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DFT Study of the Molecular Mechanism of Lewis Acid Induced [4 + 3]  
Cycloadditions of 2-Alkylacroleins with Cyclopentadiene

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The mechanism of the Lewis acid ( $\text{AlCl}_3$ ) induced [4 + 3] cycloaddition of 2-methylacrolein with cyclopentadiene (Cp) [ *J. Am. Chem. Soc.* **2004**, *126*, 2692] has been examined here through DFT calculations at the MPW1K(DCM)/6-31 + G\*\* level. Formation of these seven-membered carbocycles is a domino process that comprises three consecutive reactions. The first one is a polar Diels–Alder reaction that is initialized by the nucleophilic attack of Cp to the  $\beta$ -conjugated position of acrolein, yielding the formation of the *endo* and *exo* [4 + 2] cycloadducts. The corresponding LA–[4 + 2] cycloadduct complexes equilibrate through a skeleton rearrangement with a low free activation energy with two seven-membered zwitterionic intermediates, which undergo a rapid intramolecular hydride shift to yield irreversibly the formally *endo* and *exo* [4 + 3] cycloadducts. A comparative analysis of this mechanism with that for the Lewis acid induced [4 + 3] cycloadditions of 2-silyloxyacroleins allows establishment of the requirements for the formation of the seven-membered carbocycles.

## Introduction

The direct construction of seven-membered rings via [4 + 3] cycloadditions is the most attractive strategy for preparing this frequently observed natural product substructure.<sup>1</sup>  $\alpha,\beta$ -Unsaturated carbonyl compounds coordinated to a Lewis acid (LA) have been widely used as the three-atom component of this particular cycloaddition. The use of 2-silyloxyacroleins in the presence of a LA catalyst has received much interest in the past years (Scheme 1).<sup>2</sup>

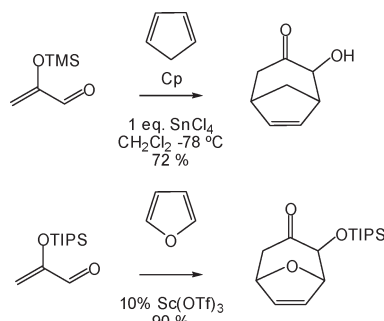
Recently, Davies and Dai<sup>3,4</sup> reported the [4 + 3] cycloaddition between 2-alkylacroleins and cyclopentadiene (Cp, **2**) in the presence on 1.1 equiv of  $\text{AlCl}_3$ . For 2-methylacrolein, **1**,

these authors found that at low temperature ( $-78^\circ\text{C}$ ), the reaction with **2** yielded the *endo* and *exo* [4 + 2] cycloadducts **3** (Scheme 2). However, when the reaction was warmed to  $0^\circ\text{C}$ , the [4 + 3] cycloadduct **4** was the major product formed with a large diastereoselectivity (96% de). These authors proposed a *tandem Diels–Alder (DA) reaction/ring expansion* for the formation of the [4 + 3] cycloadduct **4**. For Harmata's LA-induced [4 + 3] cycloadditions of 2-silyloxyacroleins, a similar mechanism was proposed.<sup>3</sup> Unfortunately, all attempts to obtain the [4 + 2] cycloadduct from the scandium triflate catalyzed DA reaction of **5** with **2** yielded a mixture of the [4 + 3] cycloadducts **7**. The [4 + 2] cycloadduct **6** was obtained by a microwave ( $\mu\omega$ )-induced cycloaddition reaction between **5** and **2** (Scheme 3). Furthermore, the isolated *exo* [4 + 2] cycloadduct **6** readily underwent a scandium triflate catalyzed rearrangement under Harmata's conditions. These experiments drove Davies and Dai to propose that the Harmata and related [4 + 3] cycloadditions were also examples of a *tandem DA reaction/ring expansion* mechanism.<sup>3</sup>

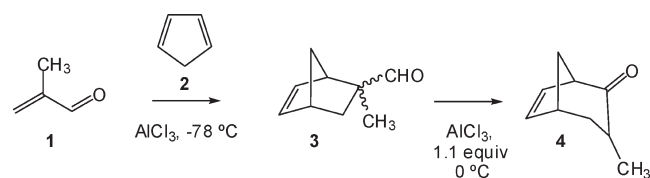
Recently, we have studied the LA-induced [4 + 3] cycloaddition of 2-silyloxyacroleins, using density functional theory

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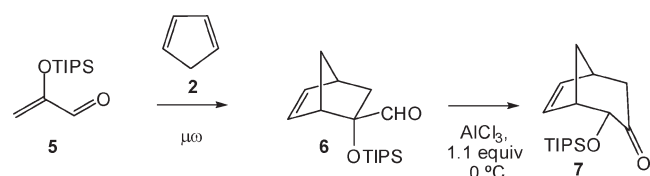
## SCHEME 1



