# Density Functional Study of the Insertion and Ring-Opening Mechanism of MCP over Cp$_2$LaH and Cp$_2$LuH Catalysts

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The strained methylenecycloalkanes, e.g., methylenecyclopropane (MCP) and methylenecyclobutane (MCB), often undergo ring-opening reactions promoted by single-site metallocene-based complexes, which has been effectively utilized in organic synthesis,[1] polymerization/copolymerization,[2] or cycloaddition with alkenes.[3] Hence, the study of metallocene catalysts has steadily grown and stimulated numerous experimental[2,4] and theoretical[5] investigations. In addition, both MCP and MCB are highly reactive with respect to C=C double bond insertion than other α,α′-disubstituted olefins such as isobutylene, and that MCP is considerably more reactive than MCB.[2b] On the other hand, an interesting but often problematic feature of MCP is their multiform reactivities that may lead to the formation of a variety of products by the opening of proximal and distal bonds as well as C=C double bond addition reaction.[1–5]

In this regard, several reaction pathways have been put forward for the insertion, ring opening, and the subsequent reaction of MCP and its derivatives with different catalysts. For example, when the exomethylene part of the MCP reacts with organometallic complexes, two types of insertion, viz., 1,2-insertion[2a,b] and 2,1-insertion,[2c] occurs. This has resulted in the cleavage of proximal or distal bonds.[1e,3e] On the other hand, MCP reaction with transition metal compounds proceeds via insertion at the proximal bond or distal bond.[3e] Thus, the selectivity of the insertion and ring-opening site depends strongly on the combination of both the substrates and the catalysts. In addition, the reactivity of MCP also varies significantly with the size of the metal ion.[2a,b]

Despite the widespread investigation, a full understanding of the reaction mechanism is still far from complete, and the following questions are yet to be answered: (i) what are the possible structures and energies of the assumed minima (M) and transitions states (TS) involved in the insertion and the subsequent cleavage of proximal or distal bonds? (ii) Are there any differences in the ring-opening mechanism over Cp$_2$LaH and Cp$_2$LuH catalysts as they give rise to different (polymerization) products? In addition, much less attention has been paid to the roles of organolanthanides that promote the MCP ring-opening process.[2a,b,5i] On the other hand, theoretical studies are relatively few[5a,i] since such studies require huge computational time. Moreover, the lanthanide-based systems are highly complicated due to the large relativistic effects.[6] Therefore, in this investigation, we focus our attention on finding an exclusive description of these unanswered queries as well as on realizing the insertion and the ring-opening pathway of MCP over Cp$_2$LaH and Cp$_2$LuH catalysts using density functional theory (DFT) method.

In the present study, we employed DMol$^3$ program (Materials Studio software, version 2.1)[7] at the level of revised Perdew−

**Scheme 1.** Insertion Types of Cp$_2$LnH-MCP Systems
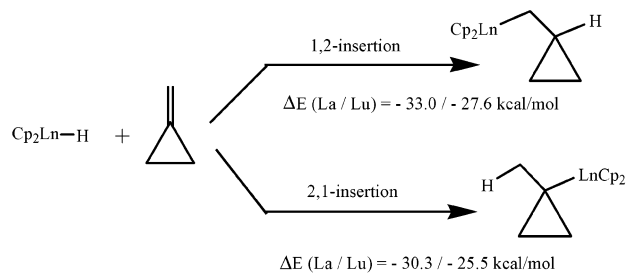


$^a$ Relative energies (ΔE) were obtained at the RPBE level.

Burke−Ernzerhodf (RPBE) functional.[8] Further, relativistic effective core potentials and double-numeric quality basis set with polarization functions were also considered. In addition, frequency calculations were carried out to determine the nature of all stationary points, viz., M and TS, as well as for the zero-point energy correction. The initial structures of both Cp$_2$LnH (Ln = La or Lu) and MCP were optimized, and the obtained results were in good agreement with the literature.[5g,i] The present method also reproduces the experimental geometrical parameters of MCP,[9] and the calculated Lu−Cp (average) distance (2.354 Å) is also in agreement with the experimental results (2.383 Å).[10] The validity of the method is also tested by computing the lanthanide contraction, i.e., $r_e$(Lu−H) − $r_e$(La−H), and the obtained value (0.170 Å) is in accordance with the accepted value of 0.179 Å.[5g]

As stated earlier, with the appropriate choice of metals and ligands, the ring-opening polymerization of MCP, in general, proceeds either by 1,2-insertion[2a,b] or by 2,1-insertion.[2c] Therefore, in the present study, we considered both types of insertion and computed their energetic stabilities. It can be seen from Scheme 1 that the calculated values favor the 1,2-insertion for both Cp$_2$LaH and Cp$_2$LuH catalysts. A similar observation was also noticed for the energetic stabilities at the level of BLYP[11] where the 1,2-insertion product is stable, as compared to 2,1-insertion, by 3.2 kcal/mol for Cp$_2$LaH, and 2.5 kcal/mol for Cp$_2$LuH.

