Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

# N,N,O-supported Tricarbonylrhenium Precatalysts for the Aerobic Deoxydehydration of Diols and Polyols

Jing Li, <sup>a</sup> Martin Lutz <sup>b</sup> and Robertus J. M. Klein Gebbink \*<sup>a</sup>

a. Organic chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584CG, Utrecht, The Netherlands.

b. Crystal and Structural Chemistry, Bijvoet Centre for Biomolecular Research, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH, Utrecht, The Netherlands.

# Contents

1. General Information	1
2. Synthesis and Characterization of LRe (CO) <sub>3</sub> Complexes	2
Synthesis of L <sup>1</sup> Re (CO) <sub>3</sub>	2
Synthesis of L <sup>2</sup> Re(CO) <sub>3</sub>	2
Synthesis of L <sup>3</sup> Re(CO) <sub>3</sub>	3
Synthesis of L <sup>4</sup> Re(CO) <sub>3</sub>	4
Synthesis of L <sup>5</sup> Re(CO) <sub>3</sub>	5
X-Ray Crystal Structure Determination of L <sup>1</sup> Re(CO) <sub>3</sub>	6
X-Ray Crystal Structure Determination of L <sup>3</sup> Re(CO) <sub>3</sub>	7
X-Ray Crystal Structure Determination of L <sup>4</sup> Re(CO) <sub>3</sub>	7
3. Catalysis	8
General Procedure for Catalytic Deoxydehydration Using PhCl as Solvent	8
General Procedure for Catalytic Deoxydehydration Using Alcohol as Solvent	8
4. <sup>1</sup> H NMR And <sup>13</sup> C NMR Spectra	11
5. References	16

#### 1. General information

PPh<sub>3</sub> was recrystallized from EtOH. Unless otherwise stated, all other chemicals were obtained commercially and used without further purification (Sigma Aldrich, Acros). 2-(((2-(dimethylamino)ethyl)(methyl)amino)methyl)phenol (HL<sup>1</sup>) was synthesized according to a known synthesize procedure.<sup>[1]</sup> NMR spectra were recorded on a Varian VNMRS400 (400 MHz) or Bruker (600 MHz) at 298 K. Infra-Red spectra were recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer in the range of 650-4000 cm<sup>-1</sup>. Elemental analysis was done by MEDAC Ltd.

# 2. Synthesis and characterization of LRe(CO)<sub>3</sub> complexes

#### Synthesis of L<sup>1</sup>Re(CO)<sub>3</sub>

A solution of HL<sup>1</sup> (363 mg, 1.74 mmol, 1.0 equiv.), Re(CO)<sub>5</sub>Br (708 mg, 0.5 mmol, 1.0 equiv.) and NaOAc (1.427 g, 17.4 mmol, 10 equiv.) in toluene (50 mL) was refluxed for 3 h under argon atmosphere. The reaction mixture was treated with aq. NH<sub>4</sub>Cl and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed under reduced pressure and the residue was purified by recrystallization (Et<sub>2</sub>O/MeCN) to obtain L<sup>1</sup>Re(CO)<sub>3</sub> as a blueish off-white solid (697 mg, 84%). Diffusion of Et<sub>2</sub>O into a MeCN solution at room temperature gave crystal of L<sup>1</sup>Re(CO)<sub>3</sub> suitable for X-ray analysis.

<sup>1</sup>H NMR (600 MHz), CD<sub>3</sub>CN (1.94 ppm):  $\delta$  = 7.10 (ddd, *J* = 8.1, 7.1, 1.9 Hz, 1H), 6.94 – 6.90 (m, 1H), 6.56 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.48 (td, *J* = 7.3, 1.2 Hz, 1H), 4.06 (d, *J* = 13.5 Hz, 1H), 3.72 (d, *J* = 13.5 Hz, 1H), 3.16 (s, 3H), 3.11 (s, 3H), 2.98 (ddd, *J* = 11.6, 5.9, 2.6 Hz, 1H), 2.88 – 2.72 (m, 3H), 2.64 (s, 3H). <sup>13</sup>C NMR (150 MHz), CD<sub>3</sub>CN (118.26 ppm):  $\delta$  = 198.36, 198.02, 197.07, 166.10, 131.07, 130.91, 123.95, 119.75, 115.62, 64.70, 62.51, 59.26, 57.52, 56.60, 50.34. Infrared v (CO) (cm<sup>-1</sup>): 1877, 1918, 2014. ESI-MS (in MeCN): calcd. for [C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>Re + H]<sup>+</sup>: 479.1, found: 479.1. Elemental analysis calcd. (%) for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>Re (477.53): C 37.73, H 4.01, N 5.86; found: C 37.38, H 3.79, N 5.86.