## SCHEME 2



## SCHEME 3



(DFT) methods at the B3LYP/6-31G\* level.<sup>5,6</sup> Formation of the formally [4 + 3] cycloadducts have a three-step mechanism that is initialized by the nucleophilic attack of furan **9** to the  $\beta$ -conjugated position of the complex **8** yielding the zwitterionic intermediate **10** (see Scheme 4). The key step on the formation of the seven-membered ring is the attack of the furan residue to the carbonyl carbon in this intermediate to yield the formally [4 + 3] cycloadduct **11**. The later migration state structure (TS) associated with the TMS migration step is located above the TS yielding the [4 + 2] cycloadduct **13**, but the [4 + 3] cycloadduct **12** is thermodynamically more stable. In consequence, while the [4 + 2] cycloadduct **13** is the product of kinetic control, the [4 + 3] cycloadduct **12** is the product of the thermodynamic control, in clear agreement with the experimental outcome.

The LA-induced [4 + 3] cycloadditions of 2-alkylacroleins reported by Davies<sup>3</sup> have not been theoretically studied. Now, a complete study about the role of the LA on the competitive formation of the formally [4 + 2] and [4 + 3] cycloadducts of 2-alkylacroleins has been carried out. With this purpose, we have performed an exhaustive exploration of the potential energy surface (PES) for the  $\text{AlCl}_3$  LA-catalyzed reaction of 2-methylacrolein,  $\text{MeACR-AlCl}_3$  **14**, with Cp **2**, as a model of the reaction experimentally studied by Davies (see Scheme 5).<sup>3</sup>

## Computational Methods

DFT calculations were carried out using the MPW1K<sup>7</sup> functionals developed by Truhlar, together with the standard 6-31 + G\*\* basis set.<sup>8</sup> Because of the problems associated with the gas-phase optimization of some species, the exploration of the PES was carried out in dichloromethane (DCM). These calculations have been referenced as MPW1K(DCM)/6-31 + G\*\*. Solvent effects have been considered at the same level of theory using a self-consistent reaction field (SCRF)<sup>9</sup> based on the polarizable continuum model (PCM) of Tomasi's group.<sup>10</sup> The dielectric constant of DCM at 298.0 K,  $\epsilon=8.93$ , was selected. The optimizations were carried out using the Berny analytical gradient optimization method.<sup>11</sup> The stationary points were characterized by frequency calculations in order to verify that TSs had one and only one imaginary frequency. The intrinsic reaction coordinate (IRC)<sup>12</sup> path was traced in order to check the energy profiles connecting each TS to the two associated minima of the proposed mechanism using the second-order González-Schlegel integration method.<sup>13</sup> The values of the enthalpies, entropies, and free energies in DCM were calculated with the standard statistical thermodynamics at 195.15 K.<sup>8</sup> Thermodynamic calculations were scaled by a factor of 0.96.<sup>14</sup> The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method.<sup>15</sup> All calculations were carried out with the Gaussian 03 suite of programs.<sup>16</sup>

The global electrophilicity index,<sup>17</sup>  $\omega$ , which measures the stabilization energy when the system acquires an additional electronic charge  $\Delta N$  from the environment, has been given by the following simple expression,<sup>17</sup>  $\omega = (\mu^2/2\eta)$ , in terms of the electronic chemical potential  $\mu$  and the chemical hardness  $\eta$ . Both quantities may be approached in terms of the one electron energies of the frontier molecular orbital HOMO and LUMO,  $\epsilon_H$  and  $\epsilon_L$ , as  $\mu \approx (\epsilon_H + \epsilon_L)/2$  and  $\eta \approx (\epsilon_L - \epsilon_H)$ , respectively.<sup>18</sup> Recently, we have introduced an empirical (relative) nucleophilicity index,<sup>19</sup>  $N$ , based on the HOMO energies obtained within the Kohn–Sham scheme<sup>20</sup> and defined as  $N = E_{\text{HOMO}}(N_U) - E_{\text{HOMO}}(\text{TCE})$ . This nucleophilicity scale is referred to tetracyanoethylene (TCE) taken as a reference. The reactivity indexes were computed from the gas-phase B3LYP/6-31G\* HOMO and LUMO energies at the ground state of the molecules.

