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Binding of Butadiene Molecules Mediated by Ni Atom and Ni^+ Ion

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Theoretical ab initio calculations based on density functional theory including gradient corrections have been performed to study the binding of *cis*- and *trans*-1,3-butadiene molecules mediated by Ni atom and Ni^+ ion. The geometries and dissociation energies are calculated to study the importance of Ni in the binding process. In the equilibrium geometry of Ni(butadiene) complex, the metal atom is found to position itself above the butadiene molecule and is bonded to all the carbon atoms in both the isomers of butadiene. The neutral and cationic $Ni(butadiene)_2$ complexes prefer three-dimensional structures with the Ni atom/ion sandwiched between the two butadiene molecules. This leads to the embedding of Ni atom or Ni^+ ion between the butadiene molecules during the binding process. The ground-state geometries of these complexes are stable against dissociation into smaller complexes, with Ni^+(butadiene) complex being the most stable one among all the complexes studied.

I. Introduction

The basic understanding of the interaction of metal atoms or clusters with hydrocarbons containing C═C double bonds is vital to organo-metallic chemistry as it may give valuable insight into the possibility of catalytic reactions. Hence, many investigations, both experimental and theoretical, have focused on studying the transition metal−unsaturated hydrocarbon complexes. Initially, IR and UV−visible spectroscopy[1,2] were employed to study the $Ni(C_2H_4)$ complexes, which predicted the presence of $Ni(C_2H_4)$, $Ni(C_2H_4)_2$, and $Ni(C_2H_4)_3$ complexes. Merle-Mejean et al.[3] employed Raman spectroscopy to study $Cu(C_2H_4)$ complexes. Later on, the same authors investigated the condensation of Ni atoms with butadiene (C_4H_6), ethylene (C_2H_4), and propylene in argon matrixes, using Raman, infrared, and UV−visible spectroscopy.[4] As a corollary of their experiment, they have proposed the possibility of formation of (i) $Ni_2(C_4H_6)$ complex, in which the Ni atoms are on either side of the *trans*-C_4H_6 molecule; (ii) $Ni(C_4H_6)_2$ complex, where the Ni atom is surrounded by two butadiene molecules, and (iii) $Ni(C_4H_6)$ complex. However, the authors have noted that the exact structures of these complexes could not be identified. Theoretical calculations on Ni−butadiene complex are limited. A semiempirical calculation on $Ni(C_4H_6)$ complex,[5] and a DFT-based calculation[6] on Ni interaction with ethylene, and butadienes have been reported previously. In the DFT-based investigation,[6] only $Ni(C_4H_6)$ and $Ni^{2+}(C_4H_6)$ complexes were taken into account. To our knowledge, no systematic calculations exist on larger complexes of $Ni(C_4H_6)$, in which the equilibrium geometries and the nature of chemical bonds between the metal atom and butadiene are analyzed. A recent gas-phase experimental study[7] has been able to produce a polymer formed out of butadiene molecules interspersed with Ni atoms and small Ni clusters. Motivated by all of these we have initiated a systematic theoretical study to investigate the equilibrium geometries and relative stabilities of $Ni_m(C_4H_6)_n$ and $Ni_m^+(C_4H_6)_n$ complexes. The focus of our work is to find out how many Ni atoms/ions it takes to bind the butadiene molecules together and to see at what point the binding begins. We also plan to examine if the binding prefers to continue in one, two, or three dimensions. In this paper, we present the results of Ni atom and Ni^+ ion interacting with up to two butadiene molecules.

The paper is organized as follows. The computational method employed in this work is discussed briefly in the next section. In Section III, the equilibrium geometries and dissociation energies of nickel−butadiene complexes are discussed. Finally, we summarize our results in Section IV.

II. Computational Procedure

The geometry optimization calculations were carried out using Density Functional Theory (DFT) including gradient corrections with the Gaussian98[8] software. The gradient corrected exchange functional due to Becke[9] combined with gradient corrected Perdew−Wang[10] correlation functional (referred to as BPW91) and a triple-ζ basis set (6-311G**) were employed for all the calculations. The geometry optimization was performed without any symmetry constraints. The reliability of the theoretical method and the basis set for systems containing transition metals and organic molecules have been confirmed in our previous calculations[11−13] of $Ni_n(Bz)_m$ and $V_n(Bz)_m$ complexes. The electron affinities, ionization potentials, and dissociation energies of these complexes, based on BPW91, agreed very well with the experiments and previous theoretical works.

III. Results and Discussions

A. Geometries. *1,3-Butadiene.* Two structural isomers of 1,3-butadiene (C_4H_6) are considered in this study, namely, *cis*-butadiene and *trans*-butadiene. Figure 1 shows the equilibrium geometries of these two forms of butadiene molecule as obtained

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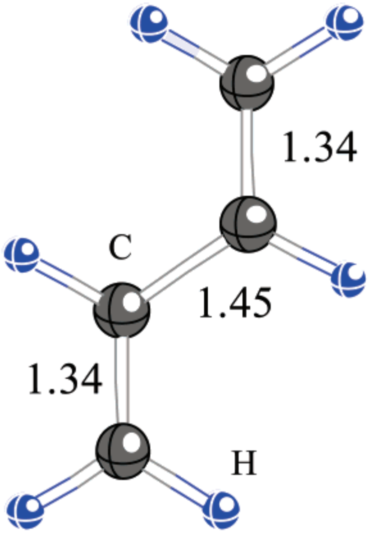
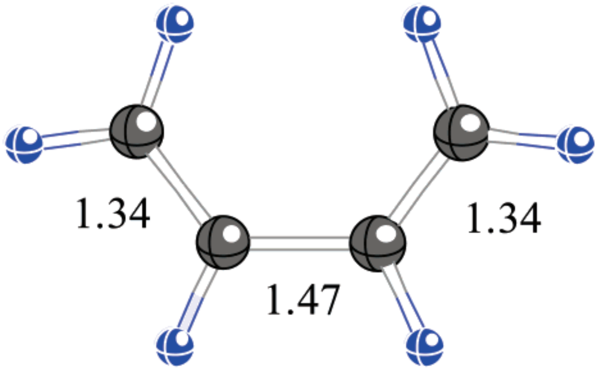


