Electronic Supplementary Information

Half-Sandwich Complexes of Rhodium Containing Cysteine-derived ligands

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1- Kinetic studies for the epimerization of complex 9

$[9] = 24.06 \text{ mM; solvent} = \text{CD}_3\text{OD}$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>192,8292</td>
</tr>
<tr>
<td>203</td>
<td>190,6314</td>
</tr>
<tr>
<td>213</td>
<td>187,8786</td>
</tr>
<tr>
<td>218</td>
<td>186,2358</td>
</tr>
<tr>
<td>223</td>
<td>182,1510</td>
</tr>
</tbody>
</table>

$\Delta G^\circ = 12.43 \pm 1.62 \text{ kcal mol}^{-1}$

$\Delta H^\circ = -0.56 \pm 0.03 \text{ kcal mol}^{-1}$

$\Delta S^\circ = -44.3 \pm 5.6 \text{ cal mol}^{-1} \cdot \text{K}^{-1}$
2- Metallacycles characterization for complexes 6Sb, 7Sb and 9

**Table S1.** Ring puckering parameters characterizing the five- and six-membered metallacycles, according to Cremer and Pople.1

<table>
<thead>
<tr>
<th></th>
<th>6Sb</th>
<th>7Sb-A</th>
<th>7Sb-B</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-O(1)-C(11)-C(12)-N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q$ (Å)</td>
<td>0.573(5)</td>
<td>0.53(2)</td>
<td>0.527(19)</td>
<td>0.513(5)</td>
</tr>
<tr>
<td>$\phi$ (°)</td>
<td>153.3(5)</td>
<td>150(2)</td>
<td>152(2)</td>
<td>147.1(5)</td>
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<tr>
<td>conformation</td>
<td>$5E/5T_1$</td>
<td>$5E/5T_1$</td>
<td>$5E/5T_1$</td>
<td>$5E$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>6Sb</th>
<th>7Sb-A</th>
<th>7Sb-B</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-S-C(13)-C(12)-N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q$ (Å)</td>
<td>0.634(4)</td>
<td>0.61(2)</td>
<td>0.62(2)</td>
<td>0.662(4)</td>
</tr>
<tr>
<td>$\phi$ (°)</td>
<td>-42.9(3)</td>
<td>-36(2)</td>
<td>-43.0(18)</td>
<td>-34.0(4)</td>
</tr>
<tr>
<td>conformation</td>
<td>$E_5$</td>
<td>$E_5$</td>
<td>$E_5$</td>
<td>$E_5$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>6Sb</th>
<th>7Sb-A</th>
<th>7Sb-B</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-S-C(13)-C(12)-C(11)-O(1)</td>
<td></td>
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</tr>
<tr>
<td>$q$ (Å)</td>
<td>1.263(3)</td>
<td>1.244(18)</td>
<td>1.256(15)</td>
<td>1.248(3)</td>
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<tr>
<td>$\phi$ (°)</td>
<td>-169.2(2)</td>
<td>-172.5(10)</td>
<td>-169.7(10)</td>
<td>-173.8(2)</td>
</tr>
<tr>
<td>$\theta$ (°)</td>
<td>102.6(2)</td>
<td>100.4(10)</td>
<td>102.4(9)</td>
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<tr>
<td>conformation</td>
<td>$B_{4,1}$</td>
<td>$B_{4,1}$</td>
<td>$B_{4,1}$</td>
<td>$B_{4,1}$</td>
</tr>
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</table>

3- Hydrogen bond interactions in 6Sb and 7Sb

![Figure S1. H-bonds of 6Sb complex](image)

**Table S2.** Complex 6Sb. Hydrogen bonds. Geometrical parameters (Å, °)

<table>
<thead>
<tr>
<th></th>
<th>D-H</th>
<th>D···A</th>
<th>H···A</th>
<th>D-H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(7)-H(7A)···O(2')</td>
<td>0.98</td>
<td>3.462(7)</td>
<td>2.50</td>
<td>166.5</td>
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<tr>
<td>N-H(1A)···O(2')</td>
<td>0.87</td>
<td>2.939(6)</td>
<td>2.32</td>
<td>127.1</td>
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</tbody>
</table>

Symmetry operation: 1-x, y-1/2, 1/2-z.

**Table S3.** Complex 7Sb. Hydrogen bonds. Geometrical parameters (Å, °)

<table>
<thead>
<tr>
<th></th>
<th>D-H</th>
<th>D···A</th>
<th>H···A</th>
<th>D-H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-H(1B)···O(52')</td>
<td>0.910(14)</td>
<td>2.80(3)</td>
<td>1.907(16)</td>
<td>168.8(10)</td>
</tr>
<tr>
<td>C(21)-H(21C)···O(51)</td>
<td>0.98(2)</td>
<td>3.54(3)</td>
<td>2.667(16)</td>
<td>148.6(15)</td>
</tr>
<tr>
<td>N(51)-H(51B)···O(2')</td>
<td>0.91(2)</td>
<td>2.81(3)</td>
<td>1.900(17)</td>
<td>174.3(14)</td>
</tr>
<tr>
<td>C(71)-H(71C)···O(1')</td>
<td>0.98(2)</td>
<td>3.54(3)</td>
<td>2.686(16)</td>
<td>145.6(14)</td>
</tr>
</tbody>
</table>