Figure 1 depicts the geometry of stationary points along with the corresponding (relative) energies of various structures. In this energy profile, the sum of the energies of Cp$_2$LnH and MCP in isolated state is considered as the reference energy, which is set to zero. It can be noticed that the coordination geometries of the various minima and transition states for both Cp$_2$LaH−MCP and Cp$_2$LuH−MCP systems are similar, suggesting that the reaction may follow an identical pathway at the initial stages although they give very different products.

The minima, M1, M2, and M3, shown in Figure 1 indicate the formation of Cp$_2$LnH−MCP complex as well as insertion and ring-opening products, respectively. More importantly, this figure also presents novel TS structures, i.e., TS1 and TS2, which show
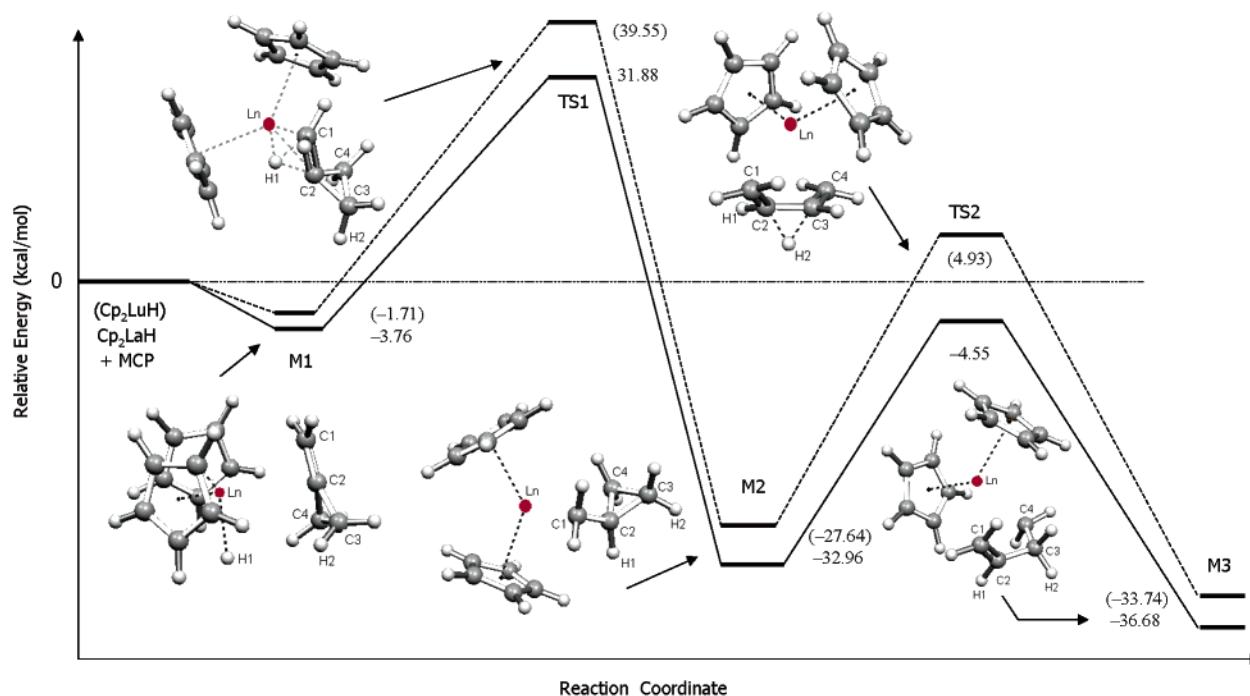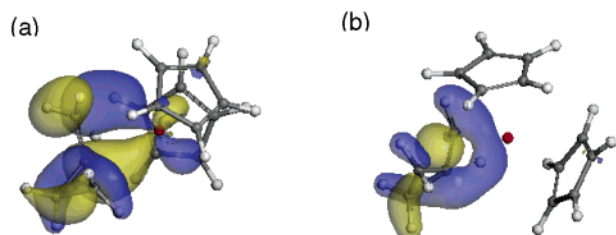
**Figure 1.** Potential energy profile of 1,2-insertion and ring-opening processes of $Cp_2LnH$-MCP systems obtained at RPBE level. The values with and without parentheses correspond to $Cp_2LuH$-MCP and $Cp_2LaH$-MCP, respectively.
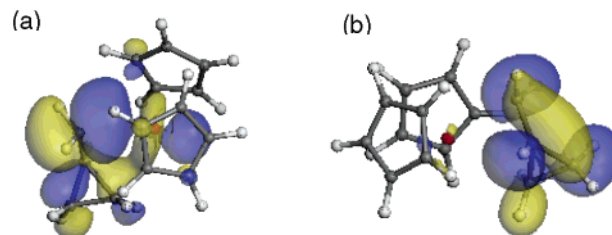


