MINDO/3 Study of Cyclopentadienylidene and Its Insertion into Molecular Hydrogen

Him-Tai Tsang and Wai-Kee Li*

Department of Chemistry, The Chinese University of Hong Kong Shatin, N. T., Hong Kong

The lowest singlet and triplet states of cyclopentadienylidene (**1**) have been studied with the MINDO/3 method. It is found that the ground state of **1** is a spin triplet, which is supported by experimental finding and some previous calculations. The relationship between the geometrical and electronic structures for these states is also discussed.

In studying the least-motion and non-least-motion paths of the hydrogen insertion of **1**, it is found that the latter is preferred energetically. In addition, as in the cases of other similar carbene-hydrogen reactions, the concerted non-least-motion path consists of, in order, electrophilic and nucleophilic steps. However, for the present reaction, in order to distinguish the two steps, the charges on the hydrogens, rather than that on the carbenic center, should be monitored.

INTRODUCTION

Considerable theoretical and experimental interest has been devoted to the chemistry of saturated and unsaturated acyclic carbenes. However, studies on cyclic carbenes are still in infancy. Therefore theoretical studies of these species should be valuable for the understanding of their chemical nature. In this work, MINDO/3 calculations have been carried out on the cyclic carbene cyclopentadienylidene, **1**,

1

which has been generated by photolyzing diazocyclopentadienylidene in a solid medium, such as hexafluorobenzene or hexachlorobutadiene at 77⁰ or 4⁰ K.[1]

The purpose of this work is twofold: (i) to investigate the geometrical properties, electronic distribution, and relative energies of different spin states of **1**; (ii) to study the reaction path of the hydrogen insertion of **1**.

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* Author for correspondence.

Pertaining to (ii), both the non-least-motion (assuming no symmetry condition) and least-motion (assuming C_{2v} symmetry throughout) paths of the reaction have been studied.

METHOD OF CALCULATION

The molecular orbital model used in this study is the MINDO/3 method[2], which has been shown to yield reasonable heats of formation and equilibrium geometries for hydrocarbons. The calculations were carried out on the IBM 3031 computing systems at the Chinese University of Hong Kong.

Referring to the optimization process, in the calculations for the singlet and triplet structures of **1**, as well as for the least-motion hydrogen insertion of singlet **1**, C_{2v} symmetry was assumed throughout. For the non-least-motion reaction, no symmetry condition was imposed on the reacting system. Thus, the reacting hydrogen molecule could move freely to attack the carbenic center.

For each of the reaction paths, a two-dimensional energy contour map has been constructed. One of the reaction coordinate is $\bar{r}$, the mean C—H distance, or $\frac{1}{2}(C-H_a + C-H_b)$, where C is the carbenic carbon and H_a and H_b are the atoms of the reacting hydrogen molecule. The remaining reaction coordinate is the H_a-H_b separation. In constructing the contour maps, for different given H_a-H_b values, $\bar{r}$ was varied over a wide range, while all other structural parameters were optimized.

RESULTS AND DISCUSSION

Singlet and Triplet States of 1

The MINDO/3 optimized geometries, heats of formation, and formal charges for the lowest singlet and triplet states of **1** are summarized in Table I. In addition, for comparison, INDO results[3] are included in the table.

TABLE I

MINDO/3 Bond Lengths (Å) (C_1 is the carbenic center, which is bonded to C_2 and C_3; C_2 and C_3 are also bonded to C_4 and C_5, respectively), *Bond Angles (°), Heats of Formation (kcal/mol) and Formal Charges (electronic charge) for the Singlet (S_0) and Triplet (T_1) States of Cyclopentadienylidene (1). For Comparison, INDO Results are Given in Brackets.*

	S_0	T_1
C_1-C_2	1.50(1.35)	1.42(1.40)
C_2-C_4	1.35(1.43)	1.39(1.37)
C_4-C_5	1.51(1.42)	1.48(1.47)
C_2-H	1.10(1.10)	1.09(1.11)
C_4-H	1.10(1.11)	1.10(1.12)
$C_2-C_1-C_3$	104(154)	117(131)
$C_1-C_2-C_4$	110(78)	101(92)
$C_2-C_4-C_5$	108(115)	110(113)
C_1-C_2-H	123(146)	129(136)
C_2-C_4-H	130(123)	127(127)
ΔH_f	136	119
$\Delta E (T_1 - S_0)$		—17(73))
For the reaction of (singlet) $1 + H_2 \rightarrow C_5H_6$, $\Delta H = -97$ kcal/mol.		
C_1	0.028	0.062
C_2	—0.087	—0.094
C_4	0.074	0.037
H (bonded to C_2)	0.011	0.034
H (bonded to C_4)	—0.013	—0.008

Although INDO calculations predict a singlet ground state for **1**, MINDO/3 study reveals a triplet ground state. The latter is supported by experimental evidence and some previous calculations.

