown to be in error by tens of kcal mol\(^{-1}\) from experimental values, rendering the results from these calculations useless for many complexes.\(^{17,18}\)

Care must also be taken when performing calculations to use a sufficient number of functions to describe the one-electron orbitals. These functions are discussed in the next section.
Section 1.3 Basis functions and orbitals.

The one-electron orbitals used in the H wavefunction are usually described by expansions in terms of basis functions:

**Equation 1.28.** \( \phi_i = \sum_{j=1}^{N_{bf}} c_{ij} \chi_j \)

Where \( \{\chi_j\} \) is a set of mathematical functions that can be used to represent the charge distributions of electrons. Most often these functions are Slater type orbitals or Gaussian type orbitals. Slater type orbitals (STOs) decay exponentially as the distance from the nuclei increases; a 1s Slater orbital is simply (where \( N \) is a normalization factor):

**Equation 1.29.** \( \chi_{STO} = Ne^{-\xi r} \)

STOs are closely related to the orbitals obtained when solving the Schroedinger equation for the hydrogen atom (for the hydrogen atom \( \xi = 1 \)). STOs have the correct behavior at the nucleus (a cusp) and are generally considered to be highly accurate but incur a very large computational cost due to the exponential term.

A ‘cheaper’ option is to use Gaussian type orbitals (GTOs). Originally proposed S.F. Boys in the 1950s and used extensively by the ‘father of Quantum Chemistry’ John Pople, GTOs use a linear combination of Gaussian functions to approximate the behavior of Slater type orbitals. For example, a 1s GTO is simply

**Equation 1.30.** \( \chi_{GTO} = \sum_i c_i N_i e^{-\xi_i r^2} \)

where \( N_i \) is again a normalization factor.

Gaussian orbitals are in most quantum chemistry programs because it is much easier to solve the HF equations when the exponential term is squared. GTO expansions
often use more than one function to describe $\chi_{GTO}$, as illustrated above; each of these individual functions, $N_i e^{-\alpha_i r^2}$, is called a primitive function and the linear combination of Gaussian functions is called a contracted function. GTOs do not have the correct asymptotic behavior at the nucleus, so many primitives are needed to correct for this shortcoming (see below). In the GAUSSIAN program, Gaussian type orbitals are given the label STO-nG which stands for a Slater type orbital derived from Gaussian functions where $n$ is equal to the number of Gaussian functions used to mimic the Slater orbital. The more GTOs used, the more the basis set approaches the STO. Figure 1.4 shows the 1D plot of STOs and GTOs as a function of the distance from the nucleus. As the number of GTOs in the basis set increases, the $\chi_{GTO}$ appears more and more similar to the STO orbitals.

At a bare minimum, one basis function is required to describe each electron or pair of electrons. A minimal basis set uses only 1 Gaussian orbital for every atomic orbital. For example, a carbon atom must have a minimum of five basis functions to create a minimal basis set; one for the “1s” orbital, one for the “2s” orbital, and three functions for the “2p” orbitals. In reality, many more functions must be used to describe the atoms: multiple functions are required to accurately describe the orbital.

If an infinite number of terms were used in the basis set, the orbitals would be exactly described by the expansion, Equation 1.28, and the calculations would be said to be at the complete basis set (CBS) limit.
Figure 1.4. Plot showing the 1-D character of Slater type orbitals and Gaussian type orbitals as the electron nucleus distance decreases. The gaussian type orbitals do not exhibit a nodal plane near the nucleus (R=0) but the STO-3G approaches STO behavior more closely than the STO-2G and STO-1G. (taken from Mcquarrie Simon)

The accuracy of the orbital descriptions can be further improved upon by using a linear combination of sets of GTO basis functions to describe the orbital. Basis sets that use two sets of functions to describe each atomic orbital are called double zeta (DZ) basis sets. Basis sets with three and four functions to describe each atomic orbital are called triple zeta (TZ) and quadruple zeta (QZ) basis sets respectively.

Although Gaussian functions are cheaper to use in calculations, the number of functions increases as the number of atoms increase. It is known that core orbitals do not change much as molecules are formed, so a suitable approximation would be to represent the core orbitals differently from the valence orbitals. In split valence basis sets, the valence orbitals are represented using more than one function but all “core” orbitals are described using a smaller grouping of functions, usually just one function (effective core
potentials may also be used.\textsuperscript{19,20} These core approximations greatly speed up the computation with relatively little loss in accuracy. Effective core potentials are regularly used for atoms in the third row or lower.

There are three different types of Gaussian type orbitals in standard usage. The most popular are the Pople basis sets\textsuperscript{21} which take the label, X-YZG where X is the number of primitive Gaussians comprising the core atomic orbitals, and Y and Z represent the number of Gaussian functions used to describe the two functions used to create the valence orbitals. Functions of this type are 6-31G, 6-311G, or 3-21G.

Of higher accuracy but increased computational cost are Dunning’s correlation consistent basis sets.\textsuperscript{22,23} Correlation consistent basis sets are built in a manner that insures systematic convergence of total energies toward their complete basis set limits.\textsuperscript{22} Saturating the one-electron basis set makes it possible to definitively compare the accuracy of different methodologies. Other commonly used basis sets (such as the Pople sets) do not have this property. Dunning basis sets are labeled cc-pV\textsubscript{N}Z where cc means correlation consistent, pV refers to polarized valence functions (discussed later), and N equals the number of valence functions.

In addition, there are the Ahlrichs type basis sets which are typically used in Turbomole.\textsuperscript{24,25} These basis sets are typically coded as NZVP where N also equals the number of valence functions and VP stands for valence polarized.

The accuracy of basis sets can be improved through the addition of polarization functions, which reflects that, in a molecule, the orbitals are not pure s or pure p as they are in the atom. Polarization functions add p character to s orbitals or d character to p orbitals, etc. Molecular orbitals are much more accurately described using basis sets that
contain polarization functions and yield more accurate energies, structures and other properties.

Examples of functions of this type include 6-31G(d) which places d functions on all atoms with p valence orbitals and 6-31G(d,p) which places d functions on all atoms with p functions and adds p functions to all atoms with just s functions. The symbols 6-31g(d) and 6-31G(d,p) are used interchangeably with 6-31G* and 6-31G**. Polarization functions are included in all correlation consistent basis sets and in Ahlrichs basis sets that end in “P” such as TZVP.

In addition to polarization functions, diffuse functions can be used for atoms where there is significant electron density far from the nuclei, like in anions. In Pople type basis sets, diffuse functions are denoted with a + sign, so 6-31G(d)+ indicates diffuse functions on all non-hydrogen atoms, while 6-31G(d)++ indicates diffuse functions on all atoms. In Dunning-type basis sets, diffuse functions are indicated with the “aug “prefix.

For heavy atoms such as osmium or bismuth, it is common to replace core electron functions with an effective potential. In addition to saving greatly on computational cost, these functions incorporate relativistic effects seen in atoms late in the periodic table. The potentials are derived from quasi-relativistic calculations for atoms and monatomic ions and can be found for all atoms on the third row or lower. Several different types of potentials exist, including the Hay-Wadt potential (also known as the Los Alamos, LAN, potentials)\textsuperscript{19,20} and the Stuttgart-Dresden potentials (SDD).\textsuperscript{27-29} It is important to pair the potential with the appropriate valence functions. For example, one should NOT use the valence functions for the LANL2DZ potential with the SDD
potential. When core potentials are paired with correlation consistent basis sets, the electrons in outermost core shell (non-valence shell) are treated implicitly (i.e., included in the effective core potential) or explicitly (i.e., included in the basis set description along with the valence electrons in shell six).\textsuperscript{30}

In practice, basis functions for atoms can either be called from the computer program or be downloaded from the Basis Set Exchange.\textsuperscript{31}

Section 1.4 Density functional theory.

While Schroedinger or wave-function based methods rely on calculation of the correct wavefunction to obtain the energetics of the system, density functional theory seeks an accurate representation of the energy density. The wavefunction is not a physical observable, but the square of the wavefunction gives the probability of finding electrons 1 to N in a particular volume, which can be physically observed. The electron density is an attractive candidate for study because while the wavefunction needs 4N variables, the density only needs three variables; three spatial and one spin variable. In addition, once one has obtained the correct density for a system, one can locate the atomic positions from the electron density map. The density can then be used to find the Hamiltonian operator, which can be used to solve the Schrodinger equation. Once one has obtained $\Psi$, physical properties of the molecule can be determined.

The theory for the density functional approach was first proposed in 1927 by Thomas and Fermi.\textsuperscript{32,33} In the earliest approximations, the energy density was separated in to two parts, the potential energy (V) and the kinetic energy (T).

\underline{Equation 1.31.} \hphantom{\text{Equation 1.31.}} \quad \rho = V + T
The potential energy was expressed as a classical charge distribution describing the attraction between positively charged nuclei and negatively charged electrons and between electrons (Equation 1.32).

\[ V = V_{ne} \rho(r) + V_{ee} \rho(r) = \sum_{k}^{\text{nuclei}} \frac{Z_k}{|r - r_k|} \rho(r) dr + \frac{1}{2} \int \int \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \]

In Equation 1.32, the first term refers to coulombic attraction between electrons and nuclei (k subscript) while the second term refers to the coulombic repulsion between electrons, which are described by electron exchange.

Information about electron correlation is contained within the kinetic energy term, which is a bit more complex to describe. In the simplest model, the uniform electron gas, the kinetic energy is the movement of the electrons in a continuous positive charge called jellium (similar to the plum pudding model of charge distribution used to describe atoms).\(^{34}\) In jellium, the kinetic energy was

\[ T_{\text{ueg}}[\rho(r)] = \frac{3}{10} (3\pi^2)^{\frac{3}{5}} \int \rho^{\frac{5}{3}}(r) dr \]

In the jellium model (also called the uniform electron gas), several approximations were made that render the theory useless for chemical systems.\(^2\) In the potential energy equation for electron electron repulsion \(V_{ee}\), repulsion is treated as a static coulomb repulsion. The effect of electron exchange (electrons of same spin) and correlation (different spin) are ignored.

**Self-interaction error in DFT.** In DFT, the classical coulomb equation for \(V_{ee}\) introduces a self interaction error since in a one electron system, the electron density \(\rho(1)\) must be greater than zero.

\[ V_{ee} \rho(1) = \frac{1}{2} \int \int \frac{\rho(1)}{r_1} dr_1 \rho(1) > 0 \]
Therefore, the $V_{\text{ee}}$ term of a one-electron system cannot be zero and solving the equation results in an unphysical situation where an electron interacts with itself. Density functional theory tries to account for correlation interactions and correct for self-interaction by providing various ways of solving for the correlation hole. Discussion of this problem is currently a matter of debate between theorists.\textsuperscript{35-38} The next section of this thesis is to explain the background of the theory and discuss the different approaches to solving the exchange correlation problem.

**Functionals.** It is important to note that the equations listed above use electron density as a variable. However, the electron density is also a function. The functions for potential energy and kinetic energy are called functionals. While a function like $3x=y$ uses variables as an input and outputs a number, a functional uses functions as an input to output a number.

<table>
<thead>
<tr>
<th>Function</th>
<th>Functional</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3x = y\ (x)$</td>
<td>$3\int x^2 \rho \ dx = y\ (\rho)$</td>
</tr>
<tr>
<td>$x = 1$ to $\infty$</td>
<td>$\rho = r^3$</td>
</tr>
</tbody>
</table>

Functionals for DFT are similar to operators in wave function based methods. Operators are functionals that operate on a wavefunction to produce a variable. For example, the Hamiltonian operator operates on the wavefunction to produce the energy of the system. Functionals are generalized versions of operators (or operators are a specific type of functional.) Functionals that operate on a density are called density functionals.
The rest of the functionals discussed in this thesis are density functionals that operate on the density to output the final energy of the system.

**Hohenberg-Kohn theorems.** DFT as applied in chemistry is formally the result of two principles that Hohenberg and Kohn set forth for the electron density which are known as the Hohenberg-Kohn theorems. The Hohenberg-Kohn theorems are

1) The ground state electron density, $\rho_0$, of a many electron system in the presence of an external potential $V_{\text{ext}}$ can be uniquely determined from the external potential $V_{\text{ext}}$. Since $V_{\text{ext}}$ determines the Hamiltonian ($H$), the Hamiltonian is a functional of the electron density, $\rho_0$.

2) The functional $E$ for the ground state energy is minimized by the ground state electron density $\rho_0$, such that $E(\rho) \geq E(\rho_0)$ for every trial electron density $\rho$.

The external potential can be viewed as the charges of the nuclei under the Born-Oppenheimer approximation. The first postulate shows that the ground state properties $\hat{H}$ of a many electron system can be determined from the external potential, which is determined from the three spatial coordinates of the electron density $\rho$. This postulate implies that the density determines all the properties of the given system and that the density determines the energy. One can use the external potential (atom positions) to determine the ground state density and then use the ground state density to obtain the external potential. As illustrated in Figure 1.5, the external potential maps to a wavefunction, which can be mapped to the electron density; or the density can be mapped to a wavefunction which can then be mapped to an external potential.
Figure 1.5. Picture showing how the potential, $V$, maps to the wavefunction, $\Psi$, and the electron density, $\rho$. The picture shows that every density $\rho$ corresponds to at least one $\Psi$ and every $\Psi$ corresponds to at least one external potential $V$.

Even after simplifying the expression from $4N$ variables to four variables, the electron-electron interaction in the kinetic energy term still cannot be solved. However, Kohn and Sham argued that it was possible to determine the kinetic energy for the ground state of a system where the electrons do NOT interact. This fictitious system of non-interacting electrons would have the same overall ground state electron density as the real system where the electrons interact. The kinetic energy of the non-interacting system would be the sum of the kinetic energies of the non-interacting electrons. Since the density determines the geometry of the atoms, the interacting systems and the non-interacting systems will have the same density and thus the same external potential.

The equations used to describe the non-interacting system are called the Kohn-Sham (KS) orbitals. These orbitals are single particle equations, similar to the one-electron equations used for Hartree-Fock theory with the main difference being that the KS are constructed post-hoc as a way to define the electron density in terms of a sum of the non-interacting electron densities (Equation 1.35).

Equation 1.35. $\rho = \sum \phi^2$

The second postulate sets up a variational rule, meaning that a trial density can be used in place of the exact density and that the energy of the system can be found from
that trial density. The energy of the trial density is greater than or equal to ground state energy density of the system. In the case of all of the DFT methods discussed in this chapter, the trial density is calculated from the non-interacting Kohn-Sham orbitals. However, despite the fact that the wavefunction system can be simplified into density, there is no guidance as to how to find the exact ground state density without solving the complete Schroedinger equation.

The generic equation for DFT could then be written as below

\[ E[\rho(r)] = T_{\text{ni}}[\rho(r)] + V_{\text{ne}}[\rho(r)] + V_{\text{ee}}[\rho(r)] + T[\rho(r)] + V_{\text{xc}}[\rho(r)] \]

The first term corresponds to the kinetic energy density of non-interacting systems, which is simply the sum of the kinetic energy of all electrons. The second and third terms are the potential energy interactions between the nuclei and electrons and between two electrons respectively. The fourth term is the correction for the kinetic energy density while the 5th term is the correction for the correlation contribution to the potential energy. The last two terms are typically grouped together to form the exchange correlation functional. Information about electron exchange is typically included in the \( V_{\text{xc}} \) term but can also be contained in the correlation part of the functional.

The Kohn-Sham procedure is this; a trial density is constructed for and then used to solve for the potentials and the KS orbitals, then the KS orbitals are used to construct a new density, then the new density is used to solve for new potentials and KS orbitals, and so on. The procedure continues until the equations become self-consistent. If one uses the correct functional to describe the ground state, the self-consistent energy should be the ground state energy. However, there is a problem with the DFT functionals available, which is discussed in the next section.
DFT is exact but unknown. Density functional theory is an exact theory. No approximations must be made in order to solve for the electron density. The problem is that we do not know what the exact functional should look like so we have to make guesses about what the functional should be. In this case, the functionals discussed below are inexact methods applied to an exact theory. In contrast, the \textit{ab initio} methods discussed previously are exact solutions to an approximation of the wavefunction (which is known for the hydrogen atom) while DFT methods are approximations to an unknown density. The exact energy density functional has been obtained for the many electron Hooke's atom but not for real systems.\textsuperscript{40} Furthermore, since DFT correlation functionals are approximations to an unknown, the variational method can fail to yield the lowest energy solution.\textsuperscript{41} As it stands, even the best DFT functionals can sometime predict total energies that are lower than the exact energy of the system. DFT is used because it is cheap and often returns results similar to those of coupled cluster calculations. Many different methods have been developed to model these equations but only the particulars of a few of these methods will be discussed.

Density Functional Methods. For the purpose of this work, it is important to know that no perfect functional exists that correctly treats electron exchange and correlation. \textit{Ab initio} theories that incorporate non-exchange correlation (CISD, CCSD, CASSCF) are mostly inaccessible to organometallic bench chemists. Approximate DFT methods, while imperfect, provide a solution to the correlation problem by providing relatively accurate results (with a few major exceptions!\textsuperscript{42,43}) for geometries, thermochemistry, and reaction barriers. Most of these errors are the result of the functionals and much work is devoted to improving DFT methods.\textsuperscript{36,38,44,45}
DFT functionals can be grouped according to Jacob’s ladder as visualized in Figure 1.6.\textsuperscript{46-48} Functionals on lower rungs use simple approximations while functionals on higher rungs use more complex approaches that should yield more accurate results. The first rung is the very basic local spin density approximations (LSDA). Generalized gradient approximation (GGA) functionals form the second rung, while meta-GGA functionals (m-GGA) form the third rung, hybrid functionals (hmGGA) form the fourth rung and functionals incorporating unoccupied (or virtual) Kohn-Sham orbitals fall into higher categories.\textsuperscript{49} More details about these approaches follow. In general functionals on the lower rungs are faster but less accurate than functionals on the higher rung.

Since there are a vast number of functionals, only a few comments will be made about the general types of functionals and the methods found within that class. More details about the functionals can be found from the references in the table below or from a few key reviews.\textsuperscript{3,50,51}

**Figure 1.6.** Jacob’s Ladder of functionals adapted from Ref. \textsuperscript{49}

<table>
<thead>
<tr>
<th>Heaven of chemical accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>unoccupied ( \psi_u (\rho') )</td>
</tr>
<tr>
<td>occupied ( \psi_o (\rho') )</td>
</tr>
<tr>
<td>( \tau (\rho) )</td>
</tr>
<tr>
<td>( \nabla n (\rho) )</td>
</tr>
<tr>
<td>( n (\rho) )</td>
</tr>
<tr>
<td>Hartree-Fock World</td>
</tr>
</tbody>
</table>
## Table 1.1. Density functional methods used in this thesis along with the correlation and exchange parts and the class of functional

<table>
<thead>
<tr>
<th>Method</th>
<th>Method type</th>
<th>%HF Exchange</th>
<th>Exchange functional</th>
<th>Correlation functional</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMK(^a)</td>
<td>HMGGA</td>
<td>42</td>
<td>BMK</td>
<td>BMK</td>
</tr>
<tr>
<td>B3LYP(^b)</td>
<td>HGGA</td>
<td>20</td>
<td>becke88</td>
<td>lee-yang-parr</td>
</tr>
<tr>
<td>BB1K(^c)</td>
<td>HMGGA</td>
<td>42</td>
<td>becke88</td>
<td>becke95</td>
</tr>
<tr>
<td>MPW1k(^d)</td>
<td>HGGA</td>
<td>42.8</td>
<td>mod PW91</td>
<td>PW91</td>
</tr>
<tr>
<td>PBE0(^e)</td>
<td>HGGA</td>
<td>25</td>
<td>perdew-burke-ernzerhof</td>
<td></td>
</tr>
<tr>
<td>M05-2X(^f)</td>
<td>HMGGA</td>
<td>56</td>
<td>m05-2x</td>
<td></td>
</tr>
<tr>
<td>TPSS(^h)</td>
<td>HMGGA</td>
<td>10</td>
<td>tao-perdew-staroverov-scuseria</td>
<td></td>
</tr>
<tr>
<td>BP86(^h)</td>
<td>GGA</td>
<td>0</td>
<td>becke88</td>
<td>perdew86</td>
</tr>
<tr>
<td>PBE(^j)</td>
<td>GGA</td>
<td>0</td>
<td>perdew-burke-ernzerhof</td>
<td></td>
</tr>
<tr>
<td>SWVN(^l)</td>
<td>LSDA</td>
<td>0</td>
<td>LSDA</td>
<td>VWN5</td>
</tr>
<tr>
<td>PBE(^k)</td>
<td>DISPERSION</td>
<td>0</td>
<td>??</td>
<td>??</td>
</tr>
</tbody>
</table>

\(^a\)\(^{52}\), \(^b\)\(^{53}\), \(^c\)\(^{54,55}\), \(^d\)\(^{56,57}\), \(^e\)\(^{58}\), \(^f\)\(^{59}\), \(^g\)\(^{60}\), \(^h\)\(^{61,62}\), \(^i\)\(^{58}\), \(^j\)\(^{63,64}\), \(^k\)\(^{65,66}\)

**Local Spin Density Approximation.** The local spin density approximation was the first approximation widely applied in chemistry. It refers to DFT methods modeled off of jellium where the energy density at some position is dependent solely on the local electron density at that point. In the LSDA (LDA is a spin-independent version of this class of functional), the exact exchange for a homogeneous electron gas is used. Popular functionals of this type include SVWN, and SVWN5. These functionals were all derived from solutions to the correlation energy for the uniform electron gas. In this gas, the density is constant, which does not apply well to molecular systems but do apply very well to calculations of periodic systems (e.g. crystals of neon atoms).\(^2\)
Generalized gradient approximation functionals (GGA). GGA functionals attempt to correct for the uniform density by introducing the density gradient that depicts how the electron density changes locally. In other words, the functional calculates how the electron density at one arbitrary point varies and then applies this gradient correction to the functional. These methods offer a large improvement over the local approximations but GGA functionals often overcorrect the error of LSDA functionals, especially in the cases of atomization energies and bond lengths. Exchange functionals of this type are B (for Becke), X, PW, and mPW for empirically derived functionals and B86, P, and PBE for non-empirically derived functionals. Correlation functionals include LYP for an empirically derived functional and B88, P86, and PW91 for non-empirically derived functionals. The exchange and correlation parts are put together to make BLYP, mPWPW91, and PBEPBE.

Meta GGA functionals are the next step in Jacob’s ladder. These functionals take two approaches to improve the model. In one approach, the second derivative of the density is used to provide information on how quickly the density is changing. Functionals of this type include BR and Lap. In the second approach, the kinetic energy density is modeled. The second approach is less expensive and has been shown to provide the same information as the second derivative. Functionals of this type include B95, B98, τ-HCTH, and TPSS. mGGA functionals are generally more accurate than GGA functionals but tax the computer resources a bit more.

Hybrid functionals. Hybrid functionals are derived by mixing parts of exact Hartree-Fock exchange with an exchange-correlation functional. Hybrid functionals are by far the most popular type of functional. Functionals of this type have the generic
equation, Equation. 1.36, where the parameters of the exchange correlation functional (a, b, c, etc.) are empirically derived.

**Equation 1.37.** \[ E_{xc} = E_{xc}^{LDA} + a(E_{x}^{HF} - E_{x}^{LDA}) + b(E_{x}^{GGA} - E_{x}^{LDA}) + c(E_{c}^{GGA} - E_{c}^{LDA}) \]

In Equation 1.37, the parameters \( E_x \) and \( E_c \) refer to the exchange and correlation energies respectively while the superscripts HF, LDA, and GGA refer to the Hartree-Fock, Local density approximation, and generalized gradient approximation respectively.

B3LYP, which combines the three-parameter exchange functional B3 with the correlation functional LYP, is an example of a semi-empirical method as the parameters were calculated by minimizing the mean absolute error of a molecule test set with the B3PW91 functional. The parameters derived from this process were then added as “fudge factors” to make the LYP exchange-correlation functional where \( a=0.20, b=0.72, \) and \( c=0.81 \). Other functionals use different parameters.

Although semi-empirical hybrid methods are not derived from first principles, they are used because they provide highly accurate results for molecules that were not in the original test set. However, one should always be careful in using semi-empirical methods outside of the range they were meant to be used. B3LYP is by far the most popular density functional (see slides and papers) but many studies have shown cases where B3LYP gives energies vastly different from experiment. B3LYP is a good method to use for an initial calculation because it can be found in nearly every computational program (vide infra). However, B3LYP fails to reproduce weak interactions like pi-pi stacking, hydrogen bonding, or van der Waal’s interactions.\(^{67,68}\) More recently, work has begun into double hybrid functionals that incorporate exact Hartree-Fock exchange but also add in correlation corrections from MP2 theory.\(^{69}\)
New developments in functionals. Dispersion corrected functionals are one of the newer editions to DFT models. These functionals seek to add in a correction for van der Waal's interactions and have been reported to achieve the accuracy of CCSD(T) at much lower computational expense. Recently, work has been successful in creating range-separated hybrids and local hybrids that seem to fix some of the problems with charge separation seen in other DFT methods.

Choosing a Functional. Picking out the correct density functional is more than an art than a science so it is not uncommon to feel overwhelmed when making a decision. The generally accepted view is that the higher the ‘rung on the DFT ladder’, the better the results. However, this is not always true. Sometimes, the lower rung functionals introduce error cancellations that lead results similar to experiment. These error cancellations are often discovered when the model is applied to other molecules or when other density functional methods are applied. Chapter three of this thesis discusses benchmarks of DFT methods and provides suggestions as to the best methods for organometallic complexes.

There are, however, a few tips to keep in mind. No matter how well-reviewed a functional may be, it is important to run a few test calculations to see how the different functionals perform. In addition, it is important to keep the functional and basis set consistent throughout all parts of a study. Results from a molecule optimized with B3LYP/6-31G are NOT directly comparable with M05-2x/aug-cc-pVTZ.

Due to simplicity of its use, cheapness of its utility, and quite good accuracy, DFT is the primary method used for computational analysis and chapter three of this work illustrates the reliability of various functionals for testing donor-acceptor interactions. Errors due to DFT approximations are typically much smaller than for HF, but the
results given by different DFT methods can vary widely. Overall, the theory has issues, but most people are in agreement that the theory is “on the right track.”\textsuperscript{41,47} DFT methods have become trusted enough so that DFT derived parameters can be utilized to make predictions about experimental complexes, as illustrated in Chapters 2 and 4 of this thesis.

**QM/MM and ONIOM methods.** All of the models discussed thus far utilize quantum mechanics, of which DFT has the most utility for donor-acceptor complexes of transition metals. Another type of model is used called molecular mechanics (MM), which is a classical approach that uses force fields and electrostatic potentials derived from quantum mechanics to solve for a chemical system. These models are fast to calculate but do not yield accurate results for many transition metal complexes. However, MM can be used in conjunction with quantum mechanics, where the inner “core” part of the molecule is treated with a QM method such as DFT or MP2 and the outer “shell” is treated with MM. The most widely implemented of these methods is called ONIOM.\textsuperscript{71} These calculations have been used for many transition metal complexes\textsuperscript{32} but have fallen out of favor as desktop computers became faster and algorithms became more efficient.

**Section 1.5 Bonding analysis methods.**

Once the structure, density, and wavefunction have been obtained for a structure from the methods discussed previously, one can use the information obtained to perform bonding or orbital analysis.

**Natural Bond Orbitals (NBO).** The natural bond orbital analysis has been called a chemists basis set. It takes the Hartree-Fock and Kohn-Sham orbitals into more
chemically intuitively localized s and p orbitals. The major strength of NBO is its basis set independence and implementation into many computational codes. NBO converts the molecular wavefunctions generated by Hartree-Fock and Kohn-Sham methods into bonding and lone electron pairs localized onto the molecular structure. The program works by converting an input basis set into a set of natural atom-centered orbitals and then using a linear combination of the atom-orbitals to create natural bond orbitals. NBO is used often to describe donor-acceptor complexes in transition metal complexes.\textsuperscript{73,74} despite discrepancies in the method.\textsuperscript{75}

**Energy decomposition analysis (EDA).** Energy decomposition analysis (EDA) describes bond formation in terms of a collection of interacting fragments and has been regularly applied to donor-acceptor complexes of transition metals and main group elements\textsuperscript{76-78} EDA has been discussed previously in detail\textsuperscript{79-85} so only a brief description is given here. The experimentally measurable bond dissociation energy of a molecule is calculated by determining the interaction and preparation energies required to change the relaxed fragments to the geometry and spin necessary for formation of the complex.

**Equation 1.38.** \[ -D_e = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \]

The preparation energy is the energy required to promote the relaxed fragments into the geometry and spin state necessary for the bond. The interaction energy is divided into three parts; the electrostatic term, the Pauli term, and the orbital term.

**Equation 1.39.** \[ \Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \]

The electrostatic term is the calculated electrostatic interaction energy between the frozen density distribution of fragments of the molecule. The Pauli term, which gauges the repulsive four-electron interactions between occupied orbitals, arises from the anti-
symmetry required in the wavefunction. The orbital interaction term is regarded as an estimate of the attractive interactions that arise from covalent bonding which comes from orbital relaxation and the mixing between occupied and unoccupied orbitals of the fragments. The key benefit of using EDA is that the orbital interaction term can be differentiated between orbitals of different symmetries, provided that the molecule processes sufficient molecular symmetry around the fragmentation point. Since the interaction and orbital terms can be broken into physically meaningful components, EDA allows the bonding of the complex to be evaluated comprehensively. EDA has proven very useful for elucidating more detailed bonding information than that determined with Tolman parameters or Hammett constants. A recent update to the EDA method, called ETS-NOCV, has been made available that allows for information on orbital contributions to be obtained without symmetry constraints on the molecule.

