

# JCTC

Journal of Chemical Theory and Computation

## Theoretical Study of the Structure and Properties of $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$

Petia Bobadova-Parvanova, David Quinonero-Santiago,<sup>†</sup> Keiji Morokuma,\* and Djamaladdin G. Musaev\*

Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received October 18, 2005

**Abstract:** Recently Pool et al. [Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, 427, 527.] showed that the  $[(\eta^5\text{-Cp}')_2\text{Zr}]_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$ ,  $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{H}$ , complex is promising for dinitrogen hydrogenation. In the present study we examine computationally the structure and relative energies of different possible positional isomers of this dimer complex as well as different isomers of the monomer complex  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$ . The relative stability of isomers of the monomer is determined by the electrostatic repulsion between the negatively charged N atoms of the  $\text{N}_2$  molecule and the negatively charged C atoms of the  $\text{Cp}'$  ring that are bound to H. Substitution of H atoms by methyl groups significantly changes the charge distribution in Cp rings, increases the negative charge of  $\text{C}_\text{H}$  atom, and affects the relative stability of the isomers. On the other hand, competition between the electrostatic effects and the steric repulsion determines the relative energy of the positional isomers of the dimer  $(\text{Cp}'_2\text{Zr})_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$ .

### Introduction

The activation of molecular nitrogen to produce nitrogen-containing compounds under mild conditions is still one of the most challenging tasks of chemistry.<sup>1</sup> Due to its nonpolar and strong triple bond, molecular nitrogen has very low reactivity. Extreme conditions are needed to convert  $\text{N}_2$  into practically useful nitrogen-containing compounds. The Haber-Bosch process, which has been used for almost a century to produce ammonia from dihydrogen and dinitrogen molecules, requires temperatures ranging from 400 to 650 °C and pressure ranging from 200 to 400 atm.<sup>2</sup> Numerous efforts have been made to develop new catalysts, which would facilitate activation of dinitrogen under milder conditions. One of the most promising of these was the synthesis of the dinuclear Zr complex  $\{[\text{P}_2\text{N}_2]\text{Zr}\}_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$ , where  $\text{P}_2\text{N}_2 = \text{PhP}(\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2$  and  $\text{Ph} = \text{phenyl}$ , which reacts with one dihydrogen molecule and forms a bridging zirconium hydride and an N–H bond.<sup>3</sup> Theoretical modeling

predicted that this complex could dissociatively add even more than one dihydrogen molecule under appropriate experimental conditions.<sup>4</sup> Recently, Pool et al.<sup>5</sup> reported the synthesis of a dinuclear Zr complex  $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$ , **1**, which reacts with dihydrogen at only 1 atm and 22 °C. Subsequent warming of the complex to 85 °C even leads to formation of a small amount of ammonia. Although the discovered reaction is still not catalytic, its significance and practical importance is undisputable.

Surprisingly, when a slightly different ligand is used,  $\text{C}_5\text{Me}_5^-$  instead of  $\text{C}_5\text{Me}_4\text{H}^-$ , the reaction follows a different path with expulsion of free  $\text{N}_2$ .<sup>6</sup> Thus, replacing only one methyl group with hydrogen completely changes the reactivity of the complex. Very recently we explained the reason behind this remarkable difference.<sup>7</sup> We examined computationally a series of side-on and end-on coordination of the  $\text{N}_2$  molecule in mono- and dinuclear complexes,  $(\text{Cp}'_2\text{Zr})(\text{N}_2)$  and  $(\text{Cp}')_2\text{Zr}(\text{N}_2)\text{Zr}(\text{Cp}')_2$ , where  $\text{Cp}' = \text{C}_5\text{H}_{5-n}\text{Me}_n$ ,  $n = 0\text{--}5$ . The results for mononuclear complexes showed that the electronic effects would favor side-on coordination, a most suitable mode for hydrogenation, when more methyl groups are added to the  $\text{Cp}'$  ring. However, the increased number of methyl groups rapidly increases the steric repul-

\* Corresponding author e-mail: dmusaev@emory.edu (D.G.M.); e-mail: morokuma@emory.edu (K.M.).

