

Addition Reaction of Cyclopropane with Magnesium Dihydride (MgH₂): A Theoretical Study

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ABSTRACT. The addition reaction of cyclopropane with MgH₂ has been investigated using the B3LYP density functional method employing several split-valence basis sets. Both along the and perpendicular to the cyclopropane ring approach has been reported. 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.

Key words: Addition reaction, Cyclopropane, Intermediate complex, Transition state

INTRODUCTION

The hydrides of magnesium are known to add to alkenes and alkynes.¹ Magnesium metal is considerably less expensive and the hydrides of magnesium can be prepared easily by reacting them with hydrogen and are easier to handle than boranes. Following the discovery of hydroboration several attempts have been made to do the hydrometallation of unsaturated organic compounds, with MgH₂.

Podall and Foster¹ showed that magnesium hydride adds to ethylene, 1-octene and isobutylene to form adduct containing Mg–C bonds in low yields. In 1978 Eugene et al.² found that magnesium hydride adds readily to carbon–carbon multiple bonds in the presence of titanium catalyst. They demonstrated that appropriate conditions and catalyst results in hydrometallation of terminal olefins with MgH₂ in nearly quantitative yield.

Theoretically, Gropen et al.³ have studied the interaction of main group metals with carbon–carbon double bonds. Their calculations at the ab initio Hartree-Fock level showed that the reaction of MgH₂ with ethylene proceeds via the formation of a weakly bonded and short lived three centered complex followed by the formation of a four centered transition structure with an energy barrier of 5.00 kcal/Mol.

Cyclopropane is known to undergo addition reactions,⁴ and computational studies on the hydroboration and hydroalumination^{5,6} of cyclopropane have been reported from this.⁵ To our knowledge there have been no reports of theoretical studies of the reaction of cyclopropane with MgH₂. In this chapter we present the results of our investigations on the reaction of cyclopropane with magnesium hydride.

In this paper, we report our studies on the addition of cyclopropane with magnesium dihydride. Unlike hydroboration of cyclopropane⁵ we found a four-centered transition states leading to the formation of addition product. Four-centered transition state occurs on the approach of MgH₂ moiety along and perpendicular to the plane of cyclopropane ring and preceded by an intermediate complex only on approach along the cyclopropane ring.

COMPUTATIONAL METHODS

All calculations have been performed on a PC running WINDOWS using the Gaussian 98⁷ suite of programs. The B3LYP hybrid density functional was used for calculation at DFT⁸ level using several split-valence basis sets. MP2^{9–13} calculations were also performed using 6-31G** basis set for comparison purposes. The nature of stationary point was confirmed by frequency calculation. Single point (SP) calculations were also performed at the geometries optimized at the B3LYP/6-31G** level at the CCSD, CCSD(T),^{14–18} QCISD, QCISD(T)¹⁸ and MP4D¹⁹ levels to see if any significant change in the energetics is observed. IRC calculations have been performed and confirm that the transition structure does fall on the path between the complex and the product.

RESULTS AND DISCUSSION

As in the case of hydroboration and hydroalumination two types of transition structures have been found in the case of reaction with MgH₂ also.

Addition of MgH₂ to Cyclopropane When MgH₂ Approaches along the Plane of Cyclopropane Ring

When MgH₂ approaches cyclopropane along the plane

of the ring an intermediate complex and a four-centered transition state is founded to form, which proceeds to the adduct. The geometries of the reactants (MgH₂ and C₃H₆),

