Supporting Information
Dimeric iminophenoxide copper complexes in rac-Lactide polymerization

Pargol Daneshmand, Leena Pinon, Frank Schaper*

Centre in Green Chemistry and Catalysis, Department of chemistry, Université de Montréal, C. P. 6128 Succ. Centre-Ville, Montréal, QC, H3T 3J7, Canada. Email: Frank.Schaper@umontreal.ca

Figure S1. Kinetics of rac-lactide polymerization with 2a without (blue squares) and with addition of 1 equiv pyridylmethanol (red diamonds).

Figure S2. X-ray structures of homoleptic bis(iminoaryloxide) copper complexes 4c-7c and 12c-15c.

Table S1. Experimental details of X-ray diffraction studies of the homoleptic complexes.

Figure S3. X-ray structure of bis(pyridylmethoxide)copper. Thermal displacements are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

Figure S4. $^1$H-NMR spectra of L4H in CDCl$_3$ (400 MHz).

Figure S5. $^1$H-NMR spectra of L5H in CDCl$_3$ (400 MHz).

Figure S6. $^1$H-NMR spectra of L6H in CDCl$_3$ (400 MHz).

Figure S7. $^1$H-NMR spectra of L7H in CDCl$_3$ (400 MHz).

Figure S8. $^1$H-NMR spectra of L12H in CDCl$_3$ (400 MHz).

Figure S9. $^1$H-NMR spectra of L13H in CDCl$_3$ (400 MHz).

Figure S11. $^1$H-NMR spectra of L15H in CDCl$_3$ (400 MHz).
Figure S1. Kinetics of rac-lactide polymerization with 2a without (blue squares) and with addition of 1 equiv pyridylmethanol (red diamonds). Linear regression provided $k_{app} = 0.69(2) \text{ h}^{-1}$ and $t_0 = -4 \text{ min (2a)}$ and $k_{app} = 1.9(1) \text{ h}^{-1}$ and $t_0 = 5 \text{ min (2a/PyCH}_2\text{OH)}$. Conditions: C$_6$D$_6$, RT, [lactide] = 200 mM, [L$_2$Cu$_2$(OR)$_2$] = 2 mM.
Figure S2. X-ray structures of homoleptic bis(iminoaryloxide) copper complexes 4c-7c and 12c-15c.

The structure of 5c has been reported before. Complex 5c, the only dimeric complex, is also the only crystal with a green colour. All other crystals have brownish colours. For 4c\textsuperscript{2} and 6c\textsuperscript{3}, the structure of a polymorph has been reported.
Table S1. Experimental details of X-ray diffraction studies of the homoleptic complexes.