<sup>†</sup> Present address: Department of Chemistry, Universitat de les Illes Balears, 07122 Palma de Mallorca, Spain.

sion between the monomer of the dinuclear complex and makes the end-on-coordinated complexes that are not suitable for hydrogenation more favorable.

In the present study we examine in detail structure, relative stability, and properties of the  $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$  complex. We investigate in detail the interplay between electronic and steric effects in this complex and examine their role in the relative stability of isomers of the complex. We analyze all possible isomers of the mononuclear  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  complex and several selected isomers of the dinuclear  $(\text{Cp}'_2\text{Zr})_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$  complex and rationalize the role of intramolecular (both steric and electronic) interactions in relative stability of these isomers.

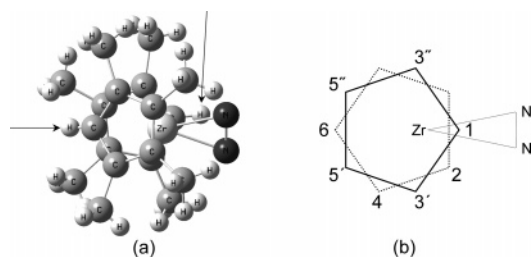
## Methodology

To find the energetically most stable structure of  $(\text{Cp}'_2\text{Zr})_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$ , we need to take into account different possible orientations of the four  $\text{Cp}'$  ligands. A complication arises from the fact that each  $\text{Cp}'$  ring has four  $\text{CH}_3$  groups and one H, which makes possible numerous isomers for  $(\text{Cp}'_2\text{Zr})_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$  that are different from each other by the mutual orientation of the  $\text{C}_5\text{Me}_4\text{H}^-$  ligands. It is very time-consuming to calculate all isomers. To simplify the task we used the following strategy. As an initial step we examined in detail all possible isomers of the mononuclear complex  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$ . Using the monomer, we hoped to select more likely monomer structures that can form stable dimers and hence reduce substantially the computational effort. As a second step, we used only the best isomers of the monomer to form several isomers of the dimer.

We used the hybrid density functional B3LYP method<sup>8</sup> and the Stevens-Basch-Krauss (SBK)<sup>9</sup> relativistic effective core potentials and the standard CEP-31G basis sets for H, C, N, and Zr atoms. Previously it was shown that d-type polarization functions on the N atoms are important for accurate prediction of the geometry and energetics of similar Zr complexes.<sup>4b</sup> Therefore we added a d-type polarization function for the two N atoms. Below, this approximation will be called as B3LYP/CEP-31G(d<sub>N</sub>). All calculations were performed using the Gaussian 03 program package.<sup>10</sup> The atomic charges were evaluated via the Natural Population Analysis (NPA) algorithm.<sup>11</sup> To estimate the steric interactions, we performed molecular mechanics (MM) calculations using Universal Force Field (UFF).<sup>12</sup>

## Results and Discussion

**A.  $\text{Cp}'_2\text{ZrN}_2$  Monomer.** The structure of the monomer  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  taken from the experimentally determined structure of the  $[(\eta^5\text{-Cp}')_2\text{Zr}]_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$  dimer is shown in Figure 1(a).<sup>5</sup> The positions of the H atoms on Cp are indicated with arrows. As can be seen, the two H atoms are oriented in opposite directions. Figure 1(b) gives a schematic representation of all possible positions of the hydrogen atoms. The solid  $\text{Cp}'$  ring is placed above the plane of the paper, and the dashed  $\text{Cp}'$  ring is placed below. We distinguish different  $\text{Cp}'$  orientations by different positions of the H atoms. Each H atom on the dashed  $\text{Cp}'$  ring can occupy positions 2, 4, or 6, while on the solid  $\text{Cp}'$  ring it can occupy positions 1, 3', 3'', 5', or 5''. Here, the larger number



**Figure 1.** (a) The monomeric unit taken from the X-ray structure of  $(\text{Cp}'_2\text{Zr})_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$ . The positions of the H atoms are indicated with arrows. (b) Schematic representation of different H positions. 1, 2, 3, 4, 5, and 6 denote different possible positions of the H atoms. The solid  $\text{Cp}'$  ring is placed above the plane of the paper and the dashed  $\text{Cp}'$  ring is placed below.