#### Synthesis of L<sup>2</sup>Re(CO)<sub>3</sub>

A mixture of *N,N,N'*-trimethylethylenediamine (1.022 g, 10 mmol), 2-hydroxy-5methoxybenzaldehyde (1.522 g, 10 mmol), and sodium triacetoxyborohydride (3.179 g, 15 mmol), in 1,2-dichloroethane (25 mL) was stirred overnight under nitrogen. The reaction mixture was quenched by adding a saturated NaHCO<sub>3</sub> solution. Dichloromethane was used to extract the mixture. The organic layer was dried with MgSO<sub>4</sub> and the solvent was removed under vacuum to obtain a red-orange oil. The oil was further purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (20:1) as the eluent. Removal of the solvent *in vacuo* gave HL<sup>2</sup> as a red-orange oil (1.260 g, 53%).

<sup>1</sup>H NMR (400 MHz), CD<sub>3</sub>CN (1.94 ppm):  $\delta$  = 6.70 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.66 – 6.60 (m, 2H), 3.69 (s, 3H), 3.52 (s, 2H), 2.47 (td, *J* = 6.1, 1.2 Hz, 4H), 2.20 (s, 6H), 2.18 (s, 3H).

A solution of  $HL^2$  (119 mg, 0.5 mmol, 1.0 equiv.),  $Re(CO)_5Br$  (203 mg, 0.5 mmol, 1.0 equiv.) and NaOAc (410 mg, 5.0 mmol, 10 equiv.) in toluene (15 mL) was refluxed for 3 h under an argon atmosphere. The reaction mixture was treated with aq.  $NH_4Cl$  and diluted with  $CH_2Cl_2$ . The organic layer was separated, dried over  $Na_2SO_4$ , and filtered. The solvent was removed under reduced pressure and the residue was purified by recrystallization  $(Et_2O/MeCN)$  to obtain  $L^2Re(CO)_3$  as an off-white solid (190 mg, 75%).

<sup>1</sup>H NMR (600 MHz), CD<sub>3</sub>CN (1.94 ppm):  $\delta$  = 6.72 (dd, *J* = 8.7, 3.2 Hz, 1H), 6.57 (d, *J* = 3.2 Hz, 1H), 6.49 (d, *J* = 8.7 Hz, 1H), 3.89 (d, *J* = 13.4 Hz, 1H), 3.72 (d, *J* = 13.4 Hz, 1H), 3.67 (s, 3H), 3.13 (s, 3H), 3.11 (s, 3H), 3.05 – 2.93 (m, 1H), 2.92 – 2.81 (m, 2H), 2.80 – 2.73 (m, 1H), 2.67 (s, 3H). <sup>13</sup>C NMR (150 MHz), CD<sub>3</sub>CN (118.26 ppm):  $\delta$  = 198.45, 197.99, 197.03, 160.66, 150.51, 124.31, 119.52, 116.32, 64.08, 62.34, 59.75, 57.52, 56.31, 56.22, 50.41. Infrared v (CO) (cm<sup>-1</sup>): 1859, 1886, 2007. ESI-MS (in MeCN): calcd. for [C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub>Re + H]<sup>+</sup>: 509.1, found: 508.1. Elemental analysis calcd. (%) for C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>O<sub>5</sub>Re (507.56): C 37.86, H 4.17, N 5.52; found: C 38.15, H 4.27, N 5.44.