<table>
<thead>
<tr>
<th>Formula</th>
<th>$M_w$ (g/mol)</th>
<th>$T$ (K); F(000)</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Unit Cell: $a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\alpha$ (°)</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
<th>$V$ (Å³)</th>
<th>$\mu$ (mm⁻¹); Z</th>
<th>$\theta$ (°); completeness</th>
<th>collected reflections; $R_{int}$</th>
<th>unique reflections; $R_{int}$</th>
<th>R1(F) (I &gt; 2σ(I))</th>
<th>wR(F²) (all data)</th>
<th>GoF(F²); Flack-x</th>
<th>Residual electron density</th>
</tr>
</thead>
<tbody>
<tr>
<td>4c</td>
<td>C$<em>{28}$H$</em>{32}$CuN$_2$O$_2$</td>
<td>484.03</td>
<td>150; 502</td>
<td>150</td>
<td>10.1218(3)</td>
<td>9.0847(2)</td>
<td>12.4074(3)</td>
<td>90</td>
<td>107.042(1)</td>
<td>90</td>
<td>1090.81(5)</td>
<td>5.555; 2</td>
<td>3.2-60.6; 1.0</td>
<td>27675; 0.026</td>
<td>2492; 0.052</td>
<td>0.080</td>
<td>0.253</td>
<td>1.068; -</td>
<td>0.80; –1.54</td>
</tr>
<tr>
<td>5c</td>
<td>C$<em>{26}$H$</em>{32}$CuN$_2$O$_2$</td>
<td>468.07</td>
<td>100; 1976</td>
<td>100</td>
<td>21.3119(6)</td>
<td>9.3432(3)</td>
<td>23.0794(7)</td>
<td>90</td>
<td>99.239(1)</td>
<td>90</td>
<td>4536.0(2)</td>
<td>1.549; 8</td>
<td>5.1-71.9; 1.0</td>
<td>122428; 0.018</td>
<td>8881; 0.040</td>
<td>0.035</td>
<td>0.100</td>
<td>1.034; -</td>
<td>0.42; –0.43</td>
</tr>
<tr>
<td>6c</td>
<td>C$<em>{28}$H$</em>{32}$CuN$_2$O$_2$</td>
<td>636.21</td>
<td>110; 1324</td>
<td>120</td>
<td>17.4037(5)</td>
<td>10.2071(3)</td>
<td>18.7364(5)</td>
<td>90</td>
<td>111.805(1)</td>
<td>90</td>
<td>3090.2(2)</td>
<td>4.012; 4</td>
<td>2.2-60.8; 0.99</td>
<td>68961; 0.024</td>
<td>7097; 0.045</td>
<td>0.047</td>
<td>0.134</td>
<td>1.052; -</td>
<td>0.68; –0.60</td>
</tr>
<tr>
<td>7c</td>
<td>C$<em>{30}$H$</em>{32}$CuN$_2$O$_2$</td>
<td>512.08</td>
<td>100; 1068</td>
<td>120</td>
<td>14.3106(5)</td>
<td>12.1062(5)</td>
<td>14.6604(6)</td>
<td>90</td>
<td>96.816(2)</td>
<td>90</td>
<td>2521.9(2)</td>
<td>4.824; 4</td>
<td>3.6-60.6; 1.0</td>
<td>43808; 0.038</td>
<td>5818; 0.060</td>
<td>0.051</td>
<td>0.130</td>
<td>1.054; -</td>
<td>0.80; –0.60</td>
</tr>
<tr>
<td>12c</td>
<td>C$<em>{28}$H$</em>{32}$ClCuN$_2$O$_2$</td>
<td>621.80</td>
<td>150; 630</td>
<td>150</td>
<td>10.5290(4)</td>
<td>6.0011(2)</td>
<td>14.6604(6)</td>
<td>90</td>
<td>99.976(1)</td>
<td>90</td>
<td>2633.6(1)</td>
<td>7.436; 2</td>
<td>3.7-60.7; 1.0</td>
<td>18642; 0.022</td>
<td>4308; 0.045</td>
<td>0.032</td>
<td>0.086</td>
<td>1.099; -</td>
<td>0.68; –0.60</td>
</tr>
<tr>
<td>13c</td>
<td>C$<em>{26}$H$</em>{32}$ClCuN$_2$O$_2$</td>
<td>605.84</td>
<td>130; 1244</td>
<td>130</td>
<td>14.7942(4)</td>
<td>12.6835(4)</td>
<td>14.0429(4)</td>
<td>90</td>
<td>91.930(1)</td>
<td>90</td>
<td>605.84</td>
<td>7.067; 4</td>
<td>2.6-54.2; 0.95</td>
<td>19086; 0.034</td>
<td>2879; 0.042</td>
<td>0.032</td>
<td>0.123</td>
<td>1.040; -</td>
<td>0.80; –0.60</td>
</tr>
<tr>
<td>14c</td>
<td>C$<em>{40}$H$</em>{32}$ClCuN$_2$O$_2$</td>
<td>773.98</td>
<td>150; 395</td>
<td>150</td>
<td>8.4189(3)</td>
<td>12.835(4)</td>
<td>14.429(4)</td>
<td>90</td>
<td>72.331(1)</td>
<td>90</td>
<td>72.893(1)</td>
<td>5.553; 1</td>
<td>3.4-60.7; 1.0</td>
<td>20783; 0.036</td>
<td>4639; 0.034</td>
<td>0.037</td>
<td>0.124</td>
<td>1.080; -</td>
<td>0.48; –1.11</td>
</tr>
<tr>
<td>15c</td>
<td>C$<em>{37}$H$</em>{32}$ClCuN$_2$O$_2$</td>
<td>741.98</td>
<td>150; 762</td>
<td>150</td>
<td>11.0291(3)</td>
<td>9.522(3)</td>
<td>16.539(5)</td>
<td>90</td>
<td>96.603(1)</td>
<td>90</td>
<td>1725.46(9)</td>
<td>5.467; 2</td>
<td>3.5-60.6; 0.77</td>
<td>87742; 0.019</td>
<td>3881; 0.060</td>
<td>0.060</td>
<td>0.060</td>
<td>1.13; –0.011(3)</td>
<td>0.24; –0.56</td>
</tr>
</tbody>
</table>
Figure S3. X-ray structure of bis(pyridylmethoxide)copper. Thermal displacements are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

Figure S4. $^1$H-NMR spectra of L4H in CDCl$_3$ (400 MHz).
Figure S5. $^1$H-NMR spectra of L5H in CDCl$_3$ (400 MHz).

Figure S6. $^1$H-NMR spectra of L6H in CDCl$_3$ (400 MHz).
Figure S7. $^1$H-NMR spectra of L7H in CDCl$_3$ (400 MHz).

Figure S8. $^1$H-NMR spectra of L12H in CDCl$_3$ (400 MHz).
Figure S9. $^1$H-NMR spectra of L13H in CDCl$_3$ (400 MHz).

Figure S10. $^1$H-NMR spectra of L14H in CDCl$_3$ (400 MHz).
Figure S11. $^1$H-NMR spectra of L15H in CDCl$_3$ (400 MHz).