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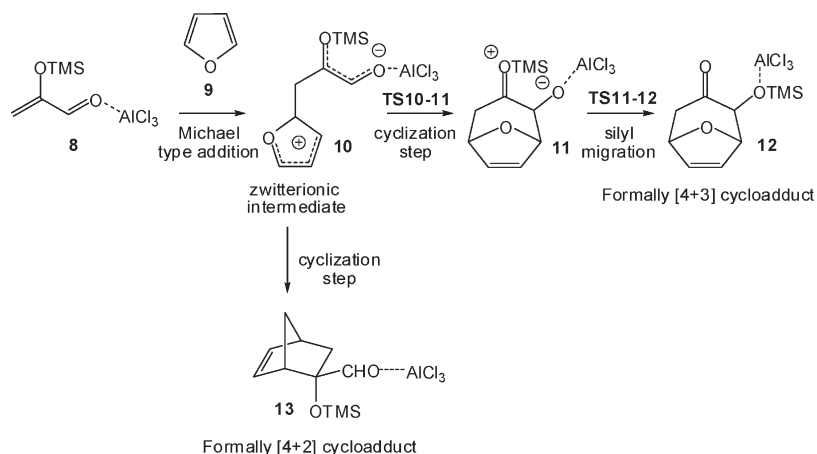
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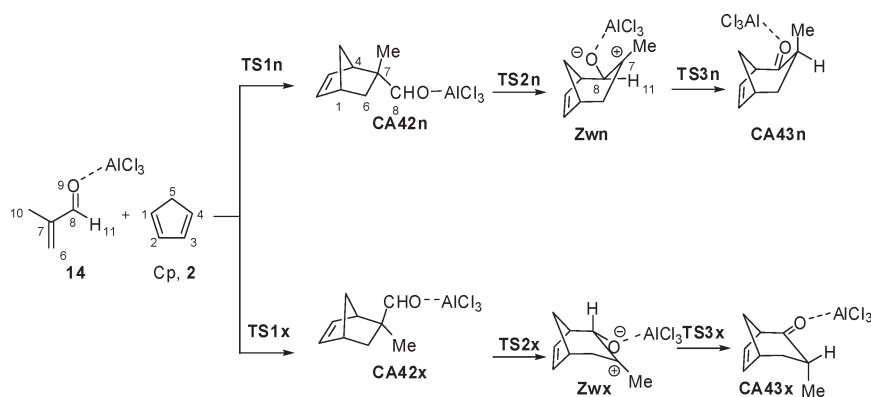
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SCHEME 4



SCHEME 5



## Results and Discussion

First, an analysis based on the reactivity indexes of the reagents involved in the LA-catalyzed DA reactions of 2-methylacrolein **1** with Cp **2** will be performed in order to state the polar character of these cycloadditions. Then, the reaction mechanism of the formation of the formally [4 + 2] and [4 + 3] cycloadducts will be studied. Finally, a comparative analysis between the mechanisms of LA-catalyzed cycloaddition reactions of 2-methylacrolein and 2-silyloxyacrolein will be performed in order to establish the main behaviors on the formations of these seven-membered carbocycles.

**Analysis of the LA-Catalyzed DA Reaction between 2-Methylacrolein **1** and Cp **2** Based on the Reactivity Indexes of the Reagents.** Recent studies carried out on cycloaddition reactions have shown that the reactivity indexes defined within the conceptual DFT<sup>21</sup> are powerful tools to establish the polar character of the reactions.<sup>22</sup> The electronic chemical potential  $\mu$  of Cp **2**,  $-0.1107$  au, is higher than that of the  $\text{AlCl}_3$ -2-methylacrolein complex **14**,  $-0.2148$  au (see Table 1). Therefore, along a polar cycloaddition, the charge

transfer (CT) will take place from Cp to this acrolein derivative, in complete agreement with the CT analysis made at the TSs (see below).

Coordination of a strong LA such as  $\text{AlCl}_3$  to the carbonyl oxygen atom of acrolein **16** increases notably the electrophilicity of the corresponding LA complex **15** to 4.62 eV. Therefore, it is expected that the LA-catalyzed DA reaction will have a large polar character. Substitution on the  $\alpha$ -position of the LA-acrolein complex **15** by an electron-releasing (ER) methyl group decreases the electrophilicity of the LA complex **14** to 4.25 eV. Note that the LA-2-methylacrolein complex **14** has a electrophilicity larger than that of 2-silyloxyacrolein **8**. Cp **2** has a low electrophilicity value, 0.83 eV, being classified as poor electrophile.<sup>22</sup> On the other hand, Cp has large nucleophilicity  $N$  value, 3.36 eV, being classified as a strong nucleophile.<sup>23</sup> Note that Cp **2** is a better nucleophile than furan **9**.