### Synthesis of L<sup>3</sup>Re(CO)<sub>3</sub>

A mixture of *N*,*N*,*N*'-trimethylethylenediamine (1.022 g, 10 mmol), 2-hydroxy-5nitrobenzaldehyde (1.671 g, 10 mmol), and sodium triacetoxyborohydride (3.179 g, 15 mmol), in 1,2-dichloroethane (25 mL) was stirred overnight under nitrogen. The reaction mixture was quenched by adding a saturated NaHCO<sub>3</sub> solution. Dichloromethane was used to extract the mixture. The organic layer was dried with MgSO<sub>4</sub> and the solvent was removed under vacuum to obtain a bright yellow oil. The oil was further purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (10:1) as the eluent. Removal of the solvent *in vacuo* gave HL<sup>3</sup> as a yellow solid (1.397g, 55%).

<sup>1</sup>H NMR (400 MHz), CD<sub>3</sub>CN (1.94 ppm): δ = 7.99 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.93 (dt, *J* = 3.0, 0.7 Hz, 1H), 6.59 (d, *J* = 9.1 Hz, 1H), 3.46 (s, 2H), 2.81 (dd, *J* = 6.7, 5.7 Hz, 2H), 2.81 (t, *J* = 6.7, 5.7 Hz, 2H), 2.65 (t, *J* = 6.1 Hz, 2H), 2.42 (s, 6H), 2.20 (s, 3H).

A solution of HL<sup>3</sup> (127 mg, 0.5 mmol, 1.0 equiv.), Re(CO)<sub>5</sub>Br (203 mg, 0.5 mmol, 1.0 equiv.) and NaOAc (410 mg, 5.0 mmol, 10 equiv.) in toluene (15 mL) was refluxed for 3 h under an argon atmosphere. The reaction mixture was treated with aq. NH<sub>4</sub>Cl and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed under reduced pressure and the residue was purified by recrystallization  $(Et_2O/MeCN)$  to obtain L<sup>3</sup>Re(CO)<sub>3</sub> as a yellow solid (190 mg, 73%). Diffusion of Et<sub>2</sub>O into a MeCN solution at room temperature gave crystals of  $L^{3}Re(CO)_{3}$  suitable for X-ray analysis. <sup>1</sup>H NMR (600 MHz), CD<sub>3</sub>CN (1.94 ppm): δ = 8.02 (dd, *J* = 9.1, 3.0 Hz, 1H), 7.94 (dd, *J* = 3.0, 0.8 Hz, 1H), 6.60 (d, J = 9.1 Hz, 1H), 4.35 (d, J = 14.1 Hz, 1H), 3.78 (d, J = 14.1 Hz, 1H), 3.23 (s, 3H), 3.13 (s, 3H), 2.98 (ddd, J = 13.8, 8.3, 3.5 Hz, 1H), 2.87 (ddd, J = 13.7, 8.3, 3.5 Hz, 1H), 2.73 (ddd, J = 13.8, 6.8, 3.5 Hz, 1H), 2.66 (ddd, J = 13.7, 6.8, 3.5 Hz, 1H), 2.54 (s, 3H). <sup>13</sup>C NMR (150 MHz), CD<sub>3</sub>CN (118.26 ppm):  $\delta$  = 198.19, 194.84, 170.79, 136.73, 135.12, 128.44, 127.45, 123.24, 120.39, 76.07, 65.04, 62.80, 58.34, 57.74, 57.32, 50.10. Infrared v (CO) (cm<sup>-1</sup>): 1884, 1921, 2016. ESI-MS (in MeCN): calcd. for [C<sub>15</sub>H<sub>18</sub>N<sub>3</sub>O<sub>6</sub>Re + H + MeCN]<sup>+</sup>: 565.1, found: 565.0. Elemental analysis calcd. (%) for C<sub>15</sub>H<sub>18</sub>N<sub>3</sub>O<sub>6</sub>Re (522.53): C 34.48, H 3.47, N 8.04; found: C 43.11, H 3.48, N 7.95.