Trans



Cis

Figure 1. Ground-state geometries of trans and cis forms of butadiene. The bond lengths are given in angstroms (Å). The shorter bonds are considered double bonds.

in our calculations. In these two forms, there exist two $C{=}C$ double bonds and one $C-C$ single bond. The *terminal* or the outer C atoms (C_t) form double bond (1.347 Å in *trans*- and 1.346 Å in *cis*-) with their corresponding inner C atoms (C_i) whereas the inner C atoms are bonded to each other by a single bond (1.455 Å in *trans*- and 1.470 Å in *cis*-). As seen in Figure 1, the calculated geometrical parameters are in very good agreement with the corresponding experimental data[14] with the $C{=}C$ and $C-C$ bond lengths being 1.349 Å and 1.467 Å, respectively. The trans and cis forms are energetically nearly degenerate with *trans*-butadiene being only 0.17 eV lower in energy than the *cis*-butadiene. Hence, both cis and trans forms are equally probable candidates for the binding process. It is expected that one or both of the double bonds of butadiene will break during the interaction with Ni, and these dangling bonds will recombine with other available broken bonds of nearby butadiene molecules leading to binding. The binding energy per bond in butadiene is 3.97 eV, and breaking of these bonds is expensive and is not expected to happen automatically. This process must be mediated by interaction with Ni atoms/ions.

Ni(butadiene). In the Ni(C_4H_6) complex, the Ni atom has a wide variety of choices where it can insert into the butadiene molecule. Hence, for each form of the butadiene molecule, there exist quite a few initial structural configurations as possible candidates for the geometry optimization. Figure 2 shows the butadiene with different possible positions of the Ni atom/ion that were used as initial geometries for geometry optimization. These include the Ni atom placed in the plane of the butadiene, directly above the plane of butadiene, and on top of the $C-C$ single and double bonds. Some starting positions lead to the same final optimized structure while some others lead to different isomers.

In Figure 3, we present the ground-state geometries of neutral Ni(*trans*-C_4H_6) and Ni(*cis*-C_4H_6) complexes. When a Ni atom is brought near a *trans*-butadiene molecule, the Ni atom prefers to bond with all the four carbon atoms of the butadiene, thereby distorting its planar configuration. This Ni(*trans*-C_4H_6) complex is termed as η^4-trans structure. In the case of Ni(*cis*-C_4H_6) complex, the ground-state geometry is a η^2-cis complex characterized by the bonding of Ni atom to the *terminal* carbon atoms (C_t) of the *cis*-butadiene. In this configuration, the Ni atom and all the four carbon atoms of the *cis*-butadiene are in the same plane. Energetically, the η^4-trans complex is 0.24 eV more stable than the ground-state geometry of Ni(*cis*-C_4H_6) complex. Hence, the addition of Ni atom to the butadiene molecule increases the energy difference between the trans and cis forms from 0.17 to 0.24 eV. In addition, there are some significant changes observed in the geometric parameters of both *trans*- and *cis*-butadiene because of their interaction with the Ni atom. In the η^4-trans structure, the bonding of Ni atom with the four carbon atoms of butadiene is accompanied by the elongation of the C_t-C_i bonds from 1.34 Å (free *trans*-C_4H_6) to 1.44 Å, thereby resulting in the breaking of these double bonds. At the same time, the C_i-C_i single bond is elongated by 0.03 Å. Thus, the interaction of the Ni atom with the *trans*-butadiene has resulted in weakening of the $C-C$ bonds in the butadiene molecule. In the case of η^2-cis structure, this weakening is more pronounced with the C_t-C_i bond length increasing from 1.34 Å (free *cis*-C_4H_6) to 1.50 Å. However, in this complex, the C_i-C_i bond length has decreased from 1.47 Å (free *cis*-C_4H_6) to 1.34 Å, thus forming a double bond between the two *inner* C atoms. This difference between the *cis*-butadiene and *trans*-butadiene can be explained by taking into consideration the two different scenarios of the Ni−butadiene bonding. In the trans form the Ni atom is forming a bond with all four carbon atoms, thus weakening all the $C-C$ bonds, whereas in the cis form the Ni atom is bonded only with the two terminal C atoms (C_t), thus leaving the two inner carbon atoms almost free to form a C_2 dimer.

We have also studied the equilibrium geometries of four higher-energy isomers of Ni(C_4H_6) complexes—two corresponding to Ni(*trans*-C_4H_6) and the other two corresponding to Ni(*cis*-C_4H_6) complex. The equilibrium geometries of these isomers along with their energies relative to the ground-state η^4-trans complex are given in Figure 4. In the higher energy isomers of Ni(*trans*-C_4H_6) complexes, the Ni atom either inserts into the $C-H$ bond of butadiene ($\Delta E = 1.27$ eV) or attaches to one of the $C{=}C$ double bonds ($\Delta E = 0.37$ eV). In the case of the first isomer, the $C-C$ bonds remained unaffected, whereas in the latter case the attaching of Ni to the $C{=}C$ double bond resulted in breaking of the corresponding double bond, leaving the remaining $C-C$ bonds unaffected. This latter isomer can be termed as an η^2-trans complex. In the case of Ni(*cis*-C_4H_6) complex, the η^4-cis complex is 0.40 eV higher in energy than