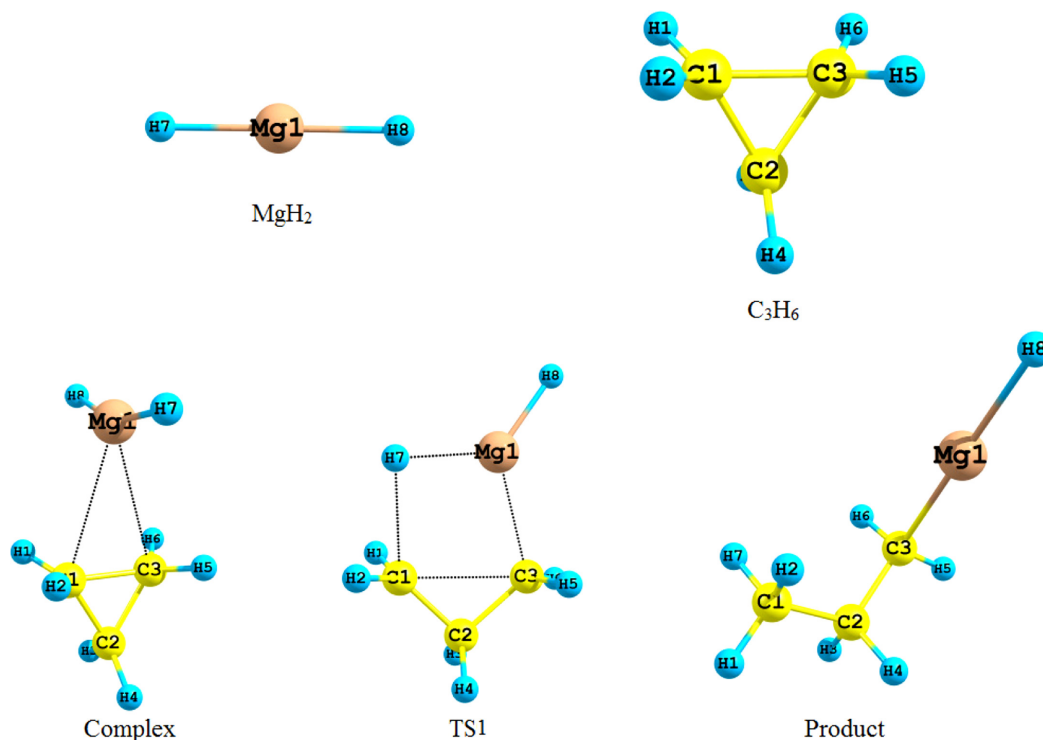


Figure 1. B3LYP/6-31G** optimized geometries of the reactants (MgH₂ and C₃H₆), complex (LM1), transition state (TS1) and product (LM2) along the plane of cyclopropane ring.

Table 1. Optimized structural parameters (bond lengths in Å and angles in degree) for the reactants, complex, transition state (TS1) and product for MgH₂+C₃H₆ reaction when MgH₂ approaches along the Plane of Cyclopropane Ring at B3LYP/6-31G**

	MgH ₂	C ₃ H ₆	Complex	TS1	Product
R(Mg1–H7)	1.708	–	1.720	1.795	3.772
R(Mg1–H8)	1.708	–	1.719	1.721	1.717
R(C1–C3)	–	1.508	1.536	2.202	2.572
R(C2–C3)	–	1.509	1.503	1.543	1.541
R(C1–C2)	–	1.508	1.503	1.469	1.532
R(C1–H1)	–	1.085	1.086	1.083	1.095
R(C1–H2)	–	1.085	1.086	1.081	1.100
R(C2–H3)	–	1.085	1.084	1.094	1.101
R(C2–H4)	–	1.085	1.084	1.093	1.098
R(C3–H5)	–	1.085	1.086	1.094	1.099
R(C3–H6)	–	1.085	1.086	1.091	1.101
R(Mg1–C1)	–	–	2.689	2.720	3.480
R(Mg1–C3)	–	–	2.689	2.217	2.117
R(C1–H7)	–	–	–	2.023	1.096
∠C1C2C3	–	60.0	61.4	93.9	113.6
∠C2C3C1	–	59.9	59.2	41.7	33.0
∠C3C1C2	–	60.0	59.2	44.3	33.2
∠H7Mg1H8	–	–	159.1	132.4	133.7
∠H7C1C3	–	–	–	91.6	91.2

the intermediate complex, the transition state and product optimized at the B3LYP/6-31G** level is shown in *Fig. 1*. The optimized geometrical parameters for these species are collected in *Table 1*.

The complex of cyclopropane with MgH₂ found here is a stable intermediate occurring on the reaction pathway as is verified by frequency calculations which resulted in all positive frequencies of vibration. The carbon–carbon (C1–C3) bond length is not significantly affected by binding to the magnesium in the complex. However, we see significant lengthening in the transition structure as the partial π -system (C1–C3 bond) in cyclopropane delocalized into the regions of the forming Mg1–C3, and C1–H7 bond regions. The molecular orbital plot in *Fig. 2* shows the degradation of the C1–C3 partial π -system in the cyclopropane ring accompanied by the formation of the C1–H7 and Mg1–C3 bonds. The carbon–carbon distance for the intermediate is 1.536 Å. While that in the transition structure is longer at 2.202 Å.