# Synthesis of L<sup>4</sup>Re(CO)<sub>3</sub>

A mixture of N,N,N'-trimethylethylenediamine (1.022 g, 10 mmol), 3,5-di-tert-butyl-2hydroxybenzaldehyde (2.343 g, 10 mmol), and sodium triacetoxyborohydride (3.179 g, 15 mmol), in 1,2-dichloroethane (25 mL) was stirred overnight under nitrogen. The reaction mixture was quenched by adding a saturated NaHCO<sub>3</sub> solution. Dichloromethane was used to extract the mixture. The organic layer was dried with MgSO<sub>4</sub> and the solvent was removed under vacuum to obtain a light-yellow oil. The oil was further purified by column chromatography on silica gel with  $CH_2Cl_2/MeOH$  (20:1) as the eluent. Removal of the solvent *in vacuo* gave HL<sup>4</sup> as a colorless solid (1.873g, 58%).

<sup>1</sup>H NMR (400 MHz), CD<sub>3</sub>CN (1.94 ppm): δ = 7.19 (d, *J* = 2.5 Hz, 1H), 6.97 – 6.82 (m, 1H), 3.63 (s, 2H), 2.53 (td, *J* = 6.4, 1.1 Hz, 2H), 2.44 (td, *J* = 6.4, 1.1 Hz, 2H), 2.23 (s, 3H), 2.16 (s, 6H), 1.38 (s, 9H), 1.26 (s, 9H).

A solution of HL<sup>4</sup> (225 mg, 0.7 mmol, 1.0 equiv.), Re(CO)<sub>5</sub>Br (406 mg, 0.7 mmol, 1.0 equiv.) and NaOAc (574 mg, 7.0 mmol, 10 equiv.) in toluene (21 mL) was refluxed for 3 h under an argon atmosphere. The reaction mixture was treated with aq. NH<sub>4</sub>Cl and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed under reduced pressure and the residue was purified by recrystallization (Et<sub>2</sub>O/hexane) to obtain L<sup>4</sup>Re(CO)<sub>3</sub> as an off-white solid (315 mg, 76%). Recrystallization from Et<sub>2</sub>O/hexane (1:2) at -30 °C gave crystals of L<sup>4</sup>Re(CO)<sub>3</sub> suitable for X-ray analysis.

<sup>1</sup>H NMR (600 MHz), CD<sub>3</sub>CN (1.94 ppm):  $\delta$  = 7.20 (d, *J* = 2.6 Hz, 1H), 6.91 (dd, *J* = 2.6, 0.6 Hz, 1H), 3.82 (d, *J* = 13.0 Hz, 1H), 3.29 (d, *J* = 13.1 Hz, 1H), 3.21 – 3.14 (m, 4H), 3.14 – 3.08 (m, 1H), 3.08 – 2.97 (m, 4H), 2.88 (s, 3H), 2.82 (ddd, *J* = 13.5, 4.2, 3.1 Hz, 1H), 1.43 (s, 9H), 1.26 (s, 9H). <sup>13</sup>C NMR (150 MHz), CD<sub>3</sub>CN (118.26 ppm):  $\delta$  = 198.90, 197.55, 196.68, 166.78, 137.73, 137.51, 126.37, 124.95, 124.05, 62.51, 61.63, 61.51, 57.28, 54.38, 51.22, 36.15, 34.11, 32.11, 30.50. Infrared v (CO) (cm<sup>-1</sup>): 1851, 1894, 2010. ESI-MS (in MeCN): calcd. for [C<sub>23</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub>Re + H]<sup>+</sup>: 591.2, found: 590.2. Elemental analysis calcd. (%) for C<sub>23</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub>Re (589.75): C 46.84, H 5.98, N 4.75; found: C 46.94, H 5.75, N 4.80.