The large  $\Delta\omega$  of the  $\text{MeACR}-\text{AlCl}_3$ (**14**)/Cp(**2**) reaction, 3.42 eV, points out the high polar character of the cycloaddition process.<sup>22</sup> This value is closer to that presented by the  $\text{SiACR}-\text{AlCl}_3$ (**8**)/furan(**9**) reaction,  $\Delta\omega = 3.52$  eV, and it is much higher than that presumably presented by the non-catalyzed process,  $\Delta\omega(\text{MeACR}(\mathbf{1})/\text{Cp}(\mathbf{2})) = 0.87$  eV. In consequence, these LA-catalyzed DA reactions will have a high polar character and low activation energy.<sup>6</sup>

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**TABLE 1.** Electronic Chemical Potential ( $\mu$ ), Chemical Hardness ( $\eta$ ), Global Electrophilicity ( $\omega$ ), and global nucleophilicity ( $N$ ) of Reagents Involved in LA-Catalyzed Cycloaddition Reactions

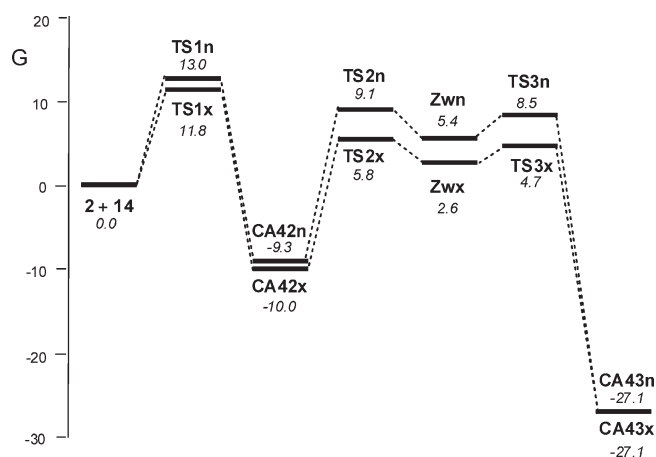
	$\mu$ (au)	$\eta$ (au)	$\omega$ (eV)	$N$ (eV)
<b>15<sup>a</sup></b>	-0.2190	0.1412	4.62	1.24
<b>14</b>	-0.2148	0.1478	4.25	1.26
<b>8</b>	-0.2120	0.1493	4.10	1.32
<b>16<sup>b</sup></b>	-0.1611	0.1921	1.84	2.12
<b>1</b>	-0.1570	0.1969	1.70	2.17
<b>2</b>	-0.1107	0.2018	0.83	3.36
<b>9</b>	-0.1024	0.2441	0.58	3.01

<sup>a</sup>**15** is the CH<sub>2</sub>=CHCHO–AlCl<sub>3</sub> complex. <sup>b</sup>**16** is CH<sub>2</sub>=CHCHO.

**Study of the Molecular Mechanism of the LA-Induced [4 + 3] Cycloaddition Reaction between Cp and 2-Methylacrolein (MeACR).** An analysis of the PES of the LA-induced [4 + 3] cycloaddition reaction between Cp and MeACR indicates that the formation of the seven-membered carbocycle is a domino process involving three consecutive reactions: (i) a polar DA reaction between Cp and the MeACR–AlCl<sub>3</sub> complex to yield the corresponding [4 + 2] cycloadduct, (ii) a skeleton rearrangement yielding a seven-membered zwitterionic intermediate, and (iii) an intramolecular hydride shift to afford the final seven-membered carbocycle. In addition, as a result of the asymmetry of both reagents, this domino reaction can take place along two stereoisomeric channels: the *endo* and the *exo* (named *n* and *x*, respectively), depending on the relative approach mode of the Cp dienic system to the formyl group of the MeACR–AlCl<sub>3</sub>. A schematic representation of the *endo* and *exo* stereoisomeric channels allowing the formation of the [4 + 2] and [4 + 3] cycloadducts is shown in Scheme 5. The energy results are given in Table 1S in Supporting Information, while the MPW1K/6-31 + G\*\* free energy profiles associated with the formation of the *endo* and *exo* seven-membered carbocycles are given in Figure 1.

The MeACR–AlCl<sub>3</sub> complex can adopt two planar conformations by rotation of the C7–C8 single bond named as *s-trans* and *s-cis*. The *s-cis* conformation is 4.5 kcal/mol higher free energy than the *s-trans*. In addition, the energy associated with the C7–C8 bond rotation, 13.8 kcal/mol, is higher than that associated with the polar DA reaction (see Table 1S in Supporting Information). In consequence, the cycloaddition reactions are expected to take place through the *s-trans* MeACR–AlCl<sub>3</sub> complex **14** (see Scheme 5).