Symmetry operation: -x, y+1/2, 1-z.
4- Circular dichroism spectra

Circular Dichroism Spectrum for 6Sb

<table>
<thead>
<tr>
<th>No.</th>
<th>nm</th>
<th>CD[mdeg]</th>
<th>No.</th>
<th>nm</th>
<th>CD[mdeg]</th>
<th>No.</th>
<th>nm</th>
<th>CD[mdeg]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>464</td>
<td>3.83625</td>
<td>2</td>
<td>370</td>
<td>-105.814</td>
<td>3</td>
<td>314</td>
<td>5.65618</td>
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<tr>
<td>4</td>
<td>308</td>
<td>-6.68981</td>
<td>5</td>
<td>300</td>
<td>5.38149</td>
<td>6</td>
<td>286</td>
<td>-6.87789</td>
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<tr>
<td>7</td>
<td>285</td>
<td>12.5585</td>
<td>8</td>
<td>253</td>
<td>-6.01917</td>
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<td>239</td>
<td>8.16381</td>
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<td>10</td>
<td>222</td>
<td>-6.54476</td>
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</table>
Circular Dichroism Spectrum for 7Sb

<table>
<thead>
<tr>
<th>No.</th>
<th>nm</th>
<th>CD[mdeg]</th>
<th>No.</th>
<th>nm</th>
<th>CD[mdeg]</th>
<th>No.</th>
<th>nm</th>
<th>CD[mdeg]</th>
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<tr>
<td>1</td>
<td>374</td>
<td>-59.4204</td>
<td>2</td>
<td>303</td>
<td>37.051</td>
<td>3</td>
<td>206</td>
<td>26.725</td>
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<tr>
<td>4</td>
<td>279</td>
<td>39.7229</td>
<td>5</td>
<td>245</td>
<td>8.96244</td>
<td>6</td>
<td>242</td>
<td>23.5622</td>
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<tr>
<td>7</td>
<td>231</td>
<td>6.81597</td>
<td>8</td>
<td>224</td>
<td>29.9358</td>
<td>9</td>
<td>212</td>
<td>-14.3534</td>
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Circular Dichroism Spectrum for 8Sb

<table>
<thead>
<tr>
<th>No.</th>
<th>nm</th>
<th>CD [mdeg]</th>
<th>No.</th>
<th>nm</th>
<th>CD [mdeg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>377</td>
<td>-28.2154</td>
<td>2</td>
<td>309</td>
<td>23.3423</td>
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Circular Dichroism Spectrum for 9

<table>
<thead>
<tr>
<th>No.</th>
<th>nm</th>
<th>CD [mdeg]</th>
<th>No.</th>
<th>nm</th>
<th>CD [mdeg]</th>
<th>No.</th>
<th>nm</th>
<th>CD [mdeg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>405</td>
<td>-4.87482</td>
<td>2</td>
<td>380</td>
<td>5.7618</td>
<td>3</td>
<td>342</td>
<td>-73.4614</td>
</tr>
<tr>
<td>4</td>
<td>303</td>
<td>16.2585</td>
<td>5</td>
<td>221</td>
<td>-3.88899</td>
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</table>
5- Preparation of HL2 by S-benzylation of IV

To a solution of 500.0 mg (2.91 mmol) of IV in EtOH (13.5 mL) 0.40 mL (2.91 mmol) of benzyl bromide were added. Then, at 5 ºC, to the resulting solution, 6 mL of an ethanolic solution of 2M NaOH were added dropwise. The precipitation of a white solid was observed. The resulting suspension was stirred for 1 h, at RT. After that time, 0.48 mL of 12M HCl was added dropwise until the pH was 6-7. The resulting suspension was filtered and the white precipitate washed consecutively with H₂O, EtOH and Et₂O and vacuum-dried to afford a white solid. Yield: 75%. M. p.: 230-232 ºC. IR (solid, cm⁻¹): 2987, 1606, 1578, 1269, 1231. [α]⁺D₂⁴: +62.4 (c = 1.075; HCl(aq) 1M). HRMS (ESI) C₁₁H₁₅NO₂S [M+H]⁺: Calcd. 226.0896, found 226.0920.

HL2·HCl. ¹H NMR (300.13 MHz, D₂O, 298 K, ppm): δ 7.38 (m, 5H, H Ar), 3.82 (s, 2H, CH₂Ph), 3.09 (AB system, Jₐₜ = 14.8 Hz, 2H, CH₂C*), 1.57 (s, 3H, Me). ¹³C (¹H) NMR (125.8 MHz, D₂O, 298 K, ppm): δ 172.55 (COOH), 137.77, 129.01, 128.84, 127.58 (6C, C Ar), 60.14 (C*), 36.85 (CH₂C*), 36.37 (CH₂Ph), 21.52 (Me).
6- Frequency list of all ground and transition states

Lower six vibrational frequencies (cm$^{-1}$) of the optimized (gas-phase) ground and transition states:

Ss-9: 20.3726, 29.6229, 33.9547, 39.1739, 43.6297, 59.5091
m1:  11.9918, 17.3250, 25.5487, 31.8023, 41.8288, 45.6620
m2:  16.4815, 21.9066, 24.2463, 30.6018, 41.4461, 48.9321
m3:  17.0428, 19.1337, 26.6523, 30.3397, 37.4974, 47.2798
m4:  15.3394, 17.7230, 28.2531, 30.8391, 40.0504, 44.0046
Rs-9: 18.7156, 28.5640, 30.7907, 37.0432, 42.7645, 50.6374
MeOH: 336.6882, 1061.1532, 1094.0672, 1179.0483, 1384.9756, 1499.3493