# Synthesis of L<sup>5</sup>Re(CO)<sub>3</sub>

A mixture of *N,N,N'*-trimethylethylenediamine (1.022 g, 10 mmol), 3,5-dichloro-2hydroxybenzaldehyde (1.910 g, 10 mmol), and sodium triacetoxyborohydride (3.179 g, 15 mmol), in 1,2-dichloroethane (25 mL) was stirred overnight under nitrogen. The reaction mixture was quenched by adding saturated NaHCO<sub>3</sub> solution. Dichloromethane was used to extract the mixture. The organic layer was dried with MgSO<sub>4</sub> and the solvent was removed under vacuum to obtain a light-yellow oil. The oil was further purified by column

5

chromatography on silica gel with  $CH_2Cl_2/MeOH$  (20:1) as the eluent. Removal of the solvent in vacuo gave  $HL^5$  as a yellow solid (1.850g, 67%).

<sup>1</sup>H NMR (400 MHz), CD<sub>3</sub>CN (1.94 ppm): δ = 7.28 (dd, *J* = 2.6, 0.5 Hz, 1H), 7.00 (dt, *J* = 2.6, 0.7 Hz, 1H), 3.52 (s, 2H), 2.63 – 2.51 (m, 4H), 2.25 (s, 6H), 2.18 (s, 3H).

A solution of  $HL^5$  (55 mg, 0.2 mmol, 1.0 equiv.),  $Re(CO)_5Br$  (81 mg, 0.2 mmol, 1.0 equiv.) and NaOAc (164 mg, 2.0 mmol, 10 equiv.) in toluene (6 mL) was refluxed for 3 h under an argon atmosphere. The reaction mixture was treated with aq.  $NH_4Cl$  and diluted with  $CH_2Cl_2$ . The organic layer was separated, dried over  $Na_2SO_4$ , and filtered. The solvent was removed under reduced pressure and the residue was purified by recrystallization (DCM/Et<sub>2</sub>O) to obtain  $L^5Re(CO)_3$  as a yellowish solid (86 mg, 79%).

<sup>1</sup>H NMR (600 MHz), CD<sub>3</sub>CN (1.94 ppm):  $\delta$  = 7.31 (d, *J* = 2.7 Hz, 1H), 6.97 (d, *J* = 2.7 Hz, 1H), 3.90 – 3.73 (m, 2H), 3.13 (s, 6H), 3.00 – 2.93 (m, 2H), 2.87 (ddd, *J* = 13.3, 8.1, 5.0 Hz, 1H), 2.77 (dt, *J* = 13.9, 4.4 Hz, 1H), 2.70 (s, 3H). <sup>13</sup>C NMR (150 MHz), CD<sub>3</sub>CN (118.26 ppm):  $\delta$  = 197.43, 161.14, 129.91, 129.27, 127.52, 124.42, 118.56, 63.39, 62.28, 60.05, 57.46, 56.75, 51.02. Infrared v (CO) (cm<sup>-1</sup>): 1855, 1873, 2007. ESI-MS (in MeCN): calcd. for [C<sub>15</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>Re + H]<sup>+</sup>: 547.0, found: 547.0. Elemental analysis calcd. (%) for C<sub>15</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>Re (546.42): C 32.97, H 3.14, N 5.12; found: C 32.98, H 3.20, N 5.10.

#### X-ray crystal structure determination of L<sup>1</sup>Re(CO)<sub>3</sub>

 $C_{15}H_{19}N_2O_4Re$ , Fw = 477.52, colourless needle, 0.53 × 0.09 × 0.07 mm<sup>3</sup>, monoclinic, P2<sub>1</sub>/c (no. 14), a = 14.6069(6), b = 8.8710(4), c = 12.0927(8) Å,  $\beta$  = 90.801(3) °, V = 1566.80(14) Å<sup>3</sup>, Z = 4, D<sub>x</sub> = 2.024 g/cm<sup>3</sup>,  $\mu$  = 7.78 mm<sup>-1</sup>. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ( $\lambda$  = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin  $\theta/\lambda$ )<sub>max</sub> = 0.65 Å<sup>-1</sup>. The crystal appeared to be cracked, with a rotation angle of 3.0 ° between the two crystal fragments. Consequently, two orientation matrices were used for the intensity integration with the Eval15 software<sup>[2]</sup>. A multi-scan absorption correction and scaling was performed with TWINABS<sup>[3]</sup> (correction range 0.17-0.43). A total of 54428 reflections was measured, 3685 reflections were unique (R<sub>int</sub> = 0.050), 3281 reflections were observed [I>2 $\sigma$ (I)]. The structure was solved with Patterson superposition methods using SHELXT<sup>[4]</sup>. Structure