According to the EHMO calculation of Hoffmann[4], the LUMO of **1** has the correct symmetry to interact with the methylenic p_π orbital, while the lone pair p_σ orbital has also been stabilized by the bending at the carbenic center, with the p_σ orbital lying 0.13 eV below the delocalized p_π. This small splitting[5] leads to a triplet ground state for **1**.

Recently, Kausch and Dürr[6] have calculated the singlet-triplet separation of **1**, using EHMO and CNDO/2 methods. For both models, they have found a triplet ground state, with the singlet state being 0.53 eV (EHMO) and 0.36 eV (CNDO/2) higher in energy. However, it should be mentioned that geometry optimization was apparently not included in the calculations.

In 1964, Wasserman et al.[1] discovered that when diazocyclopentadienylidene was photolyzed in a solid medium, such as hexafluorobenzene or hexachlorobutadiene at 77° or 4° K, a triplet ESR spectrum was observed, which they attributed to the ground state of **1**. Analysis of the ESR spectrum revealed that the unpaired electron was in the π system and the other was localized in an in-plane orbital at C_1.

Examining the structure of **1** given in Table I, it is seen that, in the singlet state, since the lone pair lies in the molecular plane and there are four π electrons in the system, extensive delocalization of the π electrons is not expected. The single and double bonds are clearly discernible in this state. However, in the triplet state, with one electron in the p_π orbital of C_1, delocalization causes the five C—C bonds to have more similar lengths, and lower energy for the system. This delocalization effect is also apparent when the formal charges of **1** are examined. In the singlet state, C_1 has a charge of 0.03. In the triplet state, the lone electron in the p_π orbital of C_1 flows toward the π system of the diene, leading to a more positive charge, 0.06.

Additionally, it is worth noting that the INDO[3] and ab initio[7] calculations for the singlet state lead to a »cumulenic« structure for **1**:

In fact, the INDO results[3] indicate that, for the singlet state, the lone pair in **1** is located in the p_π orbital at C_1. Thus there are six π electrons around the ring and the system is aromatic. As a result, INDO preducts that the singlet state of **1** is much more stable than the triplet state.

Finally, it is pointed out that single determinant models sometimes overestimate the stability of triplet species as compared to their closed shell analogs. Hence, the MINDO/3 singlet-triplet separation reported in this work should be taken with this caution in mind. However, in view of the magnitude of this quantity (19 kcal/mol), taken together with the experimental evidence as well as the results of other calculations, it seems to be conclusive that the ground state of **1** is a spin triplet.

The Non-least-motion Hydrogen Insertion of **1**

The two-dimensional energy contour map for the reaction is shown in Figure 1.