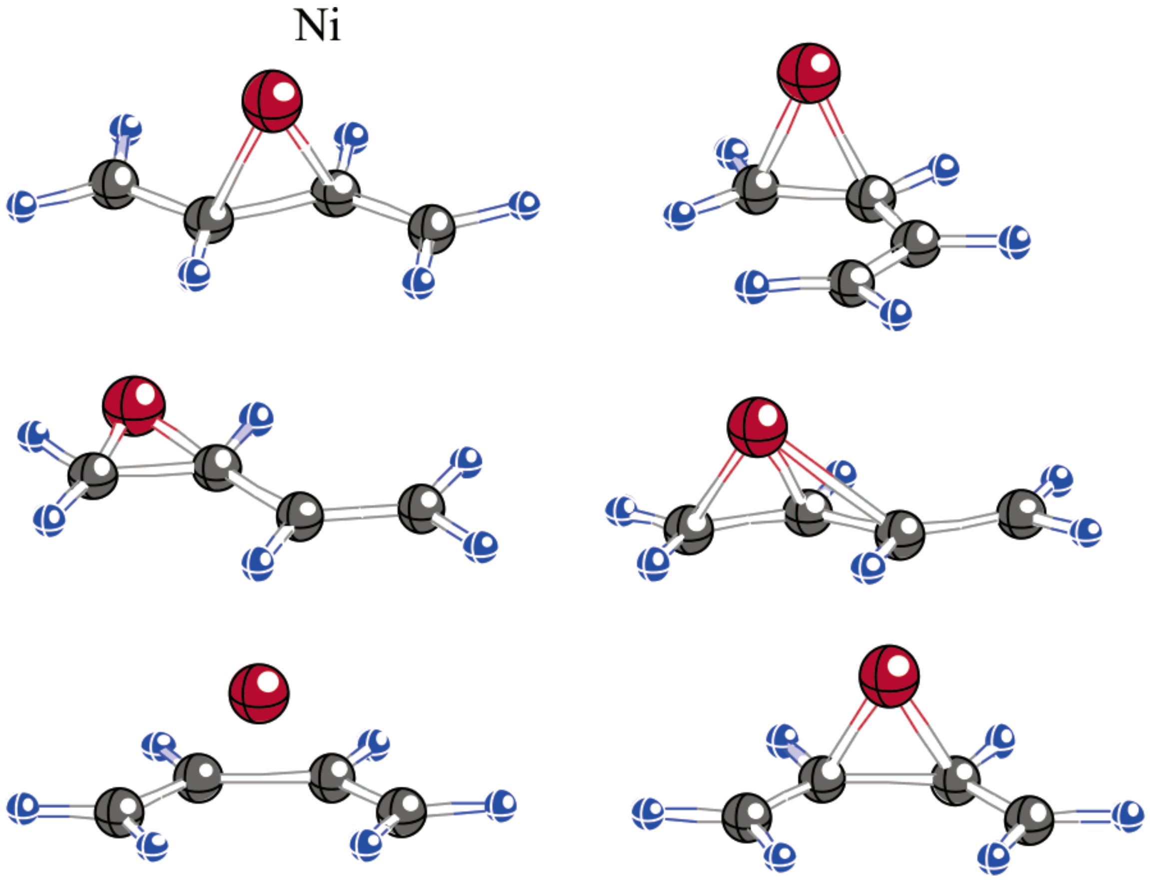


Figure 2. The possible start-up geometries for Ni(butadiene) complex.

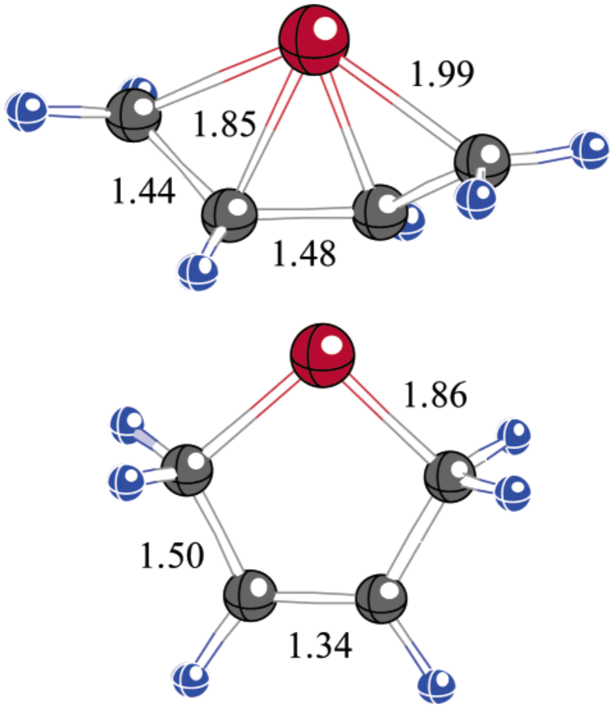


Figure 3. Ground-state geometries of neutral Ni(*trans*-butadiene) and Ni(*cis*-butadiene) complexes. Bond lengths are given in angstroms (Å).

the ground-state Ni(C_4H_6) complex. The attachment of the Ni atom to the C−C double bond of *cis*-C_4H_6 also resulted in a higher-energy isomer, with $\Delta E = 0.46$ eV, when compared to the ground-state Ni(C_4H_6). This isomer can also be termed as an η^2-cis complex. To summarize, the relative stabilities of various isomers of neutral Ni(C_4H_6) complex are given as η^4-trans < η^2-cis < η^2-trans < η^4-cis.

A previous theoretical study[6] based on B3LYP reported the relative stabilities of the Ni(C_4H_6) complex as η^2-trans < η^4-trans < η^2-cis < η^4-cis. However, in this work,[6] the energy difference between the η^4-trans and η^2-trans complexes was reported to be 0.3 kcal/mol (0.013 eV). Therefore, the authors, in their paper, commented that in view of the computational accuracy and incompleteness of basis sets, they are not sure of the ground-state geometry of Ni(C_4H_6) complex. The disagreement between our calculated relative stabilities and those of the reported ones can be attributed to the low energy differences between the various isomers and the different functional forms for the exchange-correlation energy and basis set employed in the current calculation. To assess the accuracy of our reported results, we have performed geometry optimization of the Ni(C_4H_6) using a much larger/better basis set (6-311+G**) than in the previous calculation.[6] The relative stabilities corresponding to the 6-311+G** basis set are as follows: η^4-trans < η^2-trans < η^2-cis < η^4-cis, with an energy difference of 0.15 eV between η^4-trans and η^2-trans complexes. Hence, it is observed that though there is a change in the relative stabilities, the ground-state geometry of the Ni(C_4H_6), obtained in our calculations, has remained unaffected by the choice of basis set. Therefore, on the basis of this observation, we conclude that the disagreement between our calculated results and the previous calculations[6] can be attributed to the choice of the energy functionals and to a lesser degree on the choice of different basis sets. The structural parameters of the η^4-trans and η^2-trans complexes obtained from our calculations are in good agreement with the previous calculations. The geometric parameters of η^2-cis structure (which is 0.46 eV higher in energy