refinement was performed with SHELXL-2018<sup>[5]</sup> on F<sup>2</sup> of all reflections based on an HKLF-5 file<sup>[6]</sup>. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 203 Parameters were refined with no restraints. R1/wR2 [I >  $2\sigma(I)$ ]: 0.0354 / 0.0886. R1/wR2 [all refl.]: 0.0406 / 0.0913. BASF for the two crystal fragments refined to zero. S = 1.054. Residual electron density between -3.15 and 3.40 e/Å<sup>3</sup> (in the proximity of the metal). Geometry calculations and checking for higher symmetry was performed with the PLATON program.<sup>[7]</sup>

# X-ray crystal structure determination of L<sup>3</sup>Re(CO)<sub>3</sub>

 $C_{15}H_{18}N_3O_6Re$ , Fw = 522.52, yellow needle,  $0.42 \times 0.09 \times 0.03$  mm<sup>3</sup>, orthorhombic, Pbca (no. 61), a = 8.90063(16), b = 11.9803(3), c = 31.8099(7) Å, V = 3391.95(13) Å<sup>3</sup>, Z = 8,  $D_x$  = 2.046 g/cm<sup>3</sup>,  $\mu$  = 7.20 mm<sup>-1</sup>. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ( $\lambda = 0.71073$  Å) at a temperature of 150(2) K up to a resolution of (sin  $\theta/\lambda$ )<sub>max</sub> = 0.65 Å<sup>-1</sup>. Intensity integration was performed with the Eval15 software<sup>[2]</sup>. A numerical absorption correction and scaling was performed with SADABS<sup>[3]</sup> (correction range 0.30-0.91). A total of 52093 reflections was measured, 3901 reflections were unique (R<sub>int</sub> = 0.069), 3027 reflections were observed  $[I>2\sigma(I)]$ . The structure was solved with Patterson superposition methods using SHELXT<sup>[4]</sup>. Structure refinement was performed with SHELXL-2018<sup>[5]</sup> on F<sup>2</sup> of all reflections. Nonhydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 229 Parameters were refined with no restraints. R1/wR2 [I >  $2\sigma$ (I)]: 0.0229 / 0.0403. R1/wR2 [all refl.]: 0.0402 / 0.0443. S = 1.028. Residual electron density between -0.64 and 1.14  $e/Å^3$ . Geometry calculations and checking for higher symmetry was performed with the PLATON program.<sup>[7]</sup>

# X-ray crystal structure determination of L<sup>4</sup>Re(CO)<sub>3</sub>

 $C_{23}H_{35}N_2O_4Re$ , Fw = 589.73, colourless plate,  $0.43 \times 0.20 \times 0.06 \text{ mm}^3$ , monoclinic, C2/c (no. 15), a = 23.9270(7), b = 9.4928(3), c = 22.1646(7) Å,  $\beta$  = 106.575(2) °, V = 4825.2(3) Å<sup>3</sup>, Z = 8, D<sub>x</sub> = 1.624 g/cm<sup>3</sup>,  $\mu$  = 5.07 mm<sup>-1</sup>. The diffraction experiment was performed on a Bruker