For the region $\bar{r} > 2.5$ Å, there is only weak interaction between the reactants; the energy rises only by 2 kcal/mol in this range. The only significant change is the decrease of inserting angle α from 72^0 at $\bar{r} = 3.0$ Å to 34^0 at $\bar{r} = 2.5$ Å. [The inserting angle is the angle between the line joining the mid-point of H—H bond and the carbenic center and the line perpendicular to the (carbene) molecular plane through this center. Consult Figure 2, where $\alpha = 28^0$.]
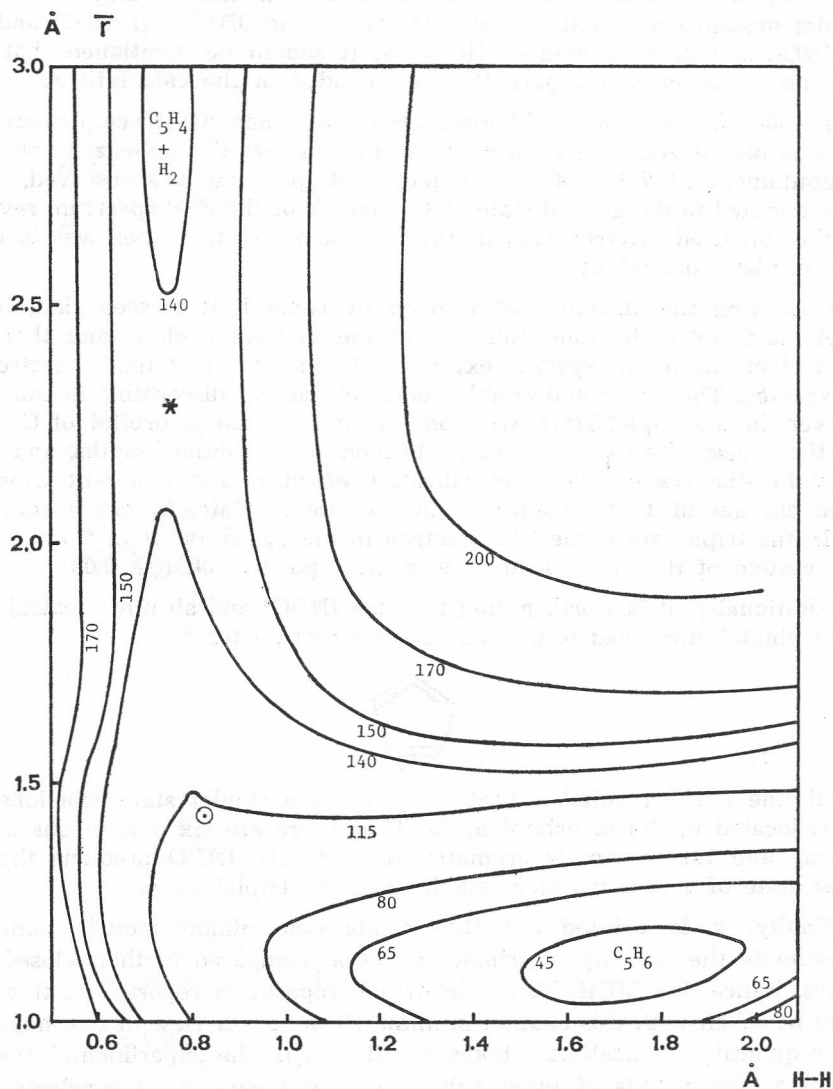