**Figure 2.** Orbital interaction isosurface of TS1: (a) 56A MO; La(5d) with 2p of C1 and C2. (b) 51A MO; H1(1s) with 2p of C1 and C2.
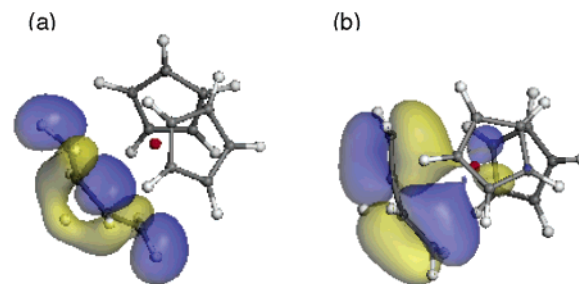


**Figure 3.** Orbital interaction isosurface of M2: (a) 56A MO; La(5d) with 2p of C1 and C4. (b) 50A MO; H1(1s) with C2(2p).

**Table 1.** Selected Bond Distances (Å) of Various Structures Shown in Figure 1

|  | Cp₂LaH+ MCP | M1 | TS1 | M2 | TS2 | M3 |
|---|---|---|---|---|---|---|
| La−H1 | 2.145 | 2.159 | 2.263 | 3.347 | 3.168 | 3.745 |
| La−C1 | / | 3.371 | 2.756 | 2.567 | 2.877 | 3.344 |
| La−C2 | / | 3.308 | 2.660 | 2.962 | 2.773 | 3.255 |
| La−C3 | / | 4.179 | 4.097 | 4.117 | 2.763 | 3.310 |
| La−C4 | / | 3.526 | 3.428 | 3.024 | 2.896 | 2.606 |
| C1−H1 | / | 4.581 | 1.345 | 2.209 | 2.164 | 2.104 |
| C2−H1 | / | 3.855 | 1.291 | 1.096 | 1.098 | 1.099 |
| C2−H2 | 2.221 | 2.229 | 2.241 | 2.250 | 1.369 | 2.137 |
| C3−H2 | 1.095 | 1.094 | 1.093 | 1.092 | 1.363 | 1.110 |
| C1−C2 | 1.335 | 1.339 | 1.561 | 1.514 | 1.423 | 1.354 |
| C2−C3 | 1.476 | 1.473 | 1.502 | 1.511 | 1.494 | 1.511 |
| C2−C4 | 1.476 | 1.478 | 1.539 | 1.585 | 2.593 | 2.509 |
| C3−C4 | 1.550 | 1.550 | 1.516 | 1.523 | 1.425 | 1.563 |



**Figure 4.** Orbital interaction isosurface of TS2: (a) 50A MO; H2(1s) with 2p of C2 and C3. (b) 51A MO, La(5d) with π-orbitals of C1=C2 and C3=C4.

interesting coordination geometry. In the case of TS1 structure, both Ln (La or Lu) and H1 coordinate ($\eta^2$ form) with C1 and C2 of MCP, resulting in the formation of a tetrahedral geometry. This observation is well supported by the examination of the various bond lengths listed in Table 1 as well as the analysis of the orbital interaction isosurfaces illustrated in Figure 2. For example, comparison of M1 and TS1 data presented in Table 1 reveals the elongation of both C1−C2 and La−H1 bonds with a simultaneous decrease in La−C1 and La−C2 distances. Further, as can be seen from Figure 2, the overlap of La(5d) orbital with C1(2p) and C2 (2p) orbitals, as well as the overlap of H1(1s) with C1(2p) and C2 (2p), clearly demonstrates the above conjecture. It is, however,

noteworthy here that the observed tetrahedral coordination for TS1 structure is very different from the usual four-center coplanar quadrilateral geometry (TS) reported for alkenes.[5c,12]

