# Computational Study of a Novel Dinuclear Metal Complex

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# COMPUTATIONAL STUDY OF A NOVEL DINUCLEAR METAL COMPLEX

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## Abstract:

*The first compound containing an M-H-M was recently reported by Vicic et al. With recent availability of large computational resources, molecular modeling has become a reliable tool for confirming experimental results. The novel dinuclear Ni complex $[(dippm)_2Ni_2Br_2](^o\text{-}H)$ was investigated in this work from a theoretical perspective. Full geometry optimization was carried on the dinuclear Ni complex at the DFT/B3LYP with the 6-31G\* basis set. The result verifies the linear Ni-H-Ni bond. Two different starting structures that converged to the same geometry confirm that a global minimum was reached. The computed structure differs from the experimentally determined one by a cis conformation adopted by the bromine atoms relative to the plane of ligands. This difference is believed to be accounted for by the preference of the theoretical model for a pseudo-tetrahedral structure of the Ni atom and by the gas-phase nature of the calculation, which neglects the crystal-packing forces present in the solid state.*

## Introduction:

A recent study by Vicic et al[1] synthesized and characterized the dinuclear Ni complex $[(dippm)_2Ni_2Br_2](^o\text{-}H)$ (**1**, dippm = bis(di-isopropylphosphino)methane) which is presented in Figure 1.
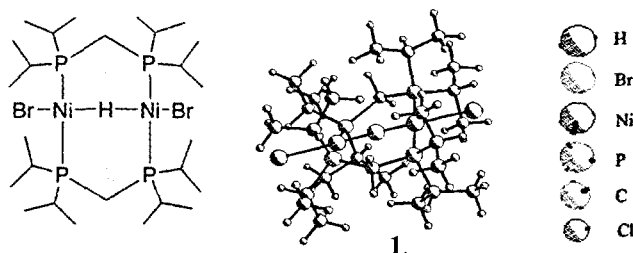


1.

*Figure 1. $[(dippm)_2Ni_2Br_2](^o\text{-}H)$ (left) Schematic structure (right) 3-D structure obtained from neutron diffraction data showing the linear Ni – H – Ni bond.*

Single-crystal neutron diffraction analysis indicates that the Ni – H – Ni bridge is virtually collinear, with an angle of 177.9∫. This was the first study to find a linear M – H – M linkage in a dinuclear metal complex, in contrast with previous research [2,3] that reported only bent geometries. The uniqueness of compound **1** for the existence of a linear M – H – M bond prompted the need for a theoretical inquiry of its existence. Compound **1** is investigated in this work from first principles using computer modeling.

The availability of inexpensive cluster computers and increasingly more accurate modeling software provides nowadays an invaluable tool for many chemists. Computer modeling of chemical reactions is used by organic chemists to predict the desirability of a reaction path at the advantage of saving the expense of unsuccessful experiments. In biochemistry modeling is used in conjunction with physical measurements to determine the complicated structures of proteins. In synthetic projects computational studies are presented as theoretical support for experimental results. In the field of organometallic chemistry papers that include calculations validating the experimental results have also become a routine [4-8]. The main goal of the present work is to employ the theoretical tool of computational chemistry to obtain a molecular model for the dinuclear complex **1**.

My previous work in the Pulay lab studied the behavior of carbon suboxide as a ligand in different organometalic compounds [8]. One example of these metal compounds is the nickel complex with phosphine ligands presented in Figure 2.
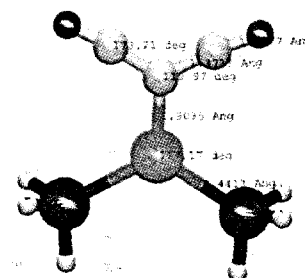


*Figure 2. Ni $C_3O_2$ $(PH_3)_2$*

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This carbon suboxide – nickel complex shares similarities with compound **1**: they both have Ni as the metallic center which is linked to phosphorus containing ligands. The successful implementation of the previous study on smaller but similar compounds led to the belief that the computational methods used are a viable approach to the current problem.