Kappa ApexII diffractometer with sealed tube and Triumph monochromator ( $\lambda = 0.71073$  Å) at a temperature of 150(2) K up to a resolution of (sin  $\theta/\lambda)_{max} = 0.65$  Å<sup>-1</sup>. Intensity integration was performed with the Eval15 software<sup>[2]</sup>. A numerical absorption correction and scaling was performed with SADABS<sup>[3]</sup> (correction range 0.26-0.80). A total of 43450 reflections was measured, 5540 reflections were unique (R<sub>int</sub> = 0.084), 4228 reflections were observed [I>2 $\sigma$ (I)]. The structure was solved with Patterson superposition methods using SHELXT<sup>[4]</sup>. Structure refinement was performed with SHELXL-2018<sup>[5]</sup> on F<sup>2</sup> of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were refined with no restraints. R1/wR2 [I > 2 $\sigma$ (I)]: 0.0296 / 0.0562. R1/wR2 [all refl.]: 0.0503 / 0.0611. S = 1.012. Residual electron density between -0.60 and 1.16 e/Å<sup>3</sup>. Geometry calculations and checking for higher symmetry was performed with the PLATON program.<sup>[7]</sup>

CCDC 1978458-1978460 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

# 3. Catalysis

#### General procedure for catalytic deoxydehydration using PhCl as solvent

1,2-octanediol (0.5 mmol), L<sup>1</sup>Re(CO)<sub>3</sub> (0.01 mmol), reductant (0.55 mmol), and mesitylene (0.5 mmol) were dissolved in chlorobenzene (5 mL) and mixed well, the mixture was then transferred to a 25 mL thick-walled glass pressure tube (Ace) fitted with a Teflon screw-cap. Then, the closed reaction vessel was brought into a preheated silicone oil bath at 180 °C. After the reaction, aliquots of the reaction mixture were diluted with acetone (for both olefin and diol analysis). GC measurements were performed using a Perkin Elmer Autosystem XL Gas Chromatograph equipped with a Perkin Elmer Elite-17 column (Length: 30m, I.D.: 0.32 mm, Film thickness: 0.50  $\mu$ m), and with FID-detector. GC method: 40 °C, 5 min; 3 °C/min to 55 °C; 20 °C/min to 250 °C; 250 °C, 10 min. All olefinic products are known compounds and were calibrated against mesitylene for quantification.

# General procedure for catalytic deoxydehydration using alcohol as solvent

Diols or polyols (0.5 mmol), LRe(CO)<sub>3</sub>/BrRe(CO)<sub>5</sub> (0.01 mmol) and mesitylene (0.5 mmol) were dissolved in an alcohol (5 mL), the mixture was then transferred to a 25 mL thick-walled glass pressure tube (Ace) fitted with a Teflon screw-cap. The closed reaction vessel was brought into a preheated silicone oil bath at 155 °C or 180 °C. The suspension became a homogeneous solution during heating. The amount of O<sub>2</sub> present in the reaction set-up was calculated as follows: volume of gas phase = total volume of reaction tube (25 mL) – total volume of reaction mixture (5 mL) = 20mL. The percentage of O2 in air is apporx. 20%; accordingly the volume of O<sub>2</sub> would be 20/5 = 4 mL. The amount of O<sub>2</sub> would be 4 mL/(22.4 mL/mmol) = 0.178 mmol.

After the reaction, the reaction vessel was opened under ambient conditions and an aliquot (~0.1 mL) of the reaction mixture was taken, diluted with CDCl<sub>3</sub> (~0.4 mL) and analyzed by <sup>1</sup>H NMR. Peaks of the olefin product were used to calculate the yield (listed below). <sup>1</sup>H NMR peak of internal standard (mesitylene) (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.78 (s, 3 H, used for calculation), 2.28 (s, 9H).

entry	product	structure	<sup>1</sup> H NMR (CDCl <sub>3</sub> , 400 MHz)
1	1-octene		δ 1.00 – 0.81 (m, 3H), 1.50 –
			1.18 (m, 8H), 2.11 – 1.98 (m,
			2H), 5.09 – 4.86 (m, 2H), 5.82
			(ddt, J = 16.9, 10.2, 6.7 Hz,
			1H).
2	1-dodecene	~~~~/	δ 0.77 (t, J = 7.4 Hz, 1H), 2.03
			(dtt, J = 7.6, 6.0, 1.9 Hz, 2H),
			4.91 (ddt, <i>J</i> = 10.1, 2.2, 1.3 Hz,
			1H), 4.98 (dq, J = 17.1, 1.8 Hz,
			1H), 5.80 (ddt, J = 16.9, 10.2,
			6.7 Hz, 1H), ), other signals
			overlapped with the signal of
			the solvent.

