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Hydrogenation of 2H-azirine by aluminium lithium hydride over palladium catalyst

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The hydrogenation of 2H-azirine by the aluminium lithium hydride (AlLiH_4) in the presence of palladium used like catalyst, was studied by Hartree Fock method. For the modelling of reaction, the catalyst was represented by one atom of palladium; we took one molecule of 2H-azirine for two molecules of aluminium lithium hydride. The reaction gave a saturated derivative of 2H-azirine ($\text{C}_2\text{H}_3\text{N}$) called aziridine ($\text{C}_2\text{H}_5\text{N}$). On the basis of the analysis of the results obtained, the probable mechanism of reaction was proposed.

Key words: 2H-azirine, aziridine, aluminium lithium hydride, palladium, modelling of reaction, Hartree Fock.

INTRODUCTION

The 2H-azirine, is an unsaturated heterocyclic molecule comprising a nitrogen atom and two carbon atoms, with a double C=N bond. The chemical compounds which contain a cycle azirine in their structure are extremely reactive and they seem intermediary in certain chemical reactions like the rearrangement of Neber (McCarty 1970). Its saturated derivative (aziridine) is an intermediate and monomer in the preparation of cationic polymers which are used to improve wet strength of paper, in fuel-oil and lubricant refining, as flocculating agents and in protective coatings, in textile finishing and for adhesives, polymer stabilizers and surfactants (Lewis, 1993; Scherr et al., 1995).

Hydrogenation is an important reaction which intervenes in the hydrotreating process of the heterocyclic molecules contained in the residues of oil, under a strong hydrogen pressure over catalysts. During this process, the hydrogenolysis of carbon-heteroatom bonds such heterocyclic molecules often occurs (Bachelier et al., 1984; Breyse et al., 1984; Bimal et al., 1999; Yermakov et al., 1985; Kasztelan et al., 1984; Murena et al., 2004).

In our present study, we modelled hydrogenation of 2H-azirine over a palladium catalyst by using as

hydrogenating reagent the aluminium lithium hydride. This reaction has been studied because experimental data exist on the same system in literature. Compared with our study, the difference is that the experimental catalyst is palladium on carbon as support, (Knouants, 1988). The objective of our study was to confront experimental results with our theoretical results in order to propose the mechanism of reaction. The calculation methods used are based on the Hartree-Fock theory and the basis set is LanL2DZ.

MATERIALS AND METHODS

Theory

The calculating method used in our work is the Hartree-Fock method (Abarenkov et al., 1989; Rivail, 1994). According to this method, the wave function is the functional of spin orbitals. The electronic energy of the ground state is obtained by applying the variation theorem. The energy has the form:

$$E_{HF} = V + \langle hP \rangle + \frac{1}{2} \langle PJ \mathbf{e} \rangle - \frac{1}{2} \langle PK \mathbf{e} \rangle \text{ where } V$$

is the nuclear disgust energy, P is the density matrix, $\langle hP \rangle$ is the one-electron (kinetic plus potential) energy, $\frac{1}{2} \langle PJ \mathbf{e} \rangle$ is the classical coulomb repulsion of the electrons, and $-\frac{1}{2} \langle PK \mathbf{e} \rangle$ is the exchange energy resulting from quantum (fermion) nature of electrons. The basis set used is LanL2DZ.

