Lanthanum-mediated dehydrogenation of 1- and 2-butynes: spectroscopy and formation of La(C_4H_4) isomers

Wenjin Cao, Dilrukshi Hewage, and Dong-Sheng Yang^a

Department of Chemistry, University of Kentucky, Lexington, KY, 40506-0055

a) Corresponding authors: dyang0@uky.edu

Tuesday, May 23, 2017
Table S1: Geometric parameters of La(η^4-CH2CCCH2) (Iso A), La(η^4-CH2CHCCH) (Iso B), and La(η^3-CHCCH3) (Iso C) in various electronic states from the DFT/B3LYP calculations. Bond lengths are in Å and bond angles in degrees. Carbon atomic numbering is shown in Figure 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>La(η^4-CH2CCCH2) (Iso A), C_{2v}</th>
<th>La(η^4-CH2CHCCH) (Iso B), C_{1}</th>
<th>La(η^3-CHCCH3) (Iso C), C_{1} or C_{s}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>^2A</td>
<td>^1A</td>
<td>^4A</td>
</tr>
<tr>
<td>C1-C2/C3-C4</td>
<td>1.416</td>
<td>1.411</td>
<td>1.363</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.248</td>
<td>1.252</td>
<td>1.255</td>
</tr>
<tr>
<td>La-C1/La-C4</td>
<td>2.597</td>
<td>2.542</td>
<td>2.995</td>
</tr>
<tr>
<td>La-C2/La-C3</td>
<td>2.449</td>
<td>2.398</td>
<td>2.621</td>
</tr>
<tr>
<td></td>
<td>^3A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.452</td>
<td>1.449</td>
<td>1.396</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.364</td>
<td>1.364</td>
<td>1.395</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.300</td>
<td>1.297</td>
<td>1.268</td>
</tr>
<tr>
<td>La-C1</td>
<td>2.568</td>
<td>2.519</td>
<td>3.057</td>
</tr>
<tr>
<td>La-C2</td>
<td>2.580</td>
<td>2.534</td>
<td>2.777</td>
</tr>
<tr>
<td>La-C3</td>
<td>2.490</td>
<td>2.438</td>
<td>2.576</td>
</tr>
<tr>
<td>La-C4</td>
<td>2.469</td>
<td>2.409</td>
<td>2.560</td>
</tr>
<tr>
<td>C1-C2-C3-C4</td>
<td>123.7</td>
<td>122.1</td>
<td>123.3</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>152.0</td>
<td>151.2</td>
<td>157.9</td>
</tr>
<tr>
<td>C1-C2-C3-C4</td>
<td>-57.1</td>
<td>-55.0</td>
<td>-76.7</td>
</tr>
<tr>
<td></td>
<td>^4A&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.324</td>
<td>1.325</td>
<td>1.338</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.312</td>
<td>1.306</td>
<td>1.341</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.499</td>
<td>1.493</td>
<td>1.493</td>
</tr>
<tr>
<td>La-C1</td>
<td>2.384</td>
<td>2.309</td>
<td>2.430</td>
</tr>
<tr>
<td>La-C2</td>
<td>2.450</td>
<td>2.409</td>
<td>2.530</td>
</tr>
<tr>
<td>La-C3</td>
<td>2.423</td>
<td>2.377</td>
<td>2.453</td>
</tr>
<tr>
<td>C4-C3-C2</td>
<td>134.0</td>
<td>138.9</td>
<td>131.2</td>
</tr>
<tr>
<td>C4-C3-C2-C1</td>
<td>140.1</td>
<td>139.0</td>
<td>180.0</td>
</tr>
</tbody>
</table>
Table S2: Excited neutral doublet and ionic singlet states and their relative energies (eV) of La(η^4-CH₂CCCH₂) (Iso A), La(η^4-CH₂CHCCH) (Iso B), and La(η^3-CHCCH₃) (Iso C) from the TDDFT and EOM-CCSD calculations.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Doublet</th>
<th>TDDFT</th>
<th>EOM-CCSD</th>
<th>Singlet</th>
<th>TDDFT</th>
<th>EOM-CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(η^4-CH₂CCCH₂) (Iso A), C₂ᵥ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>^2B₁</td>
<td>1.012</td>
<td>1.077</td>
<td>^1A₁</td>
<td>1.879</td>
<td>2.277</td>
<td></td>
</tr>
<tr>
<td>^2B₁</td>
<td>1.022</td>
<td>1.050</td>
<td>^3B₁</td>
<td>2.321</td>
<td>3.032</td>
<td></td>
</tr>
<tr>
<td>^2A₁</td>
<td>1.195</td>
<td>1.185</td>
<td>^1A₂</td>
<td>2.392</td>
<td>2.759</td>
<td></td>
</tr>
<tr>
<td>La(η^4-CH₂CHCCH) (Iso B), C₁</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>^2A</td>
<td>0.758</td>
<td>0.727</td>
<td>^1A</td>
<td>1.860</td>
<td>2.106</td>
<td></td>
</tr>
<tr>
<td>^2A</td>
<td>1.010</td>
<td>1.076</td>
<td>^1A</td>
<td>2.323</td>
<td>2.484</td>
<td></td>
</tr>
<tr>
<td>^2A</td>
<td>1.111</td>
<td>1.150</td>
<td>^1A</td>
<td>2.346</td>
<td>2.937</td>
<td></td>
</tr>
<tr>
<td>La(η^3-CHCCH₃) (Iso C), C₁</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>^2A</td>
<td>0.756</td>
<td>0.790</td>
<td>^1A</td>
<td>1.676</td>
<td>1.812</td>
<td></td>
</tr>
<tr>
<td>^2A</td>
<td>1.107</td>
<td>1.250</td>
<td>^1A</td>
<td>1.889</td>
<td>2.066</td>
<td></td>
</tr>
<tr>
<td>^2A</td>
<td>1.191</td>
<td>1.267</td>
<td>^1A</td>
<td>2.298</td>
<td>2.869</td>
<td></td>
</tr>
</tbody>
</table>
Table S3: Total energies (E, hartree) and relative energies (E_{rel}, kcal mol^{-1}) without and with zero-point energy (ZPE) corrections of the intermediates (IMn) and transition states (TSn) and imaginary frequencies (IMG, cm^{-1}) of TSn for the reactions of La with 1- and 2-butyne from the DFT/B3LYP calculations.

