Acid-Induced Liberation of Polysubstituted Cyclopentadiene Ligands from Cyclopentadienyl Cobalt: A [2 + 2 + 1] Cycloaddition Route Toward 1,2,4-Trisubstituted Cyclopentadienes

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Figure S27. ORTEP of 8-Ph-A/8-Ph-B. Thermal ellipsoids shown at 30% probability. Most hydrogen atoms are omitted for clarity. The sample was prepared from recrystallization in chloroform/hexanes at -20 °C.

Table S1. Crystal data and structure refinement for 8-Ph-A/8-Ph-B.

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<th>Identification code</th>
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<td>Molecular formula</td>
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<td>Formula weight</td>
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<td>Temperature</td>
<td>100.0 K</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>P 1 21/n 1</td>
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<tr>
<td>Unit cell dimensions</td>
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<td>a = 11.0617(8) Å</td>
<td>α = 90°</td>
</tr>
<tr>
<td>b = 10.3249(8) Å</td>
<td>β = 104.003(3)°</td>
</tr>
<tr>
<td>c = 15.3097(11) Å</td>
<td>γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1696.6(2) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.388 Mg/m³</td>
</tr>
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<td>Absorption coefficient</td>
<td>0.213 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>744</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.297 x 0.086 x 0.074 mm³</td>
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<tr>
<td>Crystal color, habit</td>
<td>Light Yellow Needle</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.737 to 25.381°</td>
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<tr>
<td>Index ranges</td>
<td>-13&lt;=h&lt;=13, -8&lt;=k&lt;=12, -18&lt;=l&lt;=18</td>
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<td>Reflections collected</td>
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<td>Independent reflections</td>
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<td>Completeness to theta = 25,000°</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
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<td>Extinction coefficient</td>
<td>n/a</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.376 and -0.344 eÅ⁻³</td>
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Figure S28. ORTEP of 8-CO\textsubscript{2}Me. Thermal ellipsoids shown at 30% probability. Most hydrogen atoms are omitted for clarity. The sample was prepared from recrystallization in CH\textsubscript{2}Cl\textsubscript{2}/hexanes.

Table S2. Crystal data and structure refinement for 8-CO\textsubscript{2}Me.

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<td>Formula weight</td>
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<tr>
<td>Temperature</td>
<td>296 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>C2/c</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a = 21.150(3) Å, α = 90°</td>
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<tr>
<td></td>
<td>b = 9.7675(13) Å, β = 104.705(2)°</td>
</tr>
<tr>
<td></td>
<td>c = 16.065(2) Å, γ = 90°</td>
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<tr>
<td>Volume</td>
<td>3209.9(8) Å\textsuperscript{3}</td>
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<td>Z</td>
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<td>Density (calculated)</td>
<td>1.392 Mg/m\textsuperscript{3}</td>
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<td>Absorption coefficient</td>
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<td>F(000)</td>
<td>1408</td>
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<td>Crystal size</td>
<td>0.50 x 0.40 x 0.40 mm\textsuperscript{3}</td>
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<td>1.99 to 25.02°</td>
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<tr>
<td>Index ranges</td>
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<td>Reflections collected</td>
<td>8117</td>
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<td>Independent reflections</td>
<td>2824 [R(int) = 0.0817]</td>
</tr>
<tr>
<td>Completeness to theta = 25.02°</td>
<td>99.6 %</td>
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<tr>
<td>Absorption correction</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.9138 and 0.8939</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F\textsuperscript{2}</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F\textsuperscript{2}</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
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<td>R indices (all data)</td>
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<td>Largest diff. peak and hole</td>
<td>0.268 and -0.241 e Å\textsuperscript{-3}</td>
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Figure S29. ORTEP of 9. Thermal ellipsoids shown at 30% probability. The sample was prepared from crystallization of the crude oil in the presence of small amount of chloroform overnight.

Table S3. Crystal data and structure refinement for 9.