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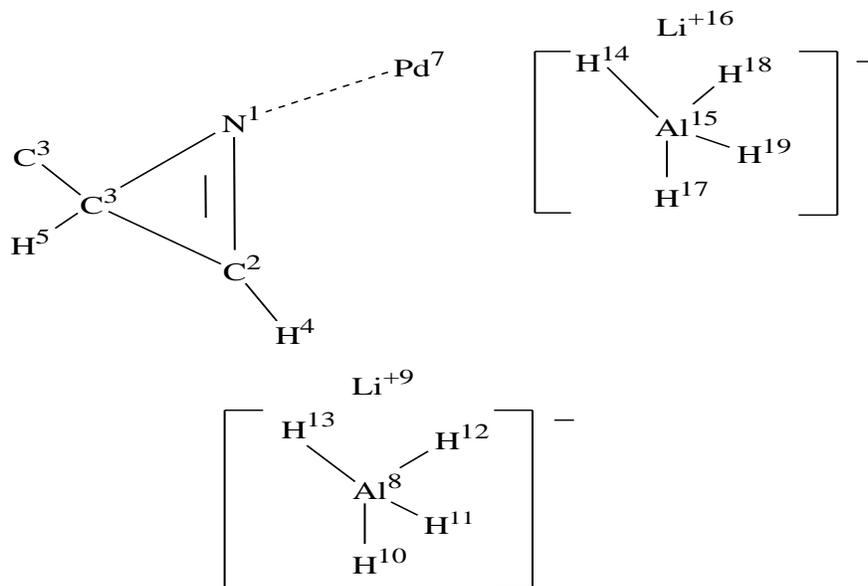


Figure 1. Chemical system studied.

Calculation program

The calculations were performed with Gaussian-98W program (Klark, 1990; Frisch et al., 1998), which carries out the quantum calculations based on *ab initio* and semi empirical methods. The program data are the geometry of systems, their multiplicity and charge. The curves and the drawings of the system studied were performed with Excel 2003 and ChemDraw Ultra 6.0, respectively. The calculations were carried out in the "Laboratoire de Chimie Théorique et de Spectroscopie Moléculaire (LACTHESMO)" of "Université d'Abomey-Calavi" in Benin Republic.

Modelling of the reaction

Two stages characterize the reaction. The first is the adsorption of the 2H-azirine (C_2H_3N) on palladium and second is the reaction between two molecules of aluminium lithium hydride and the adsorbed 2H-azirine molecule. The approach of both molecules $LiAlH_4$ was made according to two different directions in comparison with the adsorbed reactive.

The whole chemical system studied is shown in Figure 1. Two coordinates of reaction were taken into account. They are the N^1H^{14} and C^2H^{13} distances. The rapprochement of both molecules of hydride across previous both coordinates led to deep transformations of system.

In these work, we made the assumption that the active phase of catalyst used by Knouants (1988) would be palladium, and for this reason we modelled this active site of their catalyst by a palladium atom.

RESULTS

Both coordinates of reaction have as initial values 4.000 Å and 3.877 Å for N^1H^{14} and C^2H^{13} , respectively. During the process, these coordinates of reaction were gradually

decreased and the parameters whose evolutions were followed in particular are interatomic distances, angles between chemical bonds and Mulliken atomic charges.

According to both coordinates of reaction, we were interested in the evolutions of the interatomic distances C^2N^1 , C^3N^1 , $Al^{15}H^{14}$, Al^8H^{13} and N^1Pd^7 which are represented on the Figure 2. We also took in consideration angles $N^1C^2C^3$, $N^1C^3C^2$, $H^6C^3H^5$, and $H^{14}N^1C^2$ whose evolutions are represented by the Figure 3.

The analysis of the curves of the Figures 2 and 3 made it possible to determine the ruptures, formations and transformations of chemical bonds occurred during the reaction.

With regard to the atomic charges of the system, the analysis of Mulliken populations also contributes to the determination of the ruptures, formations and transformations of chemical bonds occurred during the reaction. The variations of the Mulliken atomic charges of the atoms C^2 , C^3 , N^1 , H^{13} and H^{14} are shown in Figure 4, according to the coordinates of reaction. The energy of the system also varied according to both coordinates of reaction, during the process. The variation of energy of the system is given (Figure 5).

DISCUSSION

The curves of Figure 2 show that at the end of the process, certain chemical bonds disappeared while others were formed or transformed. Indeed, the interatomic distances between the aluminium atom Al^8