<table>
<thead>
<tr>
<th>Species</th>
<th>IMG</th>
<th>E</th>
<th>E_{rel}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La + 1-butyne</td>
<td>La + 1-butyne</td>
<td></td>
</tr>
<tr>
<td></td>
<td>wo/ ZPE</td>
<td>w/ ZPE</td>
<td>wo/ ZPE</td>
</tr>
<tr>
<td>La + 1-butyne</td>
<td>-591.564145</td>
<td>-591.479751</td>
<td>0.0</td>
</tr>
<tr>
<td>IM1</td>
<td>-591.647350</td>
<td>-591.563242</td>
<td>-52.2</td>
</tr>
<tr>
<td>IM2</td>
<td>-591.615437</td>
<td>-591.540543</td>
<td>-32.2</td>
</tr>
<tr>
<td>IM3</td>
<td>-591.635574</td>
<td>-591.558082</td>
<td>-44.8</td>
</tr>
<tr>
<td>IM4</td>
<td>-591.637751</td>
<td>-591.561198</td>
<td>-46.2</td>
</tr>
<tr>
<td>IM5</td>
<td>-591.615338</td>
<td>-591.541314</td>
<td>-32.1</td>
</tr>
<tr>
<td>IM6</td>
<td>-591.637473</td>
<td>-591.560984</td>
<td>-46.0</td>
</tr>
<tr>
<td>IM7</td>
<td>-591.633270</td>
<td>-591.551503</td>
<td>-43.4</td>
</tr>
<tr>
<td>IM8</td>
<td>-591.638066</td>
<td>-591.561203</td>
<td>-46.4</td>
</tr>
<tr>
<td>IM9</td>
<td>-591.643091</td>
<td>-591.566872</td>
<td>-49.5</td>
</tr>
<tr>
<td>IM10</td>
<td>-591.620110</td>
<td>-591.547536</td>
<td>-35.1</td>
</tr>
<tr>
<td>IM11 + H2</td>
<td>-591.581017</td>
<td>-591.519454</td>
<td>-10.6</td>
</tr>
<tr>
<td>TS1</td>
<td>177i</td>
<td>-591.619491</td>
<td>-591.538142</td>
</tr>
<tr>
<td>TS2</td>
<td>688i</td>
<td>-591.619039</td>
<td>-591.534759</td>
</tr>
<tr>
<td>TS3</td>
<td>232i</td>
<td>-591.636333</td>
<td>-591.556909</td>
</tr>
<tr>
<td>TS4</td>
<td>1226i</td>
<td>-591.600818</td>
<td>-591.527411</td>
</tr>
<tr>
<td>TS5</td>
<td>162i</td>
<td>-591.634022</td>
<td>-591.557517</td>
</tr>
<tr>
<td>TS6</td>
<td>775i</td>
<td>-591.613239</td>
<td>-591.536084</td>
</tr>
<tr>
<td>TS7</td>
<td>632i</td>
<td>-591.622008</td>
<td>-591.545038</td>
</tr>
<tr>
<td>TS8</td>
<td>170i</td>
<td>-591.637567</td>
<td>-591.561357</td>
</tr>
<tr>
<td>TS9</td>
<td>1340i</td>
<td>-591.594660</td>
<td>-591.521664</td>
</tr>
<tr>
<td>TS10 + H2</td>
<td>1077i</td>
<td>-591.544764</td>
<td>-591.481907</td>
</tr>
<tr>
<td>TS11 + H2</td>
<td>977i</td>
<td>-591.554915</td>
<td>-591.492318</td>
</tr>
<tr>
<td>Iso A+H2</td>
<td>-591.619704</td>
<td>-591.549561</td>
<td>-34.9</td>
</tr>
<tr>
<td>Iso B+H2</td>
<td>-591.614006</td>
<td>-591.543503</td>
<td>-31.3</td>
</tr>
<tr>
<td>Species</td>
<td>wo/ ZPE</td>
<td>w/ ZPE</td>