3	styrene		δ 5.22 (dd, J = 10.9, 0.9 Hz,
			1H), 5.73 (dd, J = 17.6, 0.9 Hz,
			1H), 6.70 (dd, J = 17.6, 10.9
			Hz, 1H), 7.26 – 7.19 (m, 1H),
			7.34 – 7.27 (m, 2H), 7.41–
			7.36 (m, 2H).
4	cyclohexene		δ 1.98 (tt, J = 3.9, 2.0 Hz, 2H),
			5.65 (t, $J = 1.6$ Hz, 2H), the
			other two signals overlapped
			with the signal of solvent.
5	allyl alcohol	OH	δ 4.10 (d, J = 5.1 Hz, 2H), 5.11
			(dd, J = 10.4, 1.5 Hz, 1H), 5.25
			(dd, J = 17.2, 1.7 Hz, 1H), 5.97
			(ddt, J = 17.0, 10.2, 5.1 Hz,
			1H).
6	2,5-dihydrofuran	$\left[ \begin{array}{c} 0 \\ \end{array} \right]$	δ 5.87 (s, 2H), 4.62 (s, 4H).
	1,3-butadiene		0 5.14 - 5.02 (m, 2H), 5.26 -
			5.15 (m, 2H), 6.40 – 6.25 (m,
		0	
8	1,4-anhydrothreitol		$\delta$ 4.02 (dd, 2H, J = 12 Hz, 8
	(racemic)	OH	Hz), 4.15 (m, 2H), 3.76 (d, J =
			10.0 Hz, 2H)
9	fumaric acid and		Peaks at 6.80, 6.82, and 6.84
	fumarates		ppm were observed. Because
		Ö	of the overlap of acid,
			monofumarate, and
			bisfumuarete signals, the total
			value of these three was
			counted as 2 H. The aliphatic
			signals overlapped with the
			signal of the solvent.

10	muconates	HOOC $C_5H_{11}$ $C_5H_{11}$ $C_5H_{11}$ O $C_5H_{11}$ $C_5H_$	$\delta$ 6.41 – 6.09 (m, 2H), 7.56 – 7.19 (m, 2H). The aliphatic signals overlapped with the signal of the solvent.
11	furan	€°>	δ 7.41 (s, 2H), 6.36 (s, 2H)
12	2-vinylfuran		δ 5.18 (dd,1H, J = 11.3, 1.3 Hz), 5.69 (dd, 1H, J = 17.5, 1.3 Hz), 6.31 – 6.25 (m, 1H), 6.39 (dd, 1H, J = 3.3, 1.9 Hz), 6.53 (dd, 1H, J = 17.5, 11.3 Hz), 7.40 – 7.34 (m, 1H)

# 4. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra





















# 5. References

- [1] D. G. Lonnon, S. B. Colbran, D. C. Craig, *Eur. J. Inorg. Chem.* (2006), **2006**, 1190-1197.
- [2] A. M. M. Schreurs, X. Xian, L. M. J. Kroon-Batenburg. "EVAL15: a diffraction data integration method based on *ab initio* predicted profiles". J. Appl. Cryst. (2010). 43, 70-82.
- [3] G. M. Sheldrick (2014). TWINABS. Universität Göttingen, Germany.
- [4] G. M. Sheldrick. "SHELXT Integrated space-group and crystal-structure determination". Acta Cryst. (2015). A71, 3-8.
- [5] G. M. Sheldrick. "Crystal structure refinement with *SHELXL*". *Acta Cryst.* (2015). C**71**, 3-8.

[6] R. Herbst–Irmer, G. M. Sheldrick. "Refinement of Twinned Structures with SHELXL97". *Acta Cryst.* (1998). B**54**, 443-449.

[7] A. L. Spek. "Structure validation in chemical crystallography". *Acta Cryst.* (2009). D**65**, 148-155.