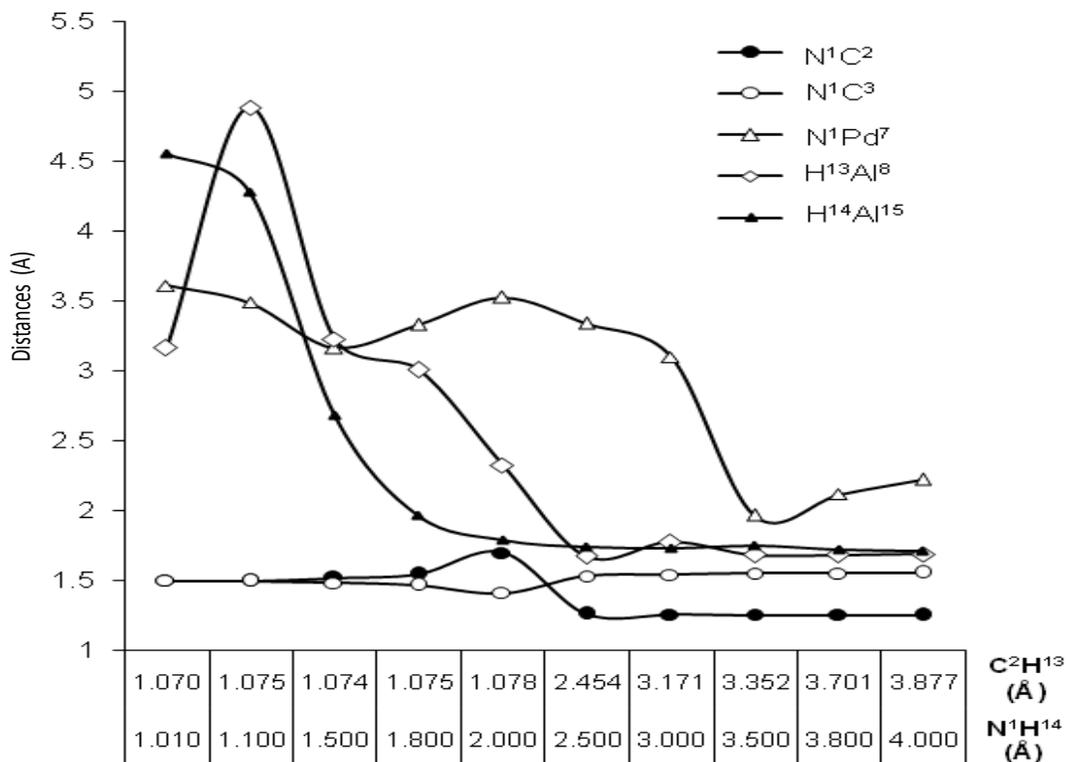


Figure 2. Variations of interatomic distances according to reaction coordinates N¹H¹⁴ and C²H¹³.