Figure 1. Energy (in kcal/mol) contour map for the non-least-motion reaction of **1** + H_2. The asterisk and ⊙ denote the saddle point and the turning point, respectively.
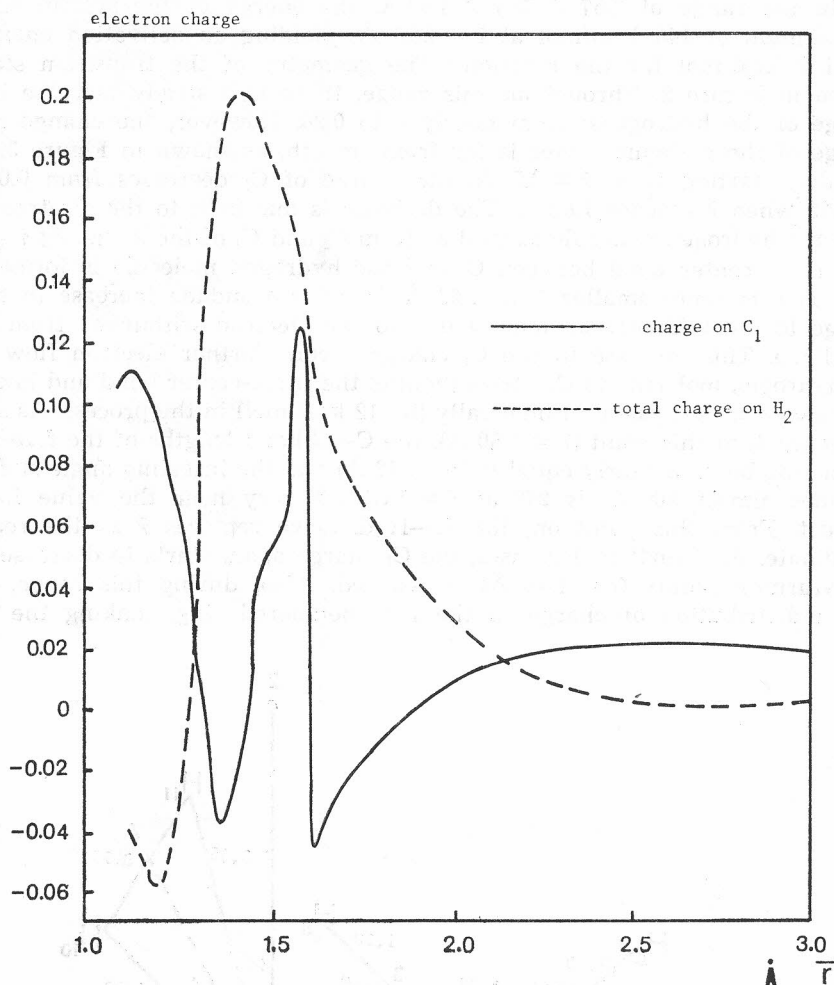
In the range of 2.57 Å $> \bar{r} >$ 1.44 Å, the energy of the system reaches a maximum of 140 kcal/mol at $\bar{r} = 2.25$ Å, yielding an activation energy of about 2 kcal/mol for the reaction.[8] The geometry of the transition state is shown in Figure 2. Throughout this range, there is a steady increase in the charge of the hydrogens: from nearly 0 to 0.20. However, the change in the charge of the carbenic center is far from smooth, as shown in Figure 3. Specifically, starting from $\bar{r} = 2.5$ Å, the charge of C_1 decreases from 0.019 to —0.045 when $\bar{r}$ reaches 1.62 Å. The decrease is due both to the electron flow from the hydrogen molecule as well as from C_2 and C_3 of the diene. At $\bar{r} = 1.62$ Å, a three-center bond between C_1 and the hydrogen molecule is formed. As soon as $\bar{r}$ becomes smaller than 1.62 Å, there is a sudden increase in the C_1 charge to 0.126 (Figure 3), mainly due to the electron withdrawl from C_1 to the diene. This increase in the C_1 charge favors further electron flow from the hydrogen molecule to C_1, strengthening the three-center bond and lowering the energy of the system dramatically (by 12 kcal/mol) in the process. As shown in Figure 4, at this point ($\bar{r} = 1.60$ Å), the C—C bond lengths of the five-membered ring become nearly equal (1.39—1.42 Å) and the inserting angle suddenly becomes almost 90⁰ (it is 27⁰ at $\bar{r} = 1.62$ Å), very near the value for the product. From this point on, the H—H distance replaces $\bar{r}$ as the reaction coordinate. As $\bar{r}$ further decreases, the C_1 charge again starts to decrease until the »turning point« ($\bar{r} = 1.44$ Å) is reached. Also, during this range, there is a redistribution of charge in the five-membered ring, making the diene

Figure 2. Geometry of the transition state for the non-least-motion reaction of $1 + H_2$. Distances are in Å.

Figure 3. Electron charge fluctuation for the non-least-motion reaction of *1* + H₂

system become distinguishable again. This concludes the electrophilic phase of the reaction.

When $\bar{r}$ becomes smaller than 1.44 Å, the nucleophilic phase begins. During this phase the lone pair of C_1 interacts with the σ^* orbital of H_2, making the H—H bond (H—H changes from 0.96 to 1.75 Å) and decreasing the charge of H_2. As far as the carbene is concerned, electron flows towards C_2 and C_3 from the other carbons, further defining the double bonds. The energy of the system decreases rapidly to that of the product.

