Homogeneous and silica-supported zinc complexes for the synthesis of propylene carbonate from propane-1,2-diol and carbon dioxide.

James W. Comerford, Sam J. Hart, Michael North* and Adrian Whitwood

Supporting information

1H NMR spectrum of propylene carbonate 2 in CDCl3.  
13C NMR spectrum of propylene carbonate 2 in CDCl3.  
High Resolution Mass Spectrum (ESI-TOF) of propylene carbonate 2.  
1H NMR spectrum of methylenebis-3,5-dimethyl-pyrazole ligand 5 in CDCl3.  
13C NMR spectrum of methylenebis-3,5-dimethyl-pyrazole ligand 5 in CDCl3.  
1H NMR spectrum of methylenebis-3,5-di-tertbutyl-pyrazole ligand 18 in CDCl3.  
13C NMR spectrum of methylenebis-3,5-di-tertbutyl-pyrazole ligand 18 in CDCl3.  
1H NMR spectrum of [Zn(5)2(CF3SO3)]+ (CF3SO3)− in CD3COCD3.  
13C NMR spectrum of [Zn(5)2(CF3SO3)]+ (CF3SO3)− in MeCN.  
19F NMR spectrum of [Zn(5)2(CF3SO3)]+ (CF3SO3)− in CD3COCD3.  
Solid state 19F NMR spectrum of [Zn(5)2(CF3SO3)]+ (CF3SO3)−.  
High Resolution Mass Spectrum (ESI-TOF) of [Zn(5)2(CF3SO3)]+ (CF3SO3)−.  
X-Ray Diffraction data for [Zn(5)2(CF3SO3)]+ (CF3SO3)−.  
1H NMR spectrum of the complex of ligand 18 and Zn(OSO2CF3)2 in CD3COCD3.  
13C NMR spectrum of the complex of ligand 18 and Zn(OSO2CF3)2 in CD3COCD3.  
19F NMR spectrum of the complex of ligand 18 and Zn(OSO2CF3)2 in CD3COCD3.  
Solid state 19F NMR spectrum of the complex of ligand 18 and Zn(OSO2CF3)2.  
Porosimetry data for silica 21a.  
Porosimetry data for silica 21b.  
Porosimetry data for silica 21c.  
Porosimetry data for heterogeneous catalyst 23a.  
Porosimetry data for heterogeneous catalyst 23b.  
Porosimetry data for heterogeneous catalyst 23c.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 21a.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 21b.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 21c.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 22a.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 22b.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 22c.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 23a.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 23b.  
Diffuse Reflectance Infrared Fourier Transform Spectrum (DRIFTS) of silica 23c.
$^1$H NMR spectrum of propylene carbonate 2 in CDCl$_3$. 
$^{13}$C NMR spectrum of propylene carbonate 2 in CDCl$_3$. 

![C NMR spectrum of propylene carbonate 2 in CDCl$_3$.](image-url)
High Resolution Mass Spectrum (ESI-TOF) of propylene carbonate 2.

York - Chemistry - Mass Spectrometry Service Report

Analysis Information

Analysis Filename: nn56477c_P1-D-9_01_63093.d
Method: 200p_meh1250_2c1s.m
Submission Name: nn56477c
Instrument: micrOTOF
ESI: Positive

Meas. m/z  #  Formula  m/z  err [ppm]  err [mDa]  mSigma  Mean err [ppm]
125.0212  1  C₄H₆O₃  125.0209  -1.9  -0.2  8.3  -2.0
$^1$H NMR spectrum of methylenebis-3,5-dimethyl-pyrazole ligand 5 in CDCl$_3$. 
$^{13}$C NMR spectrum of methylenebis-3,5-dimethyl-pyrazole ligand 5 in CDCl$_3$. 

---

11.31 13.56 148.36 140.53 106.48 60.61 148.36 140.53 106.48 60.61 13.56 11.31
$^1$H NMR spectrum of methylenebis-3,5-di-tertbutyl-pyrazole ligand 18 in CDCl$_3$. 
$^{13}$C NMR spectrum of methylenebis-3,5-di-tertbutyl-pyrazole ligand 18 in MeCN.
$^1$H NMR spectrum of [Zn(5)$_2$(CF$_3$SO$_3$)]$^+$ (CF$_3$SO$_3$)$^-$ in MeCN.
$^{13}$C NMR spectrum of $[\text{Zn(5)}_2(\text{CF}_3\text{SO}_3)]^+ (\text{CF}_3\text{SO}_3)^-$ in MeCN.
$^{19}$F NMR spectrum of $[\text{Zn}(\text{5})_2(\text{CF}_3\text{SO}_3)]^+$ (CF$_3$SO$_3$)$^-$ in CD$_3$COCD$_3$. 

-79.18 ppm
Solid state $^{19}$F NMR spectrum of $[\text{Zn}(5)(\text{CF}_3\text{SO}_3)]^+$ (CF$_3$SO$_3$).
High Resolution Mass Spectrum (ESI-TOF) of \([\text{Zn(5)}_2(\text{CF}_3\text{SO}_3)]^+ (\text{CF}_3\text{SO}_3)^-\).
X-Ray Diffraction data for [Zn(5)₂(CF₃SO₃)]⁺ (CF₃SO₃)⁻.