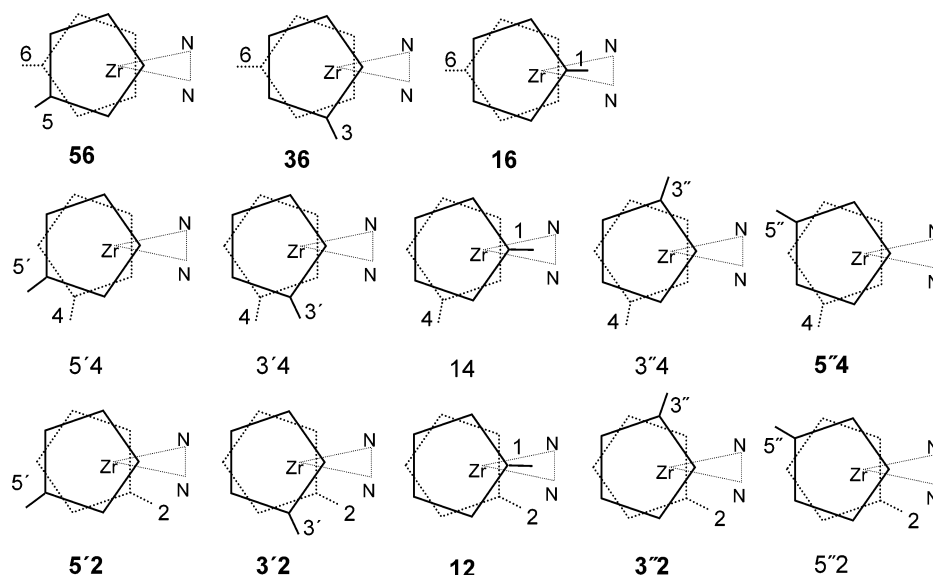
corresponds to further away from dinitrogen, and with ' and '' indicates closer or further from position 2 or 4. We will denote isomers by the positions of their H atoms. The experimentally reported structure corresponds to isomer 16, where the first number (1) corresponds to the solid  $\text{Cp}'$  ring, and the second number (6) corresponds to the dashed  $\text{Cp}'$  ring.

There are a total of 13 possible isomers of the  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  monomer, which are shown schematically in Figure 2. We attempted to optimize all these structures. However, during the optimization some of these structures converged to other isomers. As a result, we obtained only eight different stable isomers, 56, 36, 16, 5''4, 5'2, 3'2, 12, and 3''2, presented in bold in Figure 2. The barrier for  $\text{Cp}'$  rotation is found to be very small—only 2.7 kcal/mol for rotation from position 56 to position 36, for example. This indicates that different isomers correspond to points on a relatively flat potential energy surface.

Table 1 presents the relative energies of the eight optimized isomers. As can be seen, isomer 56 possesses the lowest energy of all. The experimentally reported structure, 16, is 0.90 kcal/mol higher in energy than isomer 56. At first sight, this finding does not agree with the experimental result. However, here we consider only the monomer and not the dimer, which was actually experimentally studied. As we will see later, when we will discuss the dimer, the calculated data fully agree with the experimental results.

The data in Table 1 represent calculations in a vacuum. The experiment of Chirik and co-workers was carried out in a pentane solution.<sup>5</sup> To evaluate the solvent effect, we performed single-point energy calculations of isomers 56, 16, and 12 using the PCM model.<sup>13</sup> The PCM relative energies of 0.0, 0.81, and 4.31 are very close to the values without solvent effects: 0.0, 0.90, and 4.50 kcal/mol, respectively. Thus, the nonpolar pentane solvent does not affect significantly the energy differences between different isomers.