**Computational Programs.** There are several computer programs available for computational chemistry and all programs have strengths and weaknesses. A computational chemist seeks to achieve the greatest amount of accuracy for the least amount of cost. Computation cost can be calculated in terms of the amount of time and computer power necessary for a calculation. Computational programs use different codes to perform the calculations. Calculations on different codes using the same model SHOULD produce results that are nearly identical (deviations less than those used for numerical noise between rounding rules in various chips). Gaussian03, Turbomole, and Amsterdam Density Functional are just a few of the codes available. Information on running each one of these codes can be found in the tutorials provided by the manufacturer.
References

(1) Dirac, P. A. M. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* 1929, 123, 714-733.


(5) Harvey, J. N. *Annual Reports Section "C" (Physical Chemistry)* 2006, 102, 203-226.

(6) See Appendix A for instructions on how to convert an ins file to a xyz file.


(11) See Section 2.1.2 of Szabo Ostlund for a more detailed discussion.


(13) For a more detailed discussion of electron exchange and correlation, see Koch and Holthausen Chapter 2 or Cramer Section 6.1


(26) Writing 6-31G++ for C is redundant, 6-31G++ is only necessary for H atoms.


(34) Hughes, R. I. G. Perspectives on Science 2006, 14, 457-524.


(77) Massera, C.; Frenking, G. Organometallics 2003, 22, 2758-2765.


(90) Frisch, M. J.; et al, full author list in supplementary information; Gaussian, Inc.: Wallingford CT, 2004.


CHAPTER 2. DONOR-ACCEPTOR PROPERTIES OF BIDENTATE PHOSPHINES.

Section 2.1. Introduction

Bidentate phosphines are immensely important auxiliary ligands for transition metals. Their usefulness stems in part from their ability to create a relatively rigid steric environment that can impose specific constraints on the relative positions (e.g., cis vs. trans) as well as the conformations of other ligands that bind to the metal center. In addition, the electron donating properties of the bidentate phosphine can alter the electron richness of the metal center, which in turn affects the binding and reactivity of the other ligands. These factors can greatly enhance the regiospecificity, stereospecificity, and rate of reactions catalyzed by transition metals. A detailed understanding of the influence of bidentate phosphines on the steric and electronic properties of their metal complexes is therefore highly important.

There have been many experimental\textsuperscript{1} and theoretical\textsuperscript{2-4} studies of the bonding of unidentate phosphines to transition metals, but there are very few such studies of bidentate phosphines. The effect of the phosphorus-bound substituents on the steric and electronic properties of bidentate phosphines has generally been assumed to be identical to the effect of the same substituents in unidentate phosphines, but there is some evidence that this assumption is not true. For example, metal-substrate bond dissociation energies are slightly different for metal complexes of bidentate phosphines relative to those of their unidentate phosphine counterparts.\textsuperscript{5} A few studies have compared metal-ligand bonding in a small number of bidentate phosphines,\textsuperscript{5,6} but no rigorous studies have been undertaken for a wide range of bidentate complexes.

The most widely employed experimental measure of the donor-acceptor properties of a unidentate phosphine (and many other kinds of ligands) is the Tolman electronic parameter,
which is equal to the CO stretching frequency of $A_1$ symmetry in the corresponding Ni(CO)$_3$L complex.\textsuperscript{1} The CO stretching frequency correlates well with the net donor ability of the ligand L to a metal center in other systems.\textsuperscript{7} Tolman showed that the electronic parameter $\nu$ of a phosphine $PX_1X_2X_3$ could be predicted reasonably accurately from the identities of the three substituents via the equation

$$\nu = 2056.1 + \sum_{i=1}^{3} \chi_i$$

Equation 2.1.

where $\chi_i$ is an empirically derived number characteristic of the substituent $X_i$. Crabtree and coworkers determined that ligand electron parameters of L-Ni(CO)$_3$ complexes computed at the DFT level of theory correlate well not only with the Tolman parameters, but also with other experimental gauges of electron donor/acceptor properties, such as Lever’s parameters derived from redox potentials, and Hammett constants derived from NMR chemical shifts.\textsuperscript{4} Computed electronic parameters have been used in the past to augment experimental Tolman parameters.\textsuperscript{2,8}

Carbonyl stretching frequencies measure the net donor ability of ligands, which is a combination of both $\sigma$ and $\pi$ bonding effects. In order to distinguish between $\sigma$ and $\pi$ components of the metal-ligand bonding, DFT calculations can be augmented with natural bond orbital analysis (NBO); Bader’s atoms in molecule (AIM) approach; and energy decomposition analysis (EDA). NBO converts the molecular wavefunctions generated by Hartree-Fock and Kohn-Sham methods into core orbitals, bonding orbitals and lone electron pairs localized on the molecular structure. This approach has been used to describe donor-acceptor complexes in transition metal complexes.\textsuperscript{9,10} Bader’s atoms in molecules (AIM), which uses the Laplacian of the electron density to denote regions of enhanced or depleted electron density,\textsuperscript{11} has proven useful in determining bonding properties of many weakly interacting systems.\textsuperscript{12} Energy decomposition analysis (EDA), which describes bond formation in terms of a collection of
interacting fragments, has also been regularly applied to donor-acceptor complexes of transition metals and main group elements.\textsuperscript{5,13,14}

EDA has been discussed previously in detail\textsuperscript{15-21} and only a brief conceptual description will be given here. The bond energy of a molecule is assumed to be equal to the sum of two terms: a preparation energy and an interaction energy:

$$-D_e = \Delta E_{\text{prep}} + \Delta E_{\text{int}}$$

The preparation energy is the energy required to promote the relaxed fragments into the geometry and spin state necessary for the bond. The interaction energy is divided into three parts; the electrostatic term, the Pauli term, and the orbital term.

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$

The electrostatic term is the calculated electrostatic interaction energy between the frozen fragments of the molecule, which is in most cases strongly attractive even in nonpolar molecules. The Pauli term, which gauges the repulsive four-electron interactions between occupied orbitals, arises from the anti-symmetry required in the wavefunction. The orbital interaction term can be regarded as an estimate of the attractive interactions that arise from covalent bonding, which comes from the mixing between occupied and unoccupied orbitals of the fragments. The key benefit of EDA is that the orbital interaction term can differentiate between $\sigma$ and $\pi$ interactions, provided that the molecule processes sufficient molecular symmetry. Because the interaction and orbital terms can be broken into physically meaningful components, EDA allows the bonding of the complex to be evaluated comprehensively.\textsuperscript{7,14,22}

Here, we carry out DFT calculations on bidentate phosphine complexes of stoichiometry Ni(CO)$_2$(R$_2$P(CH$_2$)$_n$PR$_2$), where $n = 1, 2, \text{ or } 3$, and R = H, Me, CF$_3$, Et, i-Pr, t-Bu, Ph, OMe, or F.
We gauge the donor ability of the bidentate phosphine from the computed CO stretching frequencies, and compare our results with available experimental data for bidentate phosphine complexes and with the properties of unidentate phosphine ligands bearing the same terminal substituents on phosphorus.

In order to exploit these results, we examine how the donor acceptor properties of the phosphine ligand affects the structures and dynamics of nickel hydride complexes of stoichiometry NiH$_2$(R$_2$P(CH$_2$)$_n$PR$_2$). As we will show, our calculations reveal that these compounds exist as non-classical elongated dihydrogen complexes (H-H distance < 1.0 Å). Depending on the phosphine, in some cases there is a higher energy classical dihydride structure (H-H distance > 1.5 Å). We also investigate hydrogen exchange mechanisms in this system, and show them to be very sensitive to steric and electronic effects.

**Section 2.2 Computational methods**

The structures of all phosphine complexes were optimized without symmetry constraints in Turbomole 6.0 using the “resolution of identity” approximation (RI-BP86) and the def2-TZVP basis set on all atoms using tight convergence criteria ($SCFConv$=8). Except when noted, all structures are local minima on the potential energy surface as confirmed by analytic frequency calculations. Nickel complexes bearing bidentate phosphines with an odd number of CH$_2$ groups in the backbone optimize to a structure that possesses near-ideal mirror symmetry, in
which the mirror plane passes through the Ni center and the central CH$_2$ group of the phosphine backbone. Nickel complexes with two CH$_2$ groups in the backbone optimize to a structure with near ideal C$_2$ symmetry, in which the C$_2$ axis passes through the Ni atom and between the two CH$_2$ groups on the phosphine backbone. These molecules can be optimized into the higher symmetry C$_3$ or C$_2$ geometry, except when very large substituents such as t-Bu are present, with negligible effects on the energy of the complex. Vibrational frequencies reported for the complexes are unscaled.

The energy of the relaxed NiH$_2$(H$_2$PCH$_2$PCH$_2$) complex as a function of the H-H distance (referred to as the relaxed H-H scan) was performed in Gaussian03 Rev. E.01 using BP-86 (BP86 ref) and def2-TZVP basis sets. Natural bond orbitals were obtained using NBO 3.1 as implemented in Gaussians03 Rev. E.01. NBO electron densities were generated from single point calculations of the molecules with BP86/def2-TZVP basis sets in Gaussian03 from Turbomole 6.0 optimized geometries. Density plots for Bader analysis were obtained from wavefunction files generated from the Turbomole structures using the tm2molden and molden2wfn utilities. Contour plots were created using AIMPAC. For the energy decomposition analysis, the selected molecules were reoptimized from Turbomole structures using the Amsterdam Density Functional program ADF 6.01b using BP86 and Slater type orbitals with the zeroth order regular approximation (ZORA) for estimating relativistic effects. The resulting structures agree well with Turbomole geometries with the exception of the H-H distance of the dihydride tautomers; the latter distance is subject to more variability because the potential energy surface is unusually flat along this structural coordinate.
Section 2.3 Results: Geometries of Ni(CO)$_2$(R$_2$P(CH$_2$)$_n$PR$_2$) complexes.

DFT calculations using the basis sets and functionals described in the Computational Methods section were employed to optimize the structures of the following nickel carbonyl complexes bearing bidentate phosphines: Ni(CO)$_2$(R$_2$P(CH$_2$)$_n$PR$_2$) where $n$ = 1, 2, or 3, and R = H, Me, CF$_3$, Et, i-Pr, t-Bu, Ph, OMe, or F. For comparison, we also determined optimized structures for two nickel carbonyl complexes of unidentate phosphines, Ni(CO)$_2$(PMe$_3$)$_2$ and Ni(CO)$_2$(PPh$_3$)$_2$. All of these compounds adopt the distorted tetrahedral geometries expected for four-coordinate complexes of Ni$_0$ as seen in Figure 2.2. Data for all structures can be found in Table 2.1. The calculated bond distances are slightly longer than those determined crystallographically. For example, the calculated CO bond distance of Ni(CO)$_2$[(t-Bu)$_2$PCH$_2$P(t-Bu)$_2$] is 1.163 Å, which is 0.02 Å longer than the experimental bond distance of 1.143 Å.

The calculated P-Ni-P angle increases by ~12° for each CH$_2$ group added to the phosphine backbone, and is 75-78°, 88-91°, and 98-103° for $n$ = 1, 2, and 3, respectively. For molecules with identical substituents R, the Ni-P distance is 0.03 Å longer when the backbone has one CH$_2$ group, vs. when there are two or three (which have essentially identical Ni-P bond lengths). Evidently, small P-Ni-P angle for the R$_2$P-CH$_2$-PR$_2$ phosphines leads to poorer overlap between nickel and phosphorus. For a given backbone length, the P-Ni-P angle is slightly larger if the terminal substituents R are larger. Thus, of all the complexes we studied, the smallest P-Ni-P angle is seen for the complexes with R = F, and the largest for complexes with R = t-Bu. As expected, the calculated P-Ni-P angle in Ni(CO)$_2$(PMe$_3$)$_2$ of 110° is larger than in any of the bidentate phosphine complexes studied. The P-Ni-C and C-Ni-C angles in all of these molecules lie close to the ideal tetrahedral value of 109.5°.
For each optimized structure, symmetric and asymmetric CO stretching frequencies were calculated and compared with those determined experimentally\textsuperscript{31,35,36} and theoretically.\textsuperscript{5} Our calculated values match the experimental trends seen in these complexes, with a high correlation coefficient of 0.942 (Figure 2.3). The symmetric carbonyl stretching frequencies are strongly correlated in the expected way with the C-O and Ni-C bond lengths: higher frequencies correspond to shorter C-O bonds and longer Ni-C bonds.

In a fashion similar to Tolman’s approach for unidentate phosphines, it is possible to derive an equation to predict the CO stretching frequencies for Ni(CO)\textsubscript{2}(R\textsubscript{2}P(CH\textsubscript{2})\textsubscript{n}PR\textsubscript{2}) complexes, given the identities of the phosphorus-bound substituents and the length of the backbone. Thus, the symmetric CO stretching frequency (in cm\textsuperscript{-1}) for Ni(CO)\textsubscript{2}(R\textsubscript{2}P(CH\textsubscript{2})\textsubscript{n}PR\textsubscript{2}) complexes in which the bidentate phosphines bears four identical substituents can be calculated from the expression ν(CO) = 1982 + 4 χ\textsubscript{B} – 4.5 n, where χ\textsubscript{B} is substituent-dependent and n is the number of carbon atoms in the phosphine backbone (1 ≤ n ≤ 3). Here, the subscript B in χ\textsubscript{B} denotes that the subsitutent parameters are deduced from data for bidentate phosphine complexes. The deduced values of χ\textsubscript{B} (in units of cm\textsuperscript{-1}) for different substituents are listed in Table 2.2.\textsuperscript{37}
Table 2.1 Geometric and vibrational data for Ni(CO)$_2$(R$_2$P(CH$_2$)$_n$PR$_3$) complexes optimized with RI-BP86/def2-TZVP.

<table>
<thead>
<tr>
<th>Label</th>
<th>n</th>
<th>R</th>
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<td>2013</td>
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$^a$ Optimized complex exhibits one imaginary frequency at -32 cm$^{-1}$.
The $\chi_B$ values for the various substituents follow the same trends as do Tolman’s $\chi$ values for the same substituents in unidentate phosphines, but there are some small differences. For example, almost all the $\chi_B$ values are larger than the corresponding Tolman parameter $\chi$ for the same substituent. This trend may be a consequence of our deducing the $\chi_B$ values from nickel dicarbonyl complexes, whereas the Tolman $\chi$ values are deduced from nickel tricarbonyl complexes. In other words, the electronic effect of the substituents on the phosphine are distributed over two carbonyl groups for $\chi_B$, but over three for $\chi$. 

Figure 2.3 Comparison between experimental and calculated symmetric CO stretching frequencies of Ni(CO)$_2$(dRpn). $^a$ Ref. 35 $^b$ Ref. 36 $^c$ Ref. 38
Table 2.2 Comparison of Tolman’s electronic substituent parameters $\chi$ for unidentate phosphines and the corresponding substituent parameters, $\chi_B$, for bidentate phosphines.

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<th>Substituent</th>
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<th>$\chi_B^b$, cm$^{-1}$</th>
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<td>0.0</td>
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<tr>
<td>iPr</td>
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<td>1.3</td>
</tr>
<tr>
<td>Et</td>
<td>1.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Me</td>
<td>2.6</td>
<td>4.5</td>
</tr>
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<td>F</td>
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</table>

$^a$ From Tolman. $^b$ From the current work

We should expect that the substituents should exert a larger effect on the carbonyl frequencies in the former case than in the latter. But there are some aspects of the behavior of $\chi_B$ with $\chi$ that are superposed on this general trend. One is that the substituent effects of methyl and phenyl are relatively similar in bidentate phosphines: the $\alpha_1$ CO stretching frequency for the methyl phosphine complex Ni(CO)$_2$(Me$_2$P(CH$_2$)$_n$PMe$_2$) is within 1 cm$^{-1}$ of that of the phenyl phosphine complex Ni(CO)$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$). In contrast, the $\alpha_1$ CO stretching frequencies of Ni(CO)$_3$(PMe$_3$) and Ni(CO)(PPh$_3$) differ by 5 cm$^{-1}$. These electronic differences may be geometric in origin. The dihedral angle between two aromatic groups in van der Waals contact is known to be highly variable$^{39}$ and the geometric constraints of the chelate ring (and the presence of the substituents on the other phosphine center) may change the preferred orientations of the phenyl rings in bidentate phosphines vs. their unidentate analogs. Different orientations with respect to the Ni-P bonds could lead to a difference in the donor/acceptor properties of the
phosphine. Furthermore, it is known that DFT calculations underestimate the interactions between aromatic rings in van der Waals contact which leads to incorrect energies.\textsuperscript{39-43} Apart from these differences, the $\chi$ and $\chi_B$ values are rather similar and suggest that the former are still mostly valid for bidentate phosphines.

One last point is that of the length of the CH$_2$ backbone does affect the CO frequency. Thus, for example, adding one methylene unit to the backbone decreases $\nu$(CO) by about as much (4 cm$^{-1}$) as changing all four substituents from Me to Et.

**Section 2.4 Results from nickel-H\textsubscript{2} complexes.**

**Geometries of NiH$_2$(R$_2$P(CH$_2$)$_n$PR$_2$) complexes.** Somewhat surprisingly, no nickel dihydrides of stoichiometry NiH$_2$(PR$_3$)$_2$ or NiH$_2$(R$_2$P(CH$_2$)$_n$PR$_2$) have ever been reported. However, cis-dihydride complexes of Pt have been reported.\textsuperscript{44,45} Our DFT results show that, irrespective of the choice of the bidentate phosphine, the lowest energy structure of NiH$_2$(R$_2$P(CH$_2$)$_n$PR$_2$) is a non-classical dihydrogen complex as shown in Figure 2.4.\textsuperscript{46} Data for these complexes are shown in Table 2.3.

![Figure 2.4 Structures of a) dhpm, Ni(H$_2$)(H$_2$PCH$_2$PH$_2$) b) dhpe, Ni(H$_2$)(H$_2$PCH$_2$CH$_2$PH$_2$) and c) dhpp, Ni(H$_2$)(H$_2$PCH$_2$CH$_2$CH$_2$PH$_2$)
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Table 2.4 H-H bond lengths (Å) for NiH$_2$(R$_2$P(CH$_2$)$_n$PR$_2$) complexes as a function of the substituent R.

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<td>0.946</td>
<td>0.936</td>
<td>0.921</td>
<td>0.901</td>
<td>0.898</td>
<td>0.867</td>
<td>0.872</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>0.937</td>
<td>0.932</td>
<td>0.927</td>
<td>0.930</td>
<td>0.918</td>
<td>0.898</td>
<td>0.891</td>
<td>0.866</td>
<td>0.870</td>
</tr>
</tbody>
</table>

The Ni-P distances in the dihydrogen complexes are typically 0.08 Å shorter than in the corresponding carbonyl complexes. This shortening causes the P-Ni-P angles for the hydride complexes to 3 to 5 degrees larger than for the carbonyl complexes. As seen in the carbonyl complexes, for molecules with identical substituents R, the Ni-P distance is 0.03 Å longer when the backbone has one CH$_2$ group, vs. when there are two or three (which have essentially identical Ni-P bond lengths) but these distances are shorter than those reported previously for Pt$^0$-P bond distances (2.24-2.68 Å). The H-H distance and Ni-H distances are essentially insensitive to the number of CH$_2$ groups in the phosphine backbone, but are sensitive to the substituents on phosphorus (Table 2.4). Specifically, the H-H bond distance is longer for alkyl substituents (being ~0.948 Å for R = t-Bu) and shorter for fluorinated substituents (~0.867 Å for R = CF$_3$). As seen for the carbonyl complexes, Me$_2$P(CH$_2$)$_n$PMe$_2$ and Ph$_2$P(CH$_2$)$_n$PPh$_2$ behave very similarly, and form nickel complexes in which the H-H bond distance is essentially equal.

It is well established that transition metal dihydrides can exist simultaneously in both classical dihydride and non-classical dihydrogen forms, and so we investigated whether the classical dihydride form of NiH$_2$(R$_2$P(CH$_2$)$_n$PR$_2$) is a stable structure. Although the dihydrogen form is the global minimum in all cases, we find that for some R groups the classical dihydride form can be located on the potential energy surface as a local minimum. Its energy can be as low as 2 kcal mol$^{-1}$ above that of the non-classical dihydrogen structure (Table 2.5). In the dihydride
In the excited state, the H-H distances of 1.6-1.8 Å are about 0.9 Å longer than in the dihydrogen tautomer. The average Ni-H distance decreases from 1.59 Å for the dihydrogen complex to 1.47 Å for the dihydride complexes. Accordingly, the H-Ni-H angle increases from ~37° in the hydrogen complexes to ~72° in the dihydride complexes. The P-Ni-P angle increases by 3° relative to the dihydrogen complexes and the Ni-P distance increases by 0.01 Å.

Table 2.5 H-H bond lengths (Å) and vibration-corrected energy, ΔE, of the dihydride excited state of NiH2(R2P(CH2)nPR2). The energy is relative to that of the dihydrogen complex, in kcal mol⁻¹.

<table>
<thead>
<tr>
<th>R</th>
<th>t-Bu</th>
<th>i-Pr</th>
<th>Et</th>
<th>Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1</td>
<td>1.630</td>
<td>1.4</td>
<td>1.734</td>
<td>0.7</td>
</tr>
<tr>
<td>n = 2</td>
<td>1.746</td>
<td>1.1</td>
<td>1.774</td>
<td>0.7</td>
</tr>
<tr>
<td>n = 3</td>
<td>1.625</td>
<td>1.1</td>
<td>1.648</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Interestingly, dihydride structures can be located on the potential energy surface only when the phosphine substituent is an electron donating alkyl group (i.e. Me, Et, i-Pr, or t-Bu). In order to determine why this is the case, we calculated the energy of the three Ni(H2)(H2P(CH2)nPH2) complexes that bear hydrogen substituents on phosphorus for a series of fixed H-H distance, allowing the rest of the structure to relax. The resulting plots of the potential energy surface along this reaction coordinate (Figure 2.5) show distinct local minima for the dihydrogen structure (H-H = 0.9 Å) but no local minimum at longer distances. Instead, there is an “incipient minimum,” (a lessening of the gradient) near H-H distances of 1.5-1.8 Å characteristic of dihydride complexes (Figure 2.4). In contrast, the relaxed surface scan for the electron donating Me substituted NiH2(Me2PCH2PMe2) complex exhibits a very flat minimum in
the potential energy surface near the dihydride distance (1.7 Å). The general trend here is as expected: electron donating phosphines increase the relative stability of the classical dihydride structure over non-classical dihydrogen alternative.\textsuperscript{48} In the present NiH\textsubscript{2}(R\textsubscript{2}P(CH\textsubscript{2})\textsubscript{n}PR\textsubscript{2}) system, the energy of the dihydride form is always at least 2 kcal mol\textsuperscript{-1} higher than that of the dihydrogen form, so that the dihydrogen form will be the predominant species (>99%) at equilibrium.

![Relaxed scan of the energy of NiH\textsubscript{2}(R\textsubscript{2}P(CH\textsubscript{2})\textsubscript{n}PR\textsubscript{2}) complexes as a function of the H-H bond length using BP86/def2-TZVP. The structure was reoptimized at each scan point, and the energies are reported relative to that of the global minimum.](image)

**Figure 2.5** Relaxed scan of the energy of NiH\textsubscript{2}(R\textsubscript{2}P(CH\textsubscript{2})\textsubscript{n}PR\textsubscript{2}) complexes as a function of the H-H bond length using BP86/def2-TZVP. The structure was reoptimized at each scan point, and the energies are reported relative to that of the global minimum.

**Section 2.5 Bonding analysis.**

In order to detail more fully the nickel-hydrogen bonding in the NiH\textsubscript{2}(R\textsubscript{2}P(CH\textsubscript{2})\textsubscript{n}PR\textsubscript{2}) complexes, we have analyzed the electron density distributions within both the nonclassical
dihydrogen and classical dihydride forms of this molecule. Three post-wavefunction methods have been employed: natural bond orbital analysis (NBO), Bader’s atoms in molecule (AIM), and energy decomposition analysis (EDA).

Contour line diagrams of the Laplacian of the density for the dihydrogen and dihydride forms of NiH$_2$(Me$_2$PCH$_2$PMe$_2$) show that there is a clear difference between the Ni-H and Ni-H$_2$ bond interactions. (Figure 2.6) The bond critical point for the Ni-H$_2$ bond is covalent ($\nabla^2 \rho(r) < 0$ a.u.) whereas the bond critical point for the Ni-H bond is ionic ($\nabla^2 \rho(r) > 0$ a.u). The contour plot of the dihydrogen complex clearly shows a buildup of charge density towards the nickel center and the energy density at that point is calculated to be 0.210 Hartrees Å$^{-3}$ (versus 0.189 Hartrees Å$^{-3}$ for the ionic Ni-H bond). In addition, NBO analysis of all of the complexes confirms that species with H-H distances less than 1.0 Å possess three-center bonds between Ni and the H$_2$ ligand, whereas complexes with H-H distances greater than 1.0 Å possess two ionic bonds between Ni and H.

**Figure 2.6** Contour plots of the Laplacian of the electron density, $\nabla^2 \rho(r)$, for the a) dihydrogen and b) dihydride tautomers of NiH$_2$(Me$_2$PCH$_2$PMe$_2$). Solid lines indicate areas of charge concentration ($\nabla^2 \rho(r) < 0$), whereas dashed lines show areas of charge depletion ($\nabla^2 \rho(r) > 0$).
We have also carried out energy decomposition analyses on selected dihydrogen and dihydride complexes. Energy decomposition analysis allows us to differentiate between σ and π orbital contributions to bonding between the Ni and hydrogen atoms in the HOMO and LUMO. In both the C₂ and C₅ point groups, the HOMO and LUMO transform differently and thus their contributions to the orbital overlap energy can be differentiated.

The relevant nickel-based orbitals on the L₂Ni fragment that interact with the hydrogen atoms should be a filled d-orbital of π symmetry and an empty d-orbital (or hybrid) of σ symmetry (Figure 2.7). The relative energies of these two orbitals are \( E(\pi) < E(\sigma) \). As the phosphine becomes more electron rich, the energies of both of these frontier orbitals on the L₂Ni fragment should increase due to shielding of the nuclear charge of the nickel atom. This effect will increase the energy difference that generate the σ interaction between Ni and H₂ (thus decreasing the overlap and σ contribution to the bond), but decrease the gap between the orbitals that generate the π interaction between Ni and H₂ (thus increasing the overlap and the π contribution to the bond). In the limit that the π contribution is very strong, the H-H bond breaks to form a dihydride.

![Figure 2.7 Diagram of σ and π interactions between the Ni(R₂PCH₂PR₂) fragment and H₂.](image)
EDA data for the elongated dihydrogen complexes are shown in Table 2.7, along with the H-H distances calculated from ADF. The distances for dihydrogen complexes match up almost perfectly with the geometric data obtained from Turbomole calculations. The distances for the dihydride complexes, however, vary by a large amount, which is not surprising considering the flatness of the potential energy surface for the dihydride complexes (Figure 2.5).

Table 2.6 EDA data for NiH₂(R₂PCH₂PR₂) dihydrogen complexes using the DCD model.

<table>
<thead>
<tr>
<th>R</th>
<th>t-Bu⁺</th>
<th>i-Pr</th>
<th>Et</th>
<th>Me</th>
<th>Ph</th>
<th>H</th>
<th>OMe</th>
<th>CF₃</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>C₅</td>
<td>C₅</td>
<td>C₅</td>
<td>C₅</td>
<td>C₅</td>
<td>C₅</td>
<td>C₅</td>
<td>C₅</td>
<td>C₅</td>
</tr>
<tr>
<td>H-Havg (Å)</td>
<td>0.980</td>
<td>0.996</td>
<td>0.959</td>
<td>0.958</td>
<td>0.962</td>
<td>0.915</td>
<td>0.916</td>
<td>0.877</td>
<td>0.879</td>
</tr>
<tr>
<td>ΔE_Pauli</td>
<td>100.35</td>
<td>97.87</td>
<td>92.13</td>
<td>92.4</td>
<td>92.59</td>
<td>83.2</td>
<td>81.88</td>
<td>74.95</td>
<td>74.86</td>
</tr>
<tr>
<td>ΔE_Elsat</td>
<td>-82.54</td>
<td>-83.18</td>
<td>-76.93</td>
<td>-77.18</td>
<td>-77.61</td>
<td>-68.91</td>
<td>-67.83</td>
<td>-60.34</td>
<td>-59.88</td>
</tr>
</tbody>
</table>

(58.28%) (58.36%) (58.33%) (58.45%) (58.61%) (58.77%) (58.64%) (58.50%) (58.18%)
(41.72%) (41.64%) (41.67%) (41.55%) (41.39%) (41.23%) (41.36%) (41.50%) (41.82%)

ΔE_Orb | -59.09 | -59.36 | -54.94 | -54.86 | -54.8 | -48.34 | -47.85 | -42.8 | -43.04 |

(41.72%) (41.64%) (41.67%) (41.55%) (41.39%) (41.23%) (41.36%) (41.50%) (41.82%)

ΔE_α | -25.32 | -24.07 | -23.92 | -24.00 | -23.64 | -23.26 | -22.73 | -23.72 | -23.68 |

(42.85%) (40.55%) (43.54%) (43.75%) (43.13%) (48.11%) (47.51%) (55.42%) (55.02%)


(57.15%) (59.45%) (56.48%) (56.25%) (56.86%) (51.90%) (52.48%) (44.56%) (44.98%)

ΔE_prep | 19.01 | 19.94 | 15.96 | 16.15 | 15.69 | 11.40 | 11.63 | 8.03  | 8.67   |


a) dtBupm in C₅ symmetry exhibits one large imaginary frequency of -43 cm⁻¹.
The relative importance of $\sigma$- or $\pi$- interactions between metals and dihydrogen ligands has been the topic of previous theoretical investigations.\textsuperscript{49,50} The EDA shows that the relative contributions of $\sigma$ and $\pi$ orbital interactions to the Ni-H$_2$ bond is strongly dependent on the nature of the substituents on the bidentate phosphine. For the complexes with R = t-Bu, i-Pr, Et, Me, Ph, H, or OMe, $\pi$ backdonation is the dominant orbital component. In contrast, for R = F or CF$_3$, the $\sigma$ component is dominant. There is also strong correlation between the relative $\sigma$ and $\pi$ contributions and the H-H distance (Figure 2.8). Although both interactions weaken the H-H bonding (Figure 2.7), the EDA results clearly indicate that the [M] $\rightarrow$ (H$_2$) $\pi$ backdonation has a much stronger effect on the H-H distance than the [M] $\leftarrow$ (H$_2$) $\sigma$ donation.