The first reaction of this domino process is a polar DA reaction, which is initialized by the nucleophilic attack of Cp **2** to the  $\beta$ -position of *s-trans* MeACR–AlCl<sub>3</sub> complex **14**. After the corresponding TS, the concomitant ring closure affords the [4 + 2] cycloadduct. The activation free energy associated with this nucleophilic attack is 13.0 (**TS1n**) and 11.8 (**TS1x**) kcal/mol (see Figure 1). **TS1x** is located 1.2 kcal/mol below **TS1n**; therefore, this nucleophilic attack presents a low *exo* selectivity. These nucleophilic attacks present very low activation barriers, 2.2 (**TS1n**) and 2.1 (**TS1x**) kcal/mol (see Table 1S in Supporting Information), as a consequence of the large nucleophilic character of Cp **2** and the large electrophilic character of MeACR–AlCl<sub>3</sub> complex **14** (see Table 1). Formation of the [4 + 2] cycloadducts is exergonic by -9.3 (**CA42n**) and -10.0 kcal/mol (**CA42x**). In consequence, with a low free activation energy, 22.3 (**TS1n**) and 21.8 (**TS1x**), these cycloadducts could revert to the separated reagents.



**FIGURE 1.** MPW1K(DCM)/6-31 + G\*\* free energy profile, *G*, in kcal/mol, for the *endo* and *exo* reaction paths of the domino reaction between Cp **2** and the MeACR–AlCl<sub>3</sub> complex **14**. The relative free energies are given in italics.

In addition, the LA complexes **CA42n** and **CA42x** can undergo a norbornene skeleton rearrangement to yield two stereoisomeric seven-membered zwitterionic intermediates, **Zwn** and **Zwx**, which are located only ca. 14 kcal/mol above the corresponding [4 + 2] cycloadducts. These rearrangements present low free activation energies, 18.4 (**TS2n**) and 15.8 (**TS2x**). Similarly to the formation [4 + 2] cycloadducts, the rearrangement along the *exo* reactive channel is 2.6 kcal/mol favored over the *endo* one. Note that **TS2x** is located 6.0 kcal/mol below **TS1x**. This large energy difference allows the stereoselective conversion of the *exo* [4 + 2] cycloadduct into the *exo* [4 + 3] one cycloadduct, without the reversion to reagents.<sup>3</sup> Finally, a rapid intramolecular hydride shift from the aldehyde carbon atom to the carbocationic  $\alpha$ -carbon of MeACR framework in these intermediates affords via **TS3n** and **TS3x** the formally [4 + 3] cycloadducts **CA43n** and **CA43x**. The free activation energies associated with these hydrogen shifts have very low values, 3.1 and 2.1 kcal/mol, respectively; formation of the final seven-membered carbocycles are strongly exergonic by ca. -27 kcal/mol (see Table 2S). Therefore, after the skeleton rearrangement yielding the zwitterionic intermediates **Zwn** and **Zwx**, formation of the formally [4 + 3] cycloadducts can be considered irreversible at room temperature.

To test the DFT energies, MP2(DCM)/6-31 + G\*\* and MP3(DCM)/6-31 + G\*\* single-point energy calculations were performed over the MPW1K(DCM)/6-31 + G\*\* geometries. The energy results are summarized in Table 2S in Supporting Information, while the corresponding *endo* and *exo* energy profiles associated to the formation of the seven-membered carbocycles are schematized in Figure 1S in Supporting Information. A comparison of the energy results given at the three computational levels shows that the MPW1K energy profile resemble to the MP3 ones (see Figure 1S). While the MPW1K activation energies associated to the polar DA reactions and the reaction energies associated with the formation of the cycloadducts are subestimated only by less of 2.0 kcal/mol, the TSs and zwitterionic intermediates associated with the skeleton rearrangement are subestimated by ca. 4.0 kcal/mol. Note that the MP2 have a more erratic response: the TS of the DA reaction disappears and the zwitterionic intermediates are located above the TSs