The energy contour map for the H_2 insertion of **1** is very similar to those for the H_2 insertion of methylene[9,10] and of vinylidene[11]. They all have low activation energies and similar positions for the transition states and turning points. Early transition states for these reactions indicate that emptiness of the carbenic p_π orbitals and the electrophilicity of the carbenic centers.
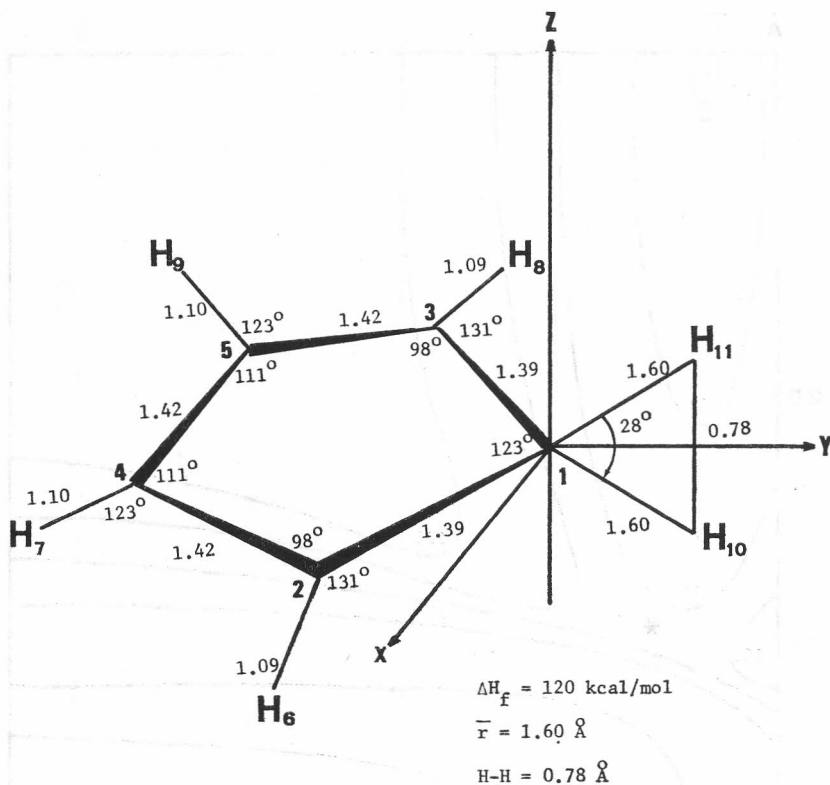
Figure 4. Geometry of the system after a rapid electron redistribution for the non-least-motion reaction of $1 + H_2$. Distances are in Å

However, the present reaction differs from other carbene-hydrogen reactions electronically. The conjugated diene π system in **1** serves as a reservoir for electron during the H_2 insertion. It leads to a complicated pattern of variation for the C_1 charge which is remarkably different from the other reactions. The fluctuation of the C_1 charge promotes the vacancy for the formation of strong $C-H_2$ three-center bonds. Besides, this fluctuation marks a sudden change of reaction coordinate, energy, electronic and geometrical structures.

The Least-motion Hydrogen Insertion of 1

In Figure 5, the two-dimensional contour map for $1 + H_2$ in C_{2v} symmetry is shown. As can be seen in the figure, the saddle point occurs in $\bar{r} = 1.55$ Å, $H-H = 0.80$ Å and the energy barrier is 37 kcal/mol, almost twenty times that of the non-least-motion path. On crossing the transition state, there is rapid fall in energy and great change in electronic distribution and geometry of the system.

Before $\bar{r} = 1.55$ Å, the carbenic center is losing electron to its neighbors. In spite of the flowing of electron from the H_2 σ bond, its charge becomes
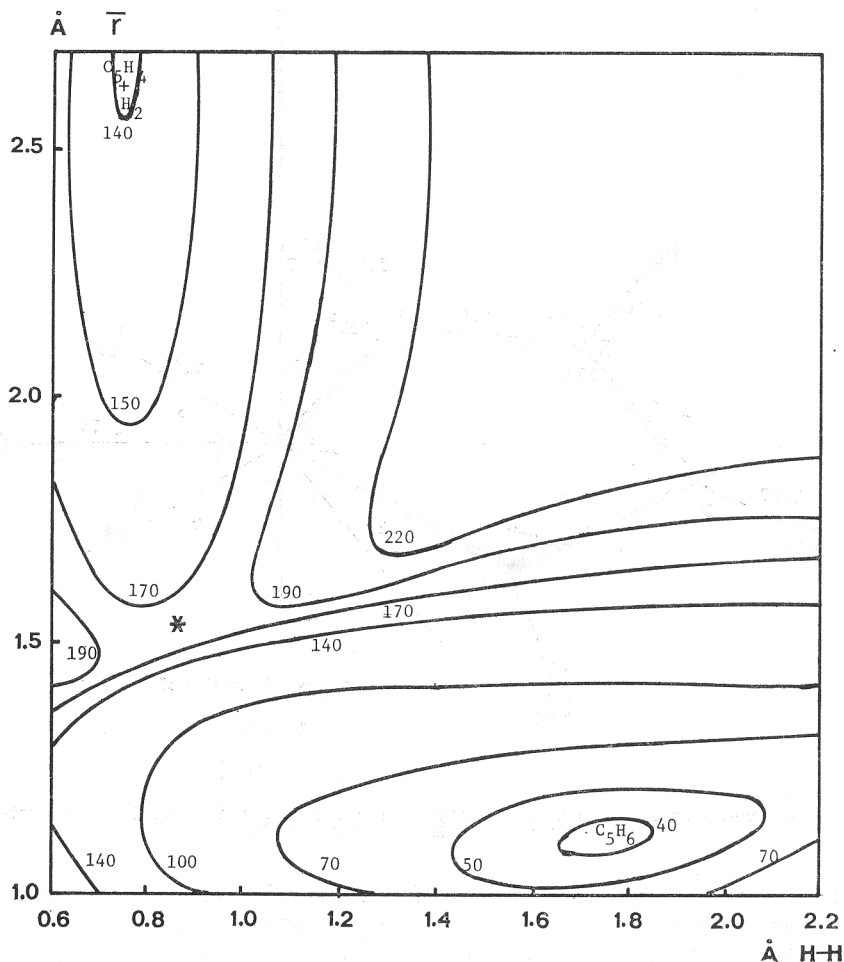
Figure 5. Energy (in kcal/mol) contour map for the least-motion reaction of $1 + H_2$. The asterisk denotes the saddle point.