Figure 2.9 compares the percent orbital contributions from the EDA data with CO$_{\text{symm}}$ stretching frequencies for the corresponding Ni(CO)$_2$(R$_2$P(CH$_2$)$_n$PR$_2$) complex. The $\% \pi$ contribution increases (and the H-H distance increases) as the carbonyl stretching frequency decreases (and the phosphine becomes more electron rich). These correlations are completely
consistent with the orbital picture in Figure 2.7. A very good correlation between the percentage \( \pi \) contribution between the metal carbon bond in metal carbonyls and the CO stretching frequencies has previously been reported for carbonyl complexes.\(^7\text{50}\)

**Figure 2.9** Plot of the \( \% \sigma \) orbital contribution (blue diamonds) and \( \% \pi \) orbital contribution (red squares) to the Ni-H\(_2\) bond versus the symmetric CO stretching frequency (cm\(^{-1}\)) of the corresponding Ni(CO)\(_2\)(R\(_2\)P(CH\(_2\))\(_n\)PR\(_3\)) complex. EDA values are from ADF calculations whereas CO stretching frequencies are from Turbomole calculations.

Interesting trends emerge also as the number of carbon atoms between the phosphine substituents is increased from one to three (Table 2.8). The H-H bond distance remains approximately constant as does the \( \% \) orbital and \( \% \) electrostatic contributions. For dhpm and dhpp, the \( \% \pi \) contribution is \(~51\%) whereas the \( \pi \) contribution for dhpe is 55%. Thus, the phosphine dhpe with two methylene units in the backbone is more electron rich than the phosphines dhpm and dhpp with an odd number of methylene units in the backbone.
Table 2.7 EDA data for NiH$_2$(H$_2$P(CH$_2$)$_n$PH$_2$) complexes where $n = 1, 2, 3$ using the DCD model. Values come from ADF calculations.

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>H$_2$PCH$_2$PH$_2$</th>
<th>H$_2$P(CH$_2$)$_2$PH$_2$</th>
<th>H$_2$P(CH$_2$)$_3$PH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular symmetry</td>
<td>C$_s$</td>
<td>C$_2$</td>
<td>C$_s$</td>
</tr>
<tr>
<td>H-H$_{avg}$ (Å)</td>
<td>0.915</td>
<td>0.917</td>
<td>0.916</td>
</tr>
<tr>
<td>$\Delta$ E$_{\text{int}}$ (kcal mol$^{-1}$)</td>
<td>-34.05</td>
<td>-35.24</td>
<td>-33.88</td>
</tr>
<tr>
<td>$\Delta$ E$_{\text{Pauli}}$ (kcal mol$^{-1}$)</td>
<td>83.2</td>
<td>80.6</td>
<td>85.26</td>
</tr>
<tr>
<td>$\Delta$ E$_{\text{Elstat}}$ (kcal mol$^{-1}$)</td>
<td>-68.91</td>
<td>-68.7</td>
<td>-70.72</td>
</tr>
<tr>
<td>(58.8%)</td>
<td>(59.3%)</td>
<td>(59.4%)</td>
<td></td>
</tr>
<tr>
<td>$\Delta$ E$_{\text{orb}}$ (kcal mol$^{-1}$)</td>
<td>-48.34</td>
<td>-47.14</td>
<td>-48.41</td>
</tr>
<tr>
<td>(41.2%)</td>
<td>(40.7%)</td>
<td>(40.6%)</td>
<td></td>
</tr>
<tr>
<td>$\Delta$ E$_{\sigma}$ (kcal mol$^{-1}$)</td>
<td>-23.26</td>
<td>-21.05</td>
<td>-23.69</td>
</tr>
<tr>
<td>(48.1%)</td>
<td>(44.6%)</td>
<td>(48.9%)</td>
<td></td>
</tr>
<tr>
<td>$\Delta$ E$_{\pi}$ (kcal mol$^{-1}$)</td>
<td>-25.09</td>
<td>-26.09</td>
<td>-24.72</td>
</tr>
<tr>
<td>(51.9%)</td>
<td>(55.4%)</td>
<td>(51.1%)</td>
<td></td>
</tr>
<tr>
<td>$\Delta$ E$_{\text{prep}}$ (kcal mol$^{-1}$)</td>
<td>11.40</td>
<td>11.76</td>
<td>13.02</td>
</tr>
<tr>
<td>$\Delta$ E =-D$_e$ (kcal mol$^{-1}$)</td>
<td>-22.65</td>
<td>-23.48</td>
<td>-20.86</td>
</tr>
</tbody>
</table>

In a recent paper, Symczak and coworkers reported that the lability of an H$_2$ ligand in a ruthenium complex is highly dependent on the electronic character of the bidentate phosphine.$^6$ Electron withdrawing substituents rendered the H$_2$ complex susceptible to substitution by H$_2$O whereas electron donating substituents stabilized the H$_2$ complex. The authors suggested that electron donating substituents increased in the $\pi$ back donation into the Ni-H$_2$ bond, increasing the Ru-H$_2$ bond dissociation energy. Our EDA results are consistent with this trend: where electron -withdrawing phosphines containing F and CF$_3$ had lower dissociations energies (~20 kcal mol$^{-1}$) than the electron donating phosphines (~23 kcal mol$^{-1}$)
Section 2.6. Conclusions.

Carbonyl stretching frequencies for bidentate phosphines maintain that substituent trends in bidentate phosphines are the same as those determined for unidentate phosphines. In bidentate phosphines the carbonyl stretching frequency is also dependent on the number of CH$_2$ groups between the phosphorous atoms. Phosphines with an even number of CH$_2$ groups show a slightly less %σ donation from versus an odd number of CH$_2$ groups. These differences could explain the differences in reactivities seen for some bidentate complexes.$^{6,51,52}$ The EDA results suggest that there is a very good linear correlation between the calculated strength of the [M]←(H$_2$) σ donation and [M]→(H$_2$) π-backdonation which clearly shows that the π-backdonation has a much stronger effect on stretching the H-H distance than the σ donation.

References


(7) Gernot Frenking; Christoph Loschen; Andreas Krapp; Stefan Fau; Steven H. Strauss J. Comput. Chem. 2007, 28, 117-126.


(37) For derivation of this equation see Appendix A.


CHAPTER 3. A DFT AND *AB INITIO* BENCHMARKING STUDY OF METAL-ALKANE INTERACTIONS AND THE ACTIVATION OF CARBON-HYDROGEN BONDS.

Section 3.1 Introduction.

The efficient conversion of alkanes into other chemical substances is a highly desirable capability for chemical industry. Alkanes are abundant feedstocks, and therefore are attractive starting materials for the synthesis of fine chemicals. To develop such syntheses, however, requires the discovery of selective methods to activate particular C-H bonds in alkanes, and to replace those hydrogen atoms with other functional groups. Of particular interest is the development of transition metal catalysts to convert alkanes into functionalized derivatives, because such catalysts are often able to promote chemical reactions with high selectivity and high yield. Alkanes, however, interact very weakly with transition metals and their complexes, and thus do not readily participate in catalytic cycles under ambient conditions.\(^1\text{-}\!^3\)

Alkanes bind weakly to transition metals for several reasons: they are electrically neutral, relatively non-polarizable, and very poor electron donors and electron acceptors, so that electrostatic, charge transfer, and covalent interactions with metals are weak. Despite these unfavorable attributes, alkanes can bind to transition metal complexes in solution under the right circumstances, and several such complexes are now known.\(^1\text{-}\!^4\) These compounds serve as instructive models for the key intermediates in alkane activation reactions, in which carbon-hydrogen bonds are broken. The structural characterization of methane coordination complexes of transition metals is a desirable goal, and the resulting fundamental understandings could assist in the creation of industrially useful catalysts in which alkanes serve as the feedstock.
Most interactions of C-H bonds with metal centers involve weak three-center-two-electron interactions analogous to those in the Dewar-Chatt-Duncanson (DCD) model for the bonding of olefins to transition metals.\textsuperscript{5-7} The bonding in such compounds (which are referred to as agostic or σ-complexes) involves σ-donation from a C-H bond into an unoccupied ‘d’ orbital on the metal center, and back donation from the metal into an unoccupied C-H σ-anti-bonding orbital. In other cases, the interaction between the metal and the C-H bond is purely electrostatic, and involves polarization of the C-H bond by the positively charged metal ion. Such interactions, which generally are weaker than agostic interactions, have been termed anagostic.\textsuperscript{4} Finally, there are examples of what appear from structural data to be σ-interactions but that actually result from delocalization of M-C bonding electrons.\textsuperscript{4,8,9}

One of us (GSG) has synthesized a family of cationic osmium complexes $L_x\text{Os}((CH_3)(H))^+$, in which a methyl group (CH$_3$) and a hydride ligand (H) occupy adjacent coordination sites.\textsuperscript{10} NMR studies demonstrated that in solution these methyl/hydride complexes are in rapid equilibrium with the tautomeric form $L_x\text{Os}((CH_4))^+$, in which the metal center is coordinated to a methane molecule formed by joining together the methyl and hydride ligands (Figure 3.1). The equilibrium between the methyl/hydride complex and the methane coordination complex is an example of the reversible activation of methane, and the activation barrier of about 8 kcal mol$^{-1}$ for this process is considerably smaller than the 20-30 kcal mol$^{-1}$ barriers that typically are characteristic of such reactions. This low barrier means that the C-H bond formation and cleavage processes in these osmium complexes are reversible and rapid enough, 100 sec$^{-1}$ at -100 °C, to be dynamic on the NMR time scale. The activation energy for loss of the bound methane to generate the dissociated state $L_x\text{Os}^+ + CH_4$ was measured to be about 13 kcal mol$^{-1}$. 

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Again, this is an unusually high dissociation barrier for metal-alkane interactions, rivaled only by those seen in certain rhenium systems.\textsuperscript{11,12}

The osmium complexes that have been studied experimentally bear two ancillary ligands: a chelating diphosphine (CH\textsubscript{3})\textsubscript{2}PCH\textsubscript{2}P(CH\textsubscript{3})\textsubscript{2} group, and a cyclopentadienyl ring (Figure 3.1). Interestingly, when the steric and electronic properties of the cyclopentadienyl ring are varied over a large range – C\textsubscript{5}H\textsubscript{x}(CH\textsubscript{3})\textsubscript{5-x}, where x = 0, 1, 4, and 5 – the relative energies of the complexes, and the barriers for the reactions that interconvert them, vary by less than 0.5 kcal mol\textsuperscript{-1}.\textsuperscript{13-15}

Two previous computational studies employed the popular B3LYP functional and Pople basis sets to explore the potential energy surface and reaction mechanisms in this osmium system.\textsuperscript{16,17,18} Both Martin and Morokuma supported the conclusions from the experimental study that the methyl/hydride complex is in equilibrium with a methane coordination complex, and that the transition state for this equilibrium is about 8 kcal mol\textsuperscript{-1} higher in energy than the methyl/hydride species. Both authors suggested that changing the cyclopentadienyl ligand from C\textsubscript{5}H\textsubscript{5} to C\textsubscript{5}Me\textsubscript{5} shifts the total energies of all species on the potential energy surface equally and therefore does not affect the barrier for H-exchange. This finding is also consistent with the experimental results, as mentioned above.\textsuperscript{13-15} In order to fully investigate the effects of ancillary ligands on the critical points in this reaction, variations due to the computational method must be smaller than the variations between the model complexes.

For most σ-complex interactions, a full configuration interaction (CI) or coupled cluster (CC) calculations remains out of reach computationally because the chemical systems are too large, often involving transition metal complexes with 20 atoms or more. Such systems are, however, within the capability of density functional theoretical (DFT) methods. Few papers have
addressed the ability of DFT methods to treat metal-alkane interactions, but generally the results suggest that calculations can provide cheap and relatively accurate descriptions of the system\textsuperscript{9,22,23} provided that care is taken to choose the correct method\textsuperscript{24-26}.

No previous benchmark study has treated σ-complexes of osmium. Pantazis et al. evaluated the ability of 24 different DFT functionals within a hybrid QM/MM protocol to predict the structure of certain niobium alkyl complexes that exhibit agostic interactions.\textsuperscript{8} Of the 24 functionals tested, eleven – including the popular B3LYP and MPW1LYP – predicted structures in conflict with experiment. The correlation part of these eleven functionals disobey the uniform electron gas (UEG) limit, either incorporating the LYP functional or versions of the B97 functionals. These eleven functionals overestimated the strength of donor-acceptor interactions with other π-bonding ligands relative to the agostic interaction. Two LDA functionals, VSXC and SVWN5, correctly predicted the agostic structure, but may have done so because these functionals tend to overestimate the correlation energy, which in turn leads to an overestimation of electron delocalization between the C-H and metal orbitals. Eleven other functionals gave more reasonable potential energy surfaces, but only six of them correctly predicted the agostic structure to have the minimum energy.

The accuracy of DFT calculations depends mostly on the choice of the functional.\textsuperscript{8,27} DFT is inherently an exact method but the form of the “exact functional” is unknown except for simple systems such as the uniform electron gas.\textsuperscript{28} There is no non-empirical way to determine the accuracy of a given functional because there is no systematic basis for improving the functional (at least in the current DFT formalism); there is no parallel to the full configuration interaction limit that allows systematic improvement of wavefunction based methods. Many different kinds of approximate functionals have been proposed,\textsuperscript{28} and their performance for
predicting structures and energies varies widely.\textsuperscript{29} As with all approximate computational methods, it is essential to benchmark DFT methods against relevant experimental results or more accurate \textit{ab initio} methods to determine how well they perform for specific applications.

The goal of the current study is to assess the accuracy and efficiency of various combinations of basis sets and DFT functionals for calculating the energetics of the methane activation reactions of the osmium complexes noted above. The benchmark calculations in the present study are compared against both experimental results and limited high-level coupled cluster calculations of the relevant chemical species (including both minima and transition states). We have investigated popular DFT functionals such as B3LYP, newer dispersion corrected functionals such as Truhlar’s M05-2X,\textsuperscript{30} and functionals such as MPW1K that were designed to model kinetics.\textsuperscript{31} Full optimizations were performed for Hartree-Fock and MP2 \textit{ab initio} methods and single point energies calculated for coupled cluster with triplet excitations (CCSD(T) and CCSD). We also evaluated the electronic structure of the relevant species in terms of the Kohn-Sham\textsuperscript{32} and natural bond orbital\textsuperscript{33} representations, in order to determine how effectively the different functionals describe the σ-complex interaction. The findings of the present study are potentially relevant to all chemical phenomena that involve weak interactions, and not just the activation of C-H bonds. Previous benchmarking studies have largely dealt with small molecules; the current paper is noteworthy because it is one of the first to benchmark the ability of different DFT methods to deal with weakly bonded complexes of transition metals and the first to test the performance of the new correlation consistent basis sets for late transition metals that have recently been developed by Peterson and co-workers.\textsuperscript{34}
**Section 3.2. Methods.**

Geometries were optimized using Gaussian03 Rev. D.01 and E.01 \(^{35}\) (M05-2X functional only) without any constraints. The crystal structure of \((\text{C}_5\text{Me}_5)\text{Os(}\text{Me}_2\text{PCH}_2\text{PMe}_2)\text{(H)}\) was used as a starting point for structure optimizations.\(^{14}\) Two different complexes were studied, the experimentally known \([\text{(C}_3\text{H}_3)\text{Os(}\text{Me}_2\text{PCH}_2\text{PMe}_2)\text{(H)}\text{CH}_3]\)^+, \(1,^{15}\) and the model complex \([\text{(C}_3\text{H}_3)\text{Os(}\text{H}_2\text{PCH}_2\text{PH}_2)\text{(H)}\text{(CH}_3)\text{]}\)^+, \(1\text{H}^+.\) For each complex, three points on the potential energy surface were characterized: the methyl hydride complex (1 and \(1\text{H}^+)\), the methane coordination complex (2 and \(2\text{H}^+)\), and the transition state (1‡ and \(1\text{H}‡\)) between them. In some cases, the energy of the dissociated state \([\text{(C}_5\text{H}_5)\text{Os(}\text{R}_2\text{PCH}_2\text{PR}_2)\text{]}^+ + \text{CH}_4\) (3 and \(3\text{H}^+)\) was also calculated; the energy of this state with respect to 2 or \(2\text{H}^+\) affords a measure of the methane binding energy.

In these latter calculations, the structure of the fragment \([\text{(C}_5\text{H}_5)\text{Os(}\text{R}_2\text{PCH}_2\text{PR}_2)\text{]}^+\) was allowed to relax. Owing to the flatness of the potential energy surface, all stationary points were determined using the GDIIS method and internal options to decrease step size. The transition states connecting the methyl hydride complex with the methane coordination complex were determined from optimizations using redundant internal coordinates. Frequency calculations were performed to confirm that optimized minima and transition states were true stationary points. For the latter, imaginary frequencies less negative than -25 cm\(^{-1}\) were considered to be close enough to 0 that they could be safely ignored. IRC calculations were used to confirm the transition state geometry.

The benchmark calculations for the basis sets were performed with the B3LYP functional. All molecules were fully optimized for each basis set, and zero point energies were computed for each molecule. The impact of basis set superposition error (BSSE) is expected to be small for these complexes when studied by DFT.\(^{36,37}\) Counterpoise corrections were
performed for selected methods and basis sets: the corrections were small (<0.2 kcal mol\(^{-1}\)) and affected all species on the potential energy surface nearly equally, confirming that the effect of BSSE is minimal (the BSSEs are small and cancellation makes the net impact even smaller.)

Structures were fully optimized for ten DFT methods. We tested one local spin density approximation (LSDA) functional (SVWN5), two pure gradient corrected (GGA) functionals (BP86, \(^{41,42}\) and PBE\(^{43}\)), three hybrid GGA (HGG A) functionals (B3LYP, \(^{41,42,44}\) MPW1K, \(^{31,43,45,46}\) and PBE0\(^{43}\)), and four hybrid meta-GGA (HMGGA) functionals (TPSSH, \(^{47}\) BB1K, \(^{41,44,48}\) BMK, \(^{49}\) and M05-2X\(^{50}\)). All benchmark comparisons for the DFT methods employed basis set combination cc10 (see Table 3). The density functional methods tested are listed in Table 1. Details about the various functionals can be found in the cited references. Keywords and IOP commands for functionals are listed in Appendix C. NBO analyses for each method were performed on the methane coordination complex 2H with NBO 3.0; \(^{51}\) NBO options included searching for delocalized orbitals (RESONANCE) and three-center bonds (3CBOND).

For the \textit{ab initio} methods, the structures of 1H, \(^{1}\text{H}\)\(^{\ddagger}\), 2H, and \(^{3}\text{H}\) were fully optimized with MP2 and HF. Single point energy calculations were performed using the CCSD and CCSD(T) methods at optimized B3LYP, M05-2X, and MP2 geometries. SCF energies are reported for all MP2, CCSD, and CCSD(T) structures.

\textbf{Section 3.3 Results and discussion.}

The results are divided into five sections. In the first section, we summarize how optimized geometric parameters vary with different methods and basis sets. In the second section, we benchmark basis sets for a fixed method (B3LYP), and in the third section, we benchmark the behavior of the functionals for a fixed basis set combination (cc10). In the fourth
section, orbital analysis is used to gain insights into the results from the various functionals. In the last section, we discuss single point energies calculated from \textit{ab initio} methods and compare them with the corresponding DFT energies.

\textbf{Geometries of stationary points.} Structures of the methyl/hydride complex 1, the transition state $1^\dagger$, and the methane coordination complex 2, as well the model complexes $1\text{H}$, $1\text{H}^\dagger$, and $2\text{H}$, have been optimized for the combinations of functionals shown in Table 3.1 (see Figure 3.1 for schematic drawings of these structures). The ranges of bond lengths, bond angles, and tilt angles\textsuperscript{52} found for 1, $1^\dagger$, and 2 are shown in Table 3.2; a selection of key structural parameters for each basis set are available in Appendix C (Table C.1). For all methods and combinations of basis sets, the optimized geometries of 1 and 2 have much in common, and the positions of the ancillary ligands are similar to those seen in the crystal structure of a related compound, the osmium hydride $(C_5\text{Me}_5)\text{Os}($Me$_2\text{PCH}_2\text{PMe}_2)\text{H}$\textsuperscript{14}.

For the methyl/hydride complex 1, the calculated Os-H bond distance varies from 1.59 to 1.62 Å, depending on the computational method used. Similarly, the calculated Os-CH$_3$ bond distance varies from 2.20 to 2.24 Å, and the calculated non-bonded C···H contact distance between the Os-CH$_3$ and Os-H groups varies from 2.13 to 2.17 Å. For the methane coordination complex 2, the bond lengths change in the expected fashion: the Os-H and Os-C(CH$_3$) distances lengthen considerably, and the C···H contact distance between the former Os-CH$_3$ and Os-H groups approaches the 1.09 Å distance seen for free methane.\textsuperscript{53} Relative to the variations in the distances calculated for 1, however, the corresponding distances in 2 show somewhat larger variations depending on the computational method employed. Thus, the calculated Os-H distance varies from 1.85 to 1.91 Å, the calculated Os-C(CH$_3$) distance varies from 2.55 to 2.68 Å, and the C-H distance between the former Os-CH$_3$ and Os-H groups varies from 1.14 to 1.17 Å. The
larger variations reflect the shallowness of the potential energy surface near this stationary point, which in turn results from the weakness of the Os-methane σ-interaction. No clear correlation could be found between these variations and nature of the calculational method used.

The geometry of the transition state $1^\dagger$ that connects 1 and 2 also varies widely depending on the computational method employed. Despite this variation, it is clear from a structural standpoint that $1^\dagger$ resembles the methane structure 2 more closely than it resembles the methyl hydride complex 1. Thus, the Os-H distance ranges from 1.47 to 1.51 Å, the Os-C(CH$_3$) distance varies from 2.26 to 2.33 Å and the incipient C⋯H bond between the hydride and methyl group ranges in length from 1.45 to 1.50 Å. Because the calculated structures of the methane coordination complex 2 and the transition state $1^\dagger$ depend most strongly on the computational method, it is not surprising that the calculated energies of these species are also most sensitive to the method employed, as will be discussed below.

**Dependence of B3LYP energies on choice of basis set.** For the osmium system described above, we carried out an extensive investigation of how different basis sets affect the potential energy surface calculated by the popular B3LYP functional.$^{42,54}$ Table 3 lists the 22 basis sets studied along with the total number of basis functions used for each complex and the energies of stationary points on the potential energy surface with respect to the methyl hydride complex. Pople style basis sets were used to analyze the experimentally-studied system (1, 2, and the transition state $1^\dagger$), whereas correlation consistent basis sets were used to analyze the simplified phosphine system (1H, 2H, and the transition state $1H^\dagger$). Pople basis sets are given symbols beginning with the letter “p”, whereas correlation consistent basis sets are given symbols beginning with the letters “cc”. Results of this study are summarized below; additional discussion of the basis set variations can be found in Appendix C.
Figures 3.2 and 3.3 show calculated energies of the transition state $1^\ddagger$ and methane complex $2$ relative to the methyl hydride complex $1$ for all basis sets tested. Calculations with the Pople basis sets predict that the transition state $1^\ddagger$ lies 5.5-8.0 kcal mol$^{-1}$ higher in energy than $1$, and that the methane coordination complex $2$ lies 0.0-2.8 kcal mol$^{-1}$ higher than $1$ (Figure 3.2). For comparison, the experimental free energy of $1^\ddagger$ is 8.1 kcal mol$^{-1}$ at -100 °C in solution. The calculated energies of the stationary points and transition states vary over a range of about 2.5 kcal mol$^{-1}$, depending, for example, on whether double zeta or triple zeta Pople basis sets are used key atoms of Os and CH$_4$. This variation is large in the context of weak interactions such as those in the present system, because the energy differences of interest (e.g., between $1$ and $2$) are of the same order. What this means is that, for weak interactions involving hydrogen atoms, a significant loss of computational accuracy results from attempts to save on computational costs by reducing the size of the Pople basis set, in particular changing the description of the Os-CH$_4$ atoms from triple zeta to double zeta.$^{48}$

Correlation consistent basis sets are excellent choices for benchmarking studies because they can be extended to approach the complete basis set limit as closely as desired and computationally feasible.$^{55-57}$ The structures of $1H$ and $2H$ and the corresponding transition state $1H^\ddagger$ (all bearing the simplified phosphine) were optimized using ten different combinations of the correlation consistent basis sets, and the energy of each optimized structure was calculated (Table 3.3 and Figure 3.3). The energies are compared to the single point energies calculated for the most complete basis set, in which quadruple zeta quality sets were used on all atoms (cc11 in Table 3). For this latter basis set, the energy of the methane coordination complex $2H$ relative to methyl hydride $1H$ is −0.58 kcal mol$^{-1}$, whereas the energy of the transition state that connects these two structures is 4.62 kcal mol$^{-1}$. The variations in the energies of the simplified
phosphine complexes $1H^\dagger$ and $2H$ relative to $1H$ computed with different correlation consistent basis sets is only 0.7 kcal mol$^{-1}$. We find that using even relatively small double zeta quality correlation consistent basis sets for the Os-CH$_4$ atoms produce results within 0.4 kcal mol$^{-1}$ of those obtained with much larger quadruple zeta quality sets (Figure 3.3). In addition, calculations with a triple zeta basis set for the Os-CH$_4$ atoms (4.98 and -0.57 kcal mol$^{-1}$ for $1^\dagger$ and $2$ respectively) are less than 0.3 kcal different from extrapolations to the estimated complete basis set limit (5.06 and -0.21 kcal mol$^{-1}$ for $1^\dagger$ and $2$ respectively).

If we assume that the results above for the B3LYP functional are representative, these calculations suggest that both Pople and correlation consistent basis sets are suitable for treating late transition metal $\sigma$-complexes, provided sufficiently large basis sets (double zeta with polarization functions, or better) are used for the Os-CH$_4$ atoms. One difference is that the Pople basis sets give energies for the methane complexes that are 1-2 kcal mol$^{-1}$ lower (relative to the methyl hydride species) than the energies calculated from the correlation consistent basis sets. We hesitate to speculate on the reasons for the differences in energies calculated using the Pople and Dunning basis sets, but it is well appreciated that these basis sets often give small but systematically different results in many systems.$^{59,60}$

**Dependence of DFT energies on choice of functional.** To determine which functionals are best able to describe the bonding in $\sigma$-complexes accurately, we used ten different DFT functionals and the cc10 basis set combination to calculate stationary points on the reaction path for the system in which the osmium bears the simplified phosphine ligand ($1H$, $1H^\dagger$, $2H$). The energies of $1H^\dagger$ and $2H$ relative to complex $1H$ are shown in Figure 3.4. Values for the zero point corrected energies for the transition state $1H^\dagger$ and methane complex $2H$ relative to the
methyl hydride $\text{1H}$ along with the zero point and Gibbs free energies for each species can be found in Appendix C.

The variation in the relative energy of the transition state $\text{1H}^\ddagger$ is $\pm 2$ kcal mol$^{-1}$, ranging from a low of 3.67 kcal mol$^{-1}$ for BMK to a high of 5.55 kcal mol$^{-1}$ for TPSSh. Interestingly, these values are all smaller than the 7.9 kcal mol$^{-1}$ obtained from single point calculations with the CCSD(T) *ab initio* correlated method (see below). This result is not surprising because DFT systematically underestimates transition state energies.$^{46,48}$ What is surprising, however, is that transition state energies obtained from the selected “fourth rung” HMGGA functionals$^{61}$ vary more than the barriers calculated using the first and second rung LSDA and GGA functionals. In the HMGGA functionals employed here, the kinetic energy density is used to provide a density functional approximation to delocalized electron exchange and an improved description of electron correlation, both of which have been proposed to be important for dispersion type interactions.$^{30,62}$ It is known that an inaccurate description of the kinetic energy density leads to the underestimation of transition state energies.$^{63,64}$

Of all the stationary points on the potential energy surface in the present system, the relative energy of the methane complex $\text{2H}$ is most strongly dependent on the choice of DFT functional (Figure 3.4). In contrast to the Pantazis benchmark study of niobium $\sigma$-complexes,$^8$ all functionals in the present study found the osmium $\sigma$-complex $\text{2H}$ to be a minimum on the potential energy surface. The relative energy of $\text{2H}$ varies from a low of -1.93 kcal mol$^{-1}$ for BMK to a high of +4.33 kcal mol$^{-1}$ for the LSDA functional SVWN5. Hartree-Fock based methods (see below) afford the lowest relative energy for $\text{2H}$. The pure DFT methods BP86, PBE, and LSDA calculate the highest energies for $\text{2H}$, perhaps due to the lack of Hartree-Fock exchange. This result suggests that pure DFT methods overestimate electron correlation between
the osmium and phosphine complex at the expense of the weakly bonded methane. Even though all of the functionals found that 2H was a local minimum, the large variation in calculated energies suggests that the functionals treat the bonding of this σ-complex rather differently. We will explore details of the bonding in the next section.