The geometrical parameters show the same qualitative

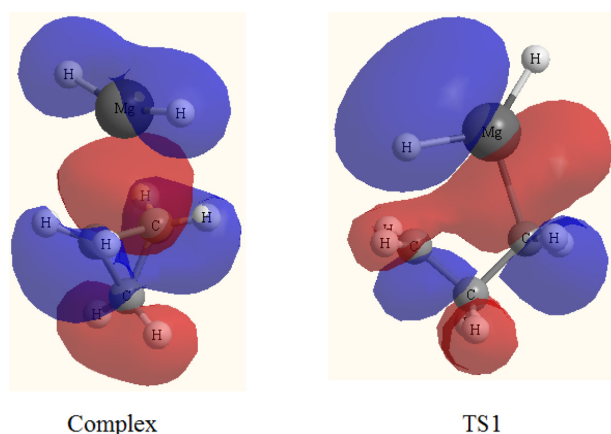


Figure 2. HOMOs of complex and transition state (TS1) for the reaction of cyclopropane with MgH₂ at B3LYP/6-31G** level along the plane of cyclopropane ring.

trends as in the foregoing results for hydroboration^{20,21} and hydroalumination.^{4,22} The transition structure is best represented as a four-centered structure.

The energies relative to the sum of the energies of the reactants, (in kcal mol⁻¹) is summarized in *Table 2*. Magnesium dihydride and cyclopropane are known to collapse without energy barrier to form the weakly bound intermediate complex²³ as no transition structure in between them has been found. The calculated stabilization energy for MgH₂ complex of cyclopropane is 5.49 kcal/mol at B3LYP/6-31G** level, while RHF/6-31G** it is 3.35 kcal/mol. At B3LYP/6-31G** level the four-centered transition structure has an energy 58.14 kcal mol⁻¹ above the complex, and the product is stabler than the reactants by 30.57 kcal mol⁻¹.

Even though the geometry of the intermediate does not change substantially as larger basis sets are used for optimization, the energy of complexation for MgH₂ bound to cyclopropane varies substantially, the various results falling with a range of approximately within a range of nearly 4 kcal mol⁻¹ with different theoretical methods used. B3LYP results with the larger basis set 6-311++G** gave calculated binding energy of -3.39 kcal mol⁻¹ for the complex compared with -5.49 kcal mol⁻¹ at the B3LYP/6-31G** level. The overall barrier is fairly high compared to that reported for addition of magnesium dihydride to ethylene, 5.23 kcal/mol.⁴

Single point (SP) values of the relative energies (in kcal mol⁻¹) of the key species calculated at several higher ab initio levels using the B3LYP/6-31G** geometries are collected in *Table 2*. These results show a larger degree of stabilization of the complex than at the B3LYP/6-31G** level, while the barriers are significantly higher. The relative energies of the product are not very sensitive to the method.

The IRC plot is shown in *Fig. 3* shows the transition

Table 2. Relative energies (in kcal/mol) at different levels and basis sets for MgH₂+C₃H₆ along the plane of cyclopropane ring

Method	Reactants	$\Delta E_{\text{Complex}}$	ΔE_{TS1}	$\Delta E_{\text{Product}}$
B3LYP/6-31G**	0.00	-5.49	52.65	-30.57
B3LYP/6-311++G**	0.00	-3.39	53.25	-29.88
MP2/6-31G**	0.00	-7.59	63.96	-31.36
RHF/6-31G**	0.00	-3.35	66.93	-26.49
^a QCISD/6-31G**	0.00	-6.42	61.73	-30.96
^a QCISD(T)/6-31G**	0.00	-7.14	59.02	-31.39
^a MP4D/6-31G**	0.00	-6.82	64.63	-31.01
^a CCSD/6-31G**	0.00	-6.40	62.78	-31.87
^a CCSD(T)/6-31G**	0.00	-7.13	59.38	-31.35