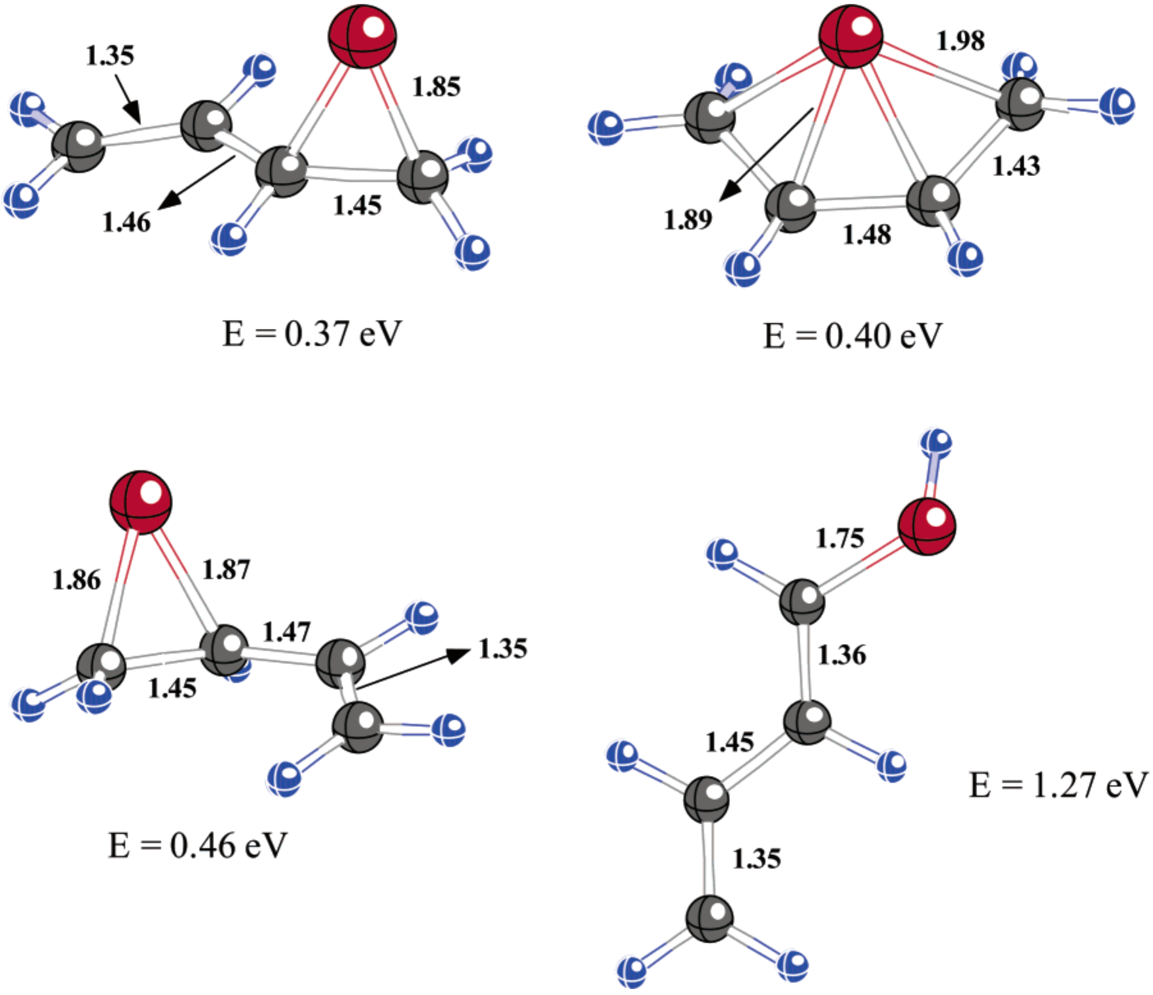


Figure 4. Equilibrium geometries of higher-energy isomers of neutral Ni(C_4H_6) complex. Energies are measured with respect to the ground-state geometry, η^4-trans structure given in Figure 3.

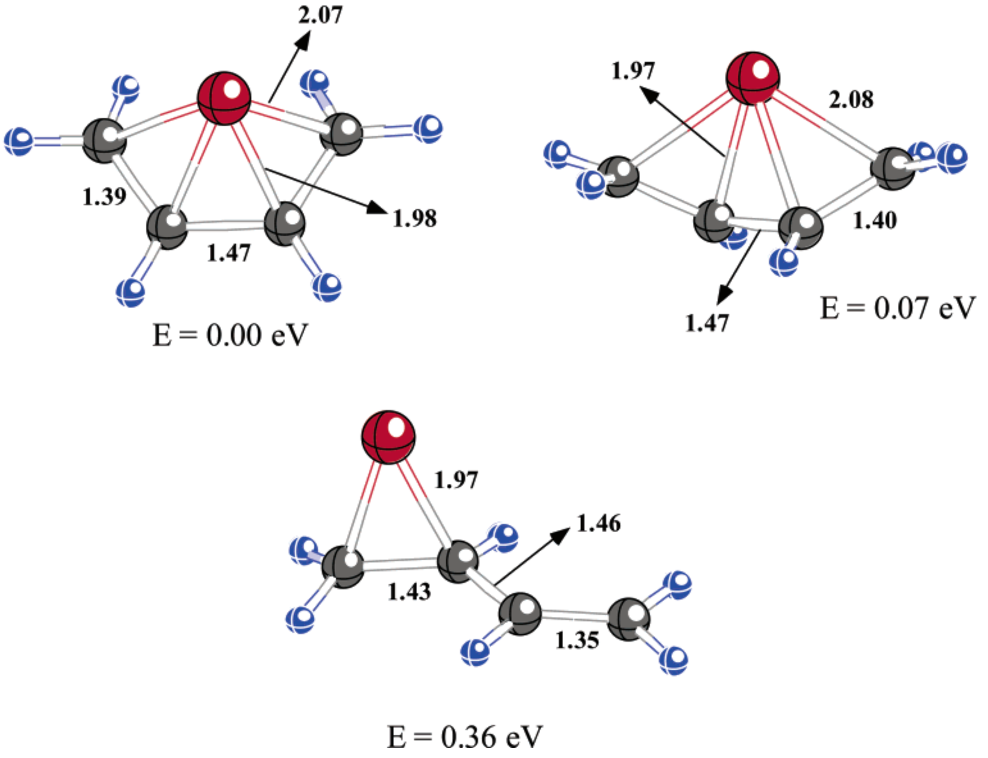


Figure 5. Equilibrium geometries of ground-state and higher-energy isomers of cationic $Ni^+(C_4H_6)$ complex.