Subsequently, H1 (of TS1) is inserted to C2 resulting in the formation of new bonds, viz., C2−H1, La−C1, and La−C4 (M2), which is reflected in the shorter bond distances (see Table 1) as well as the overlap of La(5d) with C1(2p) and C4(2p); the overlap of H1(1s) with C2(2p) (Figure 3). On the other hand, TS2 represents yet another unusual structure where the coordination ($\eta^4$ form) between Ln and MCP takes place through all four carbon atoms as a consequence of ring opening with a simultaneous "switching or oscillating" of H2 between C2 and C3. The orbital interaction isosurfaces shown in Figure 4 and the bond distances summarized
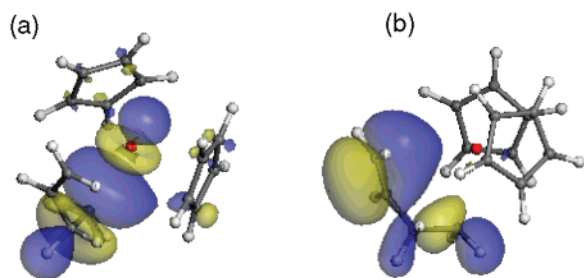
**Figure 5.** Orbital interaction isosurface of M3: (a) 56 A MO, La(5d) with C4(2p). (b) 51A MO, $\pi$-orbital of C1=C2.

**Scheme 2.** Insertion and Ring-Opening Pathway of MCP over Cp$_2$LnH
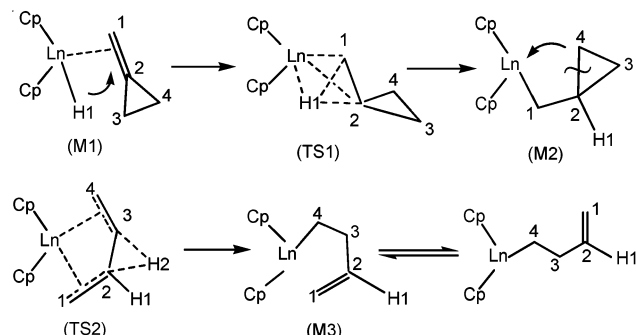


in Table 1 illustrate the binding nature of TS2. Moreover, nearly equivalent bond lengths of C2−H2 and C3−H2 as well as similar distances between La and C1∼C4 prove the above conclusion. Eventually, TS2 transforms into M3, where C4 binds with La ($\eta^1$ form; Figure 5a), with the reinstation of C1=C2 double bond (Figure 5b and Table 1), and hence no (orbital) interaction of La with C1, C2, or C3 was observed. At this juncture, it is also interesting to note that the coordination of Ln-C4 in M3 is similar to that of Ln-H1 in the parent Cp$_2$LnH catalyst, and therefore a second MCP molecule can easily approach M3, whereby a smooth polymerization may proceed in the case of Cp$_2$LuH or a dimerization in the case of Cp$_2$LaH.[2a,b]

Figure 1 also gives the relative energies for the various processes; a lower energy barrier is noted for Cp$_2$LaH than Cp$_2$LuH, suggesting that the insertion and ring opening is more facile in the case of the former. Finally, it may be concluded that the activation of MCP initiated by Cp$_2$LnH proceeds initially via the formation of Cp$_2$LnH−MCP complex followed by 1,2-insertion with the deformed MCP structure. Subsequently, the ring opening occurs at the proximal bond with a simultaneous hydrogen transfer followed by the establishment of Ln-C4 bond. It is likely that with additional

MCP molecules, the M3 may proceed to a smooth polymerization or a dimerization.[2a,b] As a result, Scheme 2 presents a schematic representation of the most probable reaction pathway of MCP activation over lanthanocene catalysts.

**Supporting Information Available:** Tables containing coordinates of stationary points, calculated and experimental geometry data, relative energies of various intermediates and transitions states at the level of BLYP as well as the orbital interaction isosurface figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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