Empirical formula  
C₂₄H₃₂F₆N₈O₆S₂Zn

Formula weight  
772.06

Temperature/K  
110.05(10)

Crystal system  
triclinic

Space group  
P1

a/Å  
8.3731(3)

b/Å  
8.6907(3)

c/Å  
11.7281(5)

α°  
68.851(3)

β°  
81.968(3)

γ°  
82.401(3)

Volume/Å³  
785.04(5)

Z  
1

ρcalc/g/cm³  
1.633

μ/mm⁻¹  
1.004

F(000)  
396.0

Crystal size/mm³  
0.2125 × 0.1858 × 0.0806

Radiation  
MoKa (λ = 0.71073)

2Θ range for data collection/°  
6.516 to 64.184

Index ranges  
-12 ≤ h ≤ 11, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17

Reflections collected  
14482

Independent reflections  
8455 [Rint = 0.0265, Rsigma = 0.0586]

Data/restraints/parameters  
8455/3/432

Goodness-of-fit on F²  
0.966

Final R indexes [I>=2σ (I)]  
R₁ = 0.0304, wR₂ = 0.0525

Final R indexes [all data]  
R₁ = 0.0331, wR₂ = 0.0539

Largest diff. peak/hole / e Å⁻³  
0.38/-0.38

Flack parameter  
0.037(4)
$^1$H NMR spectrum of the complex of ligand 18 and Zn(OSO$_2$CF$_3$)$_2$ in CD$_3$COCD$_3$. 
$^{13}$C NMR spectrum of the complex of ligand 18 and Zn(OSO$_2$CF$_3$)$_2$ in CD$_3$COCD$_3$. 

- 29.75 ppm
- 29.92 ppm
- 31.67 ppm
- 31.73 ppm
- 65.30 ppm
- 101.22 ppm
- 152.82 ppm
- 158.90 ppm
$^{19}$F NMR spectrum of the complex of ligand 18 and Zn(OSO$_2$CF$_3$)$_2$ in CD$_3$COCD$_3$. 

f$_1$ (ppm)
Solid state $^{19}$F NMR spectrum of the complex of ligand 18 and Zn(OSO$_2$CF$_3$)$_2$. 
Porosimetry data for silica 21a.

**Surface Area**
- Single point surface area at $P/P_0 = 0.238411307$: 699.3663 $\text{m}^2/\text{g}$.
- BET Surface Area: 782.5325 $\text{m}^2/\text{g}$.
- Langmuir Surface Area: 1142.6012 $\text{m}^2/\text{g}$.
- t-Plot External Surface Area: 1085.9397 $\text{m}^2/\text{g}$.
- BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 610.238 m²/g.
- BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 144.0534 m²/g.

**Pore Volume**
- Single point adsorption total pore volume of pores less than 56.6231 nm radius at $P/P_0 = 0.982756180$: 0.387883 cm³/g.
- Single point desorption total pore volume of pores less than 33.3263 nm radius at $P/P_0 = 0.970294573$: 0.386017 cm³/g.
- t-Plot micropore volume: -0.172779 cm³/g.
- BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.346690 cm³/g.
- BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.117019 cm³/g.

**Pore Size**
- Adsorption average pore width (4V/A by BET): 1.98271 nm.
- Desorption average pore width (4V/A by BET): 1.97317 nm.
- BJH Desorption average pore radius (2V/A): 1.6247 nm.

**Nanoparticle Size - Average Particle Size:** 7.6674 nm.
Porosimetry data for silica 21b.

**Surface Area**
- Single point surface area at P/Po = 0.300672136: 253.7011 m²/g.
- BET Surface Area: 268.2281 m²/g.
- Langmuir Surface Area: 386.0740 m²/g.
- T-Plot External Surface Area: 312.1251 m³/g.
- BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 274.763 m²/g.
- BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 302.0997 m²/g.

**Pore Volume**
- Single point adsorption total pore volume of pores less than 67.8719 nm radius at P/Po = 0.985666084: 0.712821 cm³/g.
- Single point desorption total pore volume of pores less than 56.2277 nm radius at P/Po = 0.982632302: 0.716998 cm³/g.
- t-Plot micropore volume: -0.026517 cm³/g.
- BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.717321 cm³/g.
- BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.740051 cm³/g.

**Pore Size**
- Adsorption average pore width (4V/A by BET): 10.63007 nm.
- Desorption average pore width (4V/A by BET): 10.69236 nm.
- BJH Adsorption average pore radius (2V/A): 5.2214 nm.
- BJH Desorption average pore radius (2V/A): 4.8994 nm.

**Nanoparticle Size - Average Particle Size:** 22.3690 nm
Porosimetry data for silica 21c.

**Surface Area**
- Single point surface area at \( P/P_0 = 0.300224030 \): 157.6600 m²/g.
- BET Surface Area: 166.7211 m²/g.
- Langmuir Surface Area: 241.1675 m²/g.
- t-Plot External Surface Area: 200.1888 m²/g.
- BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 171.675 m²/g.
- BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 186.6019 m²/g.