## Theoretical Background:

In this section a few important concepts from quantum chemistry are presented. This summary is considered necessary for understanding the computational methods used in this study.

### The Schrodinger Equation:

In quantum chemistry a function of the particles' coordinates called the wave function $Y$ is postulated to exist and contain all the information about the system [10]. The physical meaning of the wave function is that $|Y(x)|^2$ gives the probability density for finding the particle at a certain location $x$ in space. The wave function is considered to contain information about all the future states a system can be found in. From a philosophical standpoint, when an experiment is performed, the system has a quantized behavior, in the sense that it can only take one of the states preexistent in the wave function. The non-relativistic Schrödinger equation is used to "extract" information about the energy from the wavefunction:

$$\hat{H}\Psi = E\Psi$$

Here $E$ is an allowed value for the energy of the molecule, $Y$ is a function of the nuclei and electrons, namely their position, momenta, and spin. $H$ is a differential mathematical operator, called the Hamiltonian, constructed from its classical counterpart $H(p,r)=E$. The Hamiltonian is obtained by substituting the classical momentum $p$ with $\dfrac{h}{2\pi i}\dfrac{\partial}{\partial r}$. For a system of electrons and nuclei, in vacuum, at 0 K, with no magnetic interaction, the Hamiltonian is given by:

$$\hat{H} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum \frac{1}{2}\frac{1}{M_K}\nabla_K^2 - \sum_{i,K}\frac{Z_K}{|r_i - R_K|} + \sum_{i>K}\frac{1}{|r_i - r_j|} + \sum \frac{Z_K Z_L}{|R_K - R_L|}$$

In this formula $i$ and $j$ are indices for electrons with position $r$, while $K$ and $L$ are indices for nuclei with positions $R$, and charge $Z$. The first two terms that contain the Laplacian operator — are the expressions for the kinetic energy of the electrons and nuclei, respectively. The third term is the electron-nucleus coulomb attraction. The last two terms are the electron-electron and nucleus-nucleus coulomb repulsion. In the Born-Oppenheimer approximation the nuclei are considered much heavier than the electrons and thus their position is assumed to be fixed compared to that of the electrons. This is one of the most important approximations of computational chemistry and it leads to easier calculations in two ways. Firstly, the wavefunction can be written as a product of two independent wave functions, one for the nuclei and one for the electrons. Secondly, some of the terms coupling the nuclei and the electrons can be neglected and the Hamiltonian is simplified to:

$$\hat{H}_{total} \cong \hat{T}_{nuclei}(P,R) + \hat{H}_{electrons}(p,r,R)$$

The Schrodinger equation is then solved for the electrons, keeping the nuclei fixed. However, the computed potential energy of the electrons will depend on the positions R of these fixed nuclei

$$\hat{H}_{electrons}(p,r,R)\Psi_{electrons}(r,R) = V(R)\Psi_{electrons}(r,R)$$

### Hartree-Fock

In order to compute $V(R)$ one must first create an antisymmetric wavefunction $Y_{electrons}$ that has the property that when two electrons are permuted the sign of the wavefunction is changed. This behavior is imposed by the fact that electrons are Fermions and they are thus subjected to the Pauli Exclusion Principle. A form of the wavefunction that would guarantee that the Pauli principle is satisfied is the "Slater determinant". A "Slater determinant" is the determinant of a matrix which has as its elements the molecular orbital functions $f_i(x_j)$. $Y_{electrons}$ is then written as a linear combination of such Slater determinants:

$$\Psi_{electrons} = \sum C_i \Phi_{SD_i}$$

Each molecular orbital is in its turn written as a linear combination of atomic orbitals $c_j$:

$$\phi_i = \sum D_{ij}\chi_j$$

The atomic orbitals can be represented by any mathematical functions chosen so that they can properly represent the physical properties of the atom. Most used are the Gaussian type functions because they are easy to integrate analytically and therefore economical from a computational standpoint. Conventional sets of such atomic orbitals are called "basis sets" and they will be described later in greater detail.