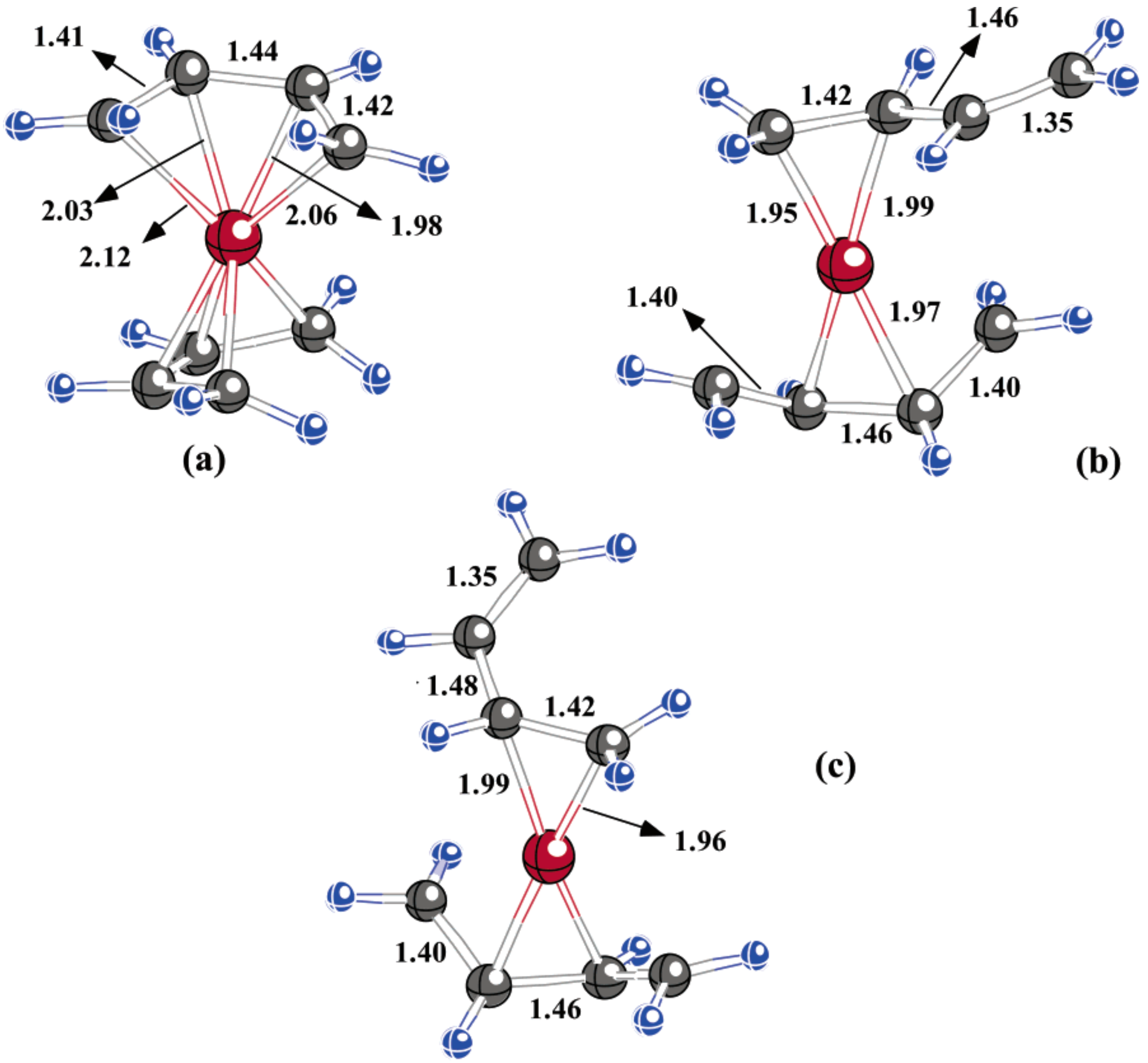


Figure 6. The equilibrium geometries of the three lowest-energy $Ni(C_4H_6)_2$ complexes.

than the ground-state $Ni(C_4H_6)$) are also in good agreement with the previously reported results.

In the cationic $Ni^+(C_4H_6)$ complex, only three equilibrium structures are found to be stable (See Figure 5). The ground-state geometry of $Ni^+(C_4H_6)$ is a η^4-cis structure, whereas the η^4-trans, the ground-state geometry in the neutral system, is energetically degenerate ($\Delta E = 0.07$ eV) with the η^4-cis structure. The η^2-cis structure could not be found in the cationic $Ni^+(C_4H_6)$ complex. The η^2-trans structure is more unstable by 0.36 eV, than the ground-state η^4-*cis* structure.

Ni(butadiene)$_2$. To check the binding of butadiene in the presence of Ni atom or Ni^+ ions, we have added the second butadiene molecule to the equilibrium geometries of various $Ni(C_4H_6)$ isomers. This second butadiene molecule can be either a cis or trans form. Hence, for a $Ni(C_4H_6)_2$ complex, we can have either Ni(*trans*-$C_4H_6)_2$, or Ni(*cis*-$C_4H_6)_2$ or a combination of *cis*- and *trans*-butadiene: *trans*-C_4H_6−Ni−*cis*-C_4H_6 as possible structures. Moreover, these butadienes can be in a chain or stacked above one another with Ni/Ni^+ in between. This leads to a large number of starting geometries that one must consider. Hence, based on the above-mentioned initial combinations, we have optimized the structure of Ni(butadiene)$_2$ and Ni^+(butadiene)$_2$ without any symmetry constraints.