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

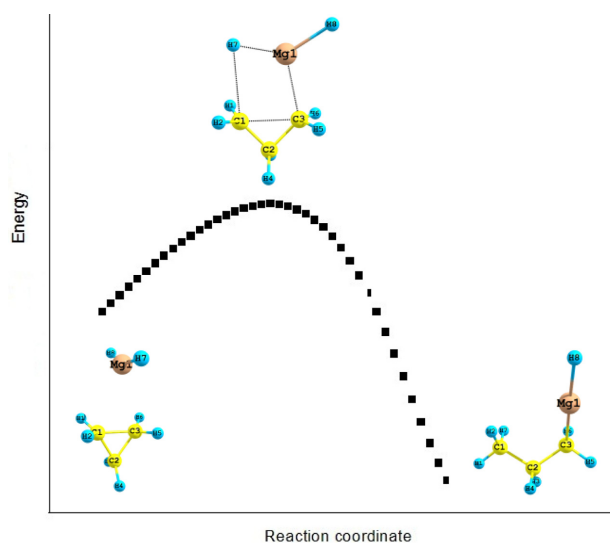


Figure 3. IRC plot for the $C_3H_6.MgH_2$, transition state at the B3LYP/6-31G** level along the plane of cyclopropane ring.

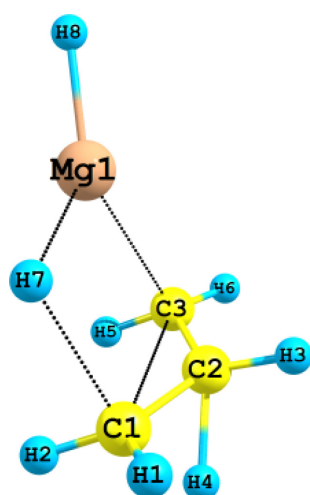


Figure 4. B3LYP/6-31G** optimized geometry of the transition state (TS2) for $C_3H_6+MgH_2$ reaction when MgH_2 approaches perpendicular to the plane of cyclopropane ring.

structure moving downhill towards the complex on one side and the product the other. Frequency calculations have been performed on all stationary structures. All positive frequencies are found for the stable species and one imaginary frequency is observed in the case of TS.

Addition of MgH_2 to Cyclopropane When MgH_2 Approaches Perpendicular to the Plane of Cyclopropane Ring

When MgH_2 approaches cyclopropane perpendicular to its plane four-centered transition structure TS2 is formed. No intermediate complex has been observed in this ori-

Table 3. Optimized structural parameters (bond lengths in Å and angles in degree) of the transition state (TS2) for $C_3H_6+MgH_2$ reaction when MgH_2 approaches perpendicular to the plane of cyclopropane ring at B3LYP/6-31G**

	TS2
R(Mg1–H7)	1.862
R(Mg1–H8)	1.729
R(C1–C3)	2.494
R(C2–C3)	1.418
R(C1–C2)	1.432
R(C1–H1)	1.083
R(C1–H2)	1.081
R(C2–H3)	1.089
R(C2–H4)	1.349
R(C3–H5)	1.093
R(C3–H6)	1.087
R(Mg1–C1)	3.076
R(Mg1–C3)	2.333
R(C1–H7)	1.885
∠ C1C2C3	122.1
∠ C2C3C1	29.0
∠ C3C1C2	28.7
∠ H7Mg1H8	139.9
∠ H7C1C3	82.1

entation. That the structure is TS is confirmed at B3LYP/6-31G** level by frequency calculations, which gave one imaginary frequency. The geometry of the transition state optimized at B3LYP/6-31G** level is shown in Fig. 4. The optimized geometrical parameters are shown in Table 3.

The distance C1–C3 in this transition state is found larger than the C1–C3 distance in the TS1 discussed in the last section. While the length of the forming bonds Mg1–C3 and C1–H7 found smaller, suggesting a ‘later’ transition state. The bond making and bond breaking phenomena can be easily visualized by the HOMO of the transition structure shown in Fig. 5.

The IRC plot shown in Fig. 6 shows the system moving downhill to the reactant on one side and to the product on the other. One imaginary frequency (1371 cm^{-1}) has been found for the transition state.

The calculated relative energies (in kcal/mol) at different levels and basis sets are collected in Table 4. Results of single point calculations at higher levels of theory are also included in the same table. In all these sets of calculations energy barriers observed are not high. The barriers for the previous case (TS1) are somewhat higher in each case, so we expect the reaction to proceed via TS2 preferentially.