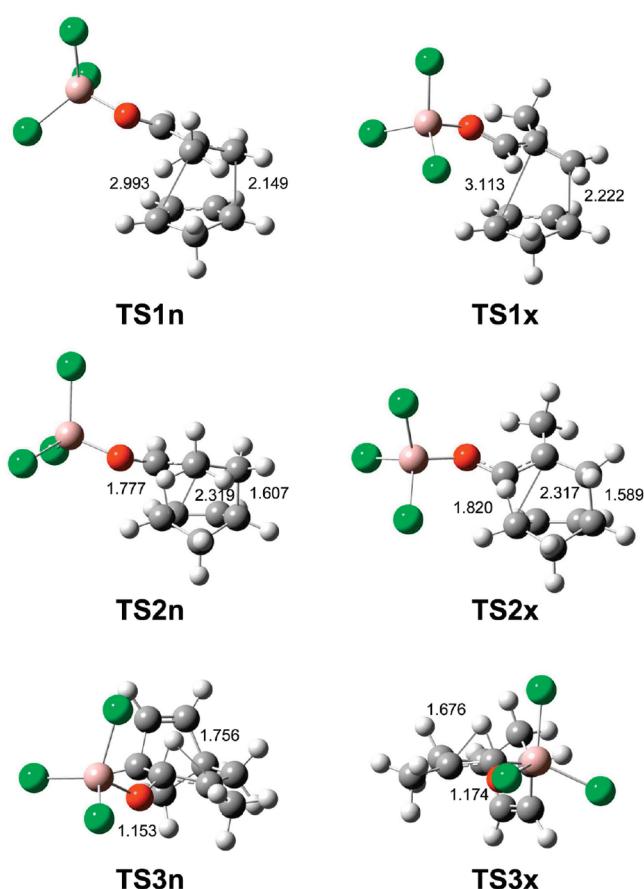
associated with the skeleton rearrangement. This comparative analysis allows us to validate the use of the MPW1K functional in the study of these domino reactions. Note that while the B3LYP affords reasonable activation energies, it underestimates the relative energy of the cycloadducts involved in the domino reactions.<sup>24</sup>

From these energies some interesting conclusions can be obtained: (i) For these polar DA reactions, after the nucleophilic attack of Cp to the MeACR–AlCl<sub>3</sub> complex, the formation of the formally [4 + 2] cycloadducts takes place without any barrier. Consequently, the [4 + 2] cycloadducts are the product of a kinetic control. (ii) Formation of the [4 + 2] cycloadducts is reversible, and with a free activation barrier of ca. 20 kcal/mol, they could revert to reagents. (iii) The LA-coordinated [4 + 2] cycloadducts can undergo a skeleton rearrangement to yield the formation of two seven-membered zwitterionic intermediates, which are located only ca. 14 kcal/mol above the corresponding LA-coordinated [4 + 2] cycloadducts. (iv) A rapid intramolecular 1,2-hydride shift at these intermediates affords the formally [4 + 3] cycloadducts, which are ca. 17 kcal/mol more stable than the [4 + 2] ones. Consequently, the [4 + 3] cycloadducts are the products of a thermodynamic control. (v) All of the stationary points belonging to the *exo* reactive channel are located below those belonging to the *endo* ones. (vi) Along the *exo* reactive channel, the TS associated with the ring expansion is clearly located below the TS associated with the [4 + 2] cycloaddition. This fact allows the stereoselective conversion of the *exo* [4 + 2] cycloadduct into the *exo* [4 + 3] cycloadduct, without the reversion to reagents. These energy results are in reasonable agreement with the experimental results reported by Davies.<sup>3</sup>

This mechanism for the formation of the seven-membered carbocycles is similar to that proposed by Davies for the LA-induced [4 + 3] cycloadditions of 2-alkylacroleins with Cp. “The most likely mechanism is a Lewis acid-induced 1,2-alkyl shift to form the tertiary carbocation **Zwx** (see Scheme 5). A suprafacial hydride migration in **Zwx** would then generate the observed [4 + 3] cycloadduct **CA43X**.”<sup>3</sup> This mechanism is consistent with the deuterium isotope study performed by Davies and can explain why crotonaldehyde fails to form the [4 + 3] cycloadduct because a less favorable secondary carbocation would be the intermediate in this case.<sup>3</sup>

The geometries of the TSs involved in this domino reaction are given in Figure 2. At the TSs associated with the nucleophilic attack of Cp 2 to MeACR–AlCl<sub>3</sub> complex 14, the lengths of the C1–C6 forming bond are 2.149 Å at **TS1n** and 2.222 Å at **TS1x**, whereas the distance between the C4 and C7 atoms remains at 2.993 and 3.113 Å, respectively. These lengths point to highly asynchronous TSs associated with the nucleophilic attack of the end of the  $\pi$ -conjugated system of Cp to the  $\beta$ -conjugated position of the MeACR–AlCl<sub>3</sub> complex 14.

At the TSs associated with the skeleton rearrangements, the lengths of the forming and breaking C4–C8 and C4–C7 bonds are 1.777 and 2.319 Å at **TS2n** and 1.829 and 2.317 Å at **TS2x**, while the lengths of the C1–C6 bond are 1.607 and



**FIGURE 2.** MPW1K(DCM)/6-31+G\*\* transition state structures involved on the cycloaddition reactions between Cp 2 and the MeACR–AlCl<sub>3</sub> complex 14. The distances of the forming and breaking bonds are given in angstroms.