The optimized geometries of the lowest energy $Ni(C_4H_6)_2$ complex, in each of the above-mentioned combination, are given in Figure 6. Of the three given geometries, the Ni(*cis*-$C_4H_6)_2$ complex is lowest in energy (Figure 6(a)). The Ni(*trans*-$C_4H_6)_2$ complex is energetically almost degenerate, with an energy difference of 0.08 eV. The $Ni(C_4H_6)_2$ complex containing both the forms of butadiene, namely, *trans*-C_4H_6)−Ni−*cis*-C_4H_6, is about 0.17 eV higher in energy than the Ni(*cis*-$C_4H_6)_2$ complex. Hence, for the neutral $Ni(C_4H_6)_2$ complex, the combination of *cis*-butadiene−Ni−*cis*-butadiene is preferred over other combinations. The ground-state geometry of neutral $Ni(C_4H_6)_2$ is characterized by two *cis*-butadiene molecules, one on top of the other, with the Ni atom sandwiched between them. In addition, the bottom *cis*-butadiene molecule is rotated with respect to the top one. In fact, in the initial geometry of this configuration, the butadiene molecules were facing in opposite directions to each other. Hence, it is a geometry optimization-induced rotation.

In the ground-state geometry of $Ni(C_4H_6)_2$ complex (Figure 6(a)), the Ni atom sandwiched between the two *cis*-butadiene molecules is bonded to all the eight carbon atoms available to it. Because of this Ni−C bonding, the C═C double bond is considerably weakened, whereas the C−C single bond is shortened by about 0.025 Å, with respect to their corresponding C−C bond lengths in the free *cis*-butadiene molecule (See Figure 1). The weakening of the C═C double bond is due to the charge transfer from Ni atom to the carbon atoms of the butadiene. The Mulliken charge analysis showed that Ni atom has a positive charge of 1.02*e*, the outer/terminal carbon atoms

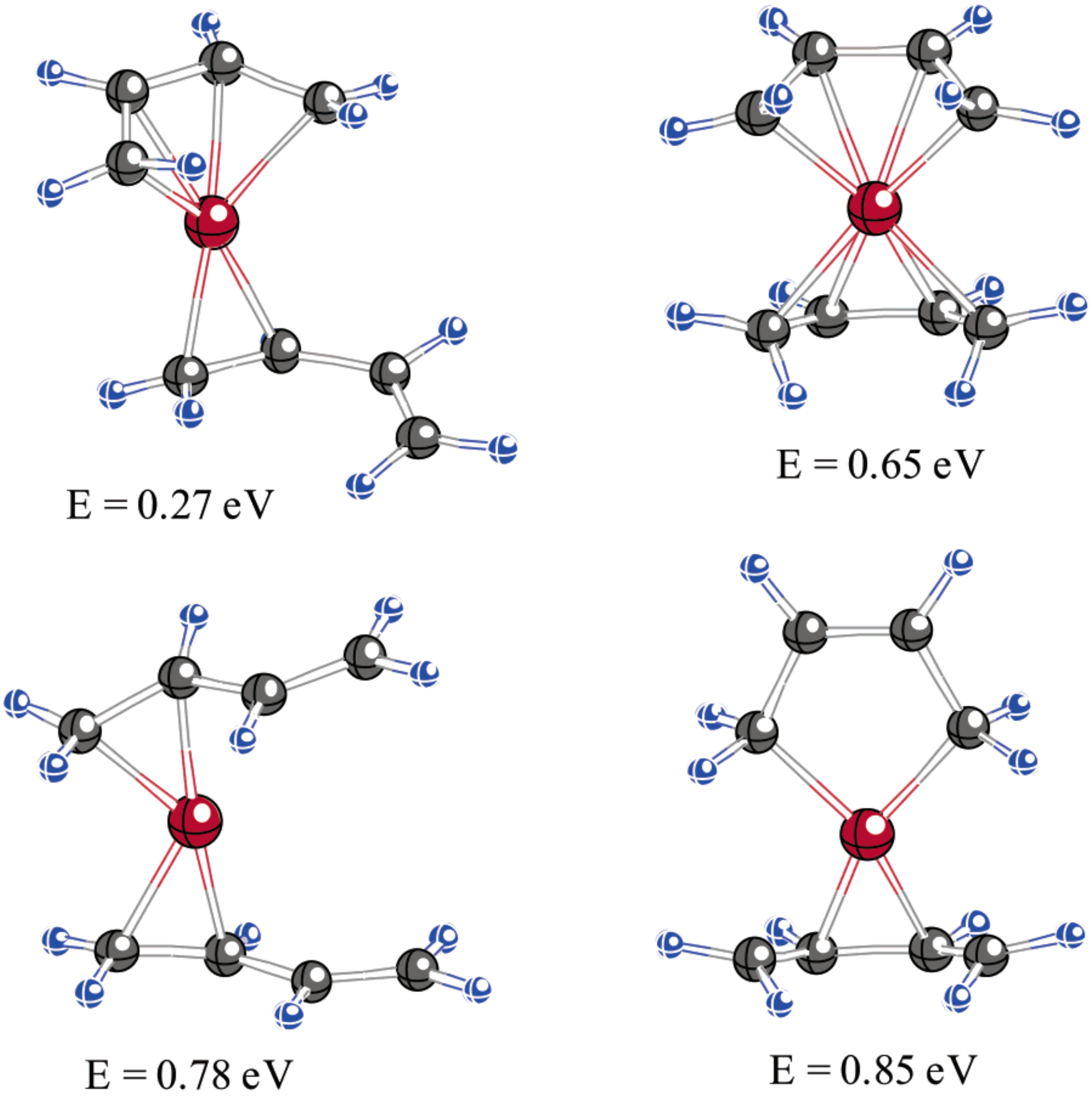


Figure 7. Equilibrium geometries of higher-energy isomers of neutral Ni(C_4H_6)$_2$ complex. Energies are measured with respect to the ground-state geometry (Figure 6(a)).

each has a charge of $-0.44e$, and inner carbon atoms have $-0.22e$; whereas in the free butadiene molecule the corresponding charges on the carbon atoms are $-0.20e$ and $-0.13e$, respectively. Hence, this charge transfer from the Ni atom to the butadiene always results in lengthening of the C═C double bond.