Another important result in quantum chemistry is the variational theorem. Finding an exact solution to the Schrodinger equation by simply varying the coefficients $C$ and $D$ is an impossible task for any molecule bigger than hydrogen. Finding just an approximate solution would be a much easier approach. The variational theorem states that by computing $E$ for different approximate wave functions $Y_{electrons}$, the lowest value of the energy is obtained for the best wave function. The problem is now reduced to minimizing the energy by varying the coefficients $C$ and $D$. Even in this case, for the complete expansion of $C$ and $D$ the computation grows fast with the size of the system.

To alleviate this computational difficulty in the Hartree-Fock approximation all but one of the $C$'s are assigned a value of zero. After mathematical derivations the Schrodinger equation is reduced to the Roothan-Hall (HF) equations. In this approach the molecular orbitals are therefore taken to be one-electron wave functions and all the electron-electron correlation is eliminated. Instead, each electron interacts with the mean field that arises from the other electrons. Because the mean-field potential changes as the coefficients of the other electrons change, there is no way of finding the solution directly. Instead, the self-consistent-field (SCF) method is used, in which the HF equations are solved iteratively until the wave function is self-consistent, i.e. it does not change within a certain threshold between two consecutive iterations. The general process is known as HF SCF. Although it contains many approximations, this approach is entirely *ab-initio* and provides the best results possible with a minimum amount of computational expense [10].

### Density Functional Theory:

In HF SCF the task is to approximate a function of 3 x $N_{electrons}$ variables, three spatial variables for each electron. To save computational expense an ingenuous solution is to substitute the wave function with a functional of the electron density, in which case the number of variables is reduced to three. A functional is a function that has as variable another function, in this case the electron density. The Hohenberg-Kohn theorem proves the existence of a one-to-one mapping between the electron density functional and the many-electron wavefunction. This existence theorem is important from a theoretical perspective, but it does not provide a method of determining such a mapping and compute the wavefunction from the density. Recent advances in the DFT theory were acknowledged by the 1998 Nobel Prize in chemistry given to Walter Kohn, whose contributions to DFT led to the development of very successful density functionals. Used in this project is the most popular functional commonly known as B3LYP, the Becke-Lee-Yang-Parr hybrid exchange-correlation functional. Because different functionals are optimized to perform better on specific chemical systems, DFT is claimed to be a slightly empirical method. However, results obtained by DFT are comparable to those given by complex wave-function methods at a fraction of the cost, making DFT the only practical approach for very large systems.

### Basis set:

We have established that a basis set is a collection of mathematical functions which are combined, in a linear fashion, to form a molecular orbital. The word "basis" has in this setting the same meaning as in the mathematical description of a space. It is intuitive to see that a very large basis set, i.e. one that contains many basis functions, would lead to a good overlap with the real wave function. In fact, an infinite basis set would be able to

describe exactly the wave function. Because such an approach is not computationally feasible more approximations are introduced. The crudest approximation is to include a minimal number of basis functions, enough so that each electron has at least one orbital to be assigned to. In this case there is no room for variation, so the calculations using minimal basis functions cannot provide much insight into the chemistry of a molecule. Because the chemical behavior of a molecule is dictated by the structure of the outer electronic shells the ideas of contracted and split-valence basis sets were introduced [9]. In this approximation, the accurate modeling of the core electrons is given less importance by averaging the primitive basis functions into fewer "contracted" ones, while the valence orbitals are "split" by being represented by more basis functions. In the Pople style notation, one of the most popular basis sets, and also the one used in this study is called 6-31G*. The dash indicates the separation between the core and valence orbitals. The core orbitals are represented by a function contracted from six primitive Gaussian functions and the valence is split into two orbitals, each represented by three, and one primitive functions respectively. "G" signifies that the basis is formed by Gaussian type functions. The " * " is equivalent to " (d) " and indicates that a polarization $d$ function was added to the metal atoms. The split-valence allows for a combination of more of the same type of atomic orbitals, offering the model the ability to change size, but not shape. In order to allow different bonds to form in different directions higher angular momentum functions are added, and these are called polarization functions. Adding a $d$ polarization function on an atom can be thought of as the $sp^3d$ hybridization in the Valence Bond Theory. For certain elements that tend to have such hybridized orbitals, like the transition metal Ni used in this work, polarization functions are imperative for modeling the actual chemical behavior of the molecule.

