Three powerful dinuclear metal-organic catalysts for converting CO$_2$ into organic carbonates

Dan Zhao, Xiao-Hui Liu, Zhuang-Zhi Shi, Chen-Dan Zhu, Yue Zhao, Peng Wang and Wei-Yin Sun*

*Corresponding author. E-mail: sunwy@nju.edu.cn

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, China.

Table of Contents

Experimental section...........................................................................................................S2
  Structures of the organic ligands HL, L2 and L3
  Crystallographic data and structure refinements
  Power X-ray diffraction (PXRD)
  Figures of HPLC

Characterization data of compounds.................................................................................S7

Copies of $^1$H NMR, $^{13}$C NMR ..................................................................................S11
Experimental section

Structure of the organic ligands HL, L2 and L3:

Chart S1 The organic ligand HL.

Chart S2 The structure of L2.

Chart S3 The structure of L3.
Crystallographic data and structure refinements:

<table>
<thead>
<tr>
<th></th>
<th>L3-Zn</th>
<th>(R)-2a</th>
<th>(S)-2a</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C_{19}H_{38}N_{3}O_{7}Cl Zn</td>
<td>C_{9}H_{8}O_{3}</td>
<td>C_{9}H_{6}O_{3}</td>
</tr>
<tr>
<td>fw</td>
<td>521.34</td>
<td>164.15</td>
<td>164.15</td>
</tr>
<tr>
<td>crystal system</td>
<td>Monoclinic</td>
<td>orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>P_2_1</td>
<td>P_2_1_2_1</td>
<td>P_2_1_2_1</td>
</tr>
<tr>
<td>T (K)</td>
<td>293(2)</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.7985(8)</td>
<td>6.1207(5)</td>
<td>6.1196(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.1054(9)</td>
<td>7.5850(6)</td>
<td>7.5799(5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>9.8329(8)</td>
<td>16.9844(14)</td>
<td>16.9823(12)</td>
</tr>
<tr>
<td>β (°)</td>
<td>97.233(3)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V(Å(^3))</td>
<td>1252.63(17)</td>
<td>788.51(11)</td>
<td>787.74(9)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>D_x (g cm(^{-3}))</td>
<td>1.382</td>
<td>1.383</td>
<td>1.384</td>
</tr>
<tr>
<td>F(000)</td>
<td>552</td>
<td>344</td>
<td>344</td>
</tr>
<tr>
<td>θ for data collection (°)</td>
<td>2.60 - 25.00</td>
<td>6.39 - 65.50</td>
<td>5.21 - 64.97</td>
</tr>
<tr>
<td>R(_1)^a, [I &gt; 2σ (I)]</td>
<td>0.0677</td>
<td>0.0255</td>
<td>0.0262</td>
</tr>
<tr>
<td>wR(_2)^a [I &gt; 2σ (I)]</td>
<td>0.1872</td>
<td>0.0676</td>
<td>0.0667</td>
</tr>
<tr>
<td>GOF</td>
<td>1.077</td>
<td>1.079</td>
<td>1.065</td>
</tr>
</tbody>
</table>

\(^a\) R\(_1\)=\sum | F_o | - | F_c | \sum | F_o | \cdot \ \ \ wR\(_2\)=\{\sum w(F_o^2-\bar{F_o}^2)^2/\sum w(F_o^2)\}^{1/2}
Power X-ray diffraction (PXRD)

Figure S1 PXRD of 1 - 3.
HPLC

Styrene oxide was isolated as a colorless solid by flash chromatography using petroleum hexane/EtOAc (5:1) as eluent. Rf = 0.41; 1H NMR (400 MHz, CDCl3) δ 7.41-7.48 (m, 3H), 7.34-7.39 (m, 2H), 5.68 (t, J = 8.0 1H), 4.80 (t, J = 8.0 1H), 4.35 (t, J = 8.0 1H); The enantiomeric excess was determined by chiral HPLC using a Chiralcel OD column (4.6 mm x 250 mm) with hexane/isopropanol (90:10) as eluent and a flow rate of 1.0 mL/min. tR=21.05 min, tS=26.53 min. Detection wavelength: 220 nm.
Figure S2 The figures of HPLC
Characterization data of compounds

4-phenyl-1,3-dioxolan-2-one 2a

Rf = 0.7 (EA/Hexane = 1:5), Yield 79%, colorless crystalline. 1H NMR (300 MHz, CDCl3): δ 7.49-7.42 (m, 3H), 7.40-7.33 (m, 2H), 5.68 (t, J = 8.1 Hz, 1H), 4.81 (t, J = 8.4 Hz, 1H), 4.35 (dd, J = 8.1 Hz, 8.7 Hz, 1H) ppm; 13C NMR (100 MHz, CDCl3): δ 154.89, 135.82, 129.74, 129.24, 125.91, 78.03, 71.20 ppm. See also: J. Melendez, M. North and P. Villuendas, Chem. Commun., 2009, 18, 2577.