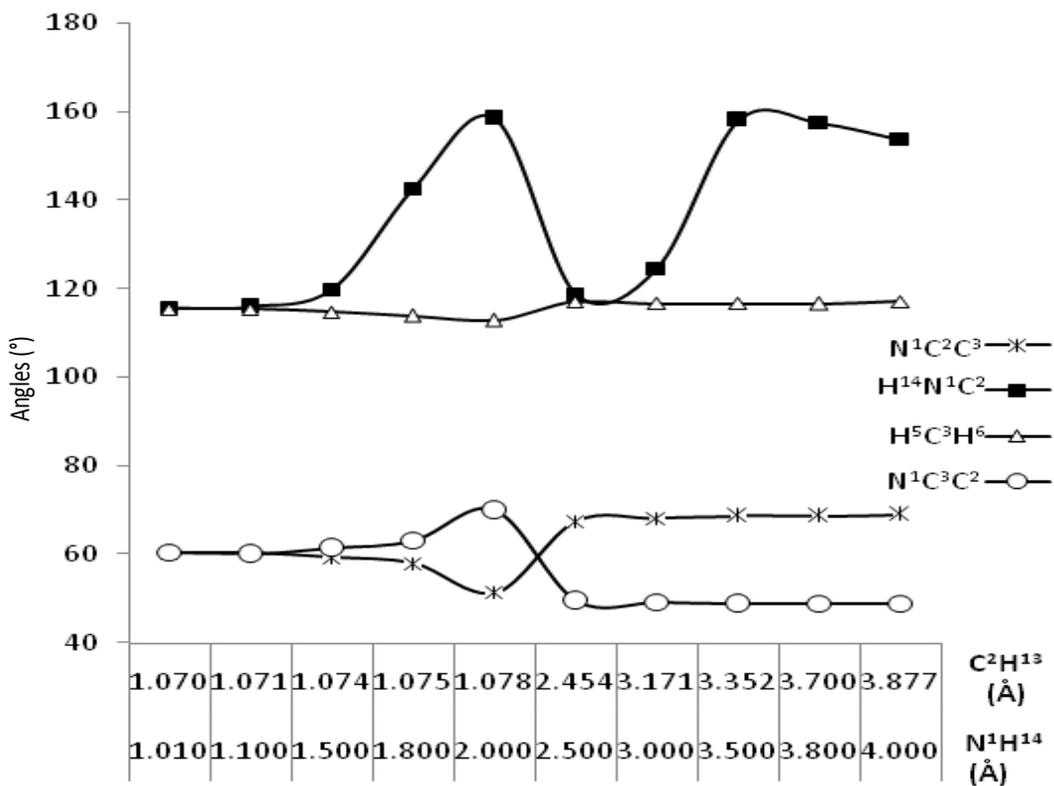


Figure 3. Variations of angles according to reaction coordinates N¹H¹⁴ and C²H¹³.

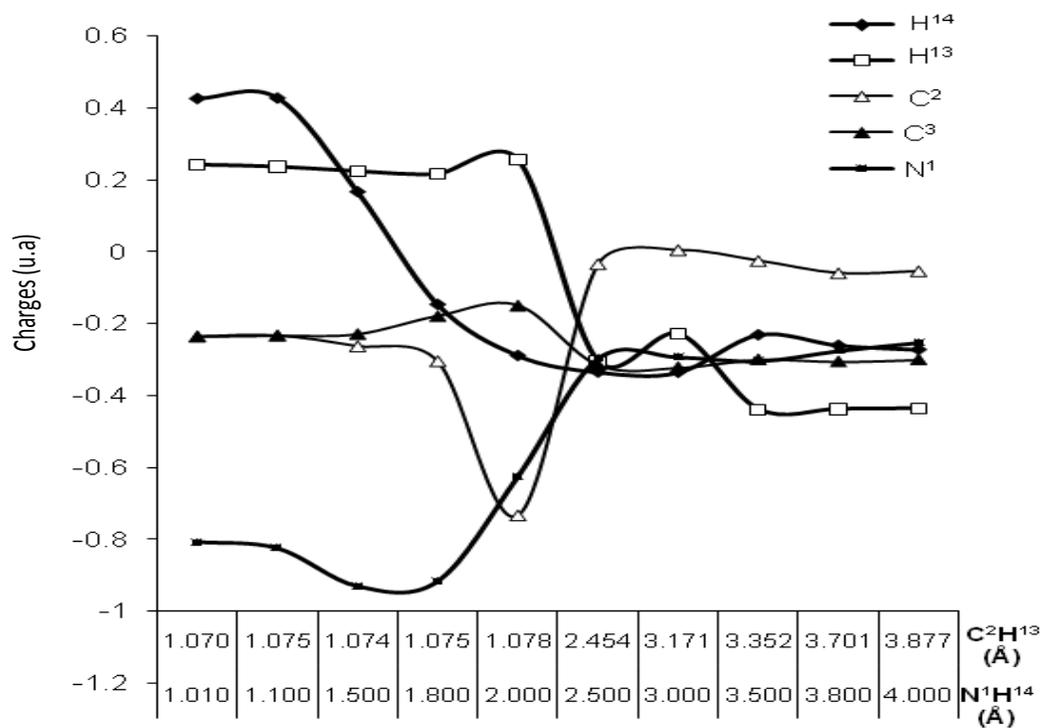


Figure 4. Variations of Mulliken atomic charges according to reaction coordinates N^1H^{14} and C^2H^{13} .

