Mechanisms of five-membered rings formation in the addition reactions of ethylene to azomethine ylide and allyl-anion

Mikhail E. Kletskii, Oleg N. Burov, Nikita S. Fedik and Sergey V. Kurbatov

Supplementary Information

1 Southern Federal University,
7 Zorge St., Rostov-on-Don 344090, Russia; e-mail: mkletskii@yandex.ru
Scheme S1. $4\pi$–electron structures.

![Diagram of molecular structures 1-7 with geometrical characteristics](Image)

Figure S1. The main geometrical characteristics of structures 1-7. Interatomic distances in Å, angles in degrees (MP2/6-311++G**, gas phase).
Scheme S2. Cycloaddition of azomethine ylide 1 to ethylene 8.

TS 2\( \Xi_{im} = -456.2 \)

TS 3\( \Xi_{im} = -445.0 \)
Figure S2. The main geometrical characteristics of the PES’s stationary points for the cycloaddition of azomethine ylide 1 to ethylene 8. Interatomic distances in Å, angles in degrees. \( \nu_{im} \) – values of imagine frequencies in cm\(^{-1}\) (MP2/6-311++G**, gas phase).

Figure S2-1. The main geometrical characteristics of the PES’s stationary points for the cycloaddition of azomethine ylide 1 to ethylene 8. Interatomic distances in Å, angles in degrees. \( \nu_{im} \) – values of imagine frequencies in cm\(^{-1}\) (MP2/6-31++G**, gas phase).
Table S1. Total (E, a.e.), relative (E_{rel}, kcal/mol), relative Gibbs free energies (G_{rel}, kcal/mol) and the relative energy values with ZPE correction [(E + ZPE)_{rel}, kcal/mol] of stationary points on scheme S1.

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>E_{rel}</th>
<th>G_{rel}</th>
<th>(E + ZPE)_{rel}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1+8</td>
<td>-211.79772</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TS 1</td>
<td>-211.80345</td>
<td>-3.6</td>
<td>9.4</td>
<td>-1.1</td>
</tr>
<tr>
<td>9</td>
<td>-211.91368</td>
<td>-72.8</td>
<td>-53.3</td>
<td>-65.0</td>
</tr>
<tr>
<td>9'</td>
<td>-250.91380</td>
<td>-72.8</td>
<td>-54.0</td>
<td>-64.9</td>
</tr>
</tbody>
</table>

Scheme S3. Cycloaddition of methylenaminometanidilithithium 2 to ethylene 8.

Figure S3. The main geometrical characteristics of the PES’s stationary points for the cycloaddition of methylenaminometanidilithithium 2 to ethylene 8. Interatomic distances in Å, angles in degrees. \( v_{im} \) – values of imagine frequencies in cm\(^{-1}\) (MP2/6-311++G**, gas phase).
Scheme S4. Cycloaddition of allyl-anion 3 to ethylene 8.

Figure S4. The main geometrical characteristics of the PES’s stationary points for cycloaddition of the allyl-anion 3 to ethylene 8. Interatomic distances in Å, angles in degrees. $v_{im}$ – values of imaginary frequencies in cm$^{-1}$. SP – second order saddle point (MP2/6-311++G**, gas phase).
**Scheme S5.** Cycloaddition of allyllithium 4 to ethylene 8.

\[
\begin{array}{c}
\text{TS 12} \quad \nu_{\text{im}} = -449.0 \\
\text{16}, \text{C}_s \\
\text{SP 2} \quad \nu_{\text{im}} = -464.3; -275.7
\end{array}
\]

**Figure S5.** The main geometrical characteristics of the PES's stationary points for the cycloaddition of allyllithium 4 to ethylene 8. Interatomic distances in Å, angles in degrees. \( \nu_{\text{im}} \) – values of imagine frequencies in cm\(^{-1}\). SP – second order saddle point (MP2/6-311++G**, gas phase).

**Scheme S6.** Cycloaddition of 2-cyanoallyl-anion 5 to ethylene 8.
Figure S6. The main geometrical characteristics of the PES’s stationary points for the cycloaddition of 2-cyanoallyl-anion 5 to ethylene 8. Interatomic distances in Å, angles in degrees. \( \nu_{\text{im}} \) – values of imaginary frequencies in cm\(^{-1}\).
**Scheme S7.** Cycloaddition of 2-borylallyl-anion 6 to ethylene 8.

**Figure S7.** The main geometrical characteristics of the PES’s stationary points for the cycloaddition of 2-borylallyl-anion 6 to ethylene 8. Interatomic distances in Å, angles in degrees. $\nu_{im}$ – values of imagine frequencies in cm$^{-1}$ (MP2/6-311++G**, gas phase).
Scheme S8. Cycloaddition of 2-aminolallyl-anion 7 to ethylene 8.
Figure S8. The main geometrical characteristics of the PES’s stationary points for the cycloaddition of 2-aminolyl-anion 6 to ethylene 8. Interatomic distances in Å, angles in degrees. $\nu_{\text{im}}$ – values of imagine frequencies in cm$^{-1}$ (MP2/6-311++G**, gas phase).