1.589 Å, respectively. These data indicate that these TSs are very advanced, in clear agreement with the endothermic character of these processes.<sup>26</sup> The IRC from **TS2n** and **TS2x** to the minimum structures connect the [4 + 2] cycloadducts **CA42n** and **CA42x** with the seven-membered intermediates **Zwn** and **Zwx**.

It is interesting to note that although **TS2n** and **TS2x** geometrically resemble **TS10–11**, associated with the formation of the seven-membered carbocycle intermediate involved in the LA-induced [4 + 3] cycloaddition of 2-silyloxyacroleins (see Scheme 4), they belong to unlike chemical process. The analysis of the atomic movement at the unique imaginary frequency associated to **TS10–11** as well as the IRC analysis from this TS indicate that they are associated to the ring closure of the zwitterionic intermediate **10<sup>6</sup>** instead of a skeleton rearrangement of the [4 + 2] cycloadducts as in the case of 2-alkylacroleins.

Finally, at the TSs associated with the 1,2-hydride shift, the distances of the C8–H11 breaking bond and the H11–C7 forming bond are 1.153 and 1.756 (TS3n) and 1.174 and 1.676 Å (TS3x), respectively. These lengths indicate that these TSs are very earlier in clear agreement with the strong exothermic character of these processes.<sup>26</sup>

The polar character of the DA reactions has been related with the CT at the corresponding TSs.<sup>22</sup> The natural charges

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at the TSs associated with the DA reactions have been shared between the Cp fragment and the MeACR–AlCl<sub>3</sub> one. At these TSs the CT from Cp to the acrolein derivative **14** is 0.37 (TS1n) and 0.30 e (TS1x). These high values, which are in clear agreement with the high electrophilicity of the MeACR–AlCl<sub>3</sub> complex **14** and the high nucleophilicity of Cp, point out the large polar character of these DA reactions.

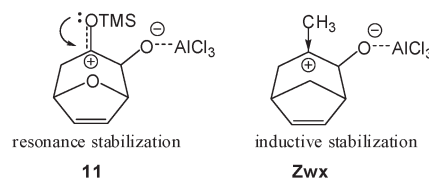
An analysis of the IRCs from TS1n and TS1x to the corresponding [4 + 2] cycloadducts indicates that these polar DA reactions have a one-step, two-stage mechanism. At the first stage of the reaction only the C1–C6 bond is formed through these highly asynchronous TSs. After the complete formation of the C1–C6 bond begins the formation of the second C4–C7 bond at the second stage of the reaction. Several theoretical studies have pointed out that for the LA-catalyzed DA reactions of acrolein derivatives both one-step<sup>27</sup> and two-step<sup>6,28</sup> mechanisms are feasible. In both mechanisms, the DA reactions are initialized by the nucleophilic attack of the diene to LA-coordinated acrolein acting as a strong electrophile through a highly asynchronous TS. At the two-step mechanisms, the zwitterionic intermediates are generally located going down the cycloadducts, and in the absence of some strain, the second step has a very low barrier. In consequence, these zwitterionic intermediates cannot be experimentally observed.

**Why the 2-Silyloxyacroleins and 2-Alkylacroleins Yield the Formally [4 + 3] Cycloadducts in Presence of Strong LA Catalysts.** A comparison of the mechanisms of the domino reactions of furan **9** with 2-silyloxyacroleins<sup>5,6</sup> and Cp **2** with 2-alkylacroleins in presence of the AlCl<sub>3</sub>–LA allows us to find some similarities in the formation of the final seven-membered carbocycles. In both cases, the reactions are initialized by a polar DA reaction characterized by the nucleophilic attack of furan or Cp dienes to the  $\beta$ -conjugated position of the LA coordinated acrolein derivatives to yield the corresponding [4 + 2] cycloadducts. In presence of 1 equiv of the LA, the formation of these [4 + 2] cycloadducts is a reversible process, and by heating, a competitive path arises from the corresponding LA-coordinated [4 + 2] cycloadducts. It consists in a norbornene skeleton rearrangement to yield a zwitterionic intermediate, which evolves to a thermodynamically more favorable seven-membered carbocycle.