### Geometry optimization:

Given the Born-Oppenheimer approximation, performing one complete SCF calculation will give the energy of the molecule only for a given set of nuclei coordinates. As the geometry of a molecule is given by the positions of the nuclei, such a calculation is often called a single point calculation. If interested in predicting the geometry of a molecule, one needs to find the nuclei coordinates that give the lowest total energy. The geometry of a molecule can be defined by different parameters: bond lengths, bond angles, dihedral angles or simply, the absolute position of each atom. Varying one of these parameters and calculating the energy for each point results in obtaining the function V(R). To illustrate, if one considers the molecule carbon suboxide $C_3O_2$ and calculates its single-point energy for different values of the C-C-C angle the following dependence is observed:

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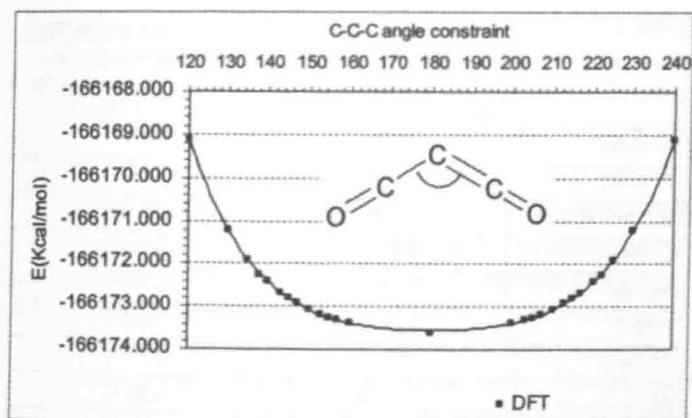CHEMISTRY AND BIOCHEMISTRY: Dragos Seghete. Computational Study of a Dinuclear Metal Complex    89



Figure 3. One variable potential energy surface for $C_3O_2$

If two parameters would be varied, i.e. the angle and a C-C bond, plotting the energy values would produce a three dimensional surface. A non-linear molecule with N atoms has 3N-6 degrees of freedom, or parameters that can be varied. The dependence of energy with these parameters defines the Potential Energy Surface (PES). Finding the most stable geometry of a molecule is equivalent to finding the absolute minimum on a PES. The general mathematical approach for finding minima of functions is to determine the zeros of the first derivative, also known as the gradient, and check for the positive second derivative. Instead of a costly numerical approach to this problem, Pulay showed how to determine the derivatives analytically, providing a cost-effective way of performing geometry optimization calculations [13].

## Methods:

In this study geometry optimizations were performed on compound 1 using the PQS software version 3.1. The calculations were carried in parallel on computer clusters containing 8 or 10 AMD Opteron™ processors. The geometry optimization calculations were performed at the DFT B3LYP level with the 6-31G* basis set. The unrestricted HF method was used and no constraints were imposed to the molecule. For a faster convergence of the first SCF step a better initial guess of the orbitals was obtained by initially performing a calculation using the smaller basis set 3-21G. A typical PQS input file is given in Appendix 5.

Because of the relative degeneracy introduced by heavy atoms like Ni, the card LVSH was used to force an energy gap between the occupied and virtual orbitals. Otherwise, excited electronic states of the molecule could be obtained, and these are not representative for the present ground state problem.

Particular attention was given to the situations where restarting a calculation was necessary. Although the geometry and orbitals were read from the previous files using the GEOM=READ card, a sequence of SCF and FORCE steps was performed before the geometry optimization. This was needed for the case when the previous calculation would have been interrupted during the force calculation procedure, thus giving an erroneous gradient as a starting point for the new calculation.

In determining the bond lengths and bond angles an "awk" script was written. Such a script for displaying the Ni-H-Ni angle in degrees is presented in Appendix 6. The script parses through the PQS output file, detects the geometry blocks and computes the bond lengths and angles from the Cartesian coordinates.