**Frontier orbital analyses.** To better understand how well the different functionals describe the bonding in the σ-complex, we compared the Kohn-Sham (KS)\(^{32}\) and natural atomic orbitals (NAO)\(^{33}\) for the methane coordination complex 2H. KS orbitals are derived naturally from the coefficients of the eigenfunctions generated in the DFT calculations. They are an improvement over the non-electron correlated Hartree-Fock orbitals and have been recommended as tools for qualitative MO descriptions.\(^{28}\) We find that, to first order, the KS HOMOs for the osmium complexes are identical irrespective of the functional chosen. The HOMO for the methane complex 2H is highly delocalized over the entire molecule (Figure 3.5), but includes a bonding interaction between the osmium atom and the C-H σ-orbitals. The delocalized nature of the HOMO suggests that the nature of the osmium-methane interaction (and the energy of 2H relative to the methyl/hydride complex 1H) should be influenced by the choice of the ancillary cyclopentadienyl and phosphine ligands.

In contrast, natural atomic orbitals (NAOs) are derived from the diagonal of the one electron density matrix.\(^{33}\) Natural bond order analysis combines the NAOs to form natural bond orbitals (NBOs). As a result, NBOs are highly sensitive to the post-hoc densities generated by the DFT calculations, and therefore should reveal differences in how different functionals describe the σ-complex interaction.\(^{8,9,22}\) NBOs have been used in the past to determine if a molecule exhibits σ-complex interactions\(^{65}\) but, in this case, we use NBOs to highlight differences between functionals. A summary of important data is shown in Table 3.4. For all ten
functionals tested, the NBO analysis shows that there are three-center bonds between the metal and the carbon atoms in the cyclopentadienyl ring. However, only five of the functionals studied – M05-2X, BMK, BB1K, MPW1K, and SVWN5 – yielded NBOs for the methane complex $\textbf{2H}$ that include a three-center bond between the osmium and the coordinated methane ligand. Of these five functionals, all include kinetic parameters except SVWN5. NBOs calculated from PBE0 do not show a three-center bond with the methane ligand, which contradicts other studies that suggested that PBE0 is useful for describing $\sigma$-complex interactions.$^{66,67}$ We conclude that PBE0 and TPSSh, along with pure GGA functionals such as BP86 and PBE, are not satisfactory choices to study molecules with weak donor-acceptor interactions such as those in the present study.

We have analyzed several functionals in greater detail. One of the oldest functionals (SVWN5) seems to outperform some functionals developed later. SVWN5 is the only functional that does not explicitly account for kinetic energy density that identifies a three-center NBO with the methane ligand. This finding is probably related to the tendency of SVWN5 to overestimate binding between atoms in molecules due to an exchange hole effect.$^{28,68}$ This effect is expressed in the large magnitude of the natural charges on osmium and the carbon atom of the coordinated methane ligand (-1.08 and -0.83, respectively). These natural charges, which are larger in magnitude than those generated from any of the other DFT functionals, illustrate that the electrons in the SVWN5 wavefunctions move freely between atoms in a molecule. This conclusion is not surprising because SVWN5 is used primarily for modeling electrons in metallic phases.$^{40}$

B3LYP is known to overestimate electron correlation between atoms in a molecule due to violations of the UEG limit that cause the description to lack the “free-electron-like” character
necessary to describe weak interactions. Consequently, this functional does a poor job of describing the osmium-methane σ-complex interaction. For the methane complex 2H, the natural charges of the osmium atom (-0.17), the methane carbon atom (-0.75) and the hydrogen atom bridging between osmium and this carbon (0.25), as calculated by B3LYP, are relatively small. More importantly, no three-center bond between osmium and methane is found by NBO analysis of the B3LYP orbitals.

Of all the functionals tested, only one specifically addresses the issue of dispersion interactions in weakly bound complexes, Truhlar’s M05-2X functional. Previous studies have shown that M05-2X, which produces results consistent with more computationally expensive ab initio methods such as CCSD(T) and CASPT2, performs well for molecules such as π-complexes and proteins that contain dispersion-like interactions. Our results suggest that M05-2X may describe σ-complex interactions as accurately as correlated methods, but for a fraction of the cost. It is likely that other dispersion corrected functionals, such as Grimme’s PBE-D, may also offer accurate descriptions of σ-complexes.

As noted in the introduction, Pantazis et al. concluded that the correlation contribution of a density functional should obey the uniform electron gas limit if the functional is to describe correctly the balance between σ-complex interactions and competing M-X π interactions. Two of the functionals we studied, B3LYP and BMK, violate this limit. Although NBO analysis of B3LYP fails to identify the osmium-methane interaction, BMK performs surprisingly well considering that in other systems it affords large errors for metal-atom binding interactions. We surmise that BMK includes too much uncorrected Hartree-Fock exchange, which causes this functional to overestimate the strength of the osmium-methane interaction. Even though NBO analysis of the BMK wavefunctions identifies the presence of a three-center interaction with the
coordinated methane ligand, this result is most likely a consequence of error cancellation rather than functional accuracy. Thus, we do not recommend BMK for studies of molecules with weak interactions.

The remaining functionals are unsuited for studying σ-complex complexes, because analysis of the wavefunctions did not find three-center NBOs with the methane ligand. Instead, we recommend that the functionals M05-2X and MPW1K are best suited for analyzing weak interactions such as the σ-complexes in the present study.

*Ab initio methods.* Due to the size of the complexes investigated in this work, and the present limitations in computational speed, calculations with correlated *ab initio* methods beyond MP2 were restricted to single point energies. In addition to calculating optimized HF and MP2 structures and frequencies, we also calculated CCSD and CCSD(T) single point energies for the methyl hydride complex 1H, the methane coordination complex 2H, and the transition state 1H‡ structures at B3LYP, M05-2X, and MP2 geometries using the cc10 basis set. The energies relative to 1H are shown in Table 3.5; the absolute energies can be found in Appendix C.

Hartree-Fock results show that the energy of the transition state 1H‡ is reasonable (4.9 kcal mol⁻¹) but the energy of 3H is calculated to be lower than that of 1H. This situation contradicts the experimental data. MP2 calculations also contradict experiment: it is unable to locate the transition state 1H‡, and the methane coordination complex 2H is calculated to be a barely bound minimum 8.7 kcal mol⁻¹ higher in energy than the methyl hydride 1H, a finding that is far out of line with all of the other results (Table 3.5). A possible explanation for our inability to locate the transition state with MP2 is that the bond energies it calculates for transition metal complexes are known to suffer from errors as large as 30 kcal mol⁻¹ due in part to large basis set superposition errors.36,74 Another contributor to this error is the inadequacy of
perturbation theory in describing strong electron correlation. Likewise, the calculated CCSD and CCSD(T) energies from MP2 geometries are in poor agreement with MP2 energies. The energy of $2\text{H}$ is 8.7 kcal mol$^{-1}$ for MP2 but 2.7 and 4.5 kcal mol$^{-1}$ for CCSD and CCSD(T), respectively. The energy of $3\text{H}$ is 9.5 kcal mol$^{-1}$ for MP2, whereas it is 18.9 and 23.0 kcal mol$^{-1}$ for CCSD and CCSD(T), respectively. This poor agreement between coupled cluster and perturbation energies suggests that MP2 should not be used to model this class of molecules.

In contrast, the calculated single point energies from M05-2X and B3LYP optimized structures are in good agreement with the CCSD and CCSD(T) single point energies. For example, the calculated energy of the transition state $1\text{H}^\ddagger$ of 5.5 kcal mol$^{-1}$ from M05-2X compares well with the equilibrium (non-corrected) energies of $1\text{H}^\ddagger$ of 7.6 and 8.0 kcal mol$^{-1}$ for CCSD and CCSD(T) respectively. Likewise, M05-2X predicts that the methane coordination complex $2\text{H}$ is 1.6 kcal mol$^{-1}$ higher in energy than the methyl/hydride $1\text{H}$, vs the CCSD and CCSD(T) values of 0.9 and 3.1 kcal mol$^{-1}$. The relative energy for the dissociated state $3\text{H}$ was identical for M05-2X and CCSD (15.9 kcal mol$^{-1}$) whereas the CCSD(T) value was much higher (26.9 kcal mol$^{-1}$). The B3LYP energies are also in good agreement with CCSD and CCSD(T) energies calculated for B3LYP optimized geometries.

**Section 3.4 Conclusions.**

This study characterizes how the choice of basis sets and functionals affects the ability of DFT methods to predict the geometries and energies of $\sigma$-complex interactions in transition metal complexes. Both Pople and correlation consistent basis sets are suitable for treating such weak interactions, provided that sufficiently large basis sets (double zeta with polarization functions, or better) are used on the Os-CH$_4$ atoms. We show that cc-pVTZ basis sets on the
atoms of importance (the metal and the interacting alkane molecule) and cc-pVDZ on other atoms provide results as good as those from the larger cc-pVQZ basis sets. Different DFT methods produce very similar potential energy surfaces, but the popular B3LYP functional systematically underestimates the energies of molecules characterized by weak interactions, such as the alkane coordination complexes in the present study. For all of the methods, the Kohn-Sham HOMO for the methane species 2 is a three-center bond between osmium and the carbon and hydrogen atoms of the coordinated methane ligand. However, natural bond order analysis shows that only five of the functionals (not including the popular B3LYP) correctly predict the presence of a three-center interaction between osmium and methane. Dispersion corrected functionals such as Truhlar’s new M05-2X functional yield energies close to CCSD(T) results and also correctly predict the presence of a covalent σ-complex interaction in the complexes. Dispersion corrected functionals used with polarized triple zeta basis sets or their equivalent are recommended for studies of weak metal σ-complexes.

Appendix C. Tables C.1-C.6 contain equilibrium point energies and geometrical parameters obtained from all basis set combinations and DFT methods.
Section 3.5. Tables and Figures.

Table 3.1 DFT methods studied

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<th>Correlation functional</th>
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Table 3.2 Sample geometric parameters of the simplified phosphine complexes

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<tr>
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<th>Methane Complex (2H)</th>
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Table 3.3 Zero-point corrected energies relative to Os-CH$_3$H (1 and 1H) for all basis sets studied using the B3LYP functional.

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Complete Basis Set Limit

| Experimental | 7.92 |

$^a$ In kcal mol$^{-1}$ relative to 1. $^b$ In kcal mol$^{-1}$ relative to 1H. $^+$ Single point energy calculation with zero point correction from cc10.
Table 3.4 NBO data including natural charges and 3-center 2-electron bonding orbital information for Os, C, and H atoms potentially involved in three center bonding.

<table>
<thead>
<tr>
<th>Method</th>
<th>Natural Charge</th>
<th>3c2e bond?</th>
<th>Obeys UEG?</th>
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<tr>
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*a UEG = uniform electron gas limit.
Table 3.5 Single point energies in kcal mol\(^{-1}\) of the transition state 1H\(^\ddagger\), the methane coordination complex 2H, and the dissociated methane state 3H, relative to the methyl/hydride 1H from \textit{ab initio} methods calculated from DFT optimized structures.

<table>
<thead>
<tr>
<th>Method</th>
<th>1H(^\ddagger)</th>
<th>2H</th>
<th>3H</th>
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<tr>
<td>CCSD//MP2(^b)</td>
<td>--</td>
<td>2.7</td>
<td>18.9</td>
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<td>CCSD(T)//MP2(^b)</td>
<td>--</td>
<td>4.5</td>
<td>23.0</td>
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<td>M05-2X</td>
<td>5.5</td>
<td>1.6</td>
<td>15.9</td>
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<td>CCSD/M05-2X(^b)</td>
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<td>CCSD(T)/B3LYP(^b)</td>
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<td>3.4</td>
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\(^{a)}\) full optimization and frequency \(^{b)}\) non-zero point corrected energies

Figure 3.1 Stationary points on the potential energy surface for methane activation: the methyl/hydride complex 1, the methane coordination complex 2, and the transition state 1\(^\ddagger\): R = CH\(_3\) for complexes, 1, 2, and 1\(^\ddagger\); R= H for the model complexes 1H, 2H, and 1H\(^\ddagger\). The chemical system 3 (and 3H) is referred to as the dissociated state in the text.
Figure 3.2 Variation in energy (kcal/mol) of the transition state $1^\ddagger$ (blue) and of the methane coordination complex $2$ (red) with respect to the methyl/hydride complex $1$, using Pople basis sets.

![Graph of Figure 3.2 showing energy variation with Pople Basis Set Label.

Figure 3.3 Variation in energy (kcal/mol) of the transition state $1H^\ddagger$ (blue) and of the methane coordination complex $2H$ (red) with respect to the methyl/hydride $1H$, using correlation consistent basis sets.

![Graph of Figure 3.3 showing energy variation with correlation consistent basis sets.]
**Figure 3.4** Variation in energy (kcal/mol) of the transition state $1H^\ddagger$ (blue) and of the methane coordination complex $2H$ (red) relative to the methyl/hydride $1H$, using various DFT functionals and the cc10 basis set.

![Energy variation](image)

**Figure 3.5** Depiction of the delocalized Kohn-Sham HOMO for $2H$ showing the mixing between the ‘d’ orbital on osmium and C-H σ-orbital on methane. The orbital shown comes from M05-2X calculations; the isovalue is 0.0767 e Å$^{-3}$ Qualitatively, the HOMO was identical for all functionals.

![HOMO depiction](image)
References


Both methods used Pople Basis sets of 6-31+G(p) quality and contractions of the Los Alamos effective core potential and double zeta valence descriptions.


The tilt angle is a measure of the steric size of the cyclopentadienyl and phosphine ligands and is defined as the dihedral angle between the mean plane of the cyclopentadienyl carbons and the plane defined by the Os atom and the two phosphorus atoms. For any particular choice of the ancillary ligands, the tilt angle calculated for the methyl hydride complex 1 and its methane tautomer 2 were essentially identical.

One conclusion of chemical importance is that changing the phosphine from the
(CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$ ligand used experimentally to the model ligand H$_2$PCH$_2$CH$_2$PH$_2$ considerably lowers the energy of the methane tautomer relative to the methyl/hydride complex. This result is not surprising in view of the poorer donor ability of the model phosphine, which will reduce the back donation from the osmium center into the antibonding C-H orbital of the coordinated methane that is necessary to cleave the bond.


CHAPTER 4. A DFT STUDY OF METAL-ALKANE INTERACTIONS AND THE
ACTIVATION OF CARBON-HYDROGEN BONDS BY A LATE TRANSITION METAL.

Section 4.1. Introduction.

The archetypal alkane, methane, is an important commodity chemical: global methane stores are estimated to be 1 to 5 trillion cubic feet.\(^1\) Methane is an excellent source of energy, producing less CO\(_2\) per unit energy than other hydrocarbons. In addition to its use as a fuel, methane is a useful feedstock: steam reforming gives hydrogen and carbon monoxide, and this mixture can be further transformed into methanol, acetic acid, and other useful chemicals.\(^2\)\(^-\)\(^5\)

Methane and other alkanes present significant challenges as chemical feedstocks owing to their chemical inertness. They are electrically neutral, relatively unpolarizable, very poor electron donors, very poor electron acceptors, and lack weak interatomic bonds that could be points of attack. For these reasons, they are poorly suited to bind to transition metals (and thus enter into catalytic cycles). Despite these attributes, alkanes can bind (albeit weakly) to transition metals under the right circumstances, and several such complexes are now known.\(^6\)\(^-\)\(^12\) These compounds serve as instructive models for the key intermediates in alkane activation reactions in which carbon-hydrogen bonds are broken.

The isolation of a methane coordination complex of a transition metal in solution near room temperature is a desirable goal, one that is made difficult by the fact that methane is the least polarizable and has the strongest C-H bonds (and is thus the most unreactive) of all alkanes. Most interactions of C-H and with metal centers involve weak three-center-two-electron covalent interactions, called agostic or σ-interactions.\(^13\),\(^14\) Most such interactions involve σ-donation from a C-H bond into an unoccupied d-orbital on the metal center and back donation of d-electrons on
the metal into an unoccupied C-H σ-anti-bonding orbital. The sigma interaction is similar to those seen in dihydrogen complexes with metals.\textsuperscript{15,16} There are also a few examples of complexes in which the interaction between C-H bonds and transition metals is purely electrostatic, and involves polarization of the C-H bond by the positively charged metal ion.\textsuperscript{17,18} Transition metals readily form both dihydride and dihydrogen complexes, depending on the choice of metal and ancillary ligands.\textsuperscript{19-22} Thus it follows that careful tuning of the electronic environment around the metal should be able to control a similar tautomerization between methyl hydride and methane complexes. (Figure 4.1)

\textbf{Figure 4.1} Figure showing how the electron environment around the metal can be tuned to favor the methane tautomer as compared to dihydrogen tautomers.

![Diagram showing electron-rich and electron-poor environments around metal]

Computational studies have been carried out on the interactions of alkanes with naked metals\textsuperscript{18,20}, with metal complexes,\textsuperscript{21-36} and with models of the active site in the protein methane monooxygenase.\textsuperscript{37-39}

Our group has synthesized a family of cationic osmium complexes, $L_x\text{Os(CH}_3\text{)}(\text{H})^+$, in which a methyl group ($\text{CH}_3$) and a hydride ligand (H) occupy adjacent coordination sites.\textsuperscript{6} NMR studies suggested that in solution these methyl/hydride complexes are in rapid equilibrium with the tautomeric form $L_x\text{Os(CH}_4\text{)}^+$, in which the metal center is coordinated to a methane molecule formed by joining together the methyl and hydride ligands (Figure 4.2). The $\sim$8 kcal mol$^{-1}$
activation barrier for the equilibrium between the methyl/hydride complex and the methane tautomer is considerably smaller than the 20-30 kcal mol$^{-1}$ barriers characteristic of most other analogous chemical systems. This low barrier means that the C-H bond formation and cleavage processes in these osmium complexes are reversible and rapid enough, 100 sec$^{-1}$ at -100 °C, to be dynamic on the NMR time scale. The activation energy for loss of the bound methane to generate the dissociated state L$_x$Os$^+$ + CH$_4$ was estimated to be ~13 kcal mol$^{-1}$. Again, this is an unusually high dissociation barrier for metal-alkane interactions, rivaled only by those seen in certain rhenium$^8$ and iridium systems.$^7$

The osmium complexes that have been studied experimentally bear two ancillary ligands: a chelating diphosphine (CH$_3$)$_2$PCH$_2$P(CH$_3$)$_2$, and a cyclopentadienyl ring. (Figure 4.2) Interestingly, when the steric and electronic properties of the cyclopentadienyl ring are varied – C$_5$H$_x$(CH$_3$)$_{5-x}$, where $x = 0, 1, 4, and 5$ – the relative energies of the complexes, and the barriers for the reactions that interconvert them, vary by less than 0.5 kcal mol$^{-1}$.$^{40-42}$ When the chelating ligand is replaced by the phenyl substituted phosphine Ph$_2$PCH$_2$PPh$_2$, loss of methane occurs so readily that no methyl hydride or methane complex could be observed.$^{43}$
Figure 4.2 Critical points on the potential energy surface for hydride exchange and reductive elimination of methane.

Two previous computational studies employed the popular B3LYP functional and Pople basis sets to explore the potential energy surface and reaction mechanisms in this osmium system.\textsuperscript{28,33} Both Martin and Morokuma determined that the methane coordination complex is in fact the intermediate responsible for the observed dynamic process that exchanges the Os-H and the Os-CH\textsubscript{3} proton environments in the methyl hydride complex. The transition state for this equilibrium is calculated to lie about 8 kcal mol\textsuperscript{-1} higher in energy than the methyl/hydride species, a value nicely in agreement with the experimentally determined exchange barrier. Finally, changing the cyclopentadienyl ligand from C\textsubscript{5}H\textsubscript{5} to C\textsubscript{5}Me\textsubscript{5} shifts the total energies of all species on the potential energy surface about equally and therefore does not affect the barrier for H-exchange.

Other computational studies of the potential energy surface for methane activation have provided evidence that the energy of the methane coordination complex changes relative to the energies of the methyl hydride when different ancillary ligands are used. For example,
computational studies using semi-empirical methods suggest that, in the complexes 
CpRe(CO)₂(CH₄), TpRe(CO)₂(CH₄) and TabRe(CO)₂(CH₄) complexes (where Cp = C₅H₅, Tp = 
HB(pyrazolyl)₃, and Tab = HB(N=NH)₃, suggest that the methane tautomer becomes much more 
stable than the methyl hydride complex when the cyclopentadienyl ring is replaced with 
trispyrazolylborate. The differences between the Tp and Cp systems were attributed primarily 
to steric effects.

In the Cp Os(Me₂PCH₂PMe₂)(CH₄)H⁺ system, the methane complex could not be 
observed directly (its equilibrium concentration is too low), but calculations suggested that its 
energy was only a few kcal/mole above that of the methyl hydride form. This small energy 
difference should be adjustable by suitable choice of the ancillary ligands, possibly to the point at 
which the methane complex would be the lowest energy species on the potential energy surface. 
If this goal can be achieved, then the methane complex would be directly observable. The 
experimental data do not make it clear, however, what choice of ancillary ligands would stabilize 
the methane tautomer sufficiently to lower its energy below that of its methyl hydride tautomer, 
and thus render it detectable by NMR spectroscopy. The focus of this work is to determine what 
modifications in the ligand environment around the osmium center in the 
(C₅H₅)Os(Me₂PCH₂PMe₂)(CH₄)⁺ system would achieve this result.

Section 4.2. Results.

Here we describe our computational studies of the chemical reactions of a methane ligand 
coordinated to an osmium complex. Two reactions are of interest: reversible breaking of one of 
the C-H bonds to form an osmium methyl hydride complex, and dissociation of the methane. 
Several different structures on the potential energy surface are examined: the methyl hydride
complex \((C_5H_xR_5-x)Os(X_2PCZ_2PXe_2)(CH_3)\)\(^{+}\) (1), the transition state for reforming the C-H bond (1\(^{\ddagger}\)), the methane coordination complex \((C_5H_xR_5-x)Os(X_2PCZ_2PX_2)(CH_4)\)\(^{+}\) (2), and the dissociated state \((C_5H_xR_5-x)Os(X_2PCZ_2PX_2)^{+} + CH_4\) (3). The stationary points on the potential energy surface are shown in Figure 4.2. As mentioned in the introduction, experimental data are available for several choices of cyclopentadienyl and phosphine ligands, to which the present results will be compared.\(^{40-44}\)

A discussion of the effects of the computational method and basis set on the potential energy surface has been published previously.\(^{45}\) Because different methods produce different results, two different functionals (BB1K and M052X) are used in the present study to calculate the effect of the ancillary ligands on the potential energy surface. The discussion will be divided into four parts: a brief discussion of parameterizing the steric and electronic properties of the ancillary ligands, a description of the geometric parameters for each complex, a comparison between the calculated and experimentally determined energies, and finally an orbital analysis of the osmium-methane binding in the coordination complex 2.

**Ligand steric and electronic parameters.** The degree of steric congestion in these osmium complexes can best be gauged by defining a tilt angle \(\tau\), (Figure 4.3) which is equal to the dihedral angle between the cyclopentadienyl ring plane and the P-Os-P plane. Sterically larger ancillary ligands will tend to increase the tilt angle. We chose to use the tilt angles for the methane coordination complexes, 2, as the best gauge of the steric sizes of the ancillary ligands.
Figure 4.3 Tilt angle defined as the dihedral angle between the cyclopentadienyl ring plane and the P-Os-P plane.

A widely employed experimental measure of the electronic environment around the metal center is Tolman’s electronic parameter, in which the CO stretching frequency of a LNi(CO)\(_3\) complex is used as a gauge of the net donor ability of the ligand L.\(^{46}\) It has been shown that carbonyl stretching frequencies computed by DFT can also be used to estimate the electronic properties of a metal complex.\(^{47,48}\) In this work, we gauged the electronic influence of the ancillary ligands on the metal from the calculated carbonyl stretching frequency of the complexes \((C_5H_xR_{5-x})Os(X_2PCZ_2PX_2)(CO)^+\), 4. (Figure 4.4)

Figure 4.4 Carbonyl complex used to determine electronic environment of the metal center.
Tilt angle and $v_{CO}$ data derived from both M05-2X and BB1K calculations are given in Tables 4.1 and 4.4. For the phosphines, the order of increasing tilt angle of the M05-2X optimized structure of 2 is: (CF$_3$)$_2$PCF$_2$P(CF$_3$)$_2$, (CF$_3$)$_2$PCH$_2$P(CF$_3$)$_2$, H$_2$PCF$_2$PH$_2$, Me$_2$PCF$_2$PMe$_2$, H$_2$PCH$_2$PH$_2$, Me$_2$PCH$_2$PMe$_2$, and Ph$_2$PCH$_2$PPh$_2$. The order of increasing electron donating ability, as measured by the carbonyl stretching frequency from M05-2X is: (CF$_3$)$_2$PCF$_2$P(CF$_3$)$_2$, (CF$_3$)$_2$PCH$_2$P(CF$_3$)$_2$, H$_2$PCF$_2$PH$_2$, H$_2$PCH$_2$PH$_2$, Me$_2$PCF$_2$PMe$_2$, Ph$_2$PCH$_2$PPh$_2$, and Me$_2$PCH$_2$PMe$_2$.

For the cyclopentadienyl rings, the order of increasing steric hindrance as measured by increasing tilt angle of the M05-2X optimized structure of 2 is: C$_5$H$_4$CF$_3$, C$_5$Me$_4$CF$_3$, C$_5$H$_5$, C$_5$H$_4$Me, C$_5$H$_4$SiH$_3$, C$_5$HMe$_4$, C$_5$Me$_5$ and C$_5$H$_4$SiMe$_3$; the order of increasing electron donating ability as measured by M05-2X carbonyl frequency is: C$_5$HMe$_4$, C$_5$H$_4$CF$_3$, C$_5$H$_5$, C$_5$H$_4$Me, C$_5$H$_4$SiH$_3$, C$_5$Me$_4$CF$_3$, C$_5$H$_4$SiMe$_3$, and C$_5$Me$_5$.

**Geometries of the osmium complexes.** Optimized geometries for 1, 1‡, 2, and 3 are shown in Figure 4.5, for the case in which the cyclopentadienyl ligand is C$_5$H$_5$ and the phosphine is H$_2$PCH$_2$PH$_2$ on the cyclopentadienyl and phosphine ligands. Similar computed structures are seen for related compounds bearing other substituents. Geometric data for all the complexes are summarized here in Table C.1. For any particular choice of ancillary ligands, the bond distances and angles calculated by BB1K and M052X are closely similar, varying by less than 0.02 Å or 2°. In contrast, changing the ancillary ligands can change certain bond distances by as much as 0.4 Å, and certain dihedral angles by as much as 10° (see below). In general, the calculated geometries for the metal-methane interaction in 2 agree well with those of other metal alkane complexes. 27,36,49
At each critical point on the potential energy surface, the osmium complex optimizes to a pseudo-piano stool geometry, but with important structural differences. For the methyl/hydride complex 1, osmium binds to the hydrogen and methyl groups separately. The metric parameters for 1 do not vary much as the ancillary ligands are changed: the calculated Os-H bond distance varies only from 1.585 to 1.592 Å, the calculated Os-CH$_3$ bond distance ranges from 2.164 to 2.168 Å, and the calculated non-bonded C⋯H contact distance between the Os-CH$_3$ and Os-H groups ranges from 2.078 to 2.158 Å. For the methane tautomer 2, the bond lengths differ from those of 1 in the expected ways: the Os-H and Os-CH$_3$ distances are considerably longer, and the C⋯H contact distance between the former Os-CH$_3$ and Os-H groups approaches the 1.09 Å distance seen for free methane.$^{50}$ The methane molecule binds to the metal center in an η¹ fashion, in which one hydrogen atom also interacts with the metal. Thus, over the range of ancillary ligands studied, the calculated Os-H distance is 1.862 to 1.925 Å, the calculated Os-C(CH$_3$) distance is 2.571 to 2.636 Å, and the C-H distance between the former Os-CH$_3$ and Os-H groups is 1.138 to 1.153 Å. Relative to the variations in the distances calculated for 1, however, the corresponding distances in 2 show somewhat larger variations depending on the ancillary substituents. The larger variations reflect the shallowness of the potential energy surface near this stationary point, which in turn results from the weakness of the Os-methane interaction.

The geometry of the transition state 1‡ that connects 1 and 2 more closely resembles the structure of the methyl hydride 1 than the methane tautomer 2. The Os-H distance ranges from
1.624 to 1.633 Å, the Os-C(CH₃) distance varies from 2.305 to 2.308 Å and the incipient C·⋯H bond between the hydride and methyl group ranges in length from 1.403 to 1.552 Å. Once again, the distances between the metal and the H and CH₃ groups are only weakly dependent on the nature of the ancillary ligands but the incipient C·⋯H distance varies widely.