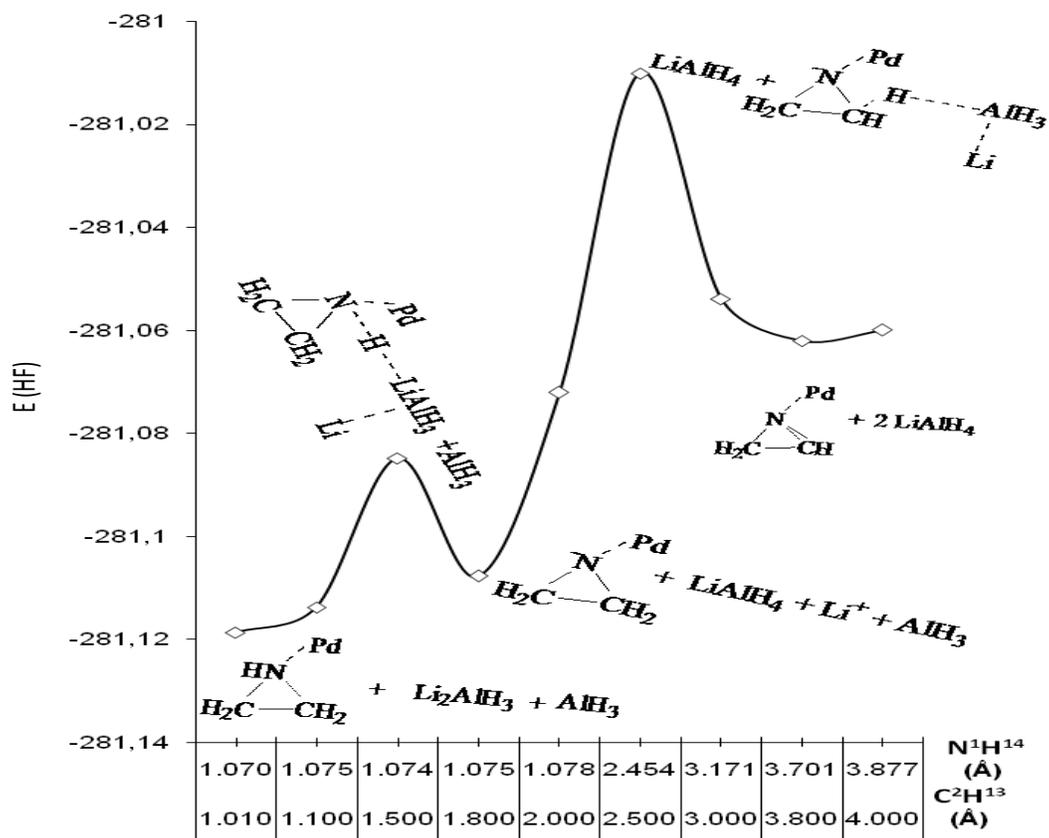


Figure 5. The variation of the energy of the system according to N^1H^{14} and C^2H^{13} coordinate.

Table 1. Calculated vibration frequencies of the reagent (2H-azirine) and the reaction product and standard IR absorption regions.

Bonds	Vibration frequencies (cm ⁻¹)		
	Before reaction (reagent 2H-azirine)	After reaction (Product aziridine)	Standard IR absorption region
C=N	1645.0	-	1500.0 - 1900.0
C-N	1092.5	1333 and 1333.7	800.0 - 1300.0
C-H	3330.0 - 3505.0	3320.0 - 3334.0	2700.0 - 3800.0
N-H	-	3700.0	2700.0 - 3800.0

and the hydrogen atom H¹³, between the aluminium atom Al¹⁵ and the hydrogen atom H¹⁴, and between the palladium atom Pd⁷ and the nitrogen atom N¹, exceed became very close at the end. This means that during the reaction, the double chemical bond N=C was transformed into a simple chemical bond between the two atoms N¹ and C². At the end of reaction, the final optimized values of N¹H¹⁴ and C²H¹³ are 1.010 Å and 1.070 Å, respectively. In addition, angles N¹C²C³ and N¹C³C² of respective initial values 68.956° and 48.715° passed to approximately 60.300°. This result confirms the transformation which took place on the level of chemical bond N¹C² during the process. The very weak variation of the value of angle H⁵C³H⁶ makes it possible to say that the carbon atom preserved its state of hybridization sp³, during the process.