## Results and Discussion:

The full geometry optimization of compound 1 was started from the structure obtained experimentally by neutron diffraction [1]. The detailed coordinates of the start and converged geometries are given in appendices 1 and 2, respectively. The calculation converged in 275 geometry optimization cycles, with a total elapsed time of 7 days on an 8 processor cluster. The starting and converged geometries are presented in Figure 4. The most important bond lengths and angles are shown in Table 1.
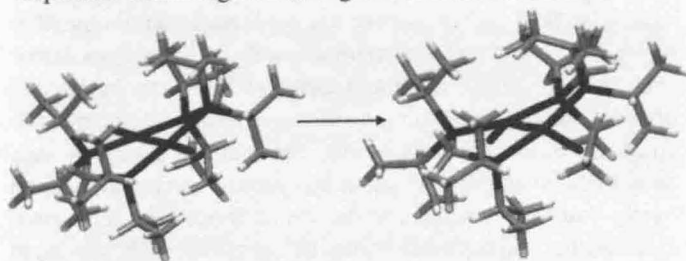


Figure 4. Starting and converged geometry of compound 1 in a DFT/6 31G* full geometry optimization. The starting geometry corresponds to the experimental structure obtained by neutron diffraction. Black=Br, Ni, Red=P, Grey=C, White=H.

|  | Starting geometry | Optimized geometry |
|---|---|---|
|  | obtained from neutron diffraction experiment Br-Ni-Ni*-Br* linear | 275 geometry cycles Total CPU time = 1199 hrs Elapsed / 8 CPU= 7 days |
| Ni-H-Ni* | 177.90 ° | 175.90 ° |
| Br-Ni-H | 177.71 ° | 154.06 ° |
| Br*-Ni*-H | 178.25 ° | 163.07 ° |
| Ni-Br | 2.37 Å | 2.53 Å |
| Ni*-Br* | 2.39 Å | 2.48 Å |
| P-Ni-P | 177.52 ° | 166.08 ° |
| P*-Ni*-P* | 175.35 ° | 169.21 ° |
| Ni-H | 1.61 Å | 1.64 Å |
| Ni*-H | 1.61 Å | 1.57 Å |
| Ni-P | 2.18 Å | 2.18 Å |
| $\Delta E = E_r - E_f(lin)$ | -60.2 kcal/mol | |

Table 1. Molecular parameters for the DFT/6-31G* full geometry optimization of Compound 1.

It can be observed that the calculation converges to a Ni-H-Ni angle of 175.90 ∞, very close to linearity. This agrees with the experimental result of Vicic et al., confirming theoretically the existence of such a bond. A general observation is that DFT tends

to overestimate the bond lengths. This can be explained by the non-locality of the functional approach. The calculation does not predict the overall experimental geometry as a minimum. The linearity along the Br-Ni-H-Ni*-Br* is not preserved, the bromine atoms preferring a *cis* position relative to the ligand system. Additionally, a slight asymmetry was obtained between equivalent Ni-Br bonds and Br-Ni-H angles. This could be explained by an error during calculation restarts. The combination of a fairly large calculation and an instability of the computer hardware led to several unwanted interruptions of the computation. It is believed that during one of the interruptions an incomplete set of forces was written, which were then read as the starting forces by the new optimization procedure. The unusually high number of optimization cycles is also to indicate that an imbalanced set of forces was introduced in the calculation which led to this asymmetry.