The osmium complex in the dissociated state, 3, shows some structural changes as a result of the removal of the methane ligand. For example, for the C₅H₅Os(H₂PCH₂PH₂) complexes, the tilt angle changes from 48.8° in 1, to 51.7° in 1‡ to 50.4° in 2 to 53.0° in 3. It is important to note that the tilt angle is not purely a measure of the steric sizes of the ligands. Specifically, the phosphine that should have the smallest steric influence, H₂PCH₂PH₂, does not have the smallest tilt angle, 53.0 and 56° for M05-2X and BB1K respectively.

In all four compounds 1, 1‡, 2, and 3, the tilt angle depends most strongly on the steric bulk of the substituents on the chelating phosphine ligand. For complexes of the type (C₅H₅)Os(X₂PCZ₂PX₂)(CH₄)⁺, the largest tilt angles are seen for the large phosphine, Ph₂PCH₂PPh₂ (63.2°) versus 54° for the next largest tilt angle. In contrast, the tilt angle depends weakly on the steric bulk of the substituents on the cyclopentadienyl ring (at least for the substituents studied). This effect is most clearly seen in the dissociated state 3: when the phosphine is H₂PCH₂PH₂, and the cyclopentadienyl ring is C₅H₅, C₅H₄Me, C₅HMe₄, C₅Me₅, C₅H₄SiH₃, and C₅H₄SiMe₃, the respective tilt angles are 53.0, 53.3, 55.0, 55.5, 51.2, and 52.7° in M05-2X, and 55.5, 55.4, 56.1, 57.1, 55.5, and 58.0° in BB1K.

Unsymmetrically substituted cyclopentadienyl rings can adopt different rotameric conformations with somewhat different steric profiles. For example, the complex (C₅H₄Me)Os(Me₂PCH₂PMe₂)(CH₃H)⁺ exhibits three different local minima differing in the location of the ring methyl group: near the phosphine backbone (Figure 4.6a), near a phosphorus
atom (Figure 4.6b), and near the methane binding site (Figure 4.6c). For these three rotamers, the optimized bond distances and bond angles for the other ligands are very similar but the tilt angles are 56.0°, 58.0°, and 54.7° for M05-2X and 54.8°, 53.0°, and 50.8° for BB1K for A, B, and C respectively. These small variations, however, affect the energies, as will be discussed below.

**Figure 4.6** Structures of three local minima for (C$_5$H$_4$Me)Os(Me$_2$PCH$_2$PMe$_2$)(CH$_3$H)$^+$ differing in rotameric conformation of the cyclopentadienyl ring.

**Section 4.3 Energies of the osmium complexes.**

The main goal of this study is to address the following questions. How do the energies of the various osmium complexes vary as the ancillary ligands are changed? Is there any combination of cyclopentadienyl and phosphine ligands that makes the methane coordination complex 2 the global minimum on the potential energy surface, rather than the methyl hydride complex 1? If the methane coordination complex 2 can be made the global minimum, will the barrier for methane loss (i.e., the energy of the dissociated state 3) be sufficiently high that isolation of 2 might be possible?

In the following sections, effects of changing the substituents on the phosphine ligand and the cyclopentadienyl ring will be examined. When considering how the phosphine affects the potential energy surface, the cyclopentadienyl ligand will always be C$_5$H$_5$; when considering
how the cyclopentadienyl ring affects the potential energy surface, the phosphine will always be the hydrogen-substituted ligand dhp, H₂PCH₂PH₂.

Energies as function of cyclopentadienyl substituent. Table 4.1 shows the calculated gas-phase Gibbs free energies at -100 °C of the transition state 1⁺, the methane complex 2, and the dissociated state 3, relative to the energy of the methyl hydride complex 1. For each combination of cyclopentadienyl ring and phosphine studied, the tables also list the calculated carbonyl stretching frequency of the analogous CO complex (C₅HₓR₅-x)Os(X₂PCZ₂PX₂)(CO)⁺, 4, (a measure of the electronic properties of the ligands) and the tilt angle of 2 (a measure of the steric properties of the ligands).

We first investigated how well M05-2X and BB1K were able to replicate the barrier for exchange between 1 and 2, which was determined experimentally by NMR spectroscopy for four complexes: (C₅HₓMe₅-x)Os(Me₂PCH₂PMe₂)H(CH₃)⁺ for x = 0, 1, 4, and 5. The M05-2X free energies were only about 1 kcal/mole smaller than the experimental values, whereas the BB1K values were about 1.5 kcal/mole smaller than the experimental values (Table 4.2). These differences are relatively small, and are on the order of the ultimate accuracy of DFT methods. Good agreement was also seen for the activation enthalpies and entropies. Such excellent agreement between theory and experiment is rare and lends credibility to the use of M05-2X to study weak interactions such as those between metals and alkanes.40-42,44
Table 4.1 Gibbs free energies at -100 °C of 1‡, 2, and 3 for complexes of the type (C_5H_xR_5-x)Os(H_2PCH_2PH_2)(CH_4)^+, listed along with the carbonyl stretching frequency of the analogous (C_5H_xR_5-x)Os(H_2PCH_2PH_2)(CO)^+ complex and the tilt angle τ of the methane coordination complex 2, for a) M05-2X and b) BB1K DFT methods.

<table>
<thead>
<tr>
<th>Cp ring</th>
<th>M05-2X</th>
<th>ΔG at 173 K (kcal mol⁻¹)</th>
<th>1‡</th>
<th>2</th>
<th>3</th>
<th>v_{CO} (cm⁻¹)</th>
<th>τ_2 (°)</th>
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<th>v_{CO} (cm⁻¹)</th>
<th>τ_2 (°)</th>
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<td></td>
<td>2161</td>
<td>51.3</td>
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<tr>
<td>C_5H_4SiMe_3</td>
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<td>5.9</td>
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</tr>
<tr>
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<td>5.0</td>
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<td>48.1</td>
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Table 4.2 Comparison between experimental activation parameters for the equilibrium between 1 and 2 (bold) and those calculated by BB1K and M052X, for \((C_5H_5Me_{5-x})Os(Me_2PCH_2PMe_2)H(CH_3)^+\) complexes with \(x = 0, 1, 4,\) and 5.

<table>
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<tr>
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<th>(C_5Me_5)</th>
<th>(C_5Me_4H^*)</th>
<th>(C_5H_4Me^*)</th>
<th>(C_5H_5)</th>
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<td>8.6 ± 0.1</td>
<td>8.4 ± 0.1</td>
<td>8.1 ± 0.1</td>
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<tr>
<td>(\Delta G^\ddagger), kcal mol(^{-1}) (BB1K)</td>
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<td>6.4</td>
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<td>6.7</td>
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<td>(\Delta G^\ddagger), kcal mol(^{-1}) (M05-2X)</td>
<td>7.1</td>
<td>7.6</td>
<td>7.2</td>
<td>7.2</td>
</tr>
<tr>
<td>(\Delta H^\ddagger), kcal mol(^{-1}) (expt)</td>
<td>7.1 ± 0.9</td>
<td>7.6 ± 0.7</td>
<td>7.7 ± 0.7</td>
<td>7.4 ± 0.7</td>
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<tr>
<td>(\Delta H^\ddagger), kcal mol(^{-1}) (BB1K)</td>
<td>6.7</td>
<td>6.1</td>
<td>6.7</td>
<td>6.5</td>
</tr>
<tr>
<td>(\Delta H^\ddagger), kcal mol(^{-1}) (M05-2X)</td>
<td>7.7</td>
<td>7.6</td>
<td>7.3</td>
<td>7.4</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), cal mol(^{-1}) K(^{-1}) (expt)</td>
<td>-7 ± 5</td>
<td>-6 ± 4</td>
<td>-4 ± 4</td>
<td>-4 ± 4</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), cal mol(^{-1}) K(^{-1}) (BB1K)</td>
<td>1</td>
<td>-2</td>
<td>-6</td>
<td>-1</td>
</tr>
<tr>
<td>(\Delta S^\ddagger), cal mol(^{-1}) K(^{-1}) (M05-2X)</td>
<td>3</td>
<td>-0.3</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

*Three rotamers for the \(C_5MeH_4\) ring are local minima; the value reported is for the highest energy rotamer, which lies 0.5 kcal/mol higher than the lowest energy rotamer. Similar trends are seen for the \(C_5Me_4H\) complexes.

We then extended our calculations to include complexes containing cyclopentadienyl rings that were not studied experimentally: \(C_5H_4CF_3\), \(C_5Me_4CF_3\), \(C_5H_4SiH_3\), and \(C_5H_4SiMe_3\). For this phase of the study, the phosphine ligand was \(H_2PCH_2PH_2\). For calculations with the M05-2X functional, the transition state 1\(^{\ddagger}\) lies 4.8 to 6.9 kcal mol\(^{-1}\) higher in energy than 1, the methane tautomer 2 lies 0.3 to 2.8 kcal mol\(^{-1}\) higher than 1, and the dissociated state 3 lies 6.9 to 10.6 kcal mol\(^{-1}\) higher than 1 (Table 4.1). For all calculations with the BB1K functional, the energies of the critical points are lower relative to the energy of the methyl hydride complex 1: the transition state 1\(^{\ddagger}\) (4.4 to 5.7 kcal mol\(^{-1}\)), the methane tautomer 2 (-2.3 to 0.2 kcal mol\(^{-1}\)), and the dissociated state 3 (2.7 to 6.2 kcal mol\(^{-1}\)).
The energies of $1^\ddagger$ and 2 relative to 1 are weakly correlated with the electronic properties of the cyclopentadienyl group, as gauged by the carbonyl stretching frequency of the analogous $(C_5H_xMe_{5-x})Os(H_2PCH_2PH_2)(CO)^+$. As the cyclopentadienyl ring becomes less strongly donating and $v_{CO}$ increases, the energies of $1^\ddagger$ and 2 drop relative to 1. For $v_{CO}$ versus the $E_{1^\ddagger}-E_1$, the correlation coefficients are 0.262 and 0.56 for M05-2X and BB1K respectively (Figure 4.7a). The correlations between $v_{CO}$ and the relative energy of 2 are higher, 0.78 and 0.35 for M05-2X and BB1K respectively. Thus, for example, the energy of the methane tautomer 2 varies as follows (all M05-2X energies in kcal mol$^{-1}$): $C_5H_4CF_3$ (0.3), $C_5HMe_4$ (0.4), $C_5H_4Me$ (0.6), $C_5H_5$ (1.1), $C_5Me_4CF_3$ (1.8), $C_5H_4SiH_3$ (1.8), $C_5H_4SiMe_3$ (2.2), and $C_5Me_5$ (2.8) in order from most stable to least stable. The CO stretching frequencies for the corresponding carbonyl complex vary in a similar order (M05-2X frequencies in cm$^{-1}$): $C_5H_4CF_3$ (2146), $C_5HMe_4$ (2161), $C_5H_4Me$ (2130), $C_5H_5$ (2140), $C_5Me_4CF_3$ (2122), $C_5H_4SiH_3$ (2123), $C_5H_4SiMe_3$ (2122), and $C_5Me_5$ (2105) $C_5H_5$ in order from least donating to most donating. Thus, the more strongly donating the substituents on the Cp ring, the more stable the methane tautomer 2 becomes relative to the methyl hydride 1. The correlation coefficients between the energy of 2 and the CO stretching frequency of 4 are 0.78 and 0.35 for M05-2X and BB1K respectively (Figure 4.7b).

The energies of $1^\ddagger$ and 2 relative to 1 are not, however, correlated with the steric bulk of the cyclopentadienyl group. The correlation coefficient between the energy and the tilt angle is 0.02 for M05-2X energies and 0.03 for BB1K energies.
Figure 4.7 Gibbs free energy values at -100 °C for complexes of the type \((C_5R_5)\text{Os(H}_2\text{PCH}_2\text{PH}_2)\) of a) 1\(^{\dagger}\) and b) 2 versus the carbonyl stretching frequency of the analogous complex for M05-2X (blue diamond) and BB1K (red squares) methods.

![Graph](image-url)
**Effect of rotamers on the potential energy surface.** For unsymmetrically substituted Cp rings, several different rotameric conformations can be located as local minima on the potential energy surface for Os(C₅H₄Me)(Me₂PCH₂PMe₂)⁺. The lowest energy structure of all rotamer combinations is the methyl hydride 1 of rotamer C, in which the Cp methyl group is located near the methane binding site. The rotamer second highest in energy (+0.6 kcal mol⁻¹) is 1B, in which the Cp methyl group is near the phosphorus atom of the phosphine. The highest energy rotamer, 1A, in which the Cp methyl group is near the methylene carbon of the phosphine, is 1.8 kcal mol⁻¹ higher than 1C. The three rotamers are close enough in energy that all three are significantly populated at -100°C. Thus, for the purpose of simplicity, the energies (M05-2X only) of all rotamers 1, 1⁺, 2, and 3 of all rotamers are reported relative to the lowest energy rotamer of 1, rotamer 1C (Table 4.3).

The transition state for 1⁺B was difficult to locate on the potential energy surface because the PES slopes 1⁺B towards a geometry resembling 1C or 2C. For the methane tautomer 2, the tautomer with the lowest energy relative to 1C is 2C (+4.8 kcal mol⁻¹) followed by 2B (+5.2 kcal mol⁻¹) and 2A (+6.0 kcal mol⁻¹). This result supports the assertion that the Cp ring rotates in solution and that the experimental barrier is the result of all three rotamers instead of one local minimum. It is likely that a similar trend will govern the behavior of other complexes bearing unsymmetrically substituted Cp rings: C₅H₄Me, C₅HMe₄, C₅H₄CF₃, C₅HMe₄CF₃, C₅H₄SiH₃, and C₅H₄SiMe₃.⁵²

The energy of 3 relative to 1C is similar for all rotamers with the energies varying from +11.1 kcal mol⁻¹ for 3C to +11.6 kcal mol⁻¹ for 3A to +12.9 kcal mol⁻¹ for 3B. This result suggests that the barrier for methane loss is not as dependent of the rotamer position as other points on the PES.
Table 4.3 Gibbs free energies at -100 °C of complexes 1, 1‡, 2, and 3 for rotamers of (C₅H₄Me)Os(Me₂PCH₂PMe₂)(CH₄)⁺ relative to the energy of the lowest energy methyl hydride complex, 1C from the M05-2X DFT method.

<table>
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<tr>
<th>Rotamer</th>
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<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.7</td>
<td>6.0</td>
<td>11.6</td>
</tr>
<tr>
<td>B</td>
<td>0.7</td>
<td>5.2</td>
<td>12.9</td>
</tr>
<tr>
<td>C</td>
<td>0.0</td>
<td>4.8</td>
<td>11.1</td>
</tr>
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</table>

**Energies as a function of phosphine substituents.** Tables 4.Xa and b show the calculated gas-phase Gibbs free energies at -100 °C of the transition state 1‡, the methane complex 2, and the dissociated state 3, relative to that of the methyl hydride complex 1 for the following of ancillary ligands: the cyclopentadienyl ring is always C₅H₅, and the chelating phosphine is Ph₂PCH₂PPh₂, H₂PCH₂PH₂, Me₂PCH₂PMe₂, F₂PCH₂PF₂, H₂PCF₂PH₂, carbonyl stretching frequencies of the analogous (C₅H₅)Os(X₂PCZ₂PX₂)(CO)⁺ complex, and the tilt angle of the methane tautomer. For the phosphines, the order of increasing electron donating ability, as measured by the carbonyl stretching frequency is: (CF₃)₂PCF₂P(CF₃)₂, (CF₃)₂PCH₂P(CF₃)₂, H₂PCF₂PH₂, H₂PCH₂PH₂, Me₂PCF₂PMe₂, Ph₂PCH₂PPh₂, and Me₂PCH₂PMe₂.

For calculations with the M05-2X functional, the energies of 1‡, 2, and 3 relative to that of 1 depend on the choice of the phosphine substituents (Figure 5.8). Thus, relative to the methyl hydride complex 1 are as follows: transition state 1‡ (2.4 to 7.1 kcal mol⁻¹), the methane tautomer 2 (-2.7 to 4.6 kcal mol⁻¹), and the dissociated state 3 (5.9 to 13.0 kcal mol⁻¹). For all calculations with the BB1K functional, the energies of the critical points relative to that of 1 are lower; the transition state 1‡ (2.0 to 6.2 kcal mol⁻¹), the methane tautomer 2 (-3.9 to 3.8 kcal mol⁻¹), and the dissociated state 3 (-1.9 to 7.8 kcal mol⁻¹). These energies vary over a larger range than when the
cyclopentadienyl substituents were varied; this result is not surprising because the diversity of phosphine substituents is larger.

Table 4.4 Gibbs free energies at -100 °C of 1‡, 2, and 3 for complexes of the type $(\text{C}_5\text{H}_5)\text{Os}(\text{X}_2\text{PCZ}_2\text{PX}_2)(\text{CH}_4)^+$, listed with the carbonyl stretching frequency of the analogous $(\text{C}_5\text{H}_5)\text{Os}(\text{X}_2\text{PCZ}_2\text{PX}_2)(\text{CO})^+$ complex and the tilt angle of 2 for a) M05-2X and b) BB1K DFT methods.

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<tr>
<th>Phosphine</th>
<th>ΔG at 173 K (kcal mol$^{-1}$)</th>
<th>v$_{\text{CO}}$ (cm$^{-1}$)</th>
<th>τ (°)</th>
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<tbody>
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<td>(F$_3$C)$_2$PCH$_2$P(CF$_3$)$_2$</td>
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<td>6.7</td>
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For comparison, the experimental free energy of the $(\text{C}_5\text{H}_5)\text{Os}(\text{Me}_2\text{PCH}_2\text{PMe}_2)(\text{CH}_4)^+$ transition state (1‡) is 8.1 kcal mol$^{-1}$ at -100 °C in solution and the experimental energy of the dissociated state (3) is estimated to be 13 kcal mol$^{-1}$.

Interesting trends emerge when the energies of critical points are compared to electronic data. As the ancillary ligand becomes less donating, the carbonyl stretching frequency increases.
and the transition state $1^\dagger$ and the methane tautomer $2$ are both stabilized relative to the methyl hydride $1$. Plots of the carbonyl stretching frequency of the analogous Os-CO complex versus the relative energy of the transition state $1^\dagger$ (Figure 4.8a) show a linear correlation, with correlation coefficients of $0.68$ and $0.87$ for M05-2X and BB1K respectively. The same plots for the methane tautomer $2$ give correlation coefficients of $0.86$ and $0.99$ for M05-2X and BB1K respectively (Figure 4.8b). We conclude that the energies of both the transition state $1^\dagger$ and the methane tautomer $2$ are sensitive to the electronic nature of the metal center: as the osmium metal becomes more electron deficient (as judged by the increase in the C-O frequency of the carbonyl analog) the methane tautomer $2$ becomes more stable relative to the methyl hydride $1$, and the barrier connecting $1$ to $2$ also decreases.

In contrast, the energy of the dissociated state $3$ is not correlated with the electronic nature of the ancillary ligands. Instead, the energy of $3$ is strongly correlated with the steric properties of the ligands, as gauged by the tilt angle: as the tilt angle becomes larger, the energy of $3$ becomes smaller (Figure 4.9). Thus, as the steric bulk of the ligands increases, the dissociation energy for methane loss becomes smaller. The correlation coefficients for these trends are $0.42$ and $0.76$ for M05-2X and BB1K respectively.
Figure 4.8 (a) Gibbs free energy at -100 °C as calculated by M05-2X (blue diamond) and BB1K (red squares) of the transition state 1‡ relative to 1, for complexes with C₅H₅ rings and different phosphines, versus the carbonyl stretching frequency of the analogous (C₅H₅)Os(X₂PCZ₂PX₂)(CO)⁺ complex. (b) Same, except for the methane coordination complex 2.
Figure 4.9 Gibbs free energy values at -100 °C as calculated by M05-2X (blue diamond) and BB1K (red squares) methods for the dissociated state \((\text{C}_5\text{H}_5)\text{Os}(\text{X}_2\text{PCZ}_2\text{PX}_2)\)\(^+\) CH\(_4\), 3, versus the tilt angle of the fragment \(\tau\).

For complexes of the methyl-substituted phosphine Me\(_2\)PCH\(_2\)PMe\(_2\), both the methyl hydride 1 and the methane complex 2 are local minima but the global minimum is the methyl hydride 1. These calculations explain why the methyl hydride complex decomposed so rapidly when the phosphine chosen was the phenyl substituted ligand dppm, Ph\(_2\)PCH\(_2\)PPh\(_2\). The dissociated state 3 has the highest energy of all, lying some 10 kcal mol\(^{-1}\) higher in energy than 1.

For complexes of the phenyl substituted phosphine Ph\(_2\)PCH\(_2\)PPh\(_2\), the methyl hydride 1 is the global minimum and the methane complex 2 is slightly higher in energy, but now the dissociated state 3 lies only 5.9 kcal mol\(^{-1}\) higher than 1 in M05-2X, which is only 1 kcal mol\(^{-1}\) higher than the barrier for hydrogen exchange. In BB1K, the dissociated state is the global minimum (1.9 kcal mol\(^{-1}\)).
kcal mol\(^{-1}\) lower in energy than \(1\)). Although replacing the electron donating dmpm ligand with the electron withdrawing dppm ligand lowers the barrier for hydrogen-exchange (\(1^2\)) and stabilizes \(2\) relative to \(1\), the methane ligand is only very weakly bound, and easily dissociates.

Overall, the data suggest that fluorine-substituted phosphines should stabilize the methane tautomer \(2\) relative to the methyl hydride \(1\), while still maintaining a large methane binding energy. Fluorinated phosphines are poorer donors to metal centers than analogous alkyl substituted phosphines.\(^\text{53}\) The strengthening of the methane binding energy upon making the ancillary ligands less strongly electron donating is supported by calculations. In one study of reaction enthalpies for a series of substituted diketiminate ligands with Ni, Co, and Fe, methane activation was less endothermic with fluorinated ligands than with non-fluorinated ligands.\(^\text{26}\) Absolutely localized molecular orbital energy decomposition analysis (ALMO-EDA) of \((\text{C}_5\text{H}_5)\text{Re(CO)}_2\text{L}\) complexes where L = various two-electron donor ligands such as CO and NH\(_3\) showed that the sigma complex was stabilized when pi-electron withdrawing groups such as fluorine are used as substituents on the Cp ring.\(^\text{36}\) Evidently, electron withdrawing groups increase the donation of electron density from the methane into the metal, thus stabilizing the complex against methane dissociation.

**The methane binding energy.** Harvey *et al* have shown that the rate limiting step in reductive elimination of methane for group 6 metallocenes of the type \(\text{C}_2\text{M(CH}_3)\text{H}\) occurs at the minimum energy crossing point between the singlet surface containing the methyl hydride exchange reaction and a triplet surface containing the free metal fragment. Thus fragment complex \(3\) is most likely an open shell complex with \(S = 1\).\(^\text{51,54}\) To save on computational time, only the closed-shell complex \(3\) with \(S = 0\) was optimized for all complexes. However, to approximate the actual barrier for dissociation for all complexes, the fragment
(C₅H₅)Os(H₂PCH₂PH₂)⁺ was optimized with two unpaired electrons (S = 1). In the optimized complex, the geometry around the osmium is rigidly linear with the tilt angle τ approaching 90°. The triplet complex is higher in energy than the singlet complex, and the barrier for the rate-limiting reductive elimination step increases by 10 kcal mol⁻¹. Thus we conclude that the barriers for methane loss are inadequately model by the calculations on the singlet complexes.

**Section 4.4 Methods.**

Geometries were optimized using Gaussian03 Rev. D.01 and E.01 (M05-2X functional only) without any constraints. Calculations were carried out using both the M05-2X and BB1K functionals with modified correlation-consistent basis sets. Benchmark calculations suggested that M05-2X afforded accurate descriptions of the methane σ-complex. Hay-Wadt effective core potentials were used to describe relativistic effects operating within the osmium center.

The crystal structure of (C₅Me₅)Os(Me₂PCH₂PMe₂)(H) was used as a starting point for structure optimizations. The structure of (C₅HₓR₅-x)Os(X₂PCZ₂PX₂)(H)(CH₃)⁺, was studied where R is H, Me, SiH₃, CF₃, or SiMe₃ and X = F, Me, H, Ph, or CF₃, and Z = H or F. For each complex, four points were calculated; the methyl hydride complex 1, the methane tautomer 2, the transition state 1‡ that connects 1 and 2, and dissociated state 3. The structure of the fragment (C₅HₓR₅-x)Os(X₂PCZ₂PX₂)⁺ was allowed to relax so the energy of the dissociated state 3 with respect to 1 affords a measure of the methane binding energy. Owing to the flatness of the potential energy surface, all stationary points were determined using the GDIIS method and internal options to decrease step size (IOP 1/8=n) The transition state 1‡ was located from optimizations using redundant internal coordinates. Frequency calculations were performed to confirm that optimized minima and transition states were true stationary points. Imaginary
frequencies less negative than -25 cm\(^{-1}\) were ignored. IRC calculations were used to confirm that the transition state geometry was a saddle point connecting 1 and 2.

Optimizations were also carried out on the carbonyl analogues \((C_5H_5R_{5-x})Os(X_2PCZ_2PX_2)(CO)\)\(^+\). The starting structures for these complexes were derived from \((C_5Me_5)Os(Me_2PCH_2PMe_2)H\) and \((C_5Me_5)Os(Ph_2PCH_2PPh_2)H\).\(^{40}\)

Energies determined by DFT methods are known to be of limited accuracy due to the hindered rigid rotor approximation used to treat internal rotation in normal mode vibrational analysis can overestimate the entropy of complexes with many degrees of freedom.\(^{58}\) However, the statistical sampling method used by Gaussian reduces the impact of this error at low temperatures, so thermochemical values calculated below room temperature are usually much more accurate.

Natural population analyses were performed on optimized complexes of the methane coordination complex 2 using both BB1K and M05-2X functionals as implemented in Gaussian03 Rev. E.01. The $\text{RESONANCE}$ keyword was used as suggested for complexes with strong delocalization, and $\text{3CBOND}$ was used to search for three-centered bonding orbitals.

Sample input files for optimization, frequency, and NBO calculations are included in Appendix D.

References


(24) Schlangen, M.; Schwarz, H. *Dalton Trans.* **2009**, *-*.


(43) Brumaghim, J. PhD, University of Illinois at Urbana-Champaign, 1994.


(45) Chapter 3 of this work.


(52) The transition states determined for the rotamers contained a large number of imaginary frequencies so they do not contain useful information.

(53) Chapter 2 of this thesis


(55) Chapter 3 of this thesis.

(56) Chapter 3 of this thesis.

CHAPTER 5. COMPUTATIONAL ANALYSIS OF AN APPARENTLY AGOSTIC INTERACTION: APPEARANCES CAN BE DECEIVING!

Section 5.1 Introduction

Agostic interactions, i.e., 3-center-2-electron interactions involving a metal and a carbon-hydrogen bond, play an important role in organometallic chemistry, being present, for example, in key intermediates in Ziegler-Natta catalysts for the polymerization of alkenes.\textsuperscript{1} From a structural viewpoint, agostic interactions can be classified as $\alpha$, $\beta$, $\gamma$, etc., according to the location of the interacting C-H bond relative to the metal center.\textsuperscript{2-6} Detailed studies suggest that $\alpha$-agostic interactions form in order to maximize the metal-carbon orbital overlap, whereas $\beta$- and more remote interactions with C-H bonds maximize metal-hydrogen overlap.\textsuperscript{4,7-10}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{agosticOverlap.png}
\caption{Line drawings showing three modes of agostic overlap.}
\end{figure}

Complexes that exhibit $\gamma$-agostic geometries are rare relative to the $\alpha$ and $\beta$ varieties.\textsuperscript{11-15} Although the presence of $\gamma$-C-H agostic geometries is usually determined crystallographically, their presence has also been deduced from unusually shielded NMR chemical shifts\textsuperscript{16} and from kinetic isotope studies.\textsuperscript{17}

Traditionally, agostic complexes are characterized on structural arguments but computational models can be used to describe the electron density. Density functional theory (DFT) can make reasonably accurate predictions of the structures of agostic geometries provided that care is taken to choose an appropriate functional.\textsuperscript{18,19} Full
computational studies of agostic complexes are rare, however, owing to the inability of many methods to accurately describe the through-space interaction between the metal and the β- or γ-carbons.\textsuperscript{20} Although the classical picture of an agostic interaction involves delocalization of C-H bonding electrons into an empty d-orbital on the metal,\textsuperscript{4,8} this simple model has been called into doubt by analysis of the wavefunctions of agostic complexes.\textsuperscript{10,20,22} For example, a computational study of the β-agostic compound TiCl\textsubscript{3}Et(dmpe) showed that the β-C-H bonding electrons delocalize principally into orbitals on the α-carbon, rather than into d-orbitals on the metal center.\textsuperscript{22} Pantazis et al furthered of this concept and suggested that agostic interactions involve delocalization of electrons from the alkyl substituent into an orbital sink, which can either be a vacant d orbital on the metal, a vacant orbital on the alkyl substituent, or a vacant orbital on another ligand.\textsuperscript{20} Computational methods to analyze the bonding in agostic complexes have recently been reviewed.\textsuperscript{10} Of the methods available, the natural bond orbital (NBO)\textsuperscript{23} and the atoms in molecules (AIM)\textsuperscript{24} methods are popular. NBO is particularly attractive owing to its implementation in many modern computational chemistry codes and robustness to basis sets employed.