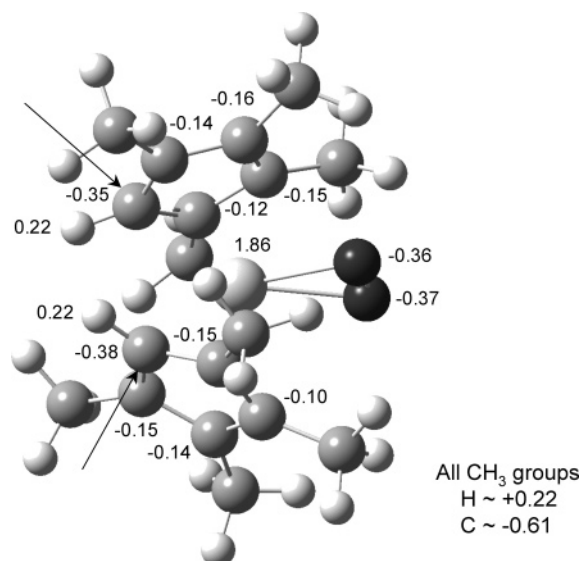
Now, let us rationalize the relative energies of the eight different isomers in terms of the specific interactions within the molecule. Analyzing the NPA atomic charges,<sup>11</sup> we found that the C atoms of  $\text{C}_5\text{Me}_4\text{H}$  rings are not equally charged. In Figure 3 we show the charge distribution only for isomer 56, as an example. The C atoms, which are bound to  $\text{CH}_3$



**Figure 2.** Schematic representation of all possible isomers of the  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  monomer. The stable structures are labeled in bold.

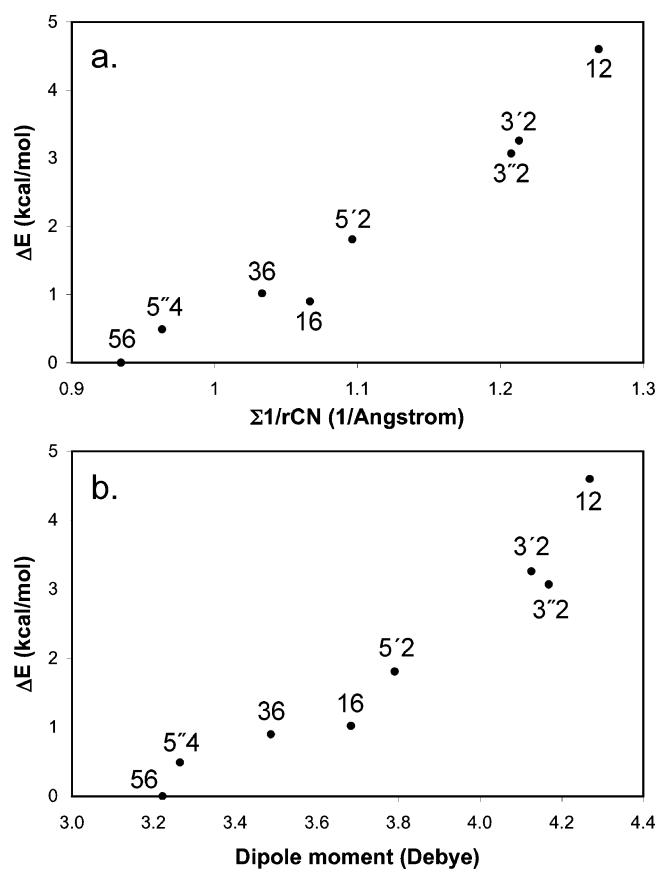
**Table 1.** B3LYP/CEP-31G(d<sub>N</sub>) Calculated Relative Energies,  $\Delta E$ , Dipole Moments,  $d$ , and Relative UFF//B3LYP/CEP-31G(d<sub>N</sub>) Energies,  $\Delta E_{\text{steric}}$ , of the Eight Stable Isomers of  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  Monomers

	$\Delta E$ (kcal/ mol)	D (Debye)	$\Delta E_{\text{steric}}$ (kcal/ mol)		$\Delta E$ (kcal/ mol)	D (Debye)	$\Delta E_{\text{steric}}$ (kcal/ mol)
56	0.00	3.22	0.00	5'2	1.81	3.79	4.74
5''4	0.49	3.26	4.50	3''2	3.07	4.17	4.18
16	0.90	3.49	5.48	3'2	3.26	4.13	4.69
36	1.02	3.68	1.45	12	4.60	4.27	4.98