Geometry optimization of large molecules poses increased difficulty because of the increased possibility of converging to a relatively "flat" saddle point or to a local minimum on the PES rather than to a global minimum. Even if the starting geometry is close to the global minimum there is a higher probability of obtaining a path away from the minimum, for many degrees of freedom. From this perspective, the starting geometry was modified and another full optimization was carried in order to verify that the obtained geometry was indeed the minimum. Because the disagreement between the calculation and experiment was in the *cis* position of the bromine atoms, the starting geometry was modified so that the Br-Ni-Ni*-Br* bonds were in *trans* to the Ni-H-Ni line, with a relative out of plane angle of 160∞. The detailed coordinates of the start and converged geometries are given in appendices 1 and 2, respectively. The calculation converged in 60 geometry optimization cycles, with a total elapsed time of 2 days on a 10 processor cluster. The starting and converged geometries are presented in Figure 5. The most important bond lengths and angles are shown in Table 2.
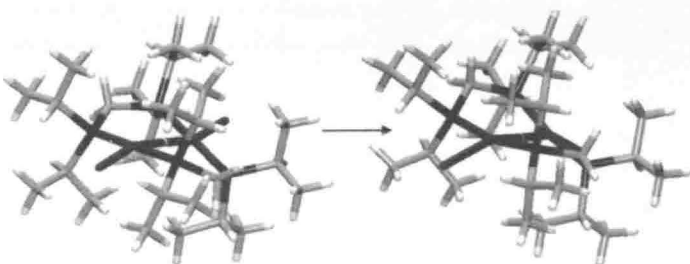


*Figure 5. Starting and converged geometry of Compound 1 in a DFT/6 31G\* full geometry optimization. The starting geometry was taken from the experimental structure obtained by neutron diffraction and modified so that the Br Ni Ni Br bonding was trans. Black=Br, Ni, Red=P, Grev=C, White=H.*

As in the previous case, the optimization converged to the structure having the bromine atoms *cis* relative to the ligand plane. This geometry is thus confirmed as a minimum. More importantly, the Ni-H-Ni was again virtually linear with an angle of 177.8∞.

|  | Starting geometry | Optimized geometry |
|---|---|---|
|  | Modified experimental structure **Br-Ni-Ni\*-Br\* trans** | 60 geometry cycles Total CPU time = 424 hrs Elapsed / 10 CPU= 2 days |
| Ni-H-Ni* | 177.90 ° | 177.84 ° |
| Br-Ni-H | 160.75 ° | 156.86 ° |
| Br*-Ni*-H | -161.33 ° | 157.20 ° |
| Ni-Br | 1.89 Å | 2.51 Å |
| Ni*-Br* | 2.05 Å | 2.51 Å |
| P-Ni-P | 177.52 | 166.99 |
| P*-Ni*-P* | 175.35 | 166.56 |
| Ni-H | 1.61 Å | 1.59 Å |
| Ni*-H | 1.61 Å | 1.59 Å |
| Ni-P | 2.18 Å | 2.22 Å |
| $\Delta E = E_r - E_f(trans)$ | -181.6 kcal/mol | |
| $\Delta E' = E_r - E_f(lin)$ | - 29.36 kcal/mol | |

*Table 2. Molecular parameters for the DFT/6-31G\* full geometry optimization of Compound 1. Starting geometry was modified to obtain a Br – Ni – Ni\* - Br\* trans structure.*

The calculated preference for the *cis* position of the bromine atoms can be explained by the Ni atom adopting a configuration in between square planar and tetrahedral. This is also verified by the P-Ni-P which diverges from linearity in the obtained geometry, the atoms P, P, Br, and H forming a flat tetrahedral arrangement around Ni. The preference of the DFT calculation for a pseudo-tetrahedral structure could be correlated with the spin-multiplicity of the complex.
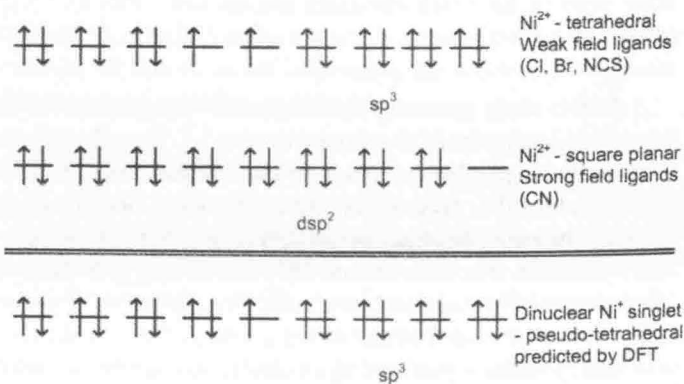


