

Hydroalumination of Cyclopropane: A Transition State Study

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Abstract: The hydroalumination of cyclopropane has been investigated using the B3LYP density functional method employing several split-valence basis sets. It is shown that the reaction proceeds via a four-centered transition state. Calculations at higher levels of theory were also performed at the geometries optimized at the B3LYP level, but only slight changes in the barriers were observed. Structural parameters for the transition state are also reported.

Keywords: Hydroalumination, Cyclopropane, Transition state, Propylalane

Introduction

Aluminium and boron belong to group III in the periodic table but there is large difference in their chemistry¹⁻³. Only a few hydrides of aluminium are known along with monomer AlH_3 and dimer Al_2H_6 while boron has a richer chemistry^{4,5} in the inorganic as well as organic chemistry. Hydrides of aluminium are good reducing agents and used as reducing agent for functional groups, hydroalumination of alkenes, alkynes, allylic rearrangement in organic chemistry⁶.

The addition of the Al-H bonds to the double or triple bonds of unsaturated organic compounds (hydroalumination) finds widespread application as a very powerful method for the reduction of specific substrates in organic synthesis⁷⁻¹⁵.

The addition of an alkene or alkyne into the Al-H bond of an alkyl aluminium hydride is a key first step in the route to the formation of a new carbon-hydrogen bond via hydroalumination. For further understand Bunden and Francl¹⁶ used *ab initio* molecular orbital methods to probe the reaction path for the addition of carbon-carbon multiple bonds into Al-H bonds.

Several theoretical studies of the hydroalumination of ethylene and acetylene have appeared. It has been suggested that the reaction involves formation of a symmetric π -complex intermediate leading to the formation of addition product via a four-centered transition state. Experimental work by Egger supports these results¹⁷. The alternative π -complex transition state proposed by Eisch¹⁸, however, is inconsistent with both the theoretical studies and the experimental work of Egger¹⁷. In 1981, Grophen and Haaland

characterized the transition structure for the addition of acetylene into the Al-H bond of alane¹⁹. One year later, they have reported the transition structure for the analogous addition reaction of AlH_3 with ethylene²⁰. Sakai described a push-pull two-stage mechanism for the analogous reaction of AlH_3 with ethylene²¹. Sakai's charge analysis on hydroalumination of ethylene suggested initial Al-C bond formation occurs which is found rapid than the breaking Al-H and the making of C-H bonds. Higashi *et al.* investigated the reverse reaction of $\text{AlH}_3 + \text{C}_2\text{H}_4$ in the context of its application to chemical vapour deposition²². They have reported a four-centered alane-ethylene transition structure using a more sophisticated theoretical model although no substantial differences were found.

Houk *et al.*^{23,24} and others²⁵ have examined the reaction path for the analogous hydroboration reaction with a variety of substrates. The intermediates and transition structures found in these studies are consistent with those for the hydroalumination pathway described earlier. Qualitatively, the energetics of these pathways compare well with those from the simple hydroalumination reaction studied earlier. Schleyer and Hommes²⁶ have examined the structure of the transition state for the reaction of dimethylborane and ethylene using correlated methods and suggest that the TS has a three-centered rather than four-centered structure. Chey *et al.*²⁷ have previously characterized the π -complex intermediates for hydroalumination of alkenes. In 1999 Bunden *et al.*²⁸ have studied the transition state for the carboalumination of alkene and alkynes at *ab initio* level of theory. They have shown that these reactions are essentially nucleophilic attacks by alkyl anions on substrate activated by Lewis acid substituents.

Togni and Grutzmacher²⁹ in 2001 have proposed metal-catalysed hydroalumination reactions of alkenes and alkynes and suggested that the catalytic hydroalumination of alkenes and alkynes is the potential tool for the functionalization of carbon-carbon multiple bonds. Among the different catalytic systems titanium (Ti), Zirconium (Zr) and Nickel (Ni) catalysts have found the widest application. Pankratyev *et al.*³⁰ has recently carried out a DFT study on the mechanism of olefin hydroalumination by XAlBu_2 in the presence of Cp_2ZrCl_2 catalyst for the mechanism of intermediate formation.

In this paper, we report our studies on the hydroalumination of cyclopropane with alane. Unlike hydroboration of cyclopropane³¹ we found a four-centered transition state leading to the formation of *n*-propyl alane. A four-centered transition state occurs on the approach of AlH_3 moiety along the plane of cyclopropane ring and proceeded by an intermediate complex.