**Figure 3.** NPA atomic charges of isomer 56.

groups, have approximately equal charges that vary between  $-0.10e$  and  $-0.16e$ . The “special” C atom bound to the H atom (denoted as  $\text{C}_\text{H}$ ) has the largest negative charge:  $-0.38e$  for the solid  $\text{Cp}'$  ring and  $-0.35e$  for the other  $\text{Cp}'$  ring, respectively. The charge distributions of the other possible isomers are similar to those discussed above.



**Figure 4.** Dependence between relative energies of different  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  isomers and (a)  $\Sigma 1/r_{\text{CN}}$  and (b) their dipole moments.

We measured the distances between the two  $\text{C}_\text{H}$  atoms and the two N atoms in every isomer ( $r_{\text{CN}}$ ) and plotted  $\Sigma 1/r_{\text{CN}}$  against the relative energy of the isomer. The result is shown in Figure 4(a). The graphical representation shows a direct relationship between the relative energies of different isomers of  $\text{Cp}'_2\text{ZrN}_2$  and  $\Sigma 1/r_{\text{CN}}$ . This indicates that the stability of the complex affected by the electrostatic repulsion between

**Table 2.** Solution of  $\sum c_i N_{ij} = \Delta E_j$  for  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  Monomers<sup>a</sup>

	$C_i$			$C_i$
H–N <sub>2</sub>	0.9520	repulsion	H–H	0.0903
Me–N <sub>2</sub>	−0.7954	attraction	Me–H	0.0281
Me–Me	0.4036	repulsion		

<sup>a</sup> See text.

the negatively charged N atoms and the negatively charged C<sub>H</sub> atoms. Another factor affecting the stability of the respective isomer is the weak electron donating CH<sub>3</sub> groups, which leads the charge redistribution in Cp-rings. As a result the C<sub>H</sub> atom becomes approximately 2–3 times more negative than the other four C atoms in the C<sub>5</sub>Me<sub>4</sub>H ring, and, consequently, the electrostatic repulsion between the N atoms and the C<sub>H</sub> atoms becomes larger. In the most stable isomer 56 these four atoms are located further away from each other, while in the less stable isomer 12 the two H atoms are at their closest distance from N<sub>2</sub> (Figure 2).

The relative stability of isomers of  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  could be also rationalized by counting the number of methyl–methyl, methyl–H, H–H, methyl–N<sub>2</sub>, and H–N<sub>2</sub> interactions in each of them. We formed the set of linear equations  $\sum c_i N_{ij} = \Delta E_j$ , where  $N_{ij}$  is the number of interactions of type (i) methyl–methyl, methyl–H, H–H, methyl–N<sub>2</sub>, and H–N<sub>2</sub>, respectively, in the  $j$ th monomer and  $\Delta E_j$  is its relative energy. In Table 2 we give the results of a least-squares fit for the coefficients  $c_i$ . As seen from this table, the largest contribution to the energy comes from the H–N<sub>2</sub> interaction, which mimics the electrostatic repulsion between the N atoms and the C<sub>H</sub> atom. As we showed above this C<sub>H</sub>–N repulsion directly affects the relative stability of the respective isomer (Figure 4(a)).

We would like to point out that in the case of C<sub>5</sub>H<sub>5</sub> or C<sub>5</sub>Me<sub>5</sub> ligands the five C atoms are equally charged, and the ligand has a zero dipole moment. However, in the case of the C<sub>5</sub>Me<sub>4</sub>H ligand, the weak electron donating methyl groups lead to a nonzero dipole moment. B3LYP/CEP-31G calculations of an individual C<sub>5</sub>Me<sub>4</sub>H ring show a dipole moment of 1.24 D. One may expect that the complex with C<sub>5</sub>Me<sub>4</sub>H ligands will be more polar and have different solubility than complexes with the nonpolar C<sub>5</sub>H<sub>5</sub> or C<sub>5</sub>Me<sub>5</sub> ligands.