*Figure 6.   The correlation between spin-multiplicity and geometry of Ni complexes*

As schematically indicated in Figure 6, $Ni^{2+}$ complexes containing low field ligands adopt a square planar geometry with two unpaired spin electrons, or spin-multiplicity of 3. On the other hand, $Ni^{2+}$ complexes containing strong field ligands exist in a tetrahedral geometry with no unpaired spin electrons, or spin-multiplicity of 1. The experiments performed by Vicic et al. on the investigated dinuclear complex formally containing $Ni^+$ indicate the presence of one unpaired spin electron [1]. The calculations were performed in accordance with the experimental result, hence the presence of the SPIN=2 card in the input file

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(Appendix 5). It can be argued that according to the DFT calculation an intermediate spin state corresponds to an intermediate geometry of the nickel coordination. Further computational study of the complex in different spin states is thus warranted.

Another reason for the slight disagreement between the calculated and experimental geometries can be explained by the ideality of the quantum chemical model. The neutron diffraction experiment was performed on a crystallized sample where the intermolecular forces play a significant role. The energy difference between the experimental structure and the *cis* Br – Ni – Ni – Br structure predicted computationally is 30 kcal/mol. Taking into account the size of the molecule and the fact that the geometry optimization included all the aliphatic groups, the energy difference can be considered small and easily accounted for by crystal packing energies. Minor differences between gas-phase theoretical predictions and experimental results are usually explained by crystal packing forces [5,7].

More detailed insight into the electronic structure of the dinuclear Nickel complex can be obtained by looking at the frontier molecular orbitals. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are presented in Figure 7. The colored wireframes correspond to isoenergetic surfaces for the indicated orbital. The probability of finding the electron inside the colored surfaces is 0.5. Bl the different spin orbitals which are employed in the open shell UHF calculation (Unrestricted Hartree Fock). The isoenergetic surfaces indicate that the Ni-H-Ni is fairly strong, as the highest electronic density is on the Ni and P atoms. The HOMO and LUMO orbitals show that the most chemically vulnerable bonds of the complex are Ni-P and P-C, which is in agreement with the increased reactivity of the ligand observed experimentally [1]. The low electronic density on the Br atom suggests that direct substitution of the halogen is not favorable.

## Conclusion:

The first reported compound that contains a linear M-H-M bond was investigated computationally. Full geometry optimizations with no bond or symmetry constraints performed at the DFT/B3LYP-6-31G* confirm the existence of a linear Ni-H-Ni bond. The gas phase computed geometries indicate a

*cis* position of the bromine atoms relative to the Ni-H-N line and the ligand plane. Two different starting geometries converging to the same structure demonstrate unequivocally that the obtained geometry is a minimum. The small differences between the experimental and theoretical results can be accounted by the intermolecular forces that exist in the solid state. The HOMO and LUMO orbitals indicate a fairly strong Ni – H bond and an increased reactivity of the phosphine ligand, which is in good agreement with the experiment.

Further improvement of this study could be obtained by using a bigger basis set (6-311G**, or vtz-alhrichs) and by performing similar calculations on compounds that display a bent M-H-M bond.

This study also demonstrates how the latest advances in computational chemistry and the increased availability of computers recommend molecular modeling as a complementary tool to synthetic chemistry.

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## Faculty Comment:

Mentor Peter Pulay made the following comment about his student's work:

Dragos Seghete has explored the structure of novel organometallic compounds computationally, using methods of modern electronic structure theory. The compounds, containing a new structural motif, a linear Ni-H-Ni bridge, were synthesized in the laboratory of Professor David Vicic, and have been the subject of much interest recently. The calculations confirm the unusual linear structure, and demonstrate that modern electronic structure theory is able to treat these complex molecules. Previously, the high cost of the calculations deterred such investigations. However, improved theoretical methods, together with inexpensive PC-based computers, have changed the situation. Given the almost limitless ways large molecules can be constructed, computer modeling prior to experiment will certainly become an important tool in chemistry, speeding up discovery.