4-(4-fluorophenyl)-1,3-dioxolan-2-one 2b

Rf = 0.6 (EA/Hexane = 1:6), Yield 80%, white solid. 1H NMR (300 MHz, CDCl3): δ 7.44-7.31 (m, 2H), 7.20-7.09 (m, 2H), 5.67 (t, J = 8.0 Hz, 1H), 4.80 (t, J = 8.4 Hz, 1H), 4.33 (dd, J = 8.7 Hz, 7.9 Hz, 1H) ppm; 13C NMR (100 MHz, CDCl3): δ 163.37 (d, J = 248.0 Hz), 154.65, 131.62 (d, J = 3.0 Hz), 128.09, 128.01, 116.45, 116.23, 77.45, 71.11 ppm. 19F NMR (376 MHz, CDCl3): δ -110.97 ppm. See also: C. William, H. Ross W, N. Michael and P. Riccardo, Chem. Eur. J., 2010, 16, 6828.

4-(4-chlorophenyl)-1,3-dioxolan-2-one 2c

Rf = 0.8 (EA/Hexane = 1:3), Yield 80%, white solid. 1H NMR (300 MHz, CDCl3): δ 7.48-7.38 (m, 2H), 7.37-7.28 (m, 2H), 5.66 (t, J = 8.0 Hz, 1H), 4.81 (t, J = 8.4 Hz, 1H), 4.31 (dd, J = 8.7 Hz, 7.8 Hz, 1H) ppm; 13C NMR (100 MHz, CDCl3): δ 154.52, 135.79, 134.29, 129.52, 127.26, 77.24, 71.00 ppm.

4-(4-bromophenyl)-1,3-dioxolan-2-one 2d

Rf = 0.7 (EA/Hexane = 1:5), Yield 78%, white solid. 1H NMR (300 MHz, CDCl3): δ 7.62-7.53 (m, 2H), 7.29-7.20 (m, 2H), 5.64 (t, J = 8.0 Hz, 1H), 4.80 (t, J = 8.4 Hz, 1H), 4.30 (dd, J = 8.7 Hz, 7.7 Hz, 1H) ppm; 13C NMR (100 MHz, CDCl3): δ 154.50, 134.82, 132.48, 127.48, 123.92, 77.25, 70.93 ppm.

4-(4-tert-butylphenyl)-1,3-dioxolan-2-one 2e

Rf = 0.8 (EA/Hexane = 1:5), Yield 71%, white solid. 1H NMR (300 MHz, CDCl3): δ 7.50-7.43 (m, 2H), 7.34-7.28 (m, 2H), 5.66 (t, J = 8.0 Hz, 1H),
Electronic Supplementary Material (ESI) for Journal Name
This journal is © The Royal Society of Chemistry

4.78 (t, J = 8.4 Hz, 1H), 4.36 (dd, J = 8.6 Hz, 8.0 Hz, 1H), 1.33 (s, 9H) ppm; 13C NMR (100 MHz, CDCl3): δ 154.91, 153.11, 132.64, 126.18, 125.83, 78.05, 71.11, 34.78, 31.22 ppm. HRMS (EI) m/z calcd for C13H16O3 [M+Na]+: 243.0997; found: 243.2875.

4-p-tolyl-1,3-dioxolan-2-one 2f

Rf = 0.6 (EA/Hexane = 1:8), Yield 75%, colorless crystalline. 1H NMR (300 MHz, CDCl3): δ 7.25 (s, 4H), 5.64 (t, J = 8.0 Hz, 1H), 4.77 (t, J = 8.3 Hz, 1H), 4.34 (dd, J = 8.6 Hz, 7.9 Hz, 1H), 2.39 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ 154.96, 139.87, 132.72, 129.87, 126.03, 78.14, 71.20 ppm. See also: J. Melendez, M. North and P. Villuendas, Chem. Commun., 2009, 18, 2577.

4-(4-methoxyphenyl)-1,3-dioxolan-2-one 2g

Rf = 0.7 (EA/Hexane = 1:10), Yield 76%, yellow solid. 1H NMR (300 MHz, CDCl3): δ 7.34-7.27 (m, 2H), 6.99-6.92 (m, 2H), 5.62 (t, J = 8.1 Hz, 1H), 4.75 (t, J = 8.4 Hz, 1H), 4.35 (dd, J = 8.7 Hz, 8.1 Hz, 3H), 3.83 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ 160.74, 154.90, 127.81, 127.40, 114.59, 78.17, 71.11, 55.41 ppm. HRMS (EI) m/z calcd for C10H10O4 [M+Na]+: 217.0477; found: 217.0472.