The different orientation of the two H atoms leads to a different dipole moment of the  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  complexes. The fourth and eighth columns of Table 1 show the calculated dipole moments of the eight  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  isomers. The smallest dipole moment, 3.22 D, belongs to the most stable isomer 56. The highest-energy isomer 12 has the biggest dipole moment, 4.27 D. Interestingly, we found a direct relationship between the relative energies of the  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  monomers and their dipole moments (Figure 4(b)). The larger the dipole moment, the less stable is the monomer.

Calculated trends in the total dipole moment of the system can be explained by analyzing its components, the dipole moment of ZrN<sub>2</sub> fragment and the two dipole moments of the two Cp' rings. The dipole moment of the individual Cp' ring is oriented along the “special” C–H bond and points

**Table 3.** Relative Energy,  $\Delta E$ , Relative Electrostatic Repulsion between the N and C<sub>H</sub> Atoms,  $\Delta E_{\text{ES}}$ , and Relative Steric Repulsion,  $\Delta E_{\text{steric}}$ , of Different Isomers of  $(\text{Cp}'_2\text{Zr})_2(\mu^2,\eta^2,\eta^2\text{-N}_2)$ <sup>a</sup>

dimer	$\Delta E$	$\Delta E_{\text{ES}}$	$\Delta E_{\text{steric}}$	dimer	$\Delta E$	$\Delta E_{\text{ES}}$	$\Delta E_{\text{steric}}$
56–56	4.64	0.00	16.74	3''2–3''2	21.65	34.91	0
16–16	0.00	26.94	7.90	12–12	2.82	46.42	4.98
36–36	7.78	22.07	10.61	56–16	1.37	10.72	12.21

<sup>a</sup> All energies are in kcal/mol.

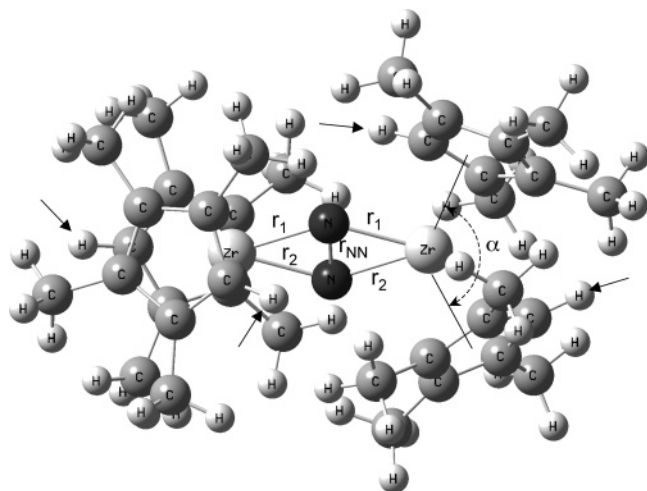
away from the H atom. The dipole moment of ZrN<sub>2</sub> is oriented toward the Zr atom. Thus, in the case of isomer 12 all three dipole moments add up, giving the largest dipole moment of all isomers. The two Cp' dipoles repel from the ZrN<sub>2</sub> dipole, and the isomer becomes the less stable. In the case of the isomer 56 the two Cp' dipoles are opposite to the ZrN<sub>2</sub> dipole, and the resulting total dipole moment is the smallest one among all eight structures. The attraction between the two Cp' dipoles and the ZrN<sub>2</sub> dipole makes isomer 56 the most stable  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  isomer.

To estimate the role of steric repulsion in the relative stability of different monomers, we calculated the UFF MM energy of the B3LYP/CEP-31G(d<sub>N</sub>) optimized structures. The results are given in the fourth and eighth columns of Table 1. As can be seen, the most stable structures 56 and 36 have the lowest steric repulsion. All other isomers have a 4.0–5.5 kcal/mol higher steric repulsion than the optimal structure 56. There is no direct relation between the steric repulsion of these structures and their relative energy. Therefore, we could conclude that in the case of  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  monomers, the steric repulsion does not play a critical role. The stability of the complex is determined predominantly by electronic effects (electrostatic and dipole–dipole interactions). The small barrier for the rotation of the Cp' rings allows the realization of the most favorable orientation.

