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Highly active Cr(III) catalysts for the reaction of CO_2 with epoxides

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Supplementary information

Materials and methods

All chemicals were obtained from commercial suppliers and used as received. Cyclohexene oxide (99.7 %) was purchased from Aldrich, dried by distillation from CaH_2 and stored over molecular sieves. The water content was determined to 20.1 ppm by Karl-Fischer-titration. Carbon dioxide (99.995%) was purchased from Westfalen AG. All manipulations involving air- and/or water-sensitive compounds were carried out under dry argon atmosphere using standard Schlenk techniques.

X-ray diffraction analyses were performed on a Stoe IPDS 2 or IPDS 2T area detector system using Mo K_α radiation (λ = 71.073 and 71.069 pm respectively) at 100 K. Stoe IPDS software[1] was used for integration and data reduction; structure solution and refinement was done with the WinGX program[2] suite using SIR-97[3] and SHELX-97.[4] Molecular graphics were produced with Diamond 3.2g.[5]

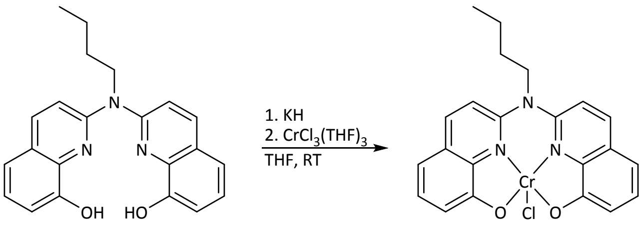
The copolymerization reaction of CHO and CO_2 were performed in a 200 mL stainless steel autoclave from Parr Instrument Deutschland GmbH. The temperature and pressure profile of the reactions were recorded using the software SpecView.

IR spectra were recorded with a Bruker MATRIX-MF spectrometer equipped with a high-pressure 3.17 mm ATR-IR fibre optical probe. The ATR-IR fibre optical probe (90° diamond prism with 1 × 2 mm basal area and 1 mm height as ATR element, 2 × 45° reflection of the IR beam, IR beam coupled *via* fibre optics) was fitted into the reactor in such a way that the diamond at the end of the optical probe was immersed entirely into the reaction mixture. IR spectra (average of 100 scans) were recorded time-resolved in the region 4000-400 cm^{-1} with a resolution of 4 cm^{-1} against argon as background and analysed with the software PEAXACT using the Hard Modeling Factor Analysis (HMFA) calculation method.[6] For quantification, the following characteristic bands were used: PO, 827 cm^{-1}; cPC 1809 cm^{-1}; CHO 835 cm^{-1}; *cis*-cCHC 1804 cm^{-1} and *trans*-cCHC 1817 cm^{-1}; pCHC 1749 cm^{-1}.

The ^1H-NMR and ^{13}C-NMR spectra were measured on a Bruker AV400 spectrometer at 400 MHz and 125 MHz, respectively. Chemical shifts are reported relative to tetramethylsilane (0 ppm). The relevant resonances used for integration are: 1.45 – 1.49 ppm methyl group of cPC, area corresponds to 3 H atoms; 2.95 – 2.99 ppm methine group of not converted PO, area corresponds to 1 H atom; 4.51 ppm methine group of pCHC, area corresponds to 2 H atoms; 3.81 ppm methine group of cCHC, area corresponds to 2 H atoms; 2.98 ppm methine group of not converted CHO, area corresponds to 2 H atoms.

Molecular weights were determined by gel permeation chromatography on a SECurity GPC System from PSS Polymer Service, which was equipped with two PSS SDV linear M, 8×300 mm, 5 µm columns and RID detector. The flow rate was 1.0 ml/min. The procedure was in accordance with DIN 55672-1: "Gel permeation chromatography, Part 1 - Tetrahydrofuran as the eluting agent". Polystyrene samples of known molecular weight were used for calibration.

Synthesis of [Cr(babhq)Cl(H_2O)]·H_2O



H_2(babhq) (513 mg, 1.43 mmol, 1.0 eq.) and potassium hydride (118 mg, 2.86 mmol, 2.0 eq.) were suspended in dry tetrahydrofuran (thf) (20 mL). This mixture was stirred until the gas evolution stopped. A purple suspension of [$CrCl_3(thf)_3$] (537 mg 1.43 mmol, 1.0 eq.) in dry thf (20 mL) was added and the colour of the reaction mixture turned to brown. After stirring at room temperature for 12 h, water (100 mL) was added. The resulting precipitate was filtered off, washed with water and dried at 50 °C / 10^{-1} mbar to get 545 mg of a yellow solid.