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<tr>
<td>Molecular formula</td>
<td>$\text{C}_4\text{H}_8\text{CoF}_6\text{O}_8$</td>
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<td>Formula weight</td>
<td>357.03</td>
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<tr>
<td>Temperature</td>
<td>100.0 K</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
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<tr>
<td>Space group</td>
<td>P-1</td>
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<tr>
<td>Unit cell dimensions</td>
<td>$a = 8.1249(14) \text{ Å}$, $\alpha = 75.059(12)^\circ$.</td>
</tr>
<tr>
<td></td>
<td>$b = 9.0422(14) \text{ Å}$, $\beta = 64.690(11)^\circ$.</td>
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<tr>
<td></td>
<td>$c = 9.2650(15) \text{ Å}$, $\gamma = 71.468(11)^\circ$.</td>
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<td>Volume</td>
<td>577.49(18) Å$^3$</td>
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<td>Z</td>
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<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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<td>F(000)</td>
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<td>Theta range for data collection</td>
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<td>Reflections collected</td>
<td>4179</td>
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<td>Completeness to theta = 25.000$^\circ$</td>
<td>100.0 %</td>
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<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
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<td>Largest diff. peak and hole</td>
<td>0.532 and -0.572 e.Å$^{-3}$</td>
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Figure S30. ORTEP of 11. Thermal ellipsoids shown at 30% probability. Most hydrogen atoms are omitted for clarity. The sample was prepared from recrystallization in chloroform/hexanes at -20 °C.

Table S4. Crystal data and structure refinement for 11.

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<tr>
<td>Crystal system</td>
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<td>Space group</td>
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<td>γ = 90°</td>
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<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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<td>Crystal color, habit</td>
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<td>Theta range for data collection</td>
<td>2.745 to 25.786°</td>
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<td>Reflections collected</td>
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<td>Completeness to theta = 25.000°</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F²</td>
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<td>0.398 and -0.377 e.Å⁻³</td>
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Figure S31. ORTEP of 15. Thermal ellipsoids shown at 30% probability. Most hydrogen atoms are omitted for clarity. The sample was prepared from recrystallization in chloroform/hexanes.

Table S5. Crystal data and structure refinement for 15.

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<td>Molecular formula</td>
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<td>Formula weight</td>
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<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
<td>Triclinic</td>
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<td>Space group</td>
<td>P-1</td>
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<td>Unit cell dimensions</td>
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<td>b</td>
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<td>c</td>
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<td>Crystal size</td>
<td>0.267 x 0.242 x 0.165 mm³</td>
</tr>
<tr>
<td>Crystal color, habit</td>
<td>Colorless Block</td>
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<tr>
<td>Theta range for data collection</td>
<td>1.590 to 26.384°</td>
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<tr>
<td>Index ranges</td>
<td>-9&lt;=h&lt;=8, -13&lt;=k&lt;=13, -16&lt;=l&lt;=17</td>
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<tr>
<td>Independent reflections</td>
<td></td>
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<tr>
<td>Completeness to theta = 25.000°</td>
<td>100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.0932 and 0.0695</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0406, wR2 = 0.0966</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0488, wR2 = 0.1029</td>
</tr>
<tr>
<td>Extinction coefficient</td>
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</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.478 and -0.353 e.Å⁻³</td>
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</table>
Figure S32. ORTEP of 17-\(\text{Cp}^*\). Thermal ellipsoids shown at 30% probability. Most hydrogen atoms are omitted for clarity. The sample was prepared from recrystallization in toluenes/hexanes at -20 °C.

Table S6. Crystal data and structure refinement for 17-\(\text{Cp}^*\).

<table>
<thead>
<tr>
<th>Identification code</th>
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<tr>
<td>Empirical formula</td>
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<tr>
<td>Molecular formula</td>
<td>C30 H32 O4 Ru S</td>
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<td>Formula weight</td>
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<tr>
<td>Temperature</td>
<td>100.0 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 1 21/c 1</td>
</tr>
</tbody>
</table>
| Unit cell dimensions| \(\begin{array}{c}
a = 15.5730(11) \text{ Å} \\
b = 15.4582(11) \text{ Å} \\
c = 11.9655(9) \text{ Å}
\end{array}\) |
| Volume              | 2767.1(3) Å\(^3\) |
| Z                   | 4 |
| Density (calculated)| 1.415 Mg/m\(^3\) |
| Absorption coefficient| 0.675 mm\(^{-1}\) |
| F(000)              | 1216 |
| Crystal size        | 0.217 x 0.153 x 0.131 mm\(^3\) |
| Crystal color, habit| Light Yellow Rod |
| Theta range for data collection | 1.361 to 26.431° |
| Index ranges        | -19<=h<=19, -19<=k<=19, -14<=l<=13 |
| Reflections collected| 58579 |
| Independent reflections| 5688 [R(int) = 0.0661, R(sigma) = 0.0376] |
| Completeness to theta = 25.000°| 100.0 % |
| Absorption correction| Semi-empirical from equivalents |
| Max. and min. transmission| 0.2468 and 0.2041 |
| Refinement method   | Full-matrix least-squares on F\(^2\) |
| Data / restraints / parameters | 5688 / 152 / 432 |
| Goodness-of-fit on F\(^2\) | 1.043 |
| Final R indices [\(1>2\text{sigma}(I)\)] | R1 = 0.0300, wR2 = 0.0743 |
| R indices (all data) | R1 = 0.0383, wR2 = 0.0814 |
| Extinction coefficient| n/a |
| Largest diff. peak and hole | 0.438 and -0.569 e.Å\(^{-3}\) |
Figure S33. Compound Index
Table S7. Computational results, Z-matrices or Cartesian coordinates, the number of imaginary frequencies, and computed total energies.