Previously, we reported the crystal structure of the titanium amide complex Ti\textsubscript{2}Cl\textsubscript{6}[N(t-Bu)\textsubscript{2}], 1,\textsuperscript{25,26} which showed that there are close contacts of 2.634(3) Å between each titanium atom and a γ-carbon on a tert-butyl group (Figure 5.2). Interestingly, the hydrogen atoms on this γ-carbon are disposed in such a way as to maximize the Ti···H distances, the shortest of which are 2.36(2) and 2.62(2) Å. The geometries of these interactions are similar to those in several metal complexes of the isosteric ligands –CH(SiMe\textsubscript{3})\textsubscript{2} and –N(SiMe\textsubscript{3})\textsubscript{2}.\textsuperscript{27} Despite the presence of these short Ti···H-C contacts, we show here from DFT calculations and other evidence that they are not agostic interactions. In fact, the Ti···H-C interaction is likely to be repulsive.
Section 5.2 DFT structure of Ti₂Cl₆[N(η-Bu)₂], 1.

In order to probe the nature of the bonding in 1, gas phase structures were optimized using three different DFT functionals: B3LYP, M05-2X, and PBE0. The calculated structure is shown in Figure 5.3. All functionals afforded optimized structures whose interatomic distances (Table 5.1) agreed within 0.1 Å of those seen for the crystal structure, except for the carbon-hydrogen distances, which as usual are systematically underestimated by ~0.15 Å by X-ray diffraction. Specifically, the calculated structure contains the same short Ti···C contact with one of the ligand methyl groups found experimentally. The calculated distances (Å) for this contact are 2.767 (B3LYP), 2.688 (PBE0), and 2.662 (M05-2X), vs. the experimental value of 2.634(2). These comparisons suggest that M05-2X does a better job than B3LYP in modeling weak M···H-C interactions, a conclusion we have also reached in a benchmark study of a different system.¹⁹ From here on, we will focus our discussion on the M05-2X calculations; results from B3LYP and PBE0 can be found in the tables and in the Supporting Information.

In the calculated structure, the hydrogen atoms attached to the methyl group are disposed in such a way as to maximize the Ti···H distances, exactly as seen crystallographically. For M05-2X, the shortest and second shortest Ti···H distances of 2.453 and 2.678 Å agree well with the experimental values of 2.36(2) and 2.62(2) Å. (The calculated and experimental Ti···H distance actually are in better agreement than it seems, owing to the underestimation of the C-H distances from X-ray crystallography). The structural similarities between these gas-phase models and the crystal structure suggest that the close Ti···H-C contacts seen in the latter are not unduly influenced by packing effects.

Although the short Ti···H contacts are in the distance range considered normal for agostic interactions,² other calculated structural features are less consistent with this interpretation. The calculated C-H bond closest to the Ti center is only 0.002 Å longer than the other C-H bonds in the molecule, whereas C-H bond lengthenings of 0.04 Å are
typical for M···H-C interactions in other transition metal complexes.\textsuperscript{10,18} Similarly, the C-C bond closest to the titanium (C11-C12) is only 0.004 to 0.006 Å longer than the two other C-C bonds in the same tert-butyl substituent (C11-C16 and C11-C20). Thus, the calculations show little evidence of significant weakening of the C-H bond or distortion of the alkyl substituent due to a Ti···H-C interaction.

Section 5.3 Orbital analysis of the bonding in Ti$_2$Cl$_6$[N(t-Bu)$_2$], 1.

**Kohn-Sham orbitals.** Kohn-Sham orbitals were calculated for 1 from the results of the DFT calculations with PBE0. The HOMO (Figure 5.4a) predominantly involves pi bonding between a titanium d-orbital and the “lone pair” p-orbital on the amide nitrogen. The titanium d-orbital is also involved in small a small $\sigma \rightarrow \pi$-antibonding overlap with both of the bridging chlorine atoms. Even at relatively inclusive electron density contour values of 0.02 e Å$^{-3}$, the HOMO clearly shows no overlap between the titanium and the $\gamma$-carbon. An examination of all occupied Kohn-Sham orbitals revealed none with a significant interaction between the titanium center and the carbon or hydrogen atoms of the proximal tert-butyl group. In contrast, the Kohn-Sham orbitals of the classical beta-agostic complex, TiCl$_3$Et(dmpe) (Figure 5.4b), show clear orbital overlap between the Ti and beta-agostic C-H bond.\textsuperscript{28}

**Natural bond orbital analysis of 1.** The natural bond orbital method has been used to test for the presence of agostic interactions in other systems\textsuperscript{18,29} and we find them useful here. In NBO, the many electron wavefunction is analyzed in terms of electron-pair bonding units on an idealized Lewis structure.\textsuperscript{23,30} In structures with delocalized electrons, perturbation theory is used to calculate donor-acceptor interactions between occupied Lewis pair orbitals and unoccupied virtual orbitals. The larger the stabilization energy due to the donor-acceptor interaction, the more stable the bond. The limit of this donor-acceptor interaction is a hypervalent 3-center-2 electron bond where two electrons are shared between three atomic centers.
One would expect a strong agostic interaction to exhibit this extreme delocalization. We find that, for all three DFT methods, there are no three center bonds between the titanium atom and any C-H or C-C bond in 1. However, a donor-acceptor interaction between the C-H bonding orbital and an empty Ti d orbital can be found. This interaction provides a stabilization energy of 2.1 kcal mol\(^{-1}\) (PBE0). For comparison, DFT calculations on a niobium complex using the PBE0 functional found that a β-agostic interaction afforded a stabilization energy of 23.8 kcal mol\(^{-1}\), whereas a similar non-bonded (i.e., non-agostic) interaction involving the same orbitals had a stabilization energy of only 1.7 kcal mol\(^{-1}\)\(^{1,18,31}\) for atomic descriptions while we used Pople and Los Alamos basis sets. The calculated NBO values should be transferable since NBO is considered robust with respect to basis sets. See Reed et al.\(^{23}\) The stabilization afforded by the donor-acceptor interaction on our complex (1) is closer to that of the non-bonded interaction rather than the agostic interaction energy.

Section 5.4 Structural analogues of 1.

As judged from the theoretical treatments and detailed structural comparisons, the close-contact in 1 is best thought of as non-bonding and is the likely result of minimization of interligand steric interactions. In order to avoid unfavorable contacts between Cl(1) and the distal tert-butyl group, the Cl(1)-Ti-N angle is large and the entire amide group is pivoted at nitrogen so that the two Ti-N-C angles are different by 15° (one is 110.6° and the other is 125.4°). The net effect of both of these effects is to place the proximal tert-butyl group close to the titanium center.

If the interaction is a result of interligand steric congestion that forces the C-H bond into close interaction with the titanium atom, then replacing the distal (i.e., non-interacting) tert-butyl group on the amide ligand with smaller substituents should allow the proximal tert-butyl group to move farther away from the titanium center. We therefore calculated gas-phase structures for Ti\(_2\)Cl\(_6\)[N(t-Bu)(R)]\(_2\) molecules in which the
distal substituent R on the amido ligand is Me, Et, or SiMe$_3$. Important geometric parameters for these molecules are shown in Table 5.2.

One of these molecules, Ti$_2$Cl$_6$[N(t-Bu)(SiMe$_3$)]$_2$, has been studied crystallographically, and adopts a structure that is very similar to 1: in this case, the tert-butyl group forms a Ti⋯C contact of 2.774 Å that is similar to (but longer than) the proximal Ti⋯C contact of 2.634(2) Å in 1. As seen in 1, the hydrogen atoms on the tert-butyl groups of Ti$_2$Cl$_6$[N(t-Bu)(SiMe$_3$)]$_2$ are oriented so as to minimize their interactions with the Ti atom. The other experimental parameters for this complex are very similar to those seen for 1: for example, the Ti-N distance is 1.838(2) Å vs 1.871(2) Å in 1.$^{32}$ The optimized DFT structure for the SiMe$_3$ analog exhibits similar parameters: the Ti⋯C close contact is 2.79 Å, the Ti-N distance is 1.82 Å and the shortest Ti⋯H distances are 2.74 and 2.60 Å.

Relative to carbon-carbon bonds, silicon-carbon bonds are longer and the relevant sigma orbitals are higher in energy, so a Si-C bond is a better donor than a C-C bond. If the driver for forming a close interaction between the Ti center and a substituent on the amide group is reducing the electron deficient nature of the titanium center, then we would expect that the SiMe$_3$ group should be the substituent that interacts with titanium center in Ti$_2$Cl$_6$[N(t-Bu)(SiMe$_3$)]$_2$. This is not what occurs, however: in both the experimental and calculated structures, the tert-butyl group occupies this position, and the SiMe$_3$ group, which takes the distal position located near the axial chlorine atom, is too remote to interact with the metal center (Figure 5.5). This overall molecular geometry is consistent with minimization of steric repulsions between the amido ligand and the chlorine atoms. By placing the tert-butyl group near the titanium and the SiMe$_3$ group near the axial chlorine, the steric interactions with those chlorine atoms are reduced. A similar minimization of steric effects can account for the structure of 1.

We carried out energy calculations on two different rotamers of this SiMe$_3$ compound: one in which the tert-butyl group is proximal to Ti (as observed
experimentally), and one in which the SiMe$_3$ group is proximal to Ti. We found that the latter rotamer is in fact higher in energy by 3.30 kcal mol$^{-1}$.

We also optimized the structures of the analogs of 1 in which the distal substituent is a methyl or ethyl group. Owing to the much smaller steric sizes of these substituents, interligand steric interactions with the chlorine atom Cl(1) are much reduced. As a result, the amide ligand pivots so that the proximal tert-butyl is located farther from the titanium center. Thus, the Ti1-H13 distance increases from 2.36 Å for R = t-Bu, to 2.63 Å for R = SiMe$_3$, to 2.81 Å for R = Et, and to 2.72 Å for R = Me. Similarly, the difference between the two Ti-N-C angles (which is a measure of how much steric interactions with Cl(1) induce pivoting of the amide group) increases in the order 112, 115, 125, and 122 for R=tBu, SiMe$_3$, Et, and Me respectively. The geometry of the R=Me complex is somewhat distorted by an interaction between the Me and the terminal chlorines.

Wiberg bond overlap indices can provide useful numbers to visualize the decreasing Ti-H interaction. In the t-Bu complex, 1, exhibited Wiberg bond overlap indices of 0.0922 for the Ti1-C12 atoms and 0.0421 for the Ti1-H13 bond. In contrast, the bond overlap indices for the beta-agostic complex, TiCl$_3$Et(dmpe) are 0.1726 and 0.1087 for Ti-C$_{beta}$ and Ti-H respectively. The bond indices decrease as interligand steric hindrance around the distal substituent decreases. The Ti-C index changes from 0.1160 to 0.0893 to 0.0030 for tBu to SiMe$_3$ to Et and the Ti-H index decreases in the same manner; from 0.0426(t-Bu) to 0.0308(SiMe$_3$) to 0.0188(Et).

The general trend is this: as interligand steric hindrance decreases, either by reducing the size of the distal ligand or increasing the size of the tertiary atom (C to Si), the Ti- C and Ti-H bond distances increase and the Ti-H bond overlap decreases. Thus, we conclude that the close Ti···H interaction in 1 is a result of the steric repulsions between the distal substituent on the amide and one of the terminal chloride ligands (see X-ray diffraction results above). This repulsion forces the C-H bond of one of the proximal methyl groups to lie close to the Ti center.
Steric effects have been known to promote agostic interactions.\textsuperscript{33,34} However, in this complex, the $\gamma$-agostic interaction is due mainly to interligand steric hindrance that forces the C-H bond into close contact with the titanium metal. This molecule illustrates a fundamental problem in computational analysis of agostic interactions; that the close metal--CH contact observed structurally may actually be best described as the result of other interactions more so than an agostic interaction. This assertion seems especially true for $\gamma$-agostic interactions.\textsuperscript{10,35,36} In the case of 1, the d$^0$ metal center is stabilized by $\pi$-backbonding from the electron rich amide nitrogen and terminal chlorines. The Wiberg bond index for the Ti-Cl overlap is 1.4738 and 1.2907 for each of the terminal chlorines and 1.2906 for the Ti-N bond while the overlap index for the Ti with the bridging chlorines is 0.6808 and 0.7488. The steric restraints placed upon the complex by this rich electron environment cause the close Ti--CH contact seen in 1. The decrease in C-H bond indices seen for C12-H13 (0.8491) versus C16-H19 (0.9046) may actually be due to destabilization of the bond as a result of repulsive forces between ligands rather than attractive forces towards the titanium metal.

Maseras and Crabtree have pointed out that a close contact between a metal and a X-Y bond can be classified as agostic only if two conditions are fulfilled: (i) there must be an empty orbital capable of overlap with the bond in question, and (ii) there must be also some evidence of weakening of the bond; the latter feature being most readily accessible by calculation.\textsuperscript{37} We have shown above that there is no evidence of significant weakening of the C-H (or C-C) bond nearest the Ti center in 1, and that overlap between the Ti d orbitals and C-H orbitals is small. All these results strongly suggest that what appears from structural data to be a $\gamma$-agostic interaction is actually a result of interligand steric repulsions between the distal tert-butyl group on the amide and one of the terminal chloride ligands. It is likely that other compounds with supposed $\gamma$-agostic interactions are actually the result of steric effects rather than bonding effects.\textsuperscript{38}
Section 5.5. Computational Methods.

All gas-phase structures were optimized in $C_i$ (inversion) symmetry using Gaussian03 Rev. E.01.\textsuperscript{39} Pople’s 6-31G(d,p) basis set\textsuperscript{40} was used for the C and H atoms, and Pople’s 6-31G basis set\textsuperscript{40} was used for the N atoms. To reduce the time required for the calculations, lanl2 effective core potentials\textsuperscript{41,42} were used on the Cl and Ti atoms. Electron affinity calculations showed that polarization functions were required to gauge accurately the electron affinity of isolated chlorine atoms, and therefore lanl2dz(d,p)\textsuperscript{43} was used in place of lanl2dz for chlorine. The crystal structure of 1 was used as a starting point for all geometry optimizations with the functionals B3LYP,\textsuperscript{44,45} PBE0 (also known as PBE1PBE),\textsuperscript{46} and M05-2X.\textsuperscript{47} Stationary points were verified to be local minima in two ways: all vibrational frequencies were non-negative, and the same structure resulted upon reoptimization after a manual distortion, such as changing the N10-C11-C12-H13 dihedral angle or the Ti1-N10-C11 angle to a value different from that in the optimized structure. Natural bond orbitals were calculated from optimized structures of each of the complexes using NBO 3.0 as implemented in Gaussian03.
Table 5.1. Geometrical parameters for Ti$_2$Cl$_6$[N(t-Bu)$_2$)$_2$, 1, from DFT and from the X-ray crystal structure.$^{25}$

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</tr>
<tr>
<td>C11-C16 (Å)</td>
<td>1.544</td>
<td>1.534</td>
<td>1.534</td>
<td>1.540(3)</td>
</tr>
<tr>
<td>C11-C20 (Å)</td>
<td>1.546</td>
<td>1.536</td>
<td>1.537</td>
<td>1.528(3)</td>
</tr>
<tr>
<td>Ti1-N10-C11 (°)</td>
<td>113.60</td>
<td>112.4</td>
<td>111</td>
<td>110.7(1)</td>
</tr>
</tbody>
</table>

Table 5.2. Geometric parameters from PBE0 for Ti$_2$Cl$_6$[NR(t-Bu)$_2$)$_2$, 1, with different distal alkyl groups on the amido ligand.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>R = Me</th>
<th>R = Et</th>
<th>R = SiMe$_3$</th>
<th>R = t-Bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-H13 (Å)</td>
<td>2.72</td>
<td>2.81</td>
<td>2.60</td>
<td>2.36</td>
</tr>
<tr>
<td>Ti-C12 (Å)</td>
<td>2.94</td>
<td>3.08</td>
<td>2.79</td>
<td>2.63</td>
</tr>
<tr>
<td>Ti-N-C (°)</td>
<td>122</td>
<td>125</td>
<td>115</td>
<td>112</td>
</tr>
</tbody>
</table>
Table 5.3. Wiberg indices calculated by PBE0 for key bonds in Ti₂Cl₆[N(t-Bu)(R)]₂
where R = Me, Et, SiMe₃ and t-Bu.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>R = Me</th>
<th>R = Et</th>
<th>R = SiMe₃</th>
<th>R = t-Bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₁-Ti₂</td>
<td>0.0473</td>
<td>0.0468</td>
<td>0.0503</td>
<td>0.0508</td>
</tr>
<tr>
<td>Ti₁-Cl5</td>
<td>0.8094</td>
<td>0.8209</td>
<td>0.7629</td>
<td>0.7488</td>
</tr>
<tr>
<td>Ti₁-Cl7</td>
<td>1.4846</td>
<td>1.4419</td>
<td>1.4722</td>
<td>1.4738</td>
</tr>
<tr>
<td>Ti₁-Cl8</td>
<td>1.3038</td>
<td>1.3369</td>
<td>1.3664</td>
<td>1.2906</td>
</tr>
<tr>
<td>Ti₁-Cl9</td>
<td>0.6125</td>
<td>0.5840</td>
<td>0.6534</td>
<td>0.6808</td>
</tr>
<tr>
<td>Ti₁-N10</td>
<td>1.2828</td>
<td>1.2929</td>
<td>1.3664</td>
<td>1.2906</td>
</tr>
<tr>
<td>Ti₁-C11</td>
<td>0.0316</td>
<td>0.0281</td>
<td>0.0411</td>
<td>0.0403</td>
</tr>
<tr>
<td>Ti₁-C12</td>
<td>0.0626</td>
<td>0.0030</td>
<td>0.0893</td>
<td>0.1160</td>
</tr>
<tr>
<td>Ti₁-H13</td>
<td>0.0235</td>
<td>0.0188</td>
<td>0.0308</td>
<td>0.0426</td>
</tr>
<tr>
<td>Ti₁-H14</td>
<td>0.0024</td>
<td>0.0017</td>
<td>0.0036</td>
<td>0.0044</td>
</tr>
<tr>
<td>Ti₁-H15</td>
<td>0.0167</td>
<td>0.0086</td>
<td>0.0235</td>
<td>0.0267</td>
</tr>
<tr>
<td>C11-C12</td>
<td>0.9920</td>
<td>0.9930</td>
<td>0.9856</td>
<td>0.9826</td>
</tr>
<tr>
<td>C11-C16</td>
<td>0.9901</td>
<td>0.9931</td>
<td>0.9893</td>
<td>0.9878</td>
</tr>
<tr>
<td>C11-C20</td>
<td>0.9863</td>
<td>0.9861</td>
<td>0.9917</td>
<td>0.9884</td>
</tr>
<tr>
<td>C12-H13</td>
<td>0.8814</td>
<td>0.8906</td>
<td>0.8687</td>
<td>0.8491</td>
</tr>
<tr>
<td>C12-H14</td>
<td>0.8977</td>
<td>0.9018</td>
<td>0.8891</td>
<td>0.8837</td>
</tr>
<tr>
<td>C12-H15</td>
<td>0.8820</td>
<td>0.9056</td>
<td>0.8756</td>
<td>0.8647</td>
</tr>
<tr>
<td>C16-H17</td>
<td>0.9121</td>
<td>0.9218</td>
<td>0.9202</td>
<td>0.9215</td>
</tr>
<tr>
<td>C16-H18</td>
<td>0.9127</td>
<td>0.9099</td>
<td>0.9141</td>
<td>0.9140</td>
</tr>
<tr>
<td>C16-H19</td>
<td>0.9100</td>
<td>0.9151</td>
<td>0.9076</td>
<td>0.9046</td>
</tr>
</tbody>
</table>
Figure 5.2. X-ray crystal structure of Ti$_2$Cl$_6$[N(t-Bu)$_2$)$_2$, 1. Ellipsoids are drawn at the 30% probability density level, except for hydrogen atoms, which are shown as arbitrarily sized spheres.

Figure 5.3. Structure of Ti$_2$Cl$_6$[N(t-Bu)$_2$)$_2$, 1, from PBE0 calculations.
Figure 5.4. HOMO of a) 1 and b) TiCl$_3$Et(dmpe) as determined by PBE0. The surface contours represent electron densities of 0.05 e Å$^{-3}$.

Figure 5.5. Skeletal structure used to determine the steric effect of distal alkyl group on Ti$_2$Cl$_6$[N(t-Bu)(R)]$_2$ (R = Me, Et, SiMe$_3$, t-Bu).

References.


(6) Scherer, W.; McGrady, G. S. Angewandte Chemie (International ed. in English) 2004, 43, 1782-806.


(25) Spicer, C., University of Illinois at Urbana-Champaign, 2008.


(28) The orbital overlap was originally studied by McGrady and coworkers. (See McGrady 1998)


(31) Pantazis and co-workers used Ahlrichs’ def2-TZVP basis sets (See Weigend, F and Ahlrichs, R; Phys. Chem. Chem. Phys. 2005, 7, 3297-3305)


(39) Frisch, M. J.; et al, full author list in supplementary information; Gaussian, Inc.: Wallingford CT, 2004.


CHAPTER 6. EDUCATIONAL STUDY: GREAT STUDENTS DON’T ALWAYS COME FROM SMALL CLASSES.

Section 6.1 Introduction.

Concern about class size effects on student learning has stretched back for centuries. In the 12th Century, the rabbinic scholar, Maimonides, proposed that class sizes should not exceed 40 students to one teacher, a rule still applied to Israeli K-12 classrooms today.¹ Colleges are often rated on their student-to-teacher ratios.² The nature of instruction dictates that students should perform better in a classroom where the primary instructor is an expert teacher and can interact with each student personally. However, over 60% of full-time undergraduates in the US attend large public universities,³ where economic and scheduling issues dictate introductory class enrollment of 150 or more students in one class. In classrooms of this size, it is very difficult for instructors to personally account for all students, and thus possible for students to fail more easily than in a small classroom setting in which the teacher can, in concept, know the students better.

Prior research suggests that smaller classes are better for students than large ones.⁴⁻⁶ A longitudinal study of class size and grade point average (GPA) at Stanford University showed a strong negative correlation between class size and course GPA of students.⁷ However, this study did not differentiate between senior seminar courses and freshman lecture courses or among instructors.

For the large and small classes taught by the same instructor, students in the small class outperform students in the larger class. In 1994, Hou taught two introductory economics courses, one with 100 students and one with 50 students.⁵ The courses were taught and evaluated in the
same manner. The author determined that student background and skill levels were comparable between courses. At the end of the course, students in the 50-member class performed significantly better on exams than students in his larger class, and also carried a higher opinion of economics.

When comparisons are made among different teachers, correlations between student satisfaction and class size are not always clear. Feldman analyzed the results of over 52 studies that related classroom achievement to student's overall evaluations of coursework. A total of 18 studies found an inverse association between class size and evaluations of the teacher and the course. However, 22 studies showed no relationship and a few studies showed a curvilinear inverse relationship where relatively large and small classes courses and the instructors who taught them received higher ratings than middle size classes. In explaining the U-shaped relationships, Feldman suggested that schools might make increased resources available to the extremely large courses (dedicated instructors, online homework, etc) that may not be available to moderately sized courses. At many institutions, specialized instructors are hired to teach these large introductory sections, where the sole responsibility of the instructor is to teach the course. The specialized teachers recruited for large introductory courses may be one of the reasons Feldman’s observed higher ratings for some large classes.

It is often difficult to recruit enough qualified teachers in order to teach introductory classes in anything other than large lectures of 150 students or more. If a large public university wanted to offer smaller sections, an economical alternative would be to use trained graduate teaching assistants. A problem with this approach is that pre-service teachers and first-year graduate students often lack the experience and knowledge necessary to successfully teach concepts to students. Bodner demonstrated that first-year graduate students at Purdue University
were unable to correctly explain the chemistry behind relatively simple phenomena such as bubbles rising from boiling water. He stated that many students understood the concepts well enough to pass exams but lacked the ability to transfer concepts learned in the classroom, such as phase changes in boiling water, to everyday events. In 1999, Lee showed that pre-service teachers, defined as undergraduates or first-year graduate students, could explain chemical equations on the macro (mole level) and the micro (atomic) level, but could not explain reactions on a level in between (particulate level).

Although first-year graduate students may not be able to teach, many studies have shown that good practices can be taught to them. Francisco, Nurrenbern, and Mickiewicz showed that the student effectiveness ratings were higher for chemistry graduate TAs who participated in a weekly development program versus TAs that only participated in a pre-semester orientation program. Students reported that the TAs in the weekly development program had more lucid explanations and were more effective in helping students to think than TAs in the general program. Shannon, Twale, and Moore showed that graduate teaching assistants (TAs) with prior teaching experience in a K-12 environment had much higher effectiveness ratings than TAs without K-12 experience. They attributed this difference to the feedback system used in many K-12 classrooms that is not available to teaching assistants. Thus, graduate teaching assistants can become effective teachers provided that they have feedback and continuous instructional support.

In an effort to provide a small and intimate classroom experience for first semester students, the UIUC chemistry department in the 1970s created a general chemistry course consisting of small discussions of 30 students taught by graduate teaching assistants. These small discussion sections met four times a week with the same teaching assistant instructor. The
traditional large lecture course consisted of lectures with a member of the teaching staff twice a week with two discussion periods of 30 students or less with a teaching assistant on days immediately following the lecture. When registering for course, students were given the choice to participate in a traditional lecture or the smaller discussion course. The current study sought to determine if student performance and satisfaction were different between the two types of sections by using three ways to assess good teaching; exam scores, attrition rates, and student satisfaction with the class (as measured by effectiveness ratings).

Section 6.2 Methodology.

The study was split into three major parts; direct comparisons of the performance of first semester chemistry students in the large lecture and small discussion sections, student evaluations of the large lecture and small discussion sections, and comparison of the dropout rate and student performance in the second semester of general chemistry.

Part 1. Evaluation of students in the same semester. Part 1 compared exam grades of students during the fall 2005 and spring 2006 semesters, in which the instructor for one section of the large lecture (Chemistry 1LB) prepared the lecture notes for the teaching assistants that taught the small discussions (Chemistry 1D). Instructors in both sets of classes covered the same content (often using the same lecture notes), assigned the same type of group work, assigned the same homework, and administered the same exams. This study compared exam grades and final grades of students in each section scaled against their ACT Math scores. In Fall 2005, exam and grade information was collected for 326 (98%) Chemistry 1LB students and 875 (98%) Chemistry 1D small-discussion students. In Spring 2006, exam and ACT information was
obtained for 282 (86%) 1LB students and 546 (98%) 1D students. Identifiable data such as names and identification numbers were replaced with generic numerical identification.

**Part 2. Evaluation of student satisfaction.** Part two consisted of anonymous evaluation surveys. Two surveys were given to students taking Chemistry 1L and 1D in Fall 2005 or Spring 2006. One survey, the Instructor and Course Evaluation System (ICES),\textsuperscript{12} was administered by the university and only a summary of the data could be obtained. The second survey, called Chemistry Large Lecture and Small Class Survey, was administered in Fall 2005 by the author to students in all general chemistry courses and requested demographic profiles of the students according to gender, major, math and chemistry background, ACT score, high school class size, and reason for taking chemistry. These data were then paired to their ranking of the course. A third survey was administered in Spring 2006 by the author to students in the subsequent section of chemistry called General Chemistry 2. In this survey, called “Chemistry 104 Student Reflections on Chemistry 102”, students were asked to rate the effectiveness of their chemistry 1 instructor in preparing them for General Chemistry 2. Students obtained two extra credit points for completing the online surveys.

All surveys were administered during the last week of class. Text versions of the surveys written by the author are included in Appendix F. Sample ICES questions can be obtained from the Center for Teaching Excellence website at www.cte.illinois.edu.

**Part 3. Longitudinal comparison of student performance.** The 3\textsuperscript{rd} part of the study consisted of a longitudinal assessment of the performance of large lecture and small discussion students in the subsequent course, general chemistry 2. Final grades for Chemistry 1 and 2, ACT scores, section identifiers for Chemistry 1, and gender data were obtained for all students who took Chemistry 2 from Fall 2002 to Fall 2005 (10 semesters total).
ACT grades were used as a control for the entire study because many institutional studies show that a student’s ACT Math score is the strongest predictor of student performance in class. In addition, the relationship between ACT scores and final grades was further supported from ANOVA results from this study.

**Data analysis.** Data analysis was performed using SPSS 14.0 and 17.0 and Microsoft Excel. Analysis of Variance results were obtained from SPSS 14.0.

All research presented in this study was approved by the Institutional Review Board of the University of Illinois at Urbana-Champaign, IRB Protocol Number 06220.

**Section 6.3 Results.**

The results of the studies are presented as: course, student, and instructor profiles as determined from the surveys; survey results from Fall 2005 and Spring 2006; exam comparison between large lecture and small discussion; grade comparison from the longitudinal study; and results for the Chemistry 2 reflection survey.

**Course Profile.** Approximately 3000 students at UIUC take first year chemistry each fall. Students are split into one of three tracks: an accelerated track for students with strong math backgrounds, an introductory track for students with a math background substantially weaker than average UIUC students, or a general track which was the focus of this study. When registering for the general course, students were given the choice between two different types of sections, a large lecture section henceforth referred to as Chemistry 1L or a small discussion henceforth called Chemistry 1D. In Fall 2005, there were three sections of Chemistry 1L were large lecture/ discussion classes that met twice a week with a professor or professional lecturer and twice a week with a TA-led discussion. Over 1000 students enrolled in the Chemistry 1L sections of over 300 students each. The lectures took place in a large, recently renovated lecture...
hall with large spaces for demonstrations and PowerPoint but little space for students to move around for group work. Discussion sections associated with Chemistry 1L were separate from the lecture, and were led by undergraduate or graduate teaching assistants. These discussion sections of 30 students or less met in small classrooms with moveable desks, a chalkboard and overhead projector.