Yield 79 %; HR-ESI/MS *m/z* calcd. for $[C_{22}H_{19}CrN_3O_2]^+$ (g/mol) 409.0878, found 409.0879; elemental analysis calcd. for $C_{22}H_{23}CrN_3O_4$ (%) C 54.95, H 4.82, N 9.74; found C 54.84, H 4.88, N 9.65; IR ν/cm^{-1} 2959, 1606, 1564, 1492, 1435, 1365, 1319, 1287, 1208, 1130, 1095, 1040, 940, 897, 859, 823, 741, 721, 676, 638, 592, 553, 526, 451, 405. NMR data could not be obtained as the complex is paramagnetic.

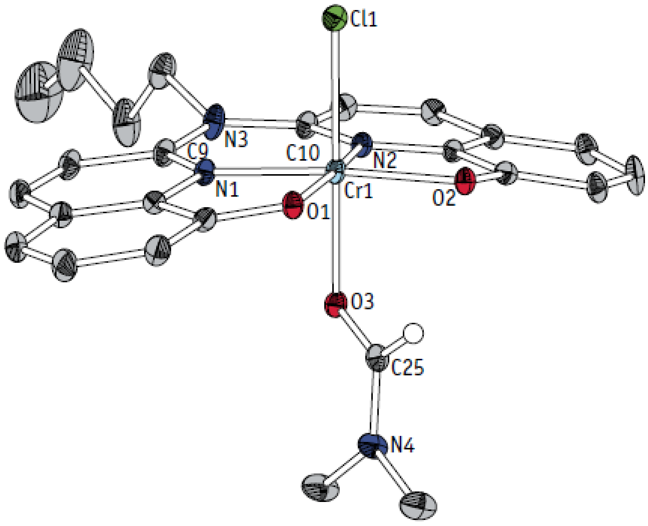
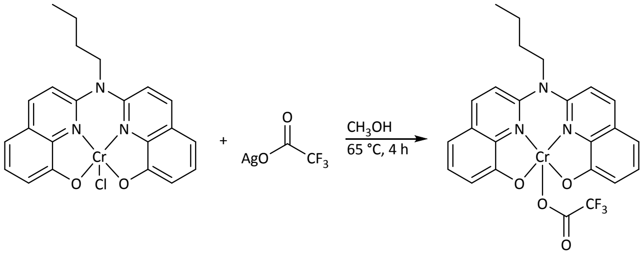


Figure S1. ORTEP drawing of the complex [Cr(babhq)Cl(dmf)] (**1b**). Hydrogen atoms and a second dmf solvent molecule are omitted for clarity. Ellipsoids are set at 30% probability.

Single crystals suitable for single crystal X-ray diffraction analysis were obtained from a saturated dmf solution, which was cooled slowly from 100 °C to room temperature.

Crystal data (CCDC deposition number 986184): $C_{28}H_{33}ClCrN_5O_4$; *MW* = 591.04 g·mol^{-1}; monoclinic; P 2_1/n; a = 9.8802(4), b = 14.1274(4), c = 19.4439(9) Å; α = 90, β = 94.197(3), γ = 90°; V = 2706.7(2) Å^3; Z = 4, $D_{calcd.}$ = 1.450 g·cm^{-3}; R_{int} = 0.0465; R_1 = 0.0452 [I>2σ(I)]; wR_2 = 0.1222 (all data).

Synthesis of [Cr(babhq)OAc^F(EtOH)]



[Cr(babhq)Cl] (545 mg, 1.13 mmol, 1.0 eq.) was suspended in ethanol (100 mL). During stirring, silver trifluoroacetate (250 mg, 1.13 mmol, 1.0 eq.) was added. The mixture was heated to reflux for 5 h. After cooling to room temperature, the solid was separated by centrifugation and extracted repeatedly with hot ethanol until the extract was nearly colourless. The volatiles were removed from the combined extracts and the residue dried at 50 C/10^{-1} mbar to yield 594 mg of a brown solid.

Yield 92 %; HR-ESI/MS *m/z* calcd. for $[C_{24}H_{19}CrF_3N_3O_4]^+$ (g/mol) 522.0727, found 522.0740; elemental analysis calcd. for $C_{26}H_{25}CrF_3N_3O_5$ (%) C 54.93, H 4.43, N 7.39; found C 54.77, H 4.46, N 7.34; infrared spectroscopy ν/cm^{-1} 2965, 1696, 1609, 1564, 1493, 1436, 1371, 1323, 1285, 1159, 1186, 1140, 1095, 1037, 937, 872, 825, 791, 745, 678, 634, 553, 520, 431. NMR data could not be obtained as the complex is paramagnetic.