Computational methods

All calculations have been performed on a PC running WINDOWS using the Gaussian 98³² suite of programs. The B3LYP hybrid density functional was used for calculation at DFT³³ level using several split-valence basis sets. The geometries of the reactants (AlH_3 and C_3H_6), transition state and the product were optimized at this level of theory using 6-31G**, 6-311++G**³⁴⁻⁴⁰, cc-pVDZ and AUG-cc-pVTZ⁴¹⁻⁴⁵ basis sets. The nature of each stationary point was confirmed in each case by frequency calculations; all the minima were verified to have all positive frequencies and the transition state to have only one imaginary frequency. MP2⁴⁶⁻⁵⁰ calculations were also performed using the chosen basis sets for comparison purposes. Single point (SP) calculations were also performed at the geometries optimized at the B3LYP/6-31G** level at the CCSD, CCSD(T)²⁷⁻³¹, QCISD, QCISD(T)⁵¹⁻⁵⁵ and MP4D levels to see if any significant change in the energetics is observed.

Results and Discussion

When aluminium approaches a C-C bond of cyclopropane along a line perpendicular to the ring plane no stable intermediate is found. However a four-centered transition structure is obtained.

The geometry of the reactants (AlH_3 and C_3H_6) four-centered transition state optimized at B3LYP/6-31G** level is shown in Figure 1. The geometrical parameters for the optimized transition structure are listed in Table 1.

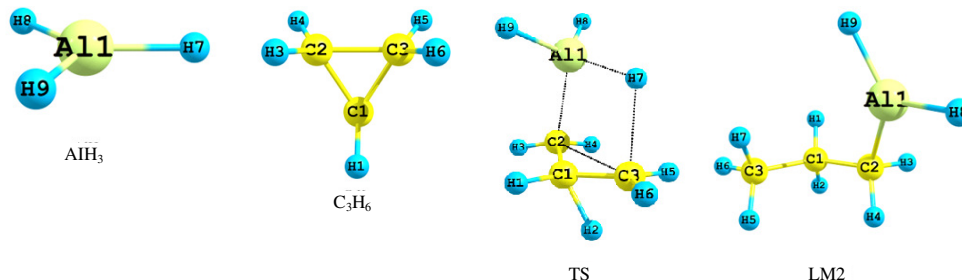


Figure 1. B3LYP/6-31G** optimized geometry of the reactants (AlH_3 and C_3H_6), four centered transition state (TS) and product

Table 1. Optimized structural parameters (bond lengths in Å and angles in degree) for the four-centered transition state (TS)

	AlH_3	C_3H_6	TS	LM
R(Al1-H7)	1.58689		1.703	3.08400
R(Al1-H8)	1.58665		1.599	1.59252
R(Al1-H9)	1.58709		1.605	1.59269
R(C1-C3)		1.50907	1.420	1.53195
R(C2-C3)		1.50899	2.474	2.56261
R(C1-C2)		1.50889	1.437	1.54117
R(C1-H1)		1.08551	1.089	1.09784
R(C1-H2)		1.08551	1.291	1.09908
R(C2-H3)		1.08550	1.089	1.10315
R(C2-H4)		1.08550	1.091	1.09998
R(C3-H5)		1.08549	1.082	1.09623
R(C3-H6)		1.08549	1.085	1.09494
R(Al1-C2)			2.162	1.97427
R(Al1-C3)			3.051	3.49260
R(C3-H7)			1.997	1.09828
∠ C1C2C3		60.006	29.8	33.387
∠ C2C3C1		59.994	30.2	33.615
∠ C3C1C2		60.000	119.8	112.998
∠ H7Al1H9	119.990		107.7	76.386
∠ H8Al1H9	119.981		118.1	118.541
∠ H8Al1H7	120.029		117.2	135.799

The C2-C3 distance in the transition state of 2.474 Å is greater than the C2-C3 distance found in the four-centered transition state in which AlH_3 moiety is oriented along the plane of cyclopropane ring by 0.309 Å. The forming C3-H7 and C2-Al1 bonds are of comparable

length in both the transition states. The HOMO of the transition state is shown in Figure 2 enabling us to visualize the electron density distribution around the forming and breaking bonds.

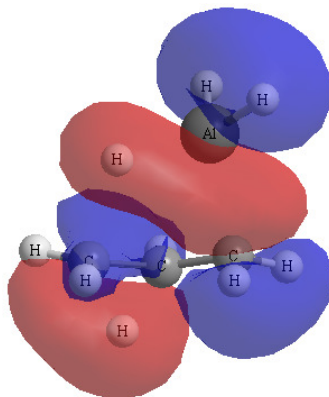


Figure 2. HOMO of the four-centered transition state (TS) for the hydroboration of cyclopropane at B3LYP/6-31G** level of calculation

The IRC plot computed from this four-centered transition state is shown in Figure 3 and shows the transition state moving downhill towards the reactants on one side and the product the other. Frequency calculation has been performed on the transition state confirms the existence of a single imaginary frequency (1275 cm^{-1}).