We notice that the barrier obtained at RHF and MP2 lev-

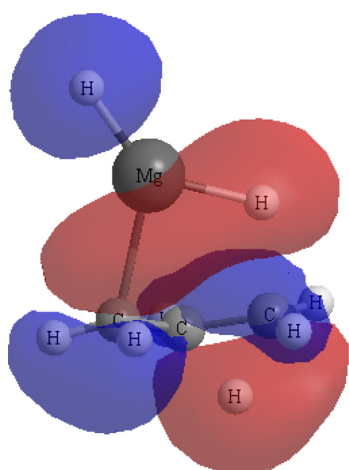


Figure 5. HOMO of the transition state (TS2) for the C₃H₆+MgH₂ reaction at B3LYP/6-31G** level of calculation perpendicular to the plane of cyclopropane ring.

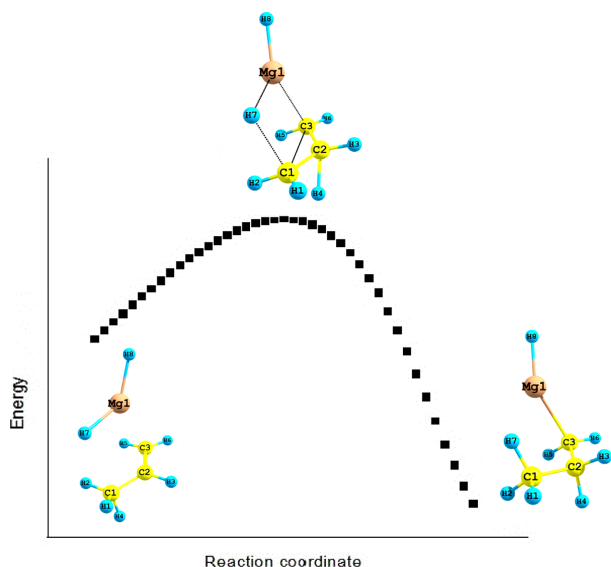


Figure 6. IRC plot of the transition state TS2 for C₃H₆+MgH₂ reaction at the B3LYP/6-31G** level when MgH₂ approaches cyclopropane perpendicularly.

els are higher than that of B3LYP level. The barriers in this case also found to be lower than the barrier calculated in the case, when MgH₂ approaches along the plane of cyclopropane ring.

In the case of the reaction of MgH₂ with cyclopropane with the in-plane approach, as in the cases of BH₃ and AlH₃, a complex is formed prior to the transition state. The MgH₂ moiety loses its linearity and is oriented perpendicular to the ring plane so as to minimize steric effects. For MgH₂ complex is stabilized to a much greater extent relative to the reactants (5.49 kcal/mol at B3LYP/6-31G**

Table 4. Total energies (in Hartree) and relative energy (in kcal/mol) for the C₃H₆+MgH₂ reaction at different levels and basis sets when MgH₂ approaches cyclopropane perpendicularly

Method	TS2 (in Hartree)	TS2 (in kcal/mol)
B3LYP/6-31G**	-319.0810973	44.73
B3LYP/6-311++G**	-319.123964	44.93
MP2/6-31G**	-318.174256	52.49
RHF/6-31G**	-317.6879061	61.45
^a QCISD/6-31G**	-318.2227006	53.55
^a QCISD(T)/6-31G**	-318.2417187	50.59
^a MP4D/6-31G**	-318.2252304	54.49
^a CCSD/6-31G**	-318.2212353	54.17
^a CCSD(T)/6-31G**	-318.2412187	50.79

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

level respectively as against 1.95 kcal/mol at the same level for the borane case). The barriers however are high and the improvement on going from RHF to MP2 and B3LYP for the same basis is not as marked as in the case of hydroboration. With the MgH₂ approaching perpendicular to the plane barriers are lower, and improve on going from RHF to MP2 and B3LYP methods to a more significant extent. We also note that while for hydroboration the in-plane approach is clearly favoured, for the hydroalumination both approaches seem equally likely as the barriers are very close and for addition of MgH₂ the perpendicular approach is preferable.

CONCLUDING REMARKS

In summary, we have investigated the stationary structures involved in the addition reaction of cyclopropane with magnesium dihydride. 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 reagents will clarify the situation.

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