Suitable crystals for single crystal X-ray diffraction analysis were obtained at room temperature by slow diffusion of diethylether into a saturated solution of [Cr(babhq)OAc^F(EtOH)] in dmf.

Crystal data (CCDC deposition number 986183): $C_{27}H_{26}CrF_3N_4O_5$; *MW* = 595.52 g·mol^{-1}; monoclinic; P 2_1/c; a = 12.2189(9), b = 13.6109(9), c = 15.9826(11) Å; α = 90, β = 102.501(5), γ = 90°; V = 2595.1(3) Å^3; Z = 4, $D_{calcd.}$ = 1.524 g·cm^{-3}; R_{int} = 0.1021; R_1 = 0.0437 [I>2σ(I)]; wR_2 = 0.1002 (all data).

Reaction of CO_2 and PO using [Cr(babhq)OAc^F(EtOH)]

The catalyst [Cr(babhq)OAc^F(EtOH)] (10.6 mg, 0.02 mmol), and *bis*(triphenylphosphine)iminium chloride (29.0 mg, 0.05 mmol) were dissolved in propylene oxide (12 ml, 0.17 mmol). After closing and degasing three times with CO_2, the autoclave was pressurized with 20 bar CO_2 at room temperature. The autoclave was then heated to 100 °C for 4 hours. The mixture was cooled down rapidly to 15 °C and the remaining pressure released slowly. A sample was taken for ^{1}H NMR analysis. The mixture was transferred into a 250 ml flask and all volatiles were removed in a partial vacuum at 50 °C to yield a bright orange solution.

Yield in cPC 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 4.45 (1H, brs), 4.14 (1H, dd), 3.61 (1H, brs), 1.01 (3H, brs); ^{13}C APT NMR (125 MHz, $CDCl_3$) δ/ppm 155.13 (C=O), 73.73 (-CH-), 70.12 (-CH_2-), 18.89 (-CH_3); ATR-IR ν/cm^{-1} 1809(t_{ini})-1793(t_{end}) (C=O), 1389, 1353, 1176, 1117, 1077, 1052(t_{ini})-1048(t_{end}) (C-O-).

Reaction of CO_2 and CHO using [Cr(babhq)OAc^F(EtOH)]

The catalyst [Cr(babhq)OAc^F(EtOH)] (13.6 mg, 0.026 mmol) and *bis*(triphenylphosphine)iminium chloride (34.8 mg, 0.061 mmol) were dissolved in cyclohexene oxide (15.3 ml, 151 mmol). After closing and degasing three times with CO_2, the autoclave was pressurized with 20 bar CO_2 at room temperature. The reaction mixture was then heated to 100 °C for 3.0 hours whereby the mixture was stirred at 700 rpm using a gas entrainment stirrer. The mixture was cooled down rapidly to 15 °C and the remaining pressure released slowly. A sample was taken for ^{1}H NMR analysis. The product was then dissolved in CH_2Cl_2 and the mixture transferred into a 250 ml flask. All volatiles were removed in a partial vacuum at 50 °C to yield a bright orange powder.

Yield in *p*CHO 75 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 4.59 (brm, -[CHR-O-C(O)-O-CHR]$_m$-), 4.21 (brm, -CHR-O-C(O)-O-X, X = end group), 3.35 (brm, -CHR-O-C(O)-O-P, P = polymer chain), 2.00-1.17 (m, 8H, -[CH_2]$_4$-); ^{13}C APT NMR (125 MHz, $CDCl_3$) δ/ppm 153.2 (C=O), 83.3 (-CH-), 71.7 (-CH_2-), 29.5 (-CH_2-), 27.9 (-CH_2-), 22.7 (-CH_2-), 19.3 (-CH_2-); M_n 3831 g/mol; PDI 1.20.