We have also studied the equilibrium geometry of the energetically nearly degenerate Ni(*trans*-C_4H_6)$_2$ complex (See Figure 6(b)). In this configuration, the Ni atom is located on top of the carbon−carbon (C_i−C_i) single bond of a distorted butadiene molecule. The second butadiene molecule is slid on top of the Ni atom in such a way that the metal atom is just below one of its C═C double bond. In addition, similar to that seen in the ground-state geometry, the top butadiene molecule was rotated upon geometry optimization. However, unlike in the ground-state geometry, here in the Ni(*trans*-C_4H_6)$_2$ configuration, the metal atom is bonded only to two carbon atoms from each of the butadiene molecules: the two inner carbon atoms (C_i) of the bottom butadiene, and to the C_t and C_i atoms of the upper butadiene molecule. In the upper butadiene, the two carbon atoms which are not interacting with the metal atom maintain the C═C double bond between them, whereas the other C═C double bond is broken because of the Ni−C bond. The interaction of Ni atom with the bottom butadiene did not result in any significant change to the C−C single bond distance, however the C═C double bonds were elongated by 0.055 Å, with respect to the corresponding bond distances in the free *trans*-butadiene. The weakening of the C═C double bond is again attributed to the charge transfer from the metal atom to the carbon atoms. The equilibrium geometries of some of the higher energy isomers of neutral Ni(C_4H_6)$_2$ are given in Figure 7. The relative energies of these isomers with respect to the ground-state Ni(*cis*-C_4H_6)$_2$ complex are also listed in Figure 7.

The ground-state geometry of cationic Ni$^+$(C_4H_6)$_2$ complex is also a Ni(*cis*-C_4H_6)$_2$ sandwich structure (Figure 8), with the bottom butadiene rotated with respect to the top one. The Ni−C bond lengths in this cationic complex are elongated when compared to the corresponding Ni−C bond lengths in the ground-state geometry of the neutral complex. Here, the Ni atom is bonded only to three carbon atoms from each of the butadiene molecules. In addition, the C═C double bond distances in the cationic complex are shortened when compared to that in the neutral complex. The elongation of the Ni−C bond and shortening of the C═C double bond in the cationic complex is

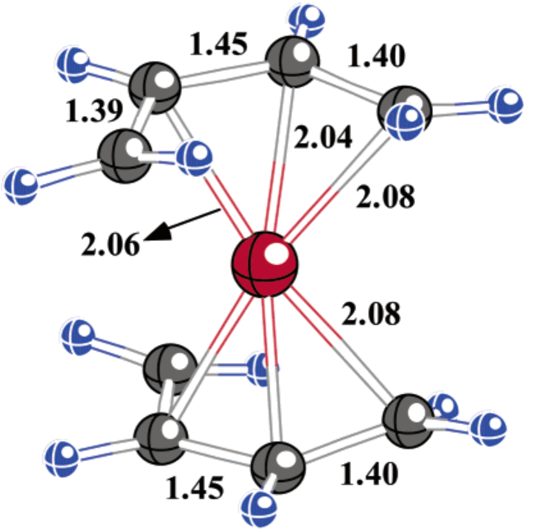


Figure 8. The ground-state geometry of cationic $Ni^+(C_4H_6)_2$ complex. Bond lengths are given in angstroms (Å).

an indication of decreasing Ni−butadiene interaction, thus a measure of the instability of $Ni^+(C_4H_6)_2$ when compared to the neutral complex. In fact, the calculations of the dissociation energies of these two complexes revealed that the neutral $Ni(C_4H_6)_2$ is more stable than the cationic $Ni^+(C_4H_6)_2$ complex (see next section for discussion). The other higher-energy isomers of the cationic complexes are collected in Figure 9. The cationic *trans*-C_4H_6−Ni−cis-C_4H_6 complex is 0.15 eV higher in energy than the ground-state Ni^+(*cis*-C_4H_6)$_2$ complex, whereas the Ni^+(*trans*-C_4H_6)$_2$ is 0.28 eV higher in energy.

TABLE 1: Dissociation Energies (eV) of Neutral and Cationic Ni(butadiene)$_n$ (n = 1, 2) Complexes along Various Dissociation Paths

complex	dissociation path	dissociation energy (eV)
$Ni(C_4H_6)$	$Ni + C_4H_6$	2.38
$Ni^+(C_4H_6)$	$Ni^+ + C_4H_6$	4.00
	$Ni + (C_4H_6)^+$	4.82
$Ni(C_4H_6)_2$	$Ni + 2(C_4H_6)$	5.68
	$Ni(C_4H_6) + C_4H_6$	3.36
	$Ni + (C_4H_6)_2$	4.22
$Ni^+(C_4H_6)_2$	$Ni^+ + 2(C_4H_6)$	6.89
	$Ni^+(C_4H_6) + C_4H_6$	2.89
	$Ni(C_4H_6) + (C_4H_6)^+$	5.40
	$Ni^+ + (C_4H_6)_2$	5.38

It is to be noted here that $Ni(C_4H_6)_2$ complex prefers a three-dimensional structure, with one of the butadiene molecules on top of the other. We have also considered few planar configurations in which the two butadiene molecules are in the same plane and either facing each other or adjacent to each other. Upon optimization, these planar structures became perfect three-dimensional structures, with the metal atom located between the two butadiene molecules.