more positive. Again, we can divide the reaction path into two phases in terms of the charge on H_2. In the first phase, electron flows from H_2 to the carbene. The flow is accelerated suddenly after the saddle point is reached. Within the carbene moiety, electron is first drawn from C_1 to the diene, then from the diene back to C_1. The second, nucleophilic phase begains at $\bar{r} = 1.46$ Å. In this phase, back-donating from the lone pair to σ^* of H_2 occurs and the H—H separation widens until the product is formed.

As in the non-least-motion reaction, the diene of 1 helps to accommodate electron from the p_π orbital of the carbenic center, which facilitates the approach of H_2 by enhancing the electron promotion from the lone pair to the empty p_π orbital. In the process, the redistribution of electrons localizes the two π bonds.

The geometry immediately after transition state is similar to that of the non-least-motion reaction. The five C—C bonds are of similar lengths, about 1.41 Å. The electrophilicity of the carbenic center contributes much to the formation of new C—H bonds.

CONCLUSION

The ground state of **1** is a spin triplet. In this state, delocalization of the π electrons is important; it constributes much for this state's stability over the singlet state. In the singlet state, the lone pair lies in the molecular plane and delocalization of the π electrons is negligible.

Referring to the non-least-motion hydrogen insertion of **1**, it is seen that reaction is a concerted process with two distinguishable steps. In the electrophilic phase, the H_2 molecule rises above the carbene molecular plane to attack the p_π orbital, forming a three-center bond. The system remains in this geometry until the rate-determining step is over. In the nucleophilic phase, at fairly small $\bar{r}$ values, the σ bond of H_2 is broken and the $H—C_1—H$ plane rotates to its final product arrangement. At the same time, back charge donation from the carbene lone pair to the H_2 σ^* orbital occurs, accompanied by a rapid fall in total energy. It is important to note that, in order to distinguish these two phases, the charges on the hydrogens, but not that on the carbenic center, should be monitored.

Due to the repulsions between the lone pair of carbenes and the H_2 σ bond, the least-motion path of the reaction involves much a higher activation energy. This study once again shows that reduction of symmetry allows interaction between the bonding orbital of H_2 and the p_π orbital of the carbenic center to occur, leading to a drastic lowering of the energy barrier. Thus the optimum reaction path avoids maximum symmetry and is determined by the topology of the orbitals involved.

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SAŽETAK

MINDO/3 studij ciklopentadienilidena i njegovog umetanja u molekulski vodik

Him-Tai Tsang i Wai-Kee Li

Pomoću MINDO/3 metode izračunane su molekulska i elektronska struktura najnižega singletnog i tripletnog stanja ciklopentadienilidena (1). Ista metoda primijenjena je zatim na ispitivanje mehanizma umetanja 1 u H—H vezu. Utvrđeno je da je tripletno stanje 1 stabilnije od singleta za 17 kcal/mol. Potencijalna ploha umetanja karbena 1 u vezu H—H izračunana je za reakcijski put koji uključuje minimalno gibanje atoma (least-motion reaction path) kao i za put u kojemu gibanje atoma nije ograničeno na minimum (non-least-motion reaction path). Rezultati su pokazali da je drugi put energijski povoljniji, što je u skladu s rezultatima prethodnih studija umetanja karbena u vezu H—H. Iscrpno su analizirane molekulske i elektronske strukture prijelaznih stanja za oba mehanizma, te promjene elektronske gustoće na karbenskom centru i pojedinim atomima vodika tijekom reakcije.