An additional 900 students took the small discussion version of the course, Chemistry 1D. These sections met four days a week in classrooms with moveable desks with chalkboards, an overhead projector, and limited space for chemical demonstrations. Each section was taught by an undergraduate or graduate teaching assistant. In Fall 2005 and Spring 2006, students in the Chemistry 1D sections took the same exams as students in one of the large lecture sections, called Chemistry 1LB.

Approximately 60% of general chemistry students took Chemistry 2, the second semester general chemistry course. All Chemistry 2 courses were taught using the same instructional format as Chemistry 1L; two one-hour lectures with a professor or professional lecturer paired with two hours of TA-led discussion. Four sections of the course were offered in Spring 2006. The survey “Chem 104 Reflections on Chem 102” was given out in one of these large sections. Students were distributed equally across the four sections according to ACT Math score and course major so the results of the survey from this one section should compare to the results from all four large lecture sections.

**Student profiles.** Student profiles were compiled from two sources, the Chemistry 1 surveys offered in Fall 2005 to 1L and 1D and internal department data. Chemistry students at the university of Illinois came from the top 10% of their high school class, had an average ACT score of 30, had an average of 1.3 years of high school chemistry, and mostly studied in the
science and related fields. A majority of the students who took this course were science majors (42% Engineering, 23% Biology, 17% other) or undeclared (15%) with 3% of students reporting other majors. ACT Math scores serve as good predictors of student performance in chemistry 1 as illustrated in Figure 6.1.

**Figure 6.1** Correlation between ACT math score and final grade in chemistry for students registered in Fall 2005 sections of chemistry 1LB (blue circles) and 1D (red squares). Points on the chart represent the mean GPA at each Math ACT score. The correlation coefficients were calculated from all data (not grouped) and were 0.387 and 0.416 for 1LB and 1D respectively.

**Instructor profiles.** The instructor of Chemistry 1LB in Fall 2005 had 10 years of experience teaching general chemistry, including multiple years on the “unofficial list of instructors ranked as excellent.” The instructor of Chemistry 1LB in Spring 2006 was a first time instructor but had spent 6+ years working as an educational specialist for the laboratory courses. The full-time teaching assistants in Chemistry 1D were all graduate students accepted
into a highly competitive, research-intensive university. Many first-year graduate students had published research papers before graduate school and/or taught a course in chemistry while the older returning TAs worked in research laboratories or pursued educational coursework. The quarter-time teaching assistants in Chemistry 1D were advanced undergraduates pursuing careers in science teaching. All teaching assistants in 1D requested to teach the discussion sections and 13 (68%) participated in the Masters of Teaching Chemistry,\textsuperscript{14} Ph.D. specialization in Chemical Education,\textsuperscript{15} or graduate teaching certificate programs\textsuperscript{16} from the university. The large percentage of graduate students in advanced teacher training programs indicated that the majority of these TAs were motivated to improve their teaching. Teaching assistants were given two sections that met for 50 minutes, four times each week, so teaching assistants had a minimum of four in-class contact hours per class per week.

In the 1D sections, teaching assistants were given detailed notes from the course director on topics to cover. Each day’s notes provided major concepts to discuss, sample problems to use, group assignments to give, and tips on how to explain difficult concepts. Many TAs used these notes verbatim in their own lecture, but TAs were allowed to write their own lecture notes and cover additional material. TAs did not exercise control over course content or exams, with exams and course schedules decided upon by the director of the course.

**Results from direct comparison study between large lecture and small discussion section.** In the direct comparison study, exam scores and final grades of students in Chemistry 1LB and 1D were used to determine how well students learned material. Data were collected for two semesters, Fall 2005 when the 1LB instructor was an experienced lecturer, and in Spring 2006 when the 1LB instructor was a first-time teacher. In both semesters, students in 1LB and 1D started with similar ACT scores and similar chemistry backgrounds. In Fall 2005, the 1LB
and 1D students had identical exams, homework, and assignments since the instructor for 1LB directed the 1D course.

Table 6.1 shows that the students in 1LB and 1D entered with similar chemistry and math backgrounds. Direct comparison data for Fall 2005 indicates that on average, students in the 1LB outperformed students in 1D on hourly examinations, as illustrated in Figure 6.2. On the first exam, which covered material most students in the course covered in high school, the average 1LB score was 76.26% while the average 1D score was 75.32%. This difference was not large enough to be statistically significant (p = 0.128). On the second, third and final exams the differences were statistically significant, with a 95% confidence interval (p = 0.017, 0.030, and 0.0254 respectively). In addition, the average final grades were statistically lower for 1D students (2.41 out of 4) than 1L students (2.55). (p = 0.022)

Table 6.1 Baseline data for Fall 2005 students including the average Math ACT score, average years of high school chemistry, and total number of students studied. All values are statistically identical.

<table>
<thead>
<tr>
<th>Statistic</th>
<th>Chemistry 1D</th>
<th>Chemistry 1LB</th>
</tr>
</thead>
<tbody>
<tr>
<td># Students</td>
<td>875</td>
<td>326</td>
</tr>
<tr>
<td>Average Math ACT</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Average Years HS Chemistry</td>
<td>1.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Figure 6.2 Comparison of scaled exam scores between large lecture and small discussion course taught in Fall 2005. The same scale was used for both courses.

Direct comparison data for Spring 2006 can not be interpreted as clearly as Fall 2005 data for two reasons. First, all of the teaching assistants in 1D sections had taught the discussion section previously and second, the instructor for the Spring 1LB course prepared notes independent of the TAs. In addition, many of 1D TAs started to develop their own lecture plans that did not directly coincide with the 1LB course. However, the exam questions and course objectives were similar between both sections so direct comparisons can be made.

Spring 2006 students in Chemistry 1LB and 1D classes also began with similar chemistry backgrounds, as shown in Table 6.2. On average, students in the professor-taught 1LB performed identically to students in the TA-taught 1D discussions, except for performance on the final exam. The average exam scores are plotted in Figure 6.3. On exam 1, the 1LB students had statistically equal results compared to the small discussion sections. On exams two and three, the 1LB students had a lower average score, but the gap was not statistically significant. On the final exam, the 1LB students scored an average of 2.12% lower than the 1D students, a statistically significant difference. The average final grades could not be obtained for this cohort of students.
Table 6.2  Average ACT Math scores and average years of high school chemistry for students in the large lecture and small discussion sections of Chemistry 1 during Spring 2006.

<table>
<thead>
<tr>
<th>Statistic</th>
<th>Small Discussion (1D)</th>
<th>Large Lecture (1L)</th>
</tr>
</thead>
<tbody>
<tr>
<td># Students</td>
<td>546</td>
<td>282</td>
</tr>
<tr>
<td>Average Math ACT</td>
<td>27</td>
<td>26</td>
</tr>
<tr>
<td>Average Years HS Chemistry</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Figure 6.3  Comparison of scaled exam scores between 1LB and 1D courses taught in Spring 2006. The same scale was used for both courses but is different from the scale used for Fall 2005.

Institutional survey results for Fall 2005. Results for the official institutional review survey (ICES) for Fall 2005 are reported in Table 6.3. This survey is given each semester to students in all classes at the University of Illinois Urbana-Champaign. Students are asked to rank their instructors on a scale from 1 to 5, with 5 being the highest rating. In the table below, students were asked to rate the effectiveness of the instructor and the average mean of these scores were reported to the department. Ratings were obtained for all 19 TA instructors of the 1D and for all 3 instructors of the 1L, including the lecture studied above. Chemistry lecturers obtained average ratings of 4.45 out of a possible 5.0 while the TA lecturers obtained average
ratings of 4.24. Both group averages are above the minimum required from the university in order for an instructor to be ranked as excellent. However, two of the three instructors of the large lecture course met the standard to be ranked as excellent (4.5 out of 5.0) while only nine (47%) of the TAs met the standard (4.2 out of 5.0) Interestingly, the instructor for the 1LB lecture received a 4.35 rating, which was not high enough to be ranked on the excellent list for professors.

Table 6.3 Summary of ICES ratings for small discussion teaching assistants for Chemistry 1D and lecturers for Chemistry 1L in Fall 2005.

<table>
<thead>
<tr>
<th>Data</th>
<th>Teaching Assistants</th>
<th>Lecturers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>19</td>
<td>3</td>
</tr>
<tr>
<td>Average</td>
<td>4.24</td>
<td>4.45</td>
</tr>
<tr>
<td>Ranked Excellent</td>
<td>9 (47%)</td>
<td>2 (67%)</td>
</tr>
</tbody>
</table>

Chemistry 1 survey results for Fall 2005. The overall response rate for the survey was 56.2% for the Fall 2005 semester. According to the survey, 60.6% of respondents were male and 39.4% were female, which matched the actual distribution of students in Chemistry 1. The response rate for the survey matched the response rate for the questions.

The data give us insight about how and why students decided on their section. The data suggest that many students were completely unaware that the course was taught in different class sizes, as 75% of students stated that they did not know there were differences between the sections.18 Students were then asked what influenced their section choice. Most students, particularly in the large lecture, said that they picked the first section available. Three out of ten students in the 1D section intentionally registered for that section because they knew that it was smaller.
Students in the discussion section were asked to rate how many factors affected their performance in Chemistry 1. The majority of students in the D section (65%) stated that the small class size of 1D helped them or helped them a lot to learn chemistry. However, females were more likely to say that the small class size helped them a lot while males were more likely to say that the class size helped them. (Figure 6.4) The difference between genders was statistically significant ($p < 0.0001$) with women ranking class size as more important (4.01 out of 7) than males (3.58 out of 7).

**Figure 6.4** Histogram showing student responses for the Fall 2005 Chemistry 1D section to the question, “Rank how much the small class size helped you learn chemistry.” The results are split by gender.

In both semesters studied, the majority of students seem satisfied with their choice of chemistry course style (Figures 6.5 and 6.6). However, students in the TA led 1D sections tended to be less satisfied with their choice than students in the larger lecture, 1L. Students in
the discussion sections were less satisfied with their choice. In Fall 2005, when comparing the 1LB and 1D directly, and nearly 90% of students indicated a desire to stay in the same 1LB section, while only 65% of students desired to stay in the small 1D sections. In Spring 2006, with the new instructor, nearly the same percentage of 1D students wanted to stay in the same 1D section while only 72% of students said they wanted to stay in the 1LB section.

**Figure 6.5** Student answers to the question “If you could take [Chemistry 1] again, what section would you choose?” for the large lecture and small discussion courses in a) Fall 2005.

**Figure 6.6** Student answers to the question “If you could take [Chemistry 1] again, what section would you choose?” for the 1LB and 1D courses in Spring 2006, when the large lecture was taught by a first time instructor.

For a semester where the instructor had a great deal of experience, as in Fall 2005, the students in the large lecture would wish to stay in their section. For a semester where the instructor had limited experience, the students in the small discussion and large lecture had about
the same percentages. For both semesters, the percentage of students in the small discussion section wanting to stay in the same type of section is approximately the same.

Results from the longitudinal study. The longitudinal study sought to determine if students in the small discussion were better prepared for and performed better in the second semester of chemistry. The reasoning behind this section of the study sought to determine if having an instructor who knew the name of the students, encouraged interaction and group work led stronger students in chemistry. Chemistry 2 was only offered as a large lecture course so students who started in the small discussion class for Chemistry 1 could only take a large lecture for chemistry 2. For the longitudinal study, the author obtained ACT Math scores, gender, and final grades for all students who enrolled in Chemistry 2 at the University of Illinois Urbana-Champaign from Fall 2002 to Fall 2005. The students were then sorted according to the type of instruction they received for Chemistry 1. Students who took an exemption exam for Chemistry 1 and enrolled directly in Chemistry 2 received AP credit, or took the course at a different school, and were removed from the analysis, leaving a total of 4341 students. Of these students, 2373 took a large lecture and 1968 students took a small discussion course for Chemistry 1. Table 6.4 shows the average grades and ACT scores for all students studied.

Table 6.4 Final Grades for Chemistry 1 and 2 sorted by the type of Chemistry 1 course.

<table>
<thead>
<tr>
<th>Final Grade</th>
<th>Large Lecture (1L)</th>
<th>Small Discussion (1D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Grade in General Chemistry 1</td>
<td>2.70</td>
<td>2.68</td>
</tr>
<tr>
<td>Final Grade in General Chemistry 2</td>
<td>2.56</td>
<td>2.64***</td>
</tr>
<tr>
<td>ACT Math Score</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td># Students</td>
<td>2373</td>
<td>1968</td>
</tr>
</tbody>
</table>

*** - Indicates Statistically significant alpha < 0.005
On the average, when students entered Chemistry 2, students who took Chemistry 1D had the same average grade as chemistry 1L students. The average ACT Math score for all Chemistry 2 students was one point higher than chemistry 1 students, indicating that students with lower ACT Math scores (which relates to math preparation) may have dropped out of the chemistry sequence due to perceived difficulty of the course or chose a major that only required one section of general chemistry. Students who took the small discussion had an average higher grade in Chemistry 2 than students who took the large lecture for Chemistry 1. Small discussion students were statistically the same going into the second semester of general chemistry, but their final grade in general chemistry 2 was statistically higher than their large lecture counterparts. (Figure 6.7)

**Figure 6.7.** Histograms showing final grades for students in Chemistry 2 split by type of Chemistry 1 class; Chemistry 1L (blue) and 1D (red).
**Results from the reflective survey of Chemistry 2 students.** In Spring 2006, an online survey was administered to two sections of students in Chemistry 2. Of the 701 responses, the data were analyzed only for the 386 students who took Chemistry 1L and 242 students who took Chemistry 1D during the previous semester. All 628 students answered the survey questions listed in Appendix F. All data reported in this section came from students who reported taking chemistry 1 during the previous semester (Fall 2005). Thus, this follow-up survey represents the same students that were tested in the survey of which the results were presented above.

First, it is interesting to note the proportion of 1D students to 1L students in those who took the survey. In Fall 2005, over 50% of Chemistry 1 students were enrolled in Chemistry 1D but in the follow-up survey, only 38.5% of students who took the survey reported taking Chemistry 1D and 61.5% of students reported taking Chemistry 1L. Four sections of Chemistry 2 were offered that semester but the survey could only be administered to two sections so it is possible that un-surveyed sections had a larger proportion of 1D students than these two sections used for the survey. However, considering that; 1) the percentage of 1D students in the longitudinal study was 45% and 2) students self-selected into one of four lecture courses; it is likely that these numbers reflect the actual distribution of students in chemistry 2. The implications of these percentages will be discussed further in the discussion.

All 628 students were asked to rate the effectiveness of their Chemistry 1 instructor using a five-point Likert scale. (Figure 6.8) In this scale, the number 1 indicates strong agreement and 5 indicates strong disagreement so the lower the average score, the more students agreed with the statement.
When asked to rate the knowledge of their Chemistry 1 instructor, 83% of students agreed with the statement that their chemistry 1 instructor knew the material. However, a smaller percentage of 1D students agreed with this statement (76%) than 1L students (91%).

**Figure 6.8** Chemistry 2 student responses to the comment, “My chemistry 1 instructor knew the material” for a) students who took Chemistry 1L and b) Chemistry 1D. The average response was statistically different (p<0.001) between courses with average scores of 1.49 and 2.00 for 1L and 1D respectively.

Although most students agreed with the statement that their instructor knew the material, a fewer proportion of students agreed that their instructors could prepare them for later course. (Figure 6.9) The majority of students (69.6%) in chemistry 2 agreed or strongly agreed with the statement that “My Chemistry 1 instructor prepared me for Chemistry 2.” However, while 74% from 1L agreed or strongly agreed, only 62% of 1D students agreed. The average score for 1D students was 2.34 while the average score for 1L was 2.12, which were statistically different (p=0.013). Interestingly, 23% of students from 1D sections were neutral on this statement while only 17% of students from 1L were neutral.
Figure 6.9 Chemistry 2 student responses to the comment, “My Chemistry 1 instructor prepared me for Chemistry 2” for a) students who took Chemistry 1L and b) Chemistry 1D. The average response was statistically different (p=0.013) between courses with average scores of 2.12 and 2.34 for 1L and 1D respectively.

Since students often vote with their feet, students were then asked, “If I had to pick my Chemistry 1 instructor again, I would pick the same instructor.” Again, the majority of students in Chemistry 2 (58%) agreed with this statement. (Figure 6.10) However, the differences between 1D and 1L were larger, with 67% of 1L students reporting satisfaction with their instructor and only 49% of 1D students reporting satisfaction. What is even more telling is that twice as many 1D students (48%) than 1L students (21%) disagreed with this statement. The average rating for this question was statistically different (p<0.001) between 1D and 1L students (2.75 and 2.19 respectively).

Figure 6.10 Chemistry 2 student responses to the comment, “If I had to pick my Chemistry 1 instructor again, I would pick the same instructor ” for a) students who took Chemistry 1L and b) Chemistry 1D. The average response was statistically different (p<0.001) between courses with average scores of 2.19 and 2.75 for 1L and 1D respectively.
Students were also asked if Chemistry 2 should offer a smaller discussion. The overall rating for this question was 2.55, indicating nearly complete neutrality on this subject. However, there were differences between section types (p<0.001) since chemistry 1L students were more likely to disagree with this statement (2.76) and small discussion students were more likely to agree (2.42). The majority of Chemistry 1L students were indifferent (neutral) to this statement while the opinions of Chemistry 1D students were more polarized. (Figure 6.11) The majority of students in 1D (55%) agreed with this statement while 22% were neutral and 23% disagreed with the formation of small sections for Chemistry 2.  

**Figure 6.11** Chemistry 2 student responses to the comment, “Chemistry 2 should offer a smaller lecture like Chemistry 1D” for a) students who took Chemistry 1L and b) Chemistry 1D. The average response was statistically different (p<0.001) between courses with average scores of 2.76 and 2.42 for 1L and 1D respectively.

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**Student performance in a section of a highly motivated TA.** The data thus far shows that in Fall 2005 students in 1D performed worse than 1L when the instructor was an experienced lecture (Fall 2005) but performed about equally with 1L when the instructor was new and relatively inexperienced. Also the 1D sections were taught by 19 different TAs so a lot of variety existed between sections. A better comparison can be made between students in 1D with an experienced TA and students in 1L with an experienced lecturer. One TA, name Cobalt, had taught 6 semesters of the 1D section and had won a departmental teaching award. The
students in his class, started with a lower average ACT score (29) than students in the large lecture. Students in cobalt’s section consistently scored an average of 1-3% points higher than students in 1L. (Table 6.5)

Table 6.5 Average exam grades of students in the Chemistry section of 1D taught by Cobalt and the large lecture section 1L in Fall 2005.

<table>
<thead>
<tr>
<th>Section</th>
<th>Exam 1</th>
<th>Exam 2</th>
<th>Exam 3</th>
<th>Final Exam</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D- Cobalt</td>
<td>75.4</td>
<td>82.3</td>
<td>80.4</td>
<td>80.1</td>
</tr>
<tr>
<td>1L</td>
<td>76.2</td>
<td>79.1</td>
<td>77.9</td>
<td>78.7</td>
</tr>
<tr>
<td>Difference</td>
<td>-0.9</td>
<td>3.2</td>
<td>2.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

In addition, low-performing students in Cobalt’s section improved. In exam one, the correlation coefficient between Exam score and ACT Math score was 0.508, meaning that the math abilities of the student prior to the course was highly correlated to their performance in the course. In Exam 2, the correlation coefficient dropped to 0.253. By final exam, the correlation between ACT Math score and final exam score dropped to 0.035. As illustrated in Figure 6.12 below, the students with lower ACT math scores had low Exam 1 scores (blue) but their scores after Exam 1 were generally higher than the first, indicating improvement.
The same can not be said for students in the 1L section of Spring 2005. In the 1L section, the correlation coefficients for Exam 1, Exam 2, Exam 3, and the Final Exam were 0.298, 0.087, 0.136, and 0.1297. These scores indicate that the initial math skills of the student became less important predictors of Exam scores but completely irrelevant as seen for the Cobalt section of Chemistry 1D in Fall 2005.

Section 6.4 Discussion.

**History of Chemistry 1D sections and motivation for study.** In preparing the study, anecdotal evidence from informal conversations with undergraduate students suggested that students were highly satisfied with the ability to directly interact with their teaching assistant in the Chemistry 1D sections and they felt that their grades had improved. In terms of student achievement, the chemistry department said that when the class was first implemented in the 1970s, students in the small lecture outperformed students in the large lecture. In the longitudinal study of students in chemistry 2 from Fall 2002 to Summer 2004, students that took chemistry
1D initially performed much better in Chemistry 2 than took Chemistry 1L. (Figure 6.13) From Fall 2001 to Fall 2003, only 25% of students took chemistry 1D from 8 specially selected TAs. In Fall 2003, the number of TAs selected to teach the small discussion increased from 10 to 13. In Fall 2004, over 15 TAs taught 40% of the Chemistry 1 students and in Fall 2005, 19 TAs taught over 50% of Chemistry 1 students. Since the number of TAs increased dramatically, it is likely that the quality of instruction from began to fail.

**Figure 6.13** Graph showing the average final grade in chemistry 2 from Fall 2002 to Fall 2005 for students that took chemistry 1D (blue) and students that took chemistry 1L (red).

Student comments from the survey seem to reinforce the fact that some of their TAs could not explain the material. When students were asked to explain why they would switch sections, some students made statements that suggested that the small discussion TAs were perceived as unable to convey information in a way necessary for students to comprehend.

“The TA tried hard and [truly] wanted to help, but it didn't seem like he knew how to TEACH the subject. He could usually do it, with the help of the guide”.

“At least with a professor, you are assured that one person teaching you will know what they're talking about.”

Students also felt that the lack of demonstrations in the small class prevented them from picturing the concepts.
“Though I did like the small class size of Section D and our TA was nice, [occasionally] there were concepts she was unclear on and I would have liked to have seen demonstrations that the lectures got to see.”

Most comments from the large lecture sections (Chemistry 1L) suggested that students felt overwhelmed by the workload and exams and thought that exams in other sections were easier. 20

“The exams seemed more reasonable for this [other] section. Our exams were almost impossible [for] me, no matter how hard [I] studied.”

However, one student noted that even though the TA was unable to convey the main concepts clearly, the group work time in class might have been more helpful than listening to a skilled lecture.

“I don't know how the lecture with a professor would have been different, but it seemed as if it might have been more focused on introducing topics and less on working through them. Because I didn't do the homework before coming to class, I may have benefited more from a thorough explanation of the topics rather than having to work through problems to learn. On the other hand, working through the problems may have been much more of a help to learning the material than just hearing about it, even if I sometimes had no idea what was going on. I think I was probably more involved in the class because I had to do group work sometimes and we spent a good amount of time in class working on problems, and I answered questions, which I probably wouldn't have done in a large lecture.”

These results suggest that the interplay between large lectures and small discussions is not dependent on class size alone and that student performance is closely linked the instructor instead of the size.

In Fall 2005, when the students in 1D were compared against students in 1L taught by an experienced lecturer, the students in 1L outperformed students in 1D. However, in Spring 2006 when the 1L instructor was new and relatively inexperienced, the 1D students performed about the same as 1L students. In addition, during Spring 2006, the average student satisfaction rating with 1D instructors were statistically identically to the ratings given to the 1L instructor. Thus it
seems clear from this data that on average, the instructors in Chemistry 1D can be compared in quality to new instructors. However, if one looks closely at the performance of one 1D section taught by a highly experienced TA versus the 1L section taught by an experienced lecturer, the students in the TA section obtained much higher exam scores than students in the 1L section and students who should have been struggling in the course (ACT Math less than 25) improved to levels equal to those of students with higher ACT math scores. Thus indicating the 1D section taught by a highly trained TA could successfully teach chemistry to incoming students.

However, great care must be taken to select highly trained TAs. In the Spring 2006 follow-up survey given to Chemistry 2 students, students from that had taken the 1D section were split between agree and disagree while Chemistry 1 students were neutral to the idea of creating small discussions in Chemistry 2. Since the results for 1D were so polarized, it was likely that the student’s opinion of 1D sections was linked to their opinion of their chemistry 1 instructor effectiveness. The survey was not set up in a manner that would allow us to correlate these scores but considering that students in Cobalt’s section outperformed the large lecture peers, the notion that a small discussion taught by a highly trained TA could provide an alternative to the traditional large lecture format merits further investigation. Overall, its important to realize that the quantity of the students instructed is not important as the quality of the instructor. Student performance depends on how well the instructor can explain concepts and interact with any number of students, from 15 to 1500.

**Inverse relationship between TA experience and student performance.** A surprising result of this study came from an ANOVA test trying to differentiate the effect of TA training on student performance. In this study, the average final grade of students was plotted against the number of years of prior TA experience for the TA. Prior TA experience was determined by
connecting section labels from the longitudinal data with TA names available in public databases. The final grades, ACT Scores, semester taken, and number of semesters TA has taught at the University of Illinois. When comparing sections from the same semester, a general trend emerged. On average, the more semesters the teaching assistant taught general chemistry, the lower their students scored. Teaching assistants with no experience had students that performed higher than students in classes with 2 or more semesters of experience. ANOVA results comparing ACT scores of students, course grade, and number of semesters of prior TA experience showed that increased TA experience had a slightly negative effect on the students grade. The Pearson coefficient was determined to be -0.055.

Common wisdom leads us to believe that all other factors considered, students with experienced teachers should outperform students with inexperienced teachers. This suggests that the longer TAs teach, the more experience they gain and thus the better they become at communicating knowledge to their students. However, Shannon, Twale, and Moore compared the demographic profiles of 624 graduate teaching assistants at a large research 1 university with student evaluations of effectiveness. They found that students rated TAs with prior TA experience less effective than TAs without prior TA experience. In contrast, TAs with prior K-12 experience were rated higher than TAs without K-12 experience. They suggest that TAs with K-12 experience received supervision and feedback while TAs rarely received mentorship after initial department university training.

The results raise the question, “Why do teaching assistants become less effective with more experience?” This study did not answer that question but some solutions have been proposed.
First, lack of a feedback system means TAs may not realize how ineffective their teaching is. Shanon and coworkers suggested the mentoring feedback of K-12 instructors was the primary reason for improved student effectiveness ratings. They further showed that TAs with great experience rated themselves much more effective than their students while TAs with K-12 experience rated themselves about the same as their students did. For this study, teaching assistants in the discussion section are rated every year by the university sponsored ICES forms and often by mid-term evaluations. However, there is no incentive for teaching assistants to improve their results by improving their methods. Due to privacy concerns, results from the ICES evaluations were never used in selecting TAs for positions.

A simple method to implement teaching mentorship would be to assign new TAs to a trained educational specialist. The specialist could meet with each TA to discuss the results of their midterm evaluations and provide strategies to improve their teaching. Mentorship could be effectively implemented into the graduate curriculum through the use of team teaching or faculty student partnerships. Tronson and Ross showed that teaching teams of experienced graduate students, instructional faculty and beginning TAs improved student performance in introductory chemistry and biology courses.\textsuperscript{22}

However, in many graduate science programs, the barrier for this active approach to teaching is quite high due to the time constraints placed on many teaching assistants, which leads to the second reason for the decline. As TAs progress through their graduate career, they could become more focused on research and less focused on teaching. GTAs must handle teaching responsibilities on top of coursework and laboratory work. Often the load increases to the point that teaching responsibilities become teaching duties. Since most chemistry PhD degrees are research based, the research demands placed on a 4th year student are often more strenuous than
those on a first year student. The 4th year student may have written lesson plans in years prior, so they may not have spent as much time preparing the plans as they would have their 1st year so they could spend the time finishing a reaction sequence. Thus 4th year TAs walk into the discussion classroom less prepared and more distracted than their 1st year counterparts.23

At this university, two experienced teaching assistants attempted to start a bi-weekly discussion group for new TAs. Interest seemed high and 15 TAs attended at the beginning. However, after the second meeting, attendance dropped to zero. Attrition was attributed to lack of time and incentive to attend the group. Perhaps labeling the mentorship as a course would improve attendance. The results of this study merit further research.

References
Instructor and Course Evaluation, Center for Teaching Excellence, University of Illinois. 

Directory of Lists of Teachers Ranked as Excellent, Center for Teaching Excellence,

Masters in the Teaching of Chemistry/ Chemistry at Illinois.
http://chemistry.illinois.edu/graduates/degrees/msteach.html (10 October, 2009).

Chemical Education Specialization / Chemistry at Illinois.
http://chemistry.illinois.edu/graduates/degrees/chem_ed_spec.html (10 October, 2009).

Teaching Certificate Program, Center for Teaching Excellence, University of Illinois at

ICES results for Spring 2006 could not be obtained.

The phrasing used for this question was possibly too vague so students may have
answered out of confusion of the unknown more than lack of awareness about different
section sizes.

In marketing studies, scales of neutral tend to indicate dissatisfaction with a product
paired with the subjects desire to provide a positive answer.(marketing bulletin 1991,
Garland) Thus we can interpret the large neutral rating indicating dislike of the 1D course
but feeling like a negative answer would indicate disrespect of the TA. The author of this
study encountered this reaction when a former student reported to a colleague “My
Chemistry 1D TA (the author) tried very hard was not very good.”

Three sections of large lecture were offered during the semester but only one lecture is
discussed here. Students thought that the exams given by other large lecture instructor
were “easier” despite the fact that the exams were quite similar and student performance on all exams was nearly identical. In addition, it is likely that students in the large lecture did not realize that small discussion students took the same exam.