<td>wo/ ZPE</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-----------</td>
<td>----------</td>
<td>---------</td>
</tr>
<tr>
<td>La + 2-butyne</td>
<td>-591.570429</td>
<td>-591.486642</td>
<td>0.0</td>
</tr>
<tr>
<td>IM12</td>
<td>-591.651699</td>
<td>-591.568154</td>
<td>-51.0</td>
</tr>
<tr>
<td>IM13</td>
<td>-591.619862</td>
<td>-591.540543</td>
<td>-31.0</td>
</tr>
<tr>
<td>IM14</td>
<td>-591.637873</td>
<td>-591.561144</td>
<td>-42.3</td>
</tr>
<tr>
<td>IM9</td>
<td>-591.643091</td>
<td>-591.566872</td>
<td>-45.6</td>
</tr>
<tr>
<td>IM10</td>
<td>-591.620110</td>
<td>-591.547536</td>
<td>-31.2</td>
</tr>
<tr>
<td>IM8</td>
<td>-591.638066</td>
<td>-591.561357</td>
<td>-42.4</td>
</tr>
<tr>
<td>IM7</td>
<td>-591.633270</td>
<td>-591.551503</td>
<td>-39.4</td>
</tr>
<tr>
<td>IM6</td>
<td>-591.637473</td>
<td>-591.560984</td>
<td>-42.1</td>
</tr>
<tr>
<td>IM3</td>
<td>-591.635574</td>
<td>-591.558082</td>
<td>-40.9</td>
</tr>
<tr>
<td>IM4</td>
<td>-591.637751</td>
<td>-591.561198</td>
<td>-42.2</td>
</tr>
<tr>
<td>IM5</td>
<td>-591.61338</td>
<td>-591.541314</td>
<td>-28.2</td>
</tr>
<tr>
<td>IM11 + H₂</td>
<td>-591.581017</td>
<td>-591.519454</td>
<td>-6.6</td>
</tr>
<tr>
<td>TS12</td>
<td>177i</td>
<td>-591.619491</td>
<td>-591.538142</td>
</tr>
<tr>
<td>TS13</td>
<td>688i</td>
<td>-591.619039</td>
<td>-591.539051</td>
</tr>
<tr>
<td>TS14</td>
<td>232i</td>
<td>-591.636333</td>
<td>-591.560060</td>
</tr>
<tr>
<td>TS9</td>
<td>1340i</td>
<td>-591.594660</td>
<td>-591.521664</td>
</tr>
<tr>
<td>TS8</td>
<td>170i</td>
<td>-591.637567</td>
<td>-591.561203</td>
</tr>
<tr>
<td>TS7</td>
<td>632i</td>
<td>-591.622008</td>
<td>-591.545038</td>
</tr>
<tr>
<td>TS6</td>
<td>775i</td>
<td>-591.613239</td>
<td>-591.536084</td>
</tr>
<tr>
<td>TS5</td>
<td>162i</td>
<td>-591.634022</td>
<td>-591.557517</td>
</tr>
<tr>
<td>TS3</td>
<td>77i</td>
<td>-591.633693</td>
<td>-591.556909</td>
</tr>
<tr>
<td>TS4</td>
<td>1226i</td>
<td>-591.600818</td>
<td>-591.527411</td>
</tr>
<tr>
<td>TS11 + H₂</td>
<td>977i</td>
<td>-591.554915</td>
<td>-591.492318</td>
</tr>
<tr>
<td>TS10 + H₂</td>
<td>1077i</td>
<td>-591.544764</td>
<td>-591.481907</td>
</tr>
<tr>
<td>Iso A + H₂</td>
<td>-591.619704</td>
<td>-591.549561</td>
<td>-30.9</td>
</tr>
<tr>
<td>Iso B + H₂</td>
<td>-591.614006</td>
<td>-591.543503</td>
<td>-27.3</td>
</tr>
</tbody>
</table>