4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one 2h

Rf = 0.7 (EA/Hexane = 1:5), Yield 72%, light yellow oil. 1H NMR (300 MHz, CDCl3): δ 7.7-7.56 (m, 3H), 7.54-7.41 (m, 1H), 6.11-5.93 (m, 1H), 4.81 (td, J = 8.7 Hz, 1.3 Hz, 1H), 4.14(dd, J = 8.8 Hz, 7.2 Hz, 1H) ppm; 13C NMR (100 MHz, CDCl3): δ 154.68, 139.98, 131.56 (q, J = 32.5 Hz), 126.20, 126.16, 126.13, 126.09, 123.71 (q, J = 270.7 Hz), 77.06, 70.98 ppm; 19F NMR (376 MHz, CDCl3): δ -62.96 ppm. HRMS (EI) m/z calcd for C10H7F3O3 [M+Na]+: 255.0245; found: 255.0240.

4-m-tolyl-1,3-dioxolan-2-one 2i

Rf = 0.6 (EA/Hexane = 1:8), Yield 84%, light yellow oil. 1H NMR (400 MHz, CDCl3): δ 7.35-7.05 (m, 4H), 5.70-5.54 (m, 1H), 4.84-4.64 (m, 1H), 4.35-4.13 (m, 1H), 2.21 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ 155.18, 139.01, 136.07, 130.32, 129.02, 126.70, 123.17, 78.17, 71.23, 21.23 ppm. HRMS (EI) m/z calcd for C10H10O3 [M+Na]+: 201.0528; found: 201.0523.
4-(3-methoxyphenyl)-1,3-dioxolan-2-one 2j

\[
\begin{align*}
R_t &= 0.7 \text{ (EA/Hexane = 1:10), Yield 84%, yellow oil. } ^1H \text{ NMR (400 MHz, DMSO-}d_6): \delta 7.38 \text{ (t, } J = 7.9 \text{ Hz, 1H), 7.16-6.93 \text{ (m, 3H), 5.84 (t, } J = 8.0 \text{ Hz, 1H), 4.89 (td, } J = 8.2 \text{ Hz, 1.2 Hz, 1H), 4.43 (ddd, } J = 8.8 \text{ Hz, 7.9 Hz, 1.0 Hz, 1H), 3.79 (s, 3H) ppm; } ^{13}C \text{ NMR (100 MHz, DMSO-}d_6): \delta 159.56, 154.71, 137.77, 130.03, 118.45, 114.81, 111.98, 77.63, 70.77, 55.11 \text{ ppm. See also: C. William, W. H. Ross, N. Michael and P. Riccardo, Chem. Eur. J., 2010, 16, 6828.}
\end{align*}
\]

4-(3-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one 2k

\[
\begin{align*}
R_t &= 0.7 \text{ (EA/Hexane = 1:5), Yield 74%, light yellow oil. } ^1H \text{ NMR (300 MHz, CDCl}_3): \delta 7.70-7.45 \text{ (m, 4H), 5.77 (t, } J = 8.0 \text{ Hz, 1H), 4.92-4.78 \text{ (m, 1H), 4.37-4.20 \text{ (m, 1H) ppm; } ^{13}C \text{ NMR (100 MHz, CDCl}_3): } \delta 154.75, 137.13, 131.29 \text{ (q, } J = 32.4 \text{ Hz), 129.88, 129.31, 126.31 \text{ (q, } J = 3.7 \text{ Hz), 123.72 \text{ (q, } J = 270.7 \text{ Hz, 1H), 122.76 \text{ (q, } J = 3.7 \text{ Hz), 77.52, 71.01 \text{ ppm; } ^{19}F \text{ NMR (376 MHz, CDCl}_3): } \delta -62.87 \text{ ppm. HRMS (EI) m/z calcd for C}_{10}H_{10}F_3O_3[M+Na]^+: 255.0245; found: 255.0241.}
\end{align*}
\]

4-o-tolyl-1,3-dioxolan-2-one 2l

\[
\begin{align*}
R_t &= 0.6 \text{ (EA/Hexane = 1:8), Yield 64%, light yellow oil. } ^1H \text{ NMR (300 MHz, CDCl}_3): \delta 7.49-7.03 \text{ (m, 4H), 5.86 (td, } J = 8.0 \text{ Hz, 6.8Hz, 3.1Hz, 1H), 4.79 (tdd, } J = 8.4 \text{ Hz, 3.2 Hz, 1.6 Hz, 1H), 4.35-4.09 \text{ (m, 1H), 2.27 (s, 3H) ppm; } ^{13}C \text{ NMR (100 MHz, CDCl}_3): } \delta 155.25, 135.03, 134.33, 131.01, 129.18, 126.72, 124.69, 75.66, 70.46, 18.84 \text{ ppm. HRMS (EI) m/z calcd for C}_{10}H_{10}O_3 [M+Na]^+: 201.0528; found: 201.0524.}
\end{align*}
\]