(21) Most students who take chemistry in the spring semester have often taken remedial chemistry courses so their exams end up with a different scale.


(23) After teaching for a total of 10 semesters as a graduate teaching assistant the author can personally attest to this fact.
APPENDIX A: CREATING PDB FILES FROM SHELL X WITH SYMMETRY EQUIVALENT ATOMS

Load the .ins file into xshell  (Make sure there is a matching .res and .html EG hi.ins, hi.res, hi.hkl)

double check the structure in shellx

open xp

type fmol (enter) to load file

type kill $q (enter) to delete q-peaks

type proj (enter) to view files

type grow (enter) to grow atoms

use proj to check the structure

type file _____ins (enter)  (enter a name different from original ins file unless you want to overwrite the original, eg hipdb.ins)

xp will ask for a .res file, give the name you started with like hi.res

type exit (enter) to exit xp

Open xpro

enter option:G

<enter> to continue

[S]

name of file - should be the .ins file you created in xp

Replace B-values? Y

Remove hydrogen atoms? N

rest Part 1 occ to 1, deleter other disorder components? Y

Remove all residues except standard amino acids? N
Remove all waters? K

Enter (integer) number of molecules per cell? ___ (obtain from ins file)

Enter space group with spaces in between each group (obtain from ins file)

pdb files to write: <enter>

Name of protein: _____ (this will be the name of the .pdb file)

Select chain: $

New ID for this chain: 1

Symmetry operator: <enter>

type [q] to exit

Then open the pdb file in a text editor like notepad

- delete disordered atoms

change partial occupancy factors of remaining atoms to 1.000

Important! - Save the file and give it to Charity if you want her to run calculations.

¹ ShellX operations derived by Gregory S. Girolami.
APPENDIX B: DERIVING THE TOLMAN ELECTRONIC PARAMETER FOR BIDENTATE PHOSPHINES

In Tolman’s original paper, the equations were derived to fit the equation of the form

\[ \text{CO}_{\text{dtBupm}} + a \, m + 4 \, S + = \text{CO}_{\text{calc}} \]

where
- \( m = n - 1 \) (n= number of CH\(_2\) groups between Phosphine atoms)
- \( a = \) a number dependent on the CH\(_2\) groups
- \( S = \) substituent parameter
- \( \text{CO}_{\text{dtBupm}} = \) symmetry CO stretching frequency of Ni(tBu\(_2\)PCH\(_2\)PtBu\(_2\))(CO)\(_2\).
- \( \text{CO}_{\text{calc}} = \) symmetric carbonyl stretching frequency predicted from data

The parameters ‘a’ and ‘S’ were determined by solving the system of equations one variable at a time.

The parameter ‘a’ was calculated from a linear least squares analysis of the CO frequency versus the number of CH\(_2\) groups, ‘n’.

The calculated slope ‘a’ for all values was -4.6 cm\(^{-1}\).

The substituent parameter ‘S’ was calculated by taking difference between the average CO frequency for all compounds with substituent R and average CO for all R from the
average for all tBu. The difference is then divided by 4 to account for the fact that four substituents are located on each bidentate phosphine.

\[
\{<\text{CO}_R>_{\text{average}} - <\text{CO}_{t\text{Bu}}>_{\text{average}} \} \div 4
\]

For example, the average CO stretching frequency for all CO\text{tBu} was 
\[
(1984 \text{ cm}^{-1} + 1977 \text{ cm}^{-1} + 1972 \text{ cm}^{-1}) / 3 = 1978
\]

The substituent parameter S for CF\text{3} was then 
\[
[(2055 \text{ cm}^{-1} + 2053 \text{ cm}^{-1} + 2048 \text{ cm}^{-1}) / 3 - 1978] \div 4 = 18.6
\]

The calculated parameters for all phosphines were then

<table>
<thead>
<tr>
<th>R</th>
<th>&lt;\text{CO}<em>R&gt;</em>{\text{average}}</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-\text{BU}</td>
<td>1978</td>
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</tr>
<tr>
<td>CF\text{3}</td>
<td>2052</td>
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<tr>
<td>Et</td>
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</tr>
<tr>
<td>F</td>
<td>2053</td>
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<tr>
<td>H</td>
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<tr>
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<tr>
<td>Ome</td>
<td>2023</td>
<td>11.3</td>
</tr>
<tr>
<td>Ph</td>
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<td>4.8</td>
</tr>
</tbody>
</table>

\text{CO}_{\text{dtBupm}} was the CO stretching frequency of Ni(tBu\text{2}PCH\text{2}PtBu\text{2})(CO)\text{2}.

The final equation was then

\[
1984 - 4.6 \text{ m} + 4 \text{ S} = \text{CO}_{\text{calc}}
\]

References

APPENDIX C: ADDITIONAL BENCHMARK DATA.

Additional Comments about B3LYP with Pople basis sets. In the following discussion, the TVP [6-311+G(d,p)] basis sets of Truhlar and coworkers will be used as benchmarks. Small but interesting changes are seen when the basis set used for the osmium atom is changed (while leaving the basis sets used for the non-metal atoms unchanged at either the double zeta level or higher). Four different effective core potentials for osmium have been tested: lanl2dz, lanl2dz with polarization functions on the outer shell, sdd, and sdd with polarization functions. Adding g functions to osmium (entries p4 and 5 versus p6-10 in Table 4) does not change the relative energies of 1 and 2, but changing the basis set description from DZ to TZ (entries p1-3 versus p4-11) leads to a 2 kcal mol\(^{-1}\) lowering of the energies of the methane tautomer 2 and the transition state 1\(^{\ddagger}\) relative to the methyl/hydride 1 (both 2 and 1\(^{\ddagger}\) remain higher in energy than 1, however). Larger variations in the energies are seen when the basis set description of all the non-osmium atoms are changed. Changing from DZ to TZ (6-31G* to 6-311G*) leads to a 1 kcal mol\(^{-1}\) increase in energy of the methane tautomer 2 and the transition state 1\(^{\ddagger}\) relative to the methyl/hydride complex 1. The energies of 1\(^{\ddagger}\) are most sensitive to the choice of basis set for the CH\(_4\) atoms (the energies vary by up to 2 kcal mol\(^{-1}\) as shown by comparing p8 to p10). Adding diffuse functions (+) to non-metal atoms also increased the relative energy of 2 relative to 1, but by only 0.3 kcal mol\(^{-1}\).

Additional Comments about B3LYP with correlation consistent basis sets. For 5d (i.e., third-row) transition metals such as osmium, a relativistic effective core potential is typically used to describe all the non-valence electrons. It is clear that such potentials work well for the inner core electrons but, for Os and other 5d transition metals, it is possible for the results of the calculations to depend on whether the electrons in shell five are treated implicitly (i.e.,
included in the effective core potential) or explicitly (i.e., included in the basis set description along with the valence electrons in shell six). For the correlation consistent sets, the effects of implicit (cc-pVDZ) and explicit (cc-pwCVDZ) descriptions of the electrons in shell five of the osmium atom were tested. Implicit treatments (entries cc1 and cc2 in Table 4) yield energies nearly identical to those obtained by explicit treatment (entries cc3 and cc4). We conclude that implicit treatment of all core electrons is sufficient for the present system.

Correlation consistent sets incorporate polarization functions on all atoms by default, but it is possible to alter the atomic description by using diffuse functions. We find that including diffuse functions (entries cc5, cc9 in Table 4) also does not significantly alter the relative energies.

We investigated whether it is possible to reduce the size of the calculation without sacrificing accuracy by using smaller basis sets to describe atoms in the ancillary phosphine and cyclopentadienyl ligands, while using large basis sets for the osmium center and the methyl and hydride groups. We find that employing triple or quadruple zeta basis sets for Os and CH₄ but double or triple zeta basis sets for all the other atoms (entries cc7-cc10), which results in a savings of 8 or more or more basis functions per atom, reduces the cost of the calculation by as much as a factor of 2 without a significant change in the energies of critical points on the potential energy surface. Removing the g functions from carbon and the f functions from hydrogen atoms on methane further reduces the cost of the calculation by removing 27 basis functions, again without significantly affecting the relative energies of the stationary points and transition states (entry cc10). These truncated correlation consistent basis sets constitute an excellent balance between computational cost and reliable accuracy.
Table C.1 Geometric data for DFT Methods

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<th>pbe0</th>
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<td></td>
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<tr>
<td>Os-H (Å)</td>
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Table C.2 Geometric data for Dunning basis sets for model complexes $1\text{H}$, $1\text{H}^\dagger$, and $2\text{H}$

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Table C.3 Geometry data for Pople basis sets for experimental complexes 1 and 2

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Table C.4 Zero point corrected energies relative to 1H for all DFT methods (kcal mol\(^{-1}\))

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Table C.5 Zero point corrected energies (Hatrees) for $1H$, $1H^\dagger$, $2H$ and the dissociated state $3H$ (Os fragment + CH$_4$) for all DFT methods studied.

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<td>0.02479</td>
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Table C.6 Equilibrium energies (Hartrees) for ab initio Methods.

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<th>Os fragment</th>
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<td>-1047.13458</td>
<td>-1047.14029</td>
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<td>-1047.24024</td>
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<td>-40.42183</td>
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References


(2) The Pople style osmium basis sets we used do not include diffuse functions because previous studies have shown that they are unnecessary for cationic metal complexes such as those in the present study.[ref]

APPENDIX D: SUPPLEMENTARY DATA FOR ANCILLARY LIGAND EFFECTS OF HYDROGEN SCRAMBLING ON A METHYL HYDRIDE COMPLEX.

Section D.1 Extra data

Geometric Data for complexes optimized with M05-2X/bs1

Table D.1 Geometric Data for all complexes optimized by M05-2X

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<tr>
<th>C₅R₅</th>
<th>Phosphine</th>
<th>CH₃H C-H (Å)</th>
<th>CH₃H Os-H (Å)</th>
<th>CH₃H Os-C (Å)</th>
<th>CH₃H H-Os-C (°)</th>
<th>Tilt Angle (°)</th>
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<td>2.174</td>
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Table D.2  Gibbs free energies at -100 °C of complexes 1‡, 2, and 3 for rotamers of (C₅H₄Me)Os(Me₂PCH₂PMe₂)(CH₄)⁺, listed with the carbonyl stretching frequency of the analogous (C₅H₄Me)Os(Me₂PCH₂PMe₂)(CO)⁺ complex and the tilt angle of 2 for a) M05-2X and b) BB1K DFT methods.

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<th>conformation</th>
<th>1‡</th>
<th>2</th>
<th>3</th>
<th>vₜ (cm⁻¹)</th>
<th>τ (°)</th>
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Section D.2 Route Sections for Gaussian03 jobs

Optimization with BB1K

# opt=(gdiis,noeigentest) bb95 gen scf=tight pseudo=read p gfprint gfinput
iop(6/7=3,1/8=3,3/76=0580004200)

Frequency with BB1K

#bb95/chkbasis pseudo=read scf=tight geom=check guess=read p freq gfinput gfprint
iop(6/7=3,3/76=0580004200) pop=full

NBO with BB1K

# p bb95/geneqc pop=nboread gfinput gfprint iop(6/7=3,3/76=0580004200)

At end of file -
$nbo bndidx RESONANCE 3CBOND plot$end

Optimization with M05-2X
Frequency with M05-2X
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NBO with M05-2X
# p m052x/geneecp pop=nboread gfinput gfprint iop(6/7=3)

at end of file –
$\text{nbo bndidx RESONANCE 3CBOND plot}$

Section D.3 Basis sets used

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    4.46183000   -0.66285600
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    0.58883000   0.50412000
    0.18326100   0.84031100
    0.08397200   -0.00774300
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| 6.962763  | 57.122503  |
P-H POTENTIAL
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| 4   |
| 10.498941  | 88.279003  |
| 9.992523  | 176.486064 |
| 6.588248  | 11.715012  |
| 5.037167  | 22.915060  |
D-H POTENTIAL
|    |    |    |
| 4   |
| 7.083441  | 44.777708 |
| 6.721179  | 67.153648 |
| 3.794626  | 5.550387  |
| 3.748125  | 8.220104  |
F-H POTENTIAL
|    |    |    |
| 2   |
| 2.826276  | 8.328332  |
| 2.781198  | 11.103102 |
G-H POTENTIAL
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| 4.496981  | -9.181343 |
| 4.467738  | -11.361604 |
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  0.1159000000D+01 0.8521620222D+00
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  0.3258000000D+00 0.1000000000D+01
S 1 1.00 0.000000000000
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  0.4133000000D+01 0.2440889849D+00
  0.1200000000D+01 0.8154920089D+00
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  0.1097000000D+01 0.1000000000D+01
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APPENDIX E. SUPPLEMENTARY INFORMATION FOR TITANIUM CHAPTER.

**Table E.1.** Electron affinities for chlorine calculated with lanl2dz and lanl2dz with polarization functions with various DFT methods

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**Table E.2** Table corresponding Crystal structure labels to theoretical model labels. Primed atoms are related to unprimed atom by crystallographic inversion center

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<td>H19</td>
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<tr>
<td>Ti1'</td>
<td>Ti2</td>
<td>C4</td>
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<tr>
<td>Cl1'</td>
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<td>H21</td>
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### Table E.3 Wiberg bond indices for key atoms for Ti\textsubscript{2}Cl\textsubscript{6}[N(t-Bu)]\textsubscript{2}, 1.

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<th>Parameter</th>
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### References

APPENDIX F: CHEMICAL EDUCATION RESEARCH EXTRAS.

Survey for CHEM 102 Students

Release for Information. You are invited to participate in a survey by Paul Kelter and Charity Flener of all UIUC CHEM 102 students to gauge opinions about the educational quality and satisfaction in CHEM 102 courses. The results of this survey will be used in a larger study to determine the success of students taking the various CHEM 102 courses. By participating in this study, you will help determine the effectiveness of the various CHEM 102 sections and help the general chemistry department place students in the section that will suit them best. Your participation in this project is completely voluntary, and you are free to withdraw at any time and for any reason without penalty. You should not experience any discomfort due to this survey. Your choice to participate or not to participate will not impact your job or status at school and you can refuse to answer any questions you do not wish to answer. You can ask receive a copy of the research results after this project is completed. The results of this study may be used for a dissertation, a scholarly report, a journal article and/or conference presentation. Any information you provide will be completely anonymous and can not be tracked to you in any way. If you have any questions about this research project, please contact Charity Flener by telephone at (217) 333-8779 or by e-mail at flener@uiuc.edu. You can also contact Paul Kelter at paulkelter@yahoo.com or (217) 333-4323. To be informed of your rights as a research participant, you can contact the Institutional Review Board at (217) 333-2670 or irb@uiuc.edu. You may call the IRB collect if you live outside the local calling area. You can print out a copy of this consent form. If you are taking this quiz to obtain the one point extra credit, you need to do the following. A copy of your survey will be sent to your uiuc account upon clicking submit. You should delete all questions except the first question (consent form) and then forward a copy of your survey to your chemistry TA for the extra credit. You can only receive two extra credit points for taking this survey and you must submit the survey before final grades are tallied. By clicking yes, you are giving us permission to use this data for research purposes and you agree that you are 18 years or older. I have read and understand the above information and voluntarily agree to participate in the research project described above

a) yes   b) no

*Students had to select yes in order for their data to be counted. They did not have to check yes in order to receive credit.
Survey

1) What is your gender?
   a) male       b) female

2) What year are you in school (by year not by credits)?
   a) freshman (first year in college)
   b) sophomore (second year in college)
   c) junior (third year in college)
   d) Senior (fourth year or higher in college)
   e) Professional (graduate student or in professional program outside of normal curriculum)
   f) none of the above ________________

3) Why did you take CHEM 102? (you may click more than one)
   a) required for major
   b) general education credit
   c) interested in chemistry
   d) other ________________

4) What school are you associated with?
   a) LAS
   b) Engineering
   c) Business
   d) Communications
   e) ACES
   f) Other

5) What of the following best describes your major?
   a) Engineering
   b) Chemistry
   c) MCB
   d) Computer Science
   e) Physics
   f) Social Science
   g) English/ Literature
   h) Languages
   i) Physical Science (other than listed above)
   j) haven’t declared a major

6) How many years of high school chemistry did you take?
7) How many years of high school math did you take?
   a) 0  b) 1  c) 2  d) 3  e) 4  f) more than 5

8) What was your ACT math score?
   a) 34-36  b) 31-33  c) 28-30  d) 25-27  e) 22-24  f) didn’t take

9) What was your SAT math score?
   a) 740-800  b) 680-739  c) 620-679  d) 560-619  e) 500-559  f) didn’t take

10) What was the size of your graduating high school class?
   a) smaller than 50  
      b) 51-100  
      c) 101-150  
      d) 150-200  
      e) 200-250  
      f) larger than 250

11) What section of CHEM 102 are you taking now?
    a) A (Kelter)  b) B (Hummel)  c) C (Harwood)  d) D (with a TA)

12) When you registered for the course, did you know that there were differences between the various sections (ABCD)?
    a) yes  b) no

13) How important were the following factors in choosing a section (A, B, C, D)?
    1 – not very important  7- very important
    a) fits best in schedule
    b) student recommendation
    c) professor recommendation
14) When you picked your section, were any of the following factors in your decision?

a) knew that D had a smaller class size, picked D
b) knew that A was engineering focused, picked A
c) knew the professor of section, picked A, B, or C
d) knew that A was engineering focused but wanted a smaller classroom, picked D
e) I just picked the first section (ABCD) available, none of the above factored into my decision

15) If you are taking 102D, do you wish you had a different TA?

a) yes b) no c) no opinion

16) For students taking 102D, rate how much the following helped you in this course.
1 - didn’t help at all 7 - helped me a lot

a) small class size
b) online homework
c) quizzes
d) demonstrations
e) interactions with my TA
f) online homework
g) written homework

17) If you took 102D, how often did you attend discussion?

a) all the time (rarely missed class)
ba) most of the time (occasionally missed class)
c) about 2 classes a week
d) on quiz days only
e) class, you mean, I was supposed to go to class?

18) If you took 102 ABC, rate how much the following helped you in this course.
1 - didn’t help at all 7 - helped me a lot

a) demonstrations
b) lecture
c) written homework
d) online homework
e) discussion section with TA
f)
19) If you took 102ABC, how often did you attend the large lecture session?

a) all the time
b) most of the time (75%-90% of the time)
c) some of the time (50%-74% of the time)
d) occasionally (around 25% of the time)
e) I rarely attended lecture

20) If you took 102ABC, how often did you attend the small discussion?

a) all the time
b) most of the time (75%-90% of the time)
c) some of the time (50%-74% of the time)
d) occasionally (quiz days only)
e) I rarely attended discussion (discussion, what’s that?)

21) If you had to choose your section again, how likely would you be to pick the same section?

1---not at all 7---- definitely pick this section again

22) If you had the option to pick your 102 class again, what class would you pick?

a) A b) B c) C d) D e) none, I wouldn’t take the class

Thank you very much for taking this survey. Please click on the submit button to receive your extra credit point.
1. You are invited to participate in a survey by Paul Kelter and Charity Flener of all UIUC CHEM 104 students to gauge opinions about the educational quality and satisfaction in CHEM 102 courses. The results of this survey will be used in a larger study to determine the success of students taking the various CHEM 102 courses. By participating in this study, you will help determine the effectiveness of the various CHEM 102 sections and help the general chemistry department place students in the section that will suit them best. Your participation in this project is completely voluntary, and you are free to withdraw at any time and for any reason without penalty. You should not experience any discomfort due to this survey. Your choice to participate or not to participate will not impact your job or status at school and you can refuse to answer any questions you do not wish to answer. You can ask receive a copy of the research results after this project is completed. The results of this study may be used for a dissertation, a scholarly report, a journal article and/or conference presentation. Any information you provide will be completely anonymous and can not be tracked to you in any way. If you have any questions about this research project, please contact Charity Flener by telephone at (217) 333-8779 or by e-mail at flener@uiuc.edu. You can also contact Paul Kelter at paulkelter@yahoo.com or (217) 333-4323. To be informed of your rights as a research participant, you can contact the Institutional Review Board at (217) 333-2670 or irb@uiuc.edu. You may call the IRB collect if you live outside the local calling area. You can print out a copy of this consent form. If you are taking this quiz to obtain the one point extra credit, you need to do the following. A copy of your survey will be sent to your uiuc account upon clicking submit. You should delete all questions except the first question (consent form) and then forward a copy of your survey to your chemistry TA for the extra credit. You can only receive two extra credit points for taking this survey and you must submit the survey before final grades are tallied. **By clicking yes, you are giving us permission to use this data for research purposes and you agree that you are 18 years or older.** I have read and understand the above information and voluntarily agree to participate in the research project described above.

2. What is your gender?
   - Male
   - Female

3. What year are you in school (by year not by credits)?
   - Freshman (first year in college)
   - Sophomore (second year in college)
   - Junior (third year in college)
   - Senior (fourth year or higher in college)
Professional (graduate student or in professional program outside of normal curriculum)
Nondegree student

4. Why did you take CHEM 104? (you may check more than one)

Required for major
General education credit
Interested in chemistry

5. Which of the following best describes your major?

Engineering
Chemistry
MCB
Computer Science
Physics
Social Science
English/ Literature
Languages
Physical Science (other than listed above)
Haven't declared a major
Other

6. What was your ACT math score?

34-36
31-33
28-30
25-27
22-24
Didn't take ACT
Other

7. What was your SAT math score?

740-800
680-739
620-679
560-619
500-559
Didn't take SAT
Other
8. What was the size of your graduating high school class?

   Smaller than 50 students
   51-100 students
   101-150 students
   150-200 students
   200-250 students
   Larger than 250 students

9. What section of CHEM 104 are you taking now?

   Section A (Harwood 9am)
   Section B (Lehman)
   Section C (Harwood 12pm)
   Section D (Vaden)

10. What section of CHEM 102 did you take?

    Section A (lecture with Kelter)
    Section B (lecture with Hummel)
    Section C (lecture with Harwood)
    Section D (lecture with a TA)
    Took CHEM 102 at another university
    Tested out of CHEM 102

11. What was your grade in CHEM 102?

    A
    A-
    B+
    B
    B-
    C+
    C
    C-
    D+
    D
    D-
    F
    Other
Answer the next four questions according to the following scale
1- Strongly Agree 2- Agree 3- Neutral
4- Disagree 5- Strongly Disagree

12. My CHEM 102 Instructor prepared me for CHEM 104.

13. If I had to pick my CHEM 102 instructor again, I would pick the same instructor.

14. My CHEM 102 instructor knew the material.

15. CHEM 104 should offer a smaller lecture like CHEM 102D (<32 students).

16. If you wanted to pick a different instructor, which of the following statements best describes your choice of a new instructor?
   I took a small lecture for CHEM 102 but I would pick another small lecture with another TA.
   I took a large lecture for CHEM 102 but I wanted to take a large lecture.
   I took a large lecture for CHEM 102 but I would pick another professor.
   I took a large lecture for CHEM 102 but I would pick the smaller lecture.
   I wouldn't take CHEM 102 at the University of Illinois.
   Other
Curriculum Vitae
Charity Flener Lovitt

Academic Training:

Doctor of Philosophy (Fall 2009)
University of Illinois Urbana-Champaign, Urbana, IL
Major: Chemistry
Advisors: Prof. Gregory Girolami and Prof. Thom Dunning
   Thesis Topic: Quantum mechanical analysis of donor-acceptor interactions in organometallic complexes
Advisor: Prof. Paul Kelter
   Thesis Topic: “Comparative analysis of students in small teaching assistant taught discussions versus large instructor taught lectures“

Bachelor of Science, Cum Laude (2003)
Kentucky Wesleyan College, Owensboro, KY
Major: Chemistry Minor: Math

Academic Experience:

Lecturer and Course Director for Chem 102
Summer 2006
“General Chemistry for Non-majors”
University of Illinois Urbana-Champaign
   • Prepared course content and schedule for 60 undergraduate students
   • Lectured and prepared discussion material, exams, and online course content
   • Coordinated and prepared three teaching assistants for two discussion sections

Course Director for Chem 105
Spring 2006, Fall 2006, Fall 2007, Spring 2008
“General Chemistry Lab II for Non-majors”
University of Illinois Urbana-Champaign
   • Arranged and conducted weekly teaching assistant training meetings for 8-15 TAs
   • Created and maintained course websites to coordinate laboratories for 600-1200 students
Teaching Assistant for Chem 102D
August 2003 – Fall 2005
“General Chemistry for Non-majors”
University of Illinois Urbana-Champaign
- Primary lecturer for two sections of chemistry majors, head TA for two semesters
- Prepared lesson plans and daily class activities for two sections of 30 students
- Wrote quizzes and answer keys for class, contributed to exams for entire course

Teaching Assistant for Chem 316
Spring 2004
“Instrumentation of Chemical Systems Laboratory”
University of Illinois Urbana-Champaign
- Provided assistance to students on operation of analytical equipment
- Prepared quizzes and grading rubrics for laboratory reports

Graduate Mentor
Summer 2004-Fall 2006
Girolami Research Group
University of Illinois Urbana-Champaign
- Trained undergraduate student in air-sensitive and moisture-sensitive techniques for synthesis
- Developed research strategy for student

Honors/ Awards:
Fulbright Fellowship to Germany August 2008 to July 2009
Central European Summer Research Institute Fellow Summer 2007
Graduate Teaching Certificate Spring 2005
University of Illinois Block Grant Summer 2005
University of Illinois John C. Bailer Fellowship Fall 2005-Spring 2006
Incomplete List of Teaching Assistants Ranked as Excellent by Their Students Spring 2004, Fall 2005
Kentucky Wesleyan College Full-Tuition James Graham Brown Scholar August 1999 to May 2003
Kentucky Wesleyan College Dean’s List, 8 semesters
Research Experience:

Visiting Scientist
August 2008 – July 2009
Philipps-Universität Marburg
Host: Dr. Prof. Gernot Frenking
- Performed bond analysis of organometallic systems using quantum chemical methods
- Worked with scientists from 10 different countries to advance research goals

Graduate Research Assistant
November 2003-December 2009
University of Illinois Urbana-Champaign
- Calculated detailed quantum mechanical models of large organometallic systems
- Synthesized molecule based magnet precursors using air-sensitive Schlenk techniques
- Mentored an undergraduate researcher
- Coordinated scientists from different groups to prepare manuscripts for publication
- Presented oral and poster presentation at national meetings

Laboratory Assistant
June 2001-July 2001
University of Georgia-Athens
Mentor: Prof. Marly Eidsness
- Developed protocol for synthesis of trigger factor and its variants
- Developed identification methods for UV-Vis Spectrophotometer and FluorChem
- Repaired minor software glitches in Alpha-Innotech Fluorchem and Cary 100 UV-Vis spectrophotometer

Service/Organizations:

American Chemical Society
Member (2006- Present), Organized and presided over symposia at American Chemical Society National Meetings (2006, 2009), Division of Chemical Education National Program Committee (2007-2010)

Careers in Academia Seminar Committee
Co-Chair (2004-2006). Host for Speakers

National Science Olympiad
Volunteer (2005)
International Center for First Year Undergraduate Chemistry Education
Member (2005-Present)
Encouraging Tomorrow’s Chemists
Led chemical demonstrations for middle school students (2004-2005)

Publications
“A DFT and ab initio Benchmarking Study of Metal-Alkane Interactions and the Activation of Carbon-Hydrogen Bonds.”
Flener Lovitt, Charity; Woon, David; Dunning, Thom; Girolami, Gregory: J. Phys. Chem. A., accepted.
“A Short Bi=Bi Double Bond Supported by a Metalloid Group 13 Ligand.”
“Donor-Acceptor Properties of Bidentate Phosphine Complexes”
Flener Lovitt, Charity; Girolami, Gregory: Frenking, Gernot: in preparation.
“Are All M···C Close Contacts Agostic Interactions? Experimental and Theoretical Analysis of Ti2Cl6[N(tBu)2]2”
Spicer, Charles; Flener Lovitt, Charity; Girolami, Gregory: in preparation.
“Great students don’t always come from small classes”

Presentations
“Computational analysis of an apparently agostic interaction: appearances can be deceiving!”
“There and back again: A grad student’s tale.”
“Electronic and steric effects of ancillary ligands on hydrogen exchange barriers and tautomer energies in osmium methyl hydride complexes”
“Modern quantum chemical bonding concepts for the general chemistry curriculum”
“Can great students come from small TA taught classes?”

“Inductive effects of cyclopentadienyl substituents on osmium dihydrogen bonds”

"Theoretical analysis of the first linear iron amide complex"

“Student assessment of first year college chemistry class size and teaching style”

“Student reflections and performance: Comparing large and small lecture”
Flener, Charity; Kelter, Paul; 231st American Chemical Society National Meeting, 10-14 Sept 2006, San Francisco, CA, CHED 491, Talk.

Technical Skills:

Ab initio Quantum Packages
Gaussian03, Amsterdam Density Functional, Turbomole, EDA, NBO 3.0

Molecular visualization software packages
Gabedit, Gaussview, Molden, ChemCraft, Facio, and Diamond

Operating Systems
Mac Os X, Windows XP, Ubuntu Linux, including unix-based command line interface

Statistical Software Packages
SAS and SPSS

Course Management Systems
Lon-CAPA and WebCT

Synthetic Techniques
Manipulation of air- and moisture- sensitive compounds including the use of standard Schlenk line techniques, glove boxes, anhydrous reagents, and solvents

Languages:

English (Native speaker), German (Proficient)