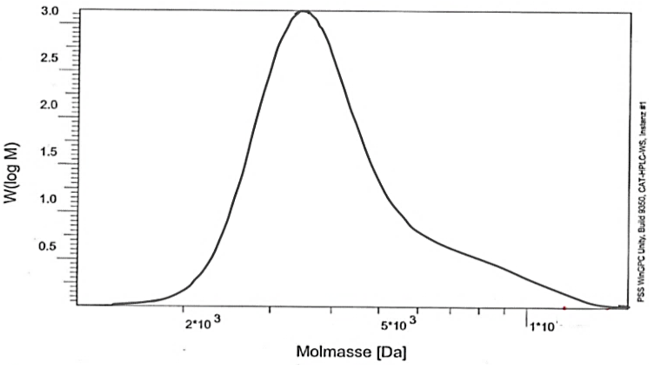


Figure S2. GPC trace of the product of the reaction of CO_2 and CHO using [Cr(babhq)OAc^F(EtOH)]

Reaction of CO_2 and PO using $[Cr(babhq)OAc^F(EtOH)]$ in the presence of 1,8-octanediol

The catalyst $[Cr(babhq)OAc^F(EtOH)]$ (13.3 mg, 0.03 mmol), tetrabutylammonium chloride (30.1 mg, 0.11 mmol) and 1,8-octanediol (158 mg, 1.08 mmol) were dissolved in propylene oxide (11.8 ml, 169 mmol). After closing and degasing three times with CO_2, the autoclave was pressurized with 20 bar CO_2 at room temperature. The autoclave was then heated to 100 °C for 20 hours. Then, the mixture was cooled down rapidly to 15 °C and the remaining pressure released slowly. A sample was taken for ^1H NMR analysis. The mixture was transferred into a 250 ml flask and all volatiles were removed in a partial vacuum at 50 °C to yield a bright orange solution ($C_4H_6O_3$).

Yield in cPC 100%; ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 4.32 (1H, s, -CH-), 4.00 (1H, dd, *cis*-CH_2-), 3.47 (1H, dd, *trans*-CH_2-), 0.88 (3H, d, -CH_3); ^{13}C APT NMR (125 MHz, $CDCl_3$) δ/ppm 155.15 (C=O), 73.76 (-CH-), 70.65 (-CH_2-), 18.92 (-CH_3); ATR-IR ν/cm^{-1} 1814(t_{ini})-1785(t_{end}) (C=O), 1386, 1352, 1170, 1114, 1075, 1054(t_{ini})-1040(t_{end}) (C-O-).

Reaction of CO_2 and CHO using $[Cr(babhq)OAc^F(EtOH)]$ in the presence of 1,8-octanediol

The catalyst $[Cr(babhq)OAc^F(EtOH)]$ (21.5 mg, 0.04 mmol), tetrabutylammonium chloride (45.5 mg, 0.165 mmol) and 1,8-octanediol (212 mg, 1.45 mmol) were dissolved in cyclohexene oxide (15 ml, 0.15 mol). After closing and degasing three times with CO_2, the autoclave was pressurized with 20 bar CO_2 at room temperature. The autoclave was then heated to 100 °C for 6 hours. The mixture was cooled rapidly to 15 °C and the remaining pressure released slowly. A sample was taken for ^1H NMR analysis. The mixture was transferred into a 250 ml flask and the volatiles were removed in a partial vacuum at 50 °C to yield a bright orange viscous liquid.

Yield in *p*CHO 69 %; ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 4.59 (brm, -$[CHR\text{-}O\text{-}C(O)\text{-}O\text{-}CHR]_m$-), 4.21 (brm, -CHR-O-C(O)-O-X, X = end group), 3.35 (brm, -CHR-O-C(O)-O-P, P = polymer chain), 2.00-1.17 (m, 8H, -$[CH_2]_4$-); ^{13}C APT NMR (125 MHz, $CDCl_3$) δ/ppm 153.2 (C=O), 83.3 (-CH-), 71.7 (-CH_2-), 29.5 (-CH_2-), 27.9 (-CH_2-), 22.7 (-CH_2-), 19.3 (-CH_2-); M_n 4543 g/mol; PDI 1.20.

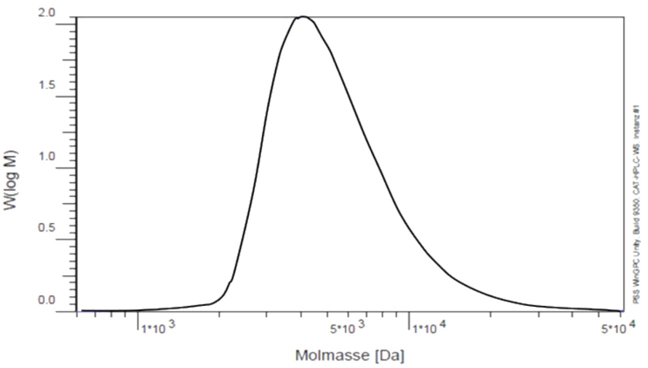


Figure S3. GPC trace of the product of the reaction of CO_2 and CHO using $[Cr(babhq)OAc^F(EtOH)]$ in the presence of 1,8-octanediol

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