**Pore Volume**
- Single point adsorption total pore volume of pores less than 60.1425 nm radius at \( P/P_0 = 0.983785703 \): 0.544113 cm³/g.
- Single point desorption total pore volume of pores less than 45.9861 nm radius at \( P/P_0 = 0.978664887 \): 0.555024 cm³/g.
- t-Plot micropore volume: -0.019020 cm³/g.
- BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.560722 cm³/g.
- BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.574331 cm³/g.

**Pore Size**
- Desorption average pore width (4V/A by BET): 13.31622 nm.

**Nanoparticle Size - Average Particle Size:** 35.9882 nm.
Porosimetry data for heterogeneous catalyst 23a

**Surface Area**
- Single point surface area at P/P₀ = 0.300156167: 40.6970 m²/g.
- BET Surface Area: 42.5908 m²/g.
- Langmuir Surface Area: 67.5899 m²/g.
- t-Plot External Surface Area: 45.5602 m²/g.
- BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 22.147 m²/g.
- BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 6.4356 m²/g.

**Pore Volume**
- Single point adsorption total pore volume of pores less than 61.1908 nm radius at P/P₀ = 0.984069088: 0.037137 cm³/g.
- Single point desorption total pore volume of pores less than 36.8255 nm radius at P/P₀ = 0.973197536: 0.035323 cm³/g.
- t-Plot micropore volume: -0.000482 cm³/g.
- BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.031584 cm³/g.
- BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.023260 cm³/g.

**Pore Size**
- Adsorption average pore width (4V/A by BET): 3.48781 nm.
- Desorption average pore width (4V/A by BET): 3.31747 nm.
- BJH Adsorption average pore radius (2V/A): 2.8522 nm.
- BJH Desorption average pore radius (2V/A): 7.2286 nm.

**Nanoparticle Size - Average Particle Size:** 140.8755 nm.
Porosimetry data for heterogeneous catalyst 23b

Surface Area
- Single point surface area at P/Po = 0.300152318: 63.0414 m²/g.
- BET Surface Area: 66.3520 m²/g.
- Langmuir Surface Area: 96.6962 m²/g.
- t-Plot External Surface Area: 76.7784 m²/g.
- BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 65.089 m²/g.
- BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: 76.7368 m²/g.

Pore Volume
- Single point adsorption total pore volume of pores less than 66.5841 nm radius at P/Po = 0.985383601: 0.250480 cm³/g.
- Single point desorption total pore volume of pores less than 46.2219 nm radius at P/Po = 0.978776436: 0.251914 cm³/g.
- t-Plot micropore volume: -0.005783 cm³/g.
- BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.262823 cm³/g.
- BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: 0.268515 cm³/g.

Pore Size
- Adsorption average pore width (4V/A by BET): 15.10006 nm.
- Desorption average pore width (4V/A by BET): 15.18651 nm.
- BJH Adsorption average pore radius (2V/A): 8.0758 nm.

Nanoparticle Size - Average Particle Size: 90.4269 nm
Porosimetry data for heterogeneous catalyst 23c

**Surface Area**

- Single point surface area at $P/P_0 = 0.299874650$: $58.3303 \text{ m}^2/\text{g}$.
- BET Surface Area: $61.1929 \text{ m}^2/\text{g}$.
- Langmuir Surface Area: $88.2629 \text{ m}^2/\text{g}$.
- t-Plot External Surface Area: $69.9641 \text{ m}^2/\text{g}$.
- BJH Adsorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: $61.510 \text{ m}^2/\text{g}$.
- BJH Desorption cumulative surface area of pores between 0.8500 nm and 150.0000 nm radius: $75.1870 \text{ m}^2/\text{g}$.

**Pore Volume**

- Single point adsorption total pore volume of pores less than 60.8452 nm radius at $P/P_0 = 0.983976764$: $0.286665 \text{ cm}^3/\text{g}$.
- Single point desorption total pore volume of pores less than 47.5567 nm radius at $P/P_0 = 0.979386600$: $0.298825 \text{ cm}^3/\text{g}$.
- t-Plot micropore volume: $-0.004894 \text{ cm}^3/\text{g}$.
- BJH Adsorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: $0.312618 \text{ cm}^3/\text{g}$.
- BJH Desorption cumulative volume of pores between 0.8500 nm and 150.0000 nm radius: $0.316537 \text{ cm}^3/\text{g}$.

**Pore Size**

- Adsorption average pore width ($4V/A$ by BET): $18.73843 \text{ nm}$.
- Desorption average pore width ($4V/A$ by BET): $19.53333 \text{ nm}$.
- BJH Adsorption average pore radius ($2V/A$): $10.1648 \text{ nm}$.
- BJH Desorption average pore radius ($2V/A$): $8.4200 \text{ nm}$.

**Nanoparticle Size - Average Particle Size:** $98.0507 \text{ nm}$.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 21a.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 21b.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 21c.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 22a.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 22b.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 22c.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 23a.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 23b.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy analysis (DRIFTS) of silica 23c.