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<th>Free Energy</th>
<th>ΔG</th>
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<tr>
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cocyclopentadieneIsoA

<p>| | | | |</p>
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H  2.0743728713  2.8715376176  -1.2424371691
H  4.0677943095  4.1201175081  -0.4631087765
H  4.8318540073  1.0581438701  2.4721188399
H  5.4591146071  3.2164147293  1.3957654993
C  1.8504003162  -1.9726966699  -0.3753688974
O  1.4709616325  -3.1080386178  -0.1199482986
O  3.1331701692  -1.6387674256  -0.6353828888
C  4.1526962337  -2.6732428998  -0.4629787344
H  3.7660438363  -3.6220788376  -0.8472433492
H  4.9784424101  -2.3314897567  -1.092503913
H  5.369006584   -1.6184673549  1.6991999465
H  0.5718376858   -0.7482502674  0.6871806677
C  1.370675862   0.4815743096  0.4373119183
C  0.5364544315   1.5493710482  0.5341035074
H  0.8108772221   2.5925941025  0.4436302103
C  1.0425979971   -2.143576265  0.4895747761
O  1.8601167663   -2.4705345902  -0.3530031462
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C  0.7347176819   -4.42298302   1.149765017
H  0.4806438276   -4.7037404668  0.1216712
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H  0.1849833209   -4.8904646287  3.191319392
H  0.1404646374  -6.2656984205  2.062597184
S  -1.9760564207   1.5441570954  -0.5744922206
O  -2.1084302425  2.994859469   -0.5351584112
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C  3.3479318427  1.5128503634  -0.6769261358
C  3.7086497569  -0.2957877324  0.89295149
C  5.0871165366  -0.1800172515  0.7073748916
C  4.7265396175  1.6238788985  -0.8660370291
H  2.6666146601  2.1588696536  -1.224982168
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H  5.7606816764  -0.8385379046  1.2508080912
H  5.1179118582  2.3652619719  -1.5587954464

cocyлыpentadieneIsoB_3
cocyclopentadieneIsoB

C  -0.817835732  1.1999673186  0.854915657
H  -1.307609544  1.8054430018  1.6277231262
C  -0.6403194225  -0.245232121  1.1972865127
H  -1.44002752005  -0.9071244737  1.5037481345
C  0.6481296806  -0.5839768608  0.9702673327
C  1.0479009855  0.6066574645  0.504937715
C  0.5474007629  1.6572112556  0.4548374025
H  0.7871922668  2.6772854552  0.1833267168
C  1.1630397666  -1.9787545337  1.1184966517
O  1.1969627467  -2.5550491585  2.1906833005
O  1.590644575  -2.620600745  0.0136230788
C  1.4109815273  -2.0341758065  -1.3240405254
H  0.4075576567  -1.6024997148  -1.3870469875
H  2.1550145751  -1.2422210085  -1.4496508462
C  1.6093870997  -3.1479066473  -2.3335182443
H  0.8654525456  -3.9402533054  -2.1926726517
H  2.6133125785  -3.5787737182  -2.2461497873
H  1.4937637294  -2.7335086621  -3.3422966283
S  -1.9548255467  1.3879949531  -0.6118639457
O  -2.1361466732  2.8190362768  -0.8166374858
O  -1.4510158986  0.570162897  -1.7062856779
C  2.8422878467  0.637842191  0.193233293
C  5.5903366071  0.723777242  -0.418789589
C  3.3284683387  1.500137849  -0.8094743145
C  3.7566260845  -0.1795854036  0.8836248583
C  5.1190457712  -0.1349820628  0.5797598534
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H  5.0474344756  2.2080684908  -1.893403926
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C  -5.8409190376  -0.418877469  0.9555513066
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cyclopentadieneIsoC