**B.  $(\text{Cp}'_2\text{Zr})_2\text{N}_2$  Dimers.** The actual complex that was studied experimentally is the dinuclear  $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu^2,\eta^2,\eta^2\text{-N}_2)$  complex, **1**. To find the lowest-energy structure of this complex, it would be best if we could consider all possible orientations of the four Cp' rings. However, the number of possible isomers of the dimer is very large, and searching for all these is not practical. Therefore we decided to limit our study to the eight candidates, which are formed by two identical monomers, 56–56, 5''4–5''4, 16–16, 36–36, 5'2–5'2, 3''2–3''2, 3'2–3'2, and 12–12, where the dimer notation combines those of the two monomers. We considered only one “mixed” dimer, 56–16, formed by the lowest-energy monomer 56 and monomer 16, which corresponds to the experimental structure. We attempted to optimize all nine structures, but during the optimization some of them converged to other isomers. As a result, we obtained six different stable dimers, 56–56, 16–16, 36–36, 3''2–3''2, 12–12, and 56–16.

The relative energies of the investigated dimers are given in Table 3. As can be seen, isomer 16–16 has the lowest energy among all examined possibilities. This is in excellent agreement with the experimentally found structure of **1** (Figure 1a). Table 3 gives also the relative electrostatic repulsion between the two negatively charged N atoms and





**Figure 5.** Optimized structure of the 16–16 isomer of  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$ . The positions of the H atoms are indicated with arrows.

the four negatively charged  $\text{C}_\text{H}$  atoms,  $\Delta E_\text{ES}$ , calculated in analogy with the monomer case. As could be expected, the electrostatic interaction favors the 56–56 dimer, formed by the two optimal monomers 56. The 56–56 dimer has the lowest electrostatic repulsion among all investigated dimers. However, the lowest energy dimer 16–16 is not formed by two 56 units but by two 16 units. This is due to the fact that, while not crucial for the monomer case, the steric interactions play an important role in the dimer. In monomer 56 the two H atoms point away from the dinitrogen molecules. Thus, when two 56 units are combined together, four H atoms point away from  $\text{N}_2$ . The two 56 units “see” each other via their methyl groups, which leads to higher steric repulsion than that in the 16–16 dimer. In the 16–16 dimer, two of the H atoms point toward the  $\text{N}_2$  molecule and thus reduce the steric repulsion. We estimated the steric effect by performing the UFF MM calculation at the B3LYP/CEP-31G(d<sub>N</sub>) optimized geometry of each dimer. The results are shown in the fourth and eighth columns of Table 3. Indeed, isomer 16–16 has 8.84 kcal/mol lower steric repulsion than the electrostatically favored 56–56 dimer. On the other hand, steric interactions do not alone govern the stability of the dimer. Isomers 3’’2-3’’2 and 12–12 have the lowest steric repulsion, but they are 21.65 and 2.82 kcal/mol, respectively, less stable than the lowest-energy dimer 16–16. Thus one can conclude that the relative stability of the dimers is determined by the competition between the electrostatic effects and the steric repulsion.

Figure 5 presents the optimized structure of the most stable dimer 16–16. Our calculations show that this structure does not have an imaginary frequency. Table 4 compares some key geometrical parameters of structure 16–16 with the experimental results, with the definition of the parameters given in Figure 5. Calculations predict a slightly shorter Zr–N bond and a slightly longer N–N bond than the experiment. The calculated bite angle,  $\alpha_{\text{Cp}'-\text{Zr}-\text{Cp}'}$ , is very close to the experimental value. In general, calculated geometries are in very good agreement with their experimental values.