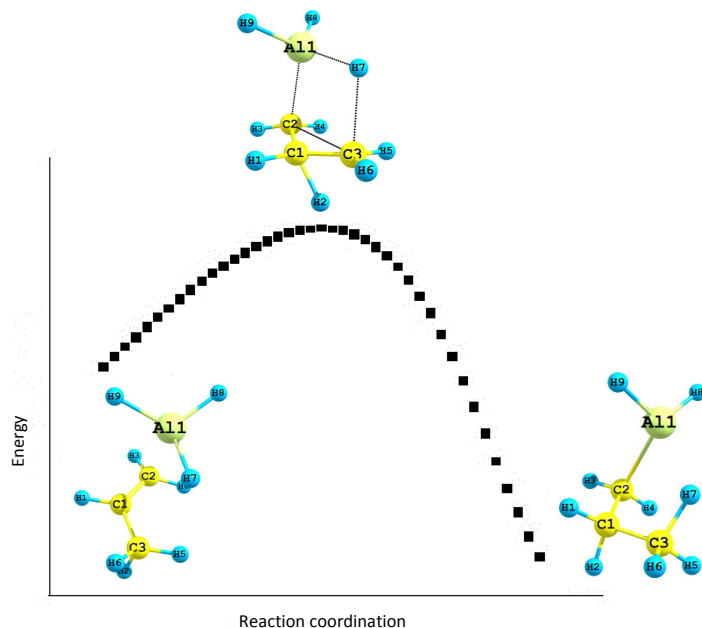


Figure 3. IRC plot for the four-centered transition state at the B3LYP/6-31G** level

Calculations at different levels and using different basis sets have been performed in this case also. The total energies (in Hartree) and the relative energies (in kcal/mol) for the reactants, transition state and product are listed below in Table 2 and Table 3 respectively.

Table 2. Total energies (in Hartree) and relative energy (in kcal/mol) for the reactants, four-centered transition state and product at different levels and basis sets

Method	AlH ₃ +C ₃ H ₆	TS	LM2
B3LYP/6-31G**	-362.1110943	-362.0469598	-362.1672311
B3LYP/cc-pVDZ	-362.1152736	-362.0513688	-362.1691517
B3LYP/6-311++G**	-362.1600749	-362.0950096	-362.2144364
B3LYP/AUG-cc-pVTZ	-362.1770811	-362.1125874	-362.2308314
MP2/6-31G**	-361.1874839	-361.1111888	-361.2450056
MP2/cc-pVDZ	-361.1998152	-361.1280688	-361.2566437
^a QCISD/6-31G**	-361.2437676	-361.1669392	-361.3010989
^a QCISD(T)/6-31G**	-361.2587135	-361.1861454	-361.3164128
^a MP4D/6-31G**	-361.2481001	-361.1693367	-361.3055561
^a CCSD/6-31G**	-361.2432854	-361.1653982	-361.3005232
^a CCSD(T)/6-31G**	-361.2585268	-361.1855883	-361.3161846

^aSingle point calculations on the B3LYP/6-31G** structures.

Table 3. Total energies (in Hartree) and relative energy (in kcal/mol) for the reactants, four-centered transition state and product at different levels and basis sets

Method	Reactants	ΔE_{TS}	$\Delta E_{Product}$
B3LYP/6-31G**	0.00	40.24	-35.22
B3LYP/cc-pVDZ	0.00	40.10	-33.80
B3LYP/6-311++G**	0.00	40.82	-34.11
B3LYP/AUG-cc-pVTZ	0.00	40.47	-33.72
MP2/6-31G**	0.00	47.87	-36.09
MP2/cc-pVDZ	0.00	45.02	-35.66
^a QCISD/6-31G**	0.00	48.21	-35.97
^a QCISD(T)/6-31G**	0.00	45.53	-36.20
^a MP4D/6-31G**	0.00	49.42	-36.05
^a CCSD/6-31G**	0.00	48.87	-35.91
^a CCSD(T)/6-31G**	0.00	45.76	-36.18

^aSingle point calculations on the B3LYP/6-31G** structures

One can notice that the barriers obtained at B3LYP levels for different basis sets are comparable. The four-centered transition state in both the cases is found to be around 40.00 kcal/mol at the B3LYP/6-31G** level. The MP2 values for the barrier are somewhat higher. The higher level *ab initio* calculations also give higher values but inclusion of triples is seen to give significantly lower barriers both in the quadratic configuration interaction (CI) and coupled cluster (CC) scheme. As the B3LYP barrier for this case are only moderately higher than for the approach along the plane discussed in the previous section, are expects that both mechanisms are viable with the approach along the plane being preferred somewhat over the perpendicular approach.

Concluding remarks

In summary, we have investigated the stationary structures involved in the hydroalumination of cyclopropane with borane. Our study posits a four-centered transition state for this reaction in contrast to the recent studies on the hydroboration of cyclopropane, in which three-centered transition state has been reported. It is also hoped that studies on reactions involving cyclopropane and its derivatives with other hydroalumination reagents will clarify the situation.

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