B. Dissociation Energies. We now turn to the most interesting aspect of this study, namely, the stability of $Ni(C_4H_6)_n$ complexes. The stability of the ground-state geometries of neutral and cationic $Ni(C_4H_6)_n$ (n = 1, 2) complexes are assessed by calculating fragmentation/dissociation energies for different dissociation pathways. The dissociation energies of neutral and cationic $Ni(C_4H_6)_n$ via different pathways are collected in Table 1. The dissociation of these complexes into smaller molecules/complexes always resulted in a positive energy, i.e., the reaction

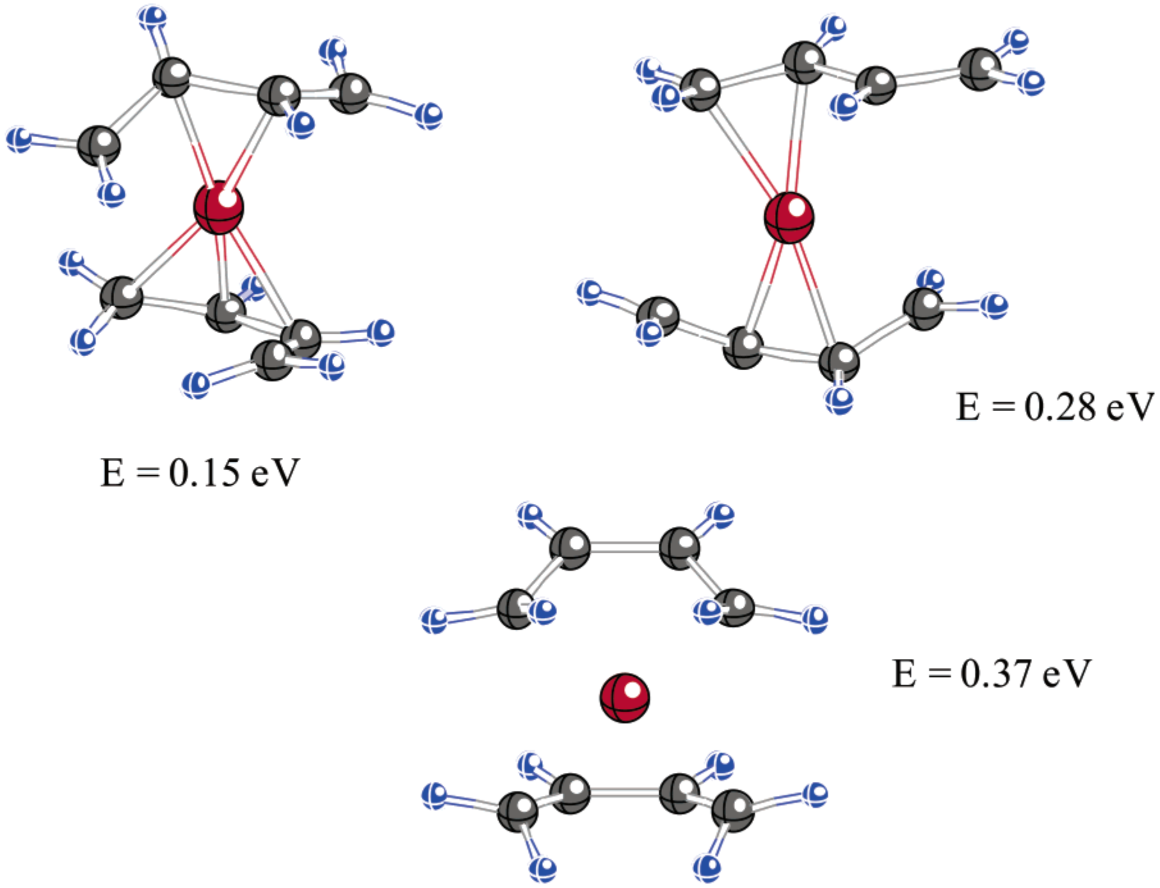


Figure 9. Equilibrium geometries of higher-energy isomers of cationic $Ni^+(C_4H_6)_2$ complex. Energies are measured with respect to the ground-state geometry, given in Figure 8.

pathways are endothermic, making the $Ni(C_4H_6)_2$ complexes stable against dissociation.

The dissociation of $Ni(C_4H_6)$ and $Ni^+(C_4H_6)$ complexes into corresponding metal atom/ion and butadiene molecule require 2.38 and 4.00 eV of energies, respectively. Hence, the Ni^+ ion is more strongly bound to the butadiene molecule than Ni atom to butadiene. For neutral and cationic $Ni(C_4H_6)_2$ complexes, different dissociation channels are considered. In neutral $Ni(C_4H_6)_2$, dissociation into butadiene molecule and $Ni(C_4H_6)$ complex is preferred, whereas in the cationic complex, dissociation leading to $Ni^+(C_4H_6)$ and butadiene molecule is the preferred path. The dissociation of cationic $Ni^+(C_4H_6)_2$ into smaller complexes requires less energy than the dissociation of neutral $Ni(C_4H_6)_2$ complex. This is because $Ni^+(C_4H_6)$ is more stable than $Ni(C_4H_6)$. It is interesting to note that the dissociation of (*cis*-butadiene)$_2$ into individual *cis*-butadiene molecules requires energy of 1.46 eV (calculated at BPW91/6-311G** level); whereas, the energy required to break the neutral/cationic $Ni(C_4H_6)_2$ complex into Ni atom/Ni^+ ion and individual butadiene molecules is calculated to be 5.68 eV/6.89 eV (See Table 1). Therefore, it is clearly seen that the Ni/Ni^+-embedded (butadiene)$_2$ complex is more stable than free (butadiene)$_2$ complex. Hence, embedding of Ni atom or Ni^+ ion between the butadiene molecules is helpful in forming a more stable complex. By examining the lowest energy dissociation pathway for each of the complexes under study, it is concluded that the cationic $Ni^+(C_4H_6)$ complex is more stable than any other complex. In fact, this cationic complex can form a building block in the binding of butadiene. Thus further theoretical study to test the stability of $[Ni_m{}^+(C_4H_6)]_n$ ($n,m = 2, 3$) is seen as the next logical step toward understanding the binding process. Calculations for the same are currently in progress.

IV. Conclusions

In this work, we have performed ab initio calculations to obtain equilibrium geometries and total energies of neutral and cationic $Ni(C_4H_6)_n$ complexes, where $n = 1-2$. The calculations on these complexes revealed a large number of higher energy isomers, which are energetically close to the ground-state structures. The elongation or breaking of C═C double bonds in butadiene molecules is an important character of the ground-state geometries of these complexes. The embedding of Ni atom/Ni^+ ion between the butadiene molecules can be seen as a better way of binding. The dissociation energies of these complexes revealed an inherent stability of $Ni^+(C_4H_6)$ complex over the other systems. Hence, it will be interesting to study the bigger complexes, such as $[Ni^+(C_4H_6)]_2$ and $[Ni^+(C_4H_6)]_3$ and see if their stability increases with the size, finally resulting in the polymerization of butadiene.

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