**Table 4.** Comparison of Experimental and B3LYP/CEP-31G(d<sub>N</sub>) Optimized Geometrical Parameters of Isomer 16–16 of  $(\text{Cp}'_2\text{Zr})(\mu^2, \eta^2, \eta^2\text{-N}_2)$  Complex, **1**<sup>a</sup>

	exptl <sup>5</sup>	calcd		exptl <sup>5</sup>	calcd
$r_1$	2.131	2.101	$r_\text{NN}$	1.377	1.404
$r_2$	2.119	2.114	$\alpha_{\text{Cp}'-\text{Zr}-\text{Cp}'}$	128.7	128.4

<sup>a</sup> Bond lengths in Å, angles in degrees. For definition of parameters see Figure 5.

## Conclusions

We have demonstrated that the stability of  $(\text{Cp}'_2\text{Zr})(\mu^2, \eta^2, \eta^2\text{-N}_2)$ ,  $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{H}$ , depends on competing electronic and steric factors. Examining all possible isomers of the  $(\text{Cp}'_2\text{Zr})(\eta^2\text{-N}_2)$  monomers, we have found a direct relationship between their relative energy and the electrostatic repulsion between the negatively charged N atoms of the  $\text{N}_2$  molecule and the negatively charged  $\text{C}_\text{H}$  atoms of the  $\text{Cp}'$  ring that are bound to H. Substitution of the H ligand by methyl groups significantly changes the charge distribution in cyclopentadienyl rings and increases the negative charge of the  $\text{C}_\text{H}$  atom and hence the electrostatic repulsion between the N atoms and the  $\text{C}_\text{H}$  atoms. As a result, the H to  $\text{CH}_3$  substitution significantly affects the relative stability of the studied isomers. This observation indicates that it would not be appropriate to use models where the methyl groups in cyclopentadienyl rings are treated with methods that do not account for electronic effects, like Molecular Mechanics. When two monomer units are combined together to form a dimer, the significance of steric factors increases and the minimal-energy structure is determined by a combination of electronic and steric factors.

**Acknowledgment.** We acknowledge Prof. P. J. Chirik for providing us with the experimental X-ray coordinates. D.Q. thanks the Ministerio de Educación y Ciencia of Spain for postdoctoral support. This work was supported in part by grant (CHE-0209660) from the U.S. National Science Foundation. Computer resources were provided in part by the Air Force Office of Scientific Research DURIP grant (FA9550-04-1-0321) as well as by the Cherry Emerson Center for Scientific Computation at Emory University.

**Supporting Information Available:** Cartesian coordinates of the lowest-energy structure of  $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu^2, \eta^2, \eta^2\text{-N}_2)$ , **1** (isomer 16–16) (Table S.1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, 200–202, 379–409. (b) *Catalytic Ammonia Synthesis*; Jennings, J. R., Ed.; Plenum: New York, 1991. (c) Fryzuk, M. D. *Nature* **2004**, 427, 498–499. (d) Shaver, M. P.; Fryzuk, M. D. *Adv. Synth. Catal.* **2003**, 345, 1061. (e) Schlögl, R. *Angew. Chem., Int. Ed.* **2003**, 42, 2004–2008. (f) Musaev, D. G. *J. Phys. Chem. B* **2004**, 108, 10012–10018. (g) Mori, M. *J. Organomet. Chem.* **2004**, 689, 4210–4227.
- (2) *Encyclopedia Britannica*; Encyclopedia Britannica Inc.: 1997.
- (3) Fryzuk, M. D.; Love, J. B.; S. J. Retting, S. J. *Science* **1997**, 275, 1445–1447.

- (4) (a) Basch, H.; Musaev, D. G.; Morokuma, K. *Organometallics* **2000**, *19*, 3393–3403. (b) Basch, H.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1999**, *121*, 5754–5761.
- (5) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527–529.
- (6) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229–6230.
- (7) Bobadova-Parvanova, P.; Wang, Q.; Morokuma, K.; Musaev, D. G. *Angew. Chem. Int. Ed.* **2005**, *44*, 7101–7103.
- (8) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (9) (a) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026–6033. (b) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612–615. (c) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555–5565.
- (10) *Gaussian 03, Revision C.01*; Frisch, M. J., et al. Gaussian, Inc.: Wallingford, CT, 2004.
- (11) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.
- (12) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, III, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.
- (13) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (b) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151–5158.

CT0502561