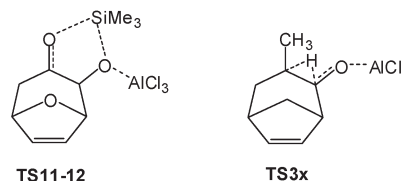
Thus, three conditions are required for the formation of the final seven-membered carbocycles: (i) the coordination of a strong LA to the [4 + 2] cycloadduct able to promote the formation of the seven-membered zwitterionic intermediates, (ii) the presence of an ER group on the  $\alpha$ -carbon of acrolein able to stabilize the carbocationic center formed at this position after the skeleton rearrangement, and (iii) a subsequent intramolecular rearrangement able to reorganize the charges at these intermediates, allowing the formation of the final [4 + 3] cycloadducts.

## SCHEME 6

*ij) Stabilization effects on the seven-membered zwitterionic intermediates.*



*ij) Transfer group involved in the formation of the final [4 + 3] cycloadducts.*



The first requirement is exerted by the use of an equimolecular quantity of a strong LA such as AlCl<sub>3</sub>, which favors the ring expansion through the formation of the corresponding complex with the [4 + 2] cycloadducts. Note that this ring expansion is achieved through unlike modes at these acrolein derivatives. While the 2-silyloxyacroleins are obtained through a ring closure at the carbonyl carbon atom at the zwitterionic intermediate **10** (see Scheme 4), 2-alkylacroleins are achieved by a skeleton rearrangement from the [4 + 2] cycloadducts.

The ER silyloxy and methyl groups meet the second requirement. While the oxygen lone pair of the silyloxy group is able to stabilize the carbocationic center by a  $\pi$  resonance effect, the inductive effect exerted by the methyl group plays a similar stabilizing effect (see the intermediates **11** and **Zwx** in Scheme 6). Note that experimentally crotonaldehyde fails to form the [4 + 3] cycloadduct because it would involve a less favorable secondary carbocationic intermediate.<sup>3</sup>

Finally, the third requirement is exerted by two different rearrangements at both acrolein derivatives: for 2-silyloxyacroleins, a silyl migration over the carbonyl oxygen allows the formation of the formally [4 + 3] cycloadduct (see Schemes 4 and 6) and for 2-methylacrolein, a hydride shift over the carbocationic center allows the stabilization (see Schemes 5 and 6).

## Conclusions

The mechanism of the Lewis acid induced [4 + 3] cycloaddition of 2-methylacrolein with cyclopentadiene has been studied using DFT calculations at the MPW1K(DCM)/6-31 + G\*\* level. Formation of the seven-membered carbocycles is a domino reaction, which is initialized by the nucleophilic attack of Cp to the  $\beta$ -conjugated position of acrolein, yielding through an one-step, two-stage mechanism the formation of the *endo* and *exo* [4 + 2] cycloadducts. The corresponding LA–[4 + 2] cycloadduct complexes equilibrate with a low free activation energy with two seven-membered zwitterionic intermediates achieved by a skeleton rearrangement. Finally, a rapid intramolecular hydride shift on these zwitterionic intermediates affords irreversibly the formation of the formally [4 + 3] cycloadducts.

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A comparison of this mechanism with that of the LA-induced [4 + 3] cycloaddition of furan with 2-silyloxyacrolein reveals some interesting behaviors. In both reactions formation of the thermodynamically more stable seven-membered carbocycles demands three analogous requirements in order to favor the formation of the seven-membered carbocycles: (i) the use of an equimolecular quantity of a strong LA in order to favor a complete complexation of the corresponding [4 + 2] cycloadducts, which assists the subsequent ring expansion; (ii) the presence of an ER silyloxy or methyl group on the  $\alpha$ -carbon able to stabilize the carbocationic center formed after the rearrangement; and (iii) a subsequent silyl group transposition or a hydride shift able to equilibrate the charges at the seven-membered zwitterionic intermediate.

The present DFT study supports the mechanism proposed by Davies for the LA-induced [4 + 3] cycloadditions of 2-alkylacroleins with cyclopentadiene through a LA-induced ring expansion of the DA cycloadducts. This mechanism is

different from that for the LA-induced [4 + 3] cycloadditions of 2-silyloxyacroleins with furan, which takes place through a two-step polar cycloaddition.

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**Supporting Information Available:** Complete citation for ref 16. MPW1K/6-31+G\*\* total and relative energies, in gas-phase and in DCM, and MPW1K(DCM)/6-31+G\*\* total and relative enthalpies, entropies and free energies. MP2-(DCM)/6-31+G\*\*//MPW1K(DCM)/6-31+G\*\* and MP3-(DCM)/6-31+G\*\*//MPW1K(DCM)/6-31+G\*\* total and relative energies. MPW1K(DCM)/6-31+G\*\* computed total energies, unique imaginary frequency, and Cartesian coordinates of **14**, **2**, TSs, intermediates and cycloadducts found along the PES of the reaction of **14** + **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.