Electronic Supplementary Information

N-Donor Ligand Supported “ReO_2^+”: A Pre-Catalyst for the Deoxydehydration of Diols and Polyols

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1. General

All chemicals including solvents were degassed by either freeze-pump-thaw cycles or degasification under vacuum. Triphenylphosphine was crystallized from ethanol and dried under vacuum. Iododioxobis(triphenylphosphine)rhenium ($IReO_2(PPh_3)_2$) was purchased from Sigma-Aldrich and used without further purification. *cis*-[(*S,S*-BPBP)ReO_2]PF_6,[1] BPMEN,[2] BP^{mdm}MEN,[2] and *trans*-[(Py_4)ReO_2]PF_6 [3] were prepared according to known literature procedures. Unless otherwise stated, all other commercial chemicals were used without further purification. NMR spectra were recorded on a Varian VNMRS400 (400 MHz) instrument at 298 K. ESI-MS spectra were recorded using a Waters LCT Premier XE instrument. IR spectra were recorded with a Perkin–Elmer Spectrum One FTIR spectrometer. All olefinic products are known compounds and were calibrated against mesitylene for quantification.

2. Synthesis of *cis*-[(BPMEN)ReO_2]PF_6

To a solution of BPMEN (136 mg, 0.5 mmol) in CH_2Cl_2 (20 mL), *cis*-[$Re^VO_2(PPh_3)_2I$] (435 mg, 0.5 mmol, 1.0 equiv.) was slowly added. The reaction mixture was stirred overnight in the dark, and the solvent was removed by rotary evaporation. Crude *cis*-[(BPMEN)ReO_2]I was then dissolved in MeOH (30 mL), NH_4PF_6 (163 mg, 1.0 mmol, 2 equiv.) was added and the mixture was stirred for 1 h. MeOH was then removered by rotary evaporation. The product was purified on a basic alumina column using 0.4% MeOH/ CH_2Cl_2 as eluent (128 mg, 0.20 mmol, 40%). Brown crystals were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex.

^1H NMR (400 MHz), CD_3CN (1.94 ppm): δ 8.02 – 7.70 (m, 4H), 7.55 (ddd, *J* = 5.7, 1.6, 0.8 Hz, 2H), 7.32 (td, *J* = 7.8, 1.6 Hz, 2H), 6.42 – 6.23 (m, 4H), 3.38 (s, 6H), 2.58 – 2.39 (m, 2H), 2.12 – 2.01 (m, 2H). ^{13}C NMR (100 MHz), C_6D_6 (118.260 ppm): δ 160.58, 150.10, 144.39, 123.28, 122.68, 78.99, 57.81, 55.99; HR-ESI-MS (in CH_3CN): calcd. for $[C_{16}H_{22}N_4O_2Re]^+$: 489.1301, found: 489.1172; IR (ATR): 523, 555, 764, 829, 905, 1302, 1442, 1475, 1613, 2937 cm^{-1}.

X-ray crystal structure determination of *cis*-[(BPMEN)ReO_2]PF_6

$[C_{16}H_{22}N_4O_2Re](PF_6)$, Fw = 633.54, black block, 0.34 × 0.09 × 0.05 mm^3, monoclinic, $P2_1$ (no. 4), a = 8.35720(19), b = 14.2848(3), c = 8.82345(17) Å, β = 106.059(1) °, V = 1012.25(4) $Å^3$, Z = 2, D_x = 2.079 g/cm^3, μ = 6.16 mm^{-1}. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. Intensity integration was done with the Eval15 software[4]. A numerical absorption correction and scaling was performed with SADABS[5] (correction range 0.34-0.80). A total of 20491 reflections was measured, 4670 reflections were unique (R_{int} = 0.023), 4619 reflections were observed [$I>2\sigma(I)$]. The structure was solved with Patterson methods using SHELXS[6] and subsequently completed with Fourier methods. Structure refinement was performed with SHELXL-2018[7] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 273 Parameters were refined with one restraint (floating origin). R1/wR2 [$I > 2\sigma(I)$]: 0.0166 / 0.0419. R1/wR2 [all refl.]: 0.0169 / 0.0420. Flack parameter[8] x = 0.005(4). S = 1.036. Residual electron density between -0.55 and 1.35 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[9]

3. Synthesis of *cis*-[(BP^{mdm}MEN)ReO$_2$]PF$_6$

This complex was prepared in an analogous manner to *cis*-[(BPMEN)ReO$_2$]PF$_6$, starting from BP^{mdm}MEN (252 mg, 0.65 mmol) and *cis*-[Re^{V}O$_2$(PPh$_3$)$_2$I] (565 mg, 0.65 mmol). Brown solid, 31% yield.

^{1}H NMR (400 MHz), CD$_3$CN (1.94 ppm): δ 7.83 (ddt, *J* = 7.8, 5.7, 1.1 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.49 (ddd, *J* = 5.7, 1.6, 0.8 Hz, 2H), 7.38 – 7.19 (m, 10H), 6.98 (t, *J* = 7.4 Hz, 8H), 6.83 (tt, *J* = 7.4, 1.6 Hz, 4H), 6.44 – 6.19 (m, 4H), 3.36 (s, 6H), 2.51 – 2.36 (m, 2H), 2.14 – 1.98 (m, 2H); IR (ATR):556, 793, 809, 829, 879, 991, 1052, 1093, 1268, 1402, 1471, 1600, 2934 cm^{-1}; elemental analysis calcd. (%) for $C_{22}H_{34}F_6N_4O_4PRe$ (750.1779): C 35.25, H 4.57, N 7.47; found: C 35.04, H 4.70, N 7.59.