At the end of the reaction, the absolute values of the dihedral angles H¹⁴N¹C²C³ and H¹³C²N¹C³ are 105.886 and 111.135, respectively. These values are equal neither to 0° nor with 180°, which means that the atoms H¹³ and H¹⁴ are not in C³C²N¹ plan.

At the beginning, atoms N¹ and C² were bound by a double bond and carried negative electronic charge. But at the beginning as at the end of the reaction, the charge carried by atom N¹ is definitely more important than that carried by C² because of its electronegativity. The atom C³, whose charge was equal to - 0.3 ua at the beginning of reaction, carries at the end of the reaction, the same charge of value -0.24 ua as atom C². This last observation confirms well that two atoms C² and C³ are found finally in the same state of hybridization (sp³). At the end of the reaction, hydrogen atoms H¹³ and H¹⁴ carry positive charge + 0.43 ua and + 0.24 ua, respectively. While fixing itself on N¹, H¹⁴ compensates for approximately 50% the N¹ electronic charge so that the remaining negative charge on N¹ corresponds only to its free electronic doublet. As for H¹³, its positive charge compensates for exactly the negative charge of C², this last carbon atom do not have a free electronic doublet.

Figure 5 representative variation of the energy of the system according to the coordinates of reaction N¹H¹⁴ and C²H¹³, presents two maximum to 2.500 and 1.500 Å for N¹H¹⁴ and 2.454 and 1.074 Å for C²H¹³. Between the two preceding values of C²H¹³, the system was relaxed concerning this coordinate of reaction. C²H¹³ then takes the optimized value of 1.075 Å T; value very close to that

3.000 Å. There are no more chemical bonds between these atoms. The interatomic distances like C²N¹ and C³N¹ which were different at the beginning of the process published in the literature for a chemical bond C–H (Potapov et al., 1981). At the second maximum of the curve of energy, the system was also released compared to the second coordinate of reaction N¹H¹⁴ whose optimized value was stabilized to 1.010 Å. This observation means that chemical bond N–H was formed, insofar as this value is of the same order of magnitude as for the length published in the literature for a N–H bond (Potapov et al., 1981).

Ultimately, the two maximum presented by the curve (Figure 5) correspond in two transition states associated with the formations of C²H¹³ and N¹H¹⁴ bonds, respectively.

In order to clarify the structure of the product of the reaction, the vibration frequencies of the reagent (2H-azirine) and the product were calculated and consigned in the Table 1, which contains also certain data on the standard IR absorption regions (Silverstein et al., 1991).

The analysis of these results shows that between 1500.0 and 1900.0 cm⁻¹, a vibration frequency (1645.0 cm⁻¹) characteristic of C=N bond contained in the molecule of reagent. This frequency disappeared with the profit from frequencies 1333.0 and 1333.7 cm⁻¹, characteristic of the C–N bond contained in the product (Table 1). All this confirms the opening of the π bond between C² and N¹ atoms and thus the transformation of C=N into C–N. The frequency 3700.0 cm⁻¹ which appeared only at the end of reaction, shows that it formed an N–H bond during the reaction. All these are only one confirmation that the results of the study carried out higher on the variation of the geometrical and different parameters.

On the basis of various stages of the reaction process indicated on Figure 6 of the geometrical parameters variations and the atomic charge of Mulliken and also on the basis of vibration frequencies of various chemical bonds on the level of the principal reagent and the product of the reaction, a probable mechanism of the reaction was proposed (Figure 6).