4-(2-methoxyphenyl)-1,3-dioxolan-2-one 2m

\[
\begin{align*}
R_t &= 0.7 \text{ (EA/Hexane = 1:10), Yield 78%, yellow oil. } ^1H \text{ NMR (400 MHz, CDCl}_3): \delta 7.40-7.25 \text{ (m, 2H), 7.00-6.87 \text{ (m, 2H), 5.75 (t, } J = 7.8 \text{ Hz, 1H), 4.76 (t, } J = 8.5 \text{ Hz, 1H), 4.21 (dd, } J = 8.4 \text{ Hz, 7.1 Hz, 1H), 3.79 (s, 3H) ppm; } ^{13}C \text{ NMR (100 MHz, CDCl}_3): } \delta 156.50, 155.37, 130.53, 126.51, 124.71, 120.66, 110.91, 75.23, 70.45, 55.48 \text{ ppm. HRMS (EI) m/z calcd for C}_{10}H_{10}O_4 [M+Na]^+: 217.0477; found: 217.0473.}
\end{align*}
\]

4-(2-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one 2n
Rₜ = 0.7 (EA/Hexane = 1:5), Yield 31%, light yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 7.75-7.40 (m, 4H), 6.03 (m, 1H), 4.88-4.73 (m, 1H), 4.14 (dd, J = 8.8 Hz, 7.2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 154.60, 135.01, 133.09, 129.34, 126.78(d, J = 31.0 Hz), 126.28 (q, J = 6.1 Hz), 125.86, 123.89 (q, J = 271.1 Hz), 73.88 (q, J = 2.8 Hz), 71.45 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -58.93 ppm. HRMS (EI) m/z calcd for C₁₀H₁₀F₃O₃[M+Na]^+: 255.0245; found: 255.0242.

4-(naphthalen-1-yl)-1,3-dioxolan-2-one 2o

Rₜ = 0.7 (EA/Hexane = 1:5), Yield 76%, brown yellow solid. ¹H NMR (300 MHz, CDCl₃): δ 8.02-7.87 (m, 2H), 7.75-7.47 (m, 5H), 6.42 (t, J = 7.8 Hz, 1H), 5.06 (t, J = 8.4 Hz, 1H), 4.39 (dd, J = 8.5 Hz, 7.4 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 154.82, 133.81, 131.72, 129.75, 129.47, 129.20, 127.21, 126.37, 125.50, 122.33, 121.54, 75.55, 70.79 ppm. HRMS (EI) m/z calcd for C₁₃H₁₀O₃ [M+Na]^+: 237.0528; found: 237.0523.

hexahydrobenzo[d]-1,3-dioxolan-2-one 2p

Rₜ = 0.6 (EA/Hexane = 1:10), Yield 61%, brown yellow oil.¹H NMR (400 MHz, CDCl₃) δ 5.05 (m, 2H), 2.04 (m, 2H), 1.72 (m, 4H) ppm ¹³C NMR (100 MHz, CDCl₃) δ 155.36, 81.75, 33.12, 21.46 ppm. See also: C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, J. Am. Chem. Soc. 2013, 135, 1228.

5-methylhexahydrobenzo[d]-1,3-dioxolan-2-one 2q

Rₜ = 0.7 (EA/Hexane = 1:8), Yield 52%, brown yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 4.71 (m, 4H), 2.34 (m, 1H), 2.27 (m, 1H), 2.14 (m, 2H), 1.77 (m, 3H), 1.66 (m, 3H), 1.38 (m, 2H), 1.22 (m, 2H), 1.00 (m, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 155.24, 155.21, 76.49, 75.86, 75.60, 75.24, 36.32, 34.40, 28.36, 27.86, 27.42, 27.17, 26.04, 25.10, 21.87, 21.34 ppm. See also: V. Laserna, G. Fiorani, C. J. Whiteoak, E. Martin, E. Escudero-Adán and A. W. Kleij, Angew. Chem. Int. Ed., 2014, 53, 10416.
$^1$H- and $^{13}$C-NMR spectra
4-(4-tert-butylphenyl)-1,3-dioxolan-2-one 2e
4-(4-methoxyphenyl)-1,3-dioxolan-2-one 2g
4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one 2h
4-m-tolyl-1,3-dioxolan-2-one 2i
4-(3-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one 2k
4-o-tolyl-1,3-dioxolan-2-one 2l

[Chemical structure image]

[Chemical spectra and data]
4-(2-methoxyphenyl)-1,3-dioxolan-2-one 2m
4-(2-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one 2n
4-(naphthalen-1-yl)-1,3-dioxolan-2-one 2o