C 1.2155706603 -0.7536559643 -0.5188175257
C 1.1542947930 0.6222048546 -0.4789237478
C -0.9585277535 -0.2591503554 -1.0495609604
S -2.6447252957 -0.4093493806 -1.5029812334
O -2.9323453079 0.5944424419 -2.521748391
O -2.9260518219 -1.812782398 -1.7787780262
C 2.4195019812 -1.6777161375 -0.6040549968
C 2.0663275922 -2.8514818353 0.049433171
C 2.1691533416 1.6051105601 -0.109215141
C 4.0667137953 3.5527586272 0.6347262136
C 2.1873766834 2.8706245479 -0.7326909829
C 3.1089291481 1.3433483782 0.9085400259
C 4.0452415385 2.3076857894 1.2763733504
C 3.135749282 3.8300967643 -0.3703723618
H 1.471473395 3.0921640223 -1.5195700974
H 3.0870094549 0.3877816181 1.4218433517
H 4.7570194996 2.0907880099 2.0693183662
H 3.1423466912 4.794201235 -0.8730753458
H 4.8011239375 4.3019573293 0.9204599161
C -3.5158469376 0.0575423618 -0.0054999187
C -4.8161777027 0.779090478 2.3414005269
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H 2.6346544998 -4.793032547 0.1497927735
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S39
cocyclopentadieneIsoD

C  1.4511363722  0.6000560437 -0.6458473065
C  0.2408695154  1.208615836  0.6000560437
H  0.0049845553  2.1089441587  0.0050316759
C  1.3453169778  0.6260201719 -1.531534191
H  0.562613935  1.3561565253 -2.5824994338
S  2.9203869848  1.8728253821  3.1113040593
O  3.0339959937  0.0775576069 -2.4601098673
C  3.0278034136  0.4240855193  0.1412572837
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C  3.6710757733 -1.2533329546  0.7446282003
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O  3.8023869848  1.8728253821  3.1113040593
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C  1.6957663395 -1.9410583131 -0.8365102248
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O  2.5661890135  2.0399118067  0.8334568304
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H  4.235839671  1.7102610213  2.0360202611
H  4.475442484  2.8652299666  0.7042970361
C  3.3680587153  3.6767605886  2.3974992324
H  2.6635448441  3.3301953316  3.1624952468
H  2.9035995424  4.4892310046  1.8267107043
H  4.2607911731  4.06958986  2.8987998378

cocyclopentadieneIsoE


cocyclopentadieneIsoANMe2

C  -0.021632548  1.1981492701 -0.6745899263
H  -0.1521089561  2.2741679885 -0.6604768758
C  -0.9779746299  0.2885499639 -0.9687361985
C  1.0021694005  0.8510273213 -0.4637027261

S 41
cocyclopentadieneIsoCNMe2

C  1.3064133856  -0.716942983 -0.4227552756
S 43

C   1.2650534629  0.6743419597 -0.4248519261
C  -0.850829177 -0.2072951632 -1.0244163773
S  -2.5199660848 -0.3530230586 -1.5062080379
O  -2.7937100148  0.6456771753 -2.5367623311
O  -2.8105638651 -1.7567993264 -1.7717892624
C  2.4813007162 -1.5991776873 -0.260481239
O  3.6460088979 -1.2872029254 -0.455529861
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C  2.2535331516  1.6591495734 -0.0525570971
C  4.1458039501  3.6807201766  0.7126417968
C  2.1737649197  2.9829013284 -0.2072951632
C  3.2942601853  1.3923698487  0.8688110035
C  4.2042976646  2.3615776628  1.2498284531
C  3.0873470717  3.9615146951 -0.1982184496
C  4.9643472817  2.1029251257  1.978408683
C  2.9870963497  4.9500080569 -0.6319649861
C  -3.423580876  0.1276625874 -0.029538069
C  -4.7642520237  0.8728327047  2.289728653
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C  -0.253329204 -2.2896065168 -0.837671093
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