Conclusion

By methods of quantum chemistry and the hydrogenation

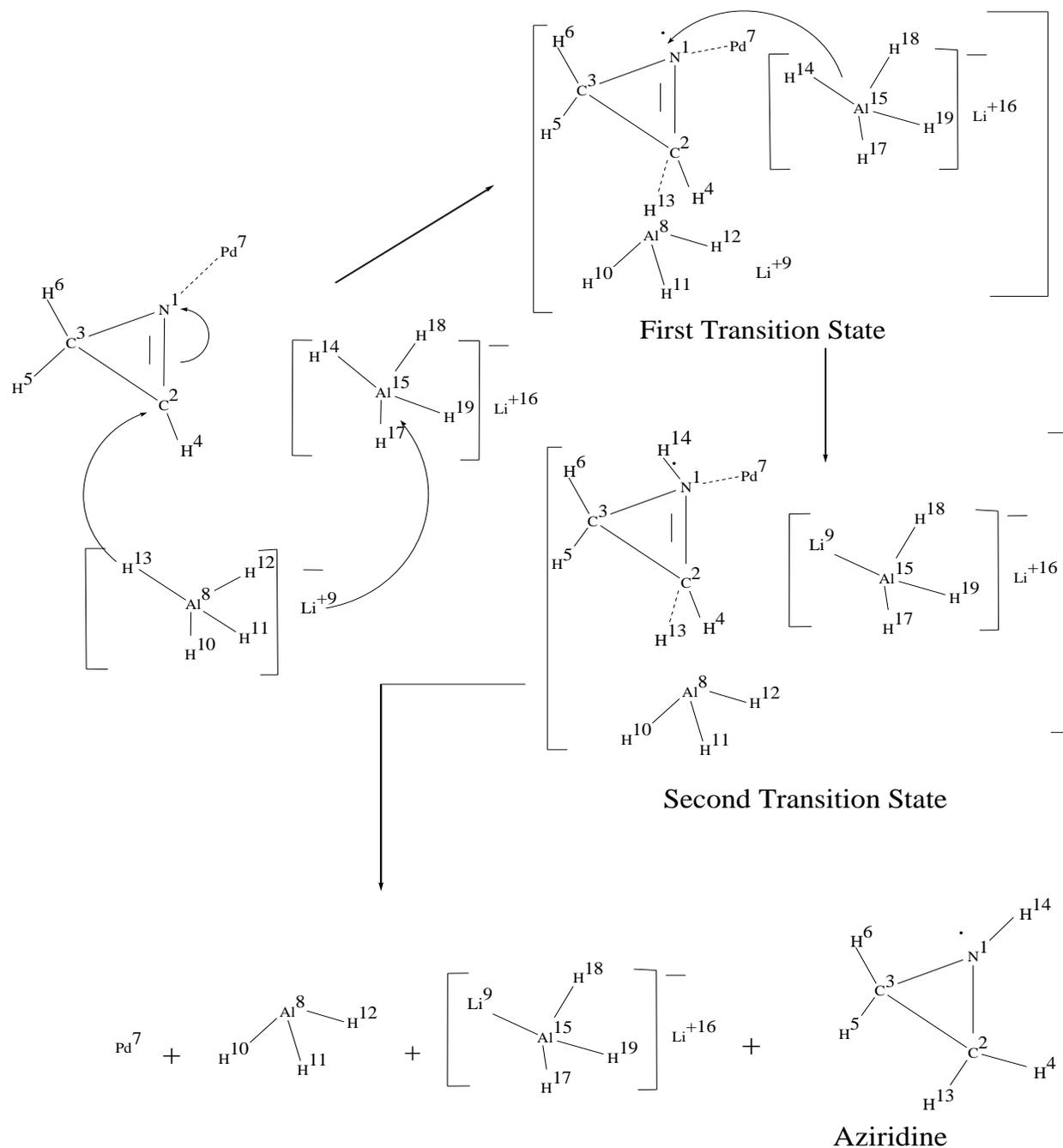


Figure 6. Probable mechanism of Hydrogenation of 2H-azirine by aluminium lithium hydride over palladium catalyst.

of 2H-azirine by aluminium lithium hydride over palladium catalyst was studied. The catalytic site was modeled by a palladium atom, insofar as the same reaction was carried out in experiments by other authors who used palladium supported by carbon as catalyst. According to the data of the literature and our results, it appeared that

two molecules of aluminium lithium hydride reacted by providing each one to the molecule of 2H-azirine a hydrogen atom to give a molecule of aziridine, according to a mechanism confirmed by several studied parameters.

The results of our work made, once more, the proof of

the utility of the quantum chemistry in the field of the molecular reactivity, in the sense that it makes it possible to highlight steps of chemical conversions that the experiment alone cannot elucidate.

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