X-ray crystal structure determination of *cis*-[(BP^{mdm}MEN)ReO$_2$]PF$_6$

[$C_{22}H_{34}N_4O_4Re$](PF_6) · 0.5CH$_3$OH, Fw = 765.72, brown plate, 0.49 × 0.18 × 0.04 mm^3, monoclinic, P2$_1$/n (no. 14), a = 14.4596(4), b = 7.9988(3), c = 24.5644(5) Å, β = 102.635(2) °, V = 2772.30(13) Å^3, Z = 4, D_x = 1.835 g/cm^3, μ = 4.52 mm^{-1}. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. The crystal appeared to be twinned with a twofold rotation about *uvw*=[1,0,1] as twin operation. Consequently, two orientation matrices were used for the integration with the Eval15 software[4]. A multiscan absorption correction and scaling was performed with TWINABS[5] (correction range 0.24-0.43). A total of 73003 reflections was measured, 6395 reflections were unique (R_{int} = 0.044), 5825 reflections were observed [$I>2\sigma(I)$]. The structure was solved with Patterson superposition methods using SHELXT.[10] Structure refinement was performed with SHELXL-2018[7] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. The PF_6 anion was refined with a disorder model, and the methanol solvent molecule was disordered on an inversion center. 417 Parameters were refined with 529 restraints (distances, angles and displacement parameters of the disordered groups). R1/wR2 [$I > 2\sigma(I)$]: 0.0329 / 0.0870. R1/wR2 [all refl.]: 0.0371 / 0.0901. Twin fraction BASF = 0.1086(7). S = 1.036. Residual electron density between -2.46 and 2.44 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[9]

4. Synthesis of *cis*-[(BPMEN)ReO_2]BPh_4

This complex was prepared in an analogous manner to *cis*-[(BPMEN)ReO_2]PF_6, starting from BPMEN (270 mg, 1.0 mmol) and *cis*-[$Re^VO_2(PPh_3)_2I$] (869 mg, 1.0 mmol). Instead of NH_4PF_6, $NaBPh_4$ was used for salt metathesis. Brown solid, 45% yield.

^{1}H NMR (400 MHz), CD_3CN (1.94 ppm): δ 7.16 (s, 2H), 6.46 (d, *J* = 15.4 Hz, 2H), 6.07 (d, *J* = 15.4 Hz, 2H), 3.83 (s, 6H), 3.46 (s, 6H), 2.61 – 2.37 (m, 2H), 2.10 (s, 8H). ^{13}C NMR (100 MHz), C_6D_6 (118.260 ppm): δ 171.48, 158.40, 149.36, 149.28, 126.61, 125.76, 76.93, 76.83, 63.89, 63.77, 59.14, 59.06, 56.45, 14.48, 14.44, 12.59, 12.54; HR-ESI-MS (in CH_3CN): calcd. for $[C_{22}H_{34}N_4O_4Re]^+$: 605.2139, found: 605.2003; IR (ATR):611, 704, 733,768, 813, 891, 965, 1031, 1157, 1296, 1428, 1445, 1470, 1478, 1578, 2983, 3051 cm^{-1}; elemental analysis calcd. (%) for $C_{40}H_{42}BN_4O_2Re$ (807.8190): C 59.47, H 5.24, N 6.93; found: C 59.76, H 5.23, N 7.14.

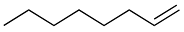
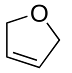
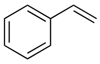
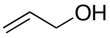
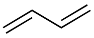
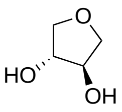
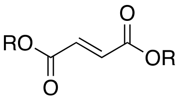
5. General procedure for catalytic deoxydehydration using a secondary alcohol as solvent

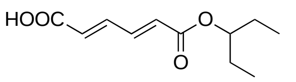
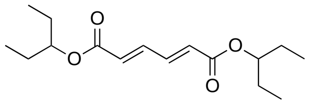
Unless otherwise noted, all reaction mixtures were prepared inside a Glove box under nitrogen atmosphere in a 15 mL thick-walled glass pressure tube (Ace) fitted with a Teflon screw-cap. Polyols (0.5 mmol), dioxorhenium complexes (0.01 mmol), and mesitylene (0.5 mmol) were dissolved in secondary alcohol (5 mL) and mixed well. Then, the closed reaction vessel was brought into a preheated silicone oil bath at 180 °C. After reaction, an aliquot

(~0.1 mL) of the reaction mixture was taken, diluted with $CDCl_3$ (~0.4 mL) and analyzed by ^{1}H NMR.

6. ^{1}H NMR data for olefin products

The intensity of the signals of the olefin products relative to aromatic signal of the mesitylene internal standard were used to calculate reaction yields (listed below). ^{1}H NMR peak of internal standard (mesitylene) (400 MHz, $CDCl_3$): δ 6.78 (s, 3 H, used for calculations), 2.28 (s, 9H).

entry	product	structure	^{1}H NMR ($CDCl_3$, 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	2,5-dihydrofuran		δ 5.87 (s, 2H), 4.62 (s, 4H).
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	allyl alcohol		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).
5	1,3-butadiene		δ 5.14 – 5.02 (m, 2H), 5.26 – 5.15 (m, 2H), 6.40 – 6.25 (m, 2H).
6	1,4-anhydrothreitol (racemic)		δ 4.02 (dd, 2H, J = 12 Hz, 8 Hz), 4.15 (m, 2H), 3.76 (d, J = 10.0 Hz, 2H)
7	fumaric acid and fumarates		δ 6.80 (s, 2H), 6.82 (d, J = 0.8 Hz, 2H), 6.84 (s, 2H). The aliphatic part was overlapped by the peak of solvent.

8	muconates	 	δ 6.41 – 6.09 (m, 2H), 7.56 – 7.19 (m, 2H). The aliphatic part was overlapped by the peak of solvent.

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