Supporting Information for:

New cobalt, iron and chromium catalysts based on easy-to-handle N₄-chelating ligands for the coupling reaction of epoxides with CO₂

M. Adolph, T. A. Zevaco*, C. Altesleben, O. Walter, E. Dinjus

a Institut für Katalyseforschung und -Technologie (IKFT), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.
Fax: +49 721 608-22244; Tel: +49 721 608-24385;
E-mail: thomas.zevaco@kit.edu, eckhard.dinjus@kit.edu

Contents:

Page 2 - 26: Experimental data for 1 - 23.
Page 27 - 29: X-ray structure determination of 6, 22 and 23.
Page 30: evaluation of the operating conditions for screening tests (with catalyst 10)
Page 31 - 32: PCHC characterization.
Page 33: PC characterization.
Page 34 – 36: Characterization of products displayed in table 7
Page 37: Recycle experiment with 23 (¹H NMR)
Experimental data for I:

The bpb-ligand was prepared according to the procedure described by Vagg et al. [1]. 0.12 mol picolinic acid in 48 ml abs. pyridine was mixed with 0.06 mol o-phenylenediamine in 12 ml abs. pyridine. After adding 31.5 ml (0.12 mol) triphenylphosphite the reaction solution was heated for 4 h at 120 °C and subsequently stirred at room temperature overnight. The solvent was removed under vacuum and the raw product was obtained as a brown solid. Through washing with 50 ml of ethanol and following drying under vacuum the pure product was obtained as a white powder. Yield: 9.39 g (50%).

IR (cm⁻¹): 3061 (m), 1942 (w), 1673 (s), 1592 (s), 1521 (s), 1451 (s), 1430 (s), 1300 (m), 1238 (m), 1127 (m), 1100 (m), 996 (m), 748 (m), 687 (m). ¹H-NMR: δ (ppm, DMSO-d₆) = 7.30 (dd, J = 5.9 Hz, J = 3.6 Hz, 2 H), 7.60 - 7.70 (m, 2 H), 7.73 - 7.82 (m, 2 H), 8.10 (dt, J = 7.8 Hz, J = 1.4 Hz, 2 H), 8.14 - 8.22 (m, 2H) 8.64 (d, J = 4.2 Hz, 2 H), 10.72 (s, 2 H). ¹³C{¹H}NMR / DEPT135 (prim. =primary carbon ; sec.=secondary carbon ; tert.=tertiary carbon ; quat.= quaternary carbon): δ (ppm, CDCl₃) = 123.2 (tert., 2 C), 126.6 (tert., 2 C), 127.0 (tert., 2 C), 127.9 (tert, 2 C), 132.4 (quat., 2 C), 139.2 (tert., 2 C), 149.9 (tert., 2 C), 150.3 (quat., 2 C), 163.4 (quat., 2 C). MS: (EI⁺) m/z = 319 [M+H]⁺. Anal. Calcd for C₁₈H₁₄N₄O₂: C, 67.91; H, 4.43; N, 17.60 Found: C, 67.75; H, 4.36; N, 17.82.

¹H-spectrum in DMSO-d₆ of I:
Experimental data for 2:

The bpCl₂-ligand was prepared according to the procedure described by Vagg et al. [1]. 0.06 mol picolinic acid in 24 ml abs. pyridine was mixed with 0.03 mol 4,5-dichloro-o-phenylenediamine in 6 ml abs. pyridine. After adding 15.72 ml (0.06 mol) triphenylphosphite the reaction solution was heated for 4 h at 120 °C and subsequently stirred at room temperature overnight. The solvent was removed under vacuum and the raw product was obtained as a brown solid. Through washing with 50 ml of ethanol and following drying under vacuum the pure product was obtained as a white powder. Yield: 7.18 g (62 %).

IR (cm⁻¹): 3290 (m), 3053 (w), 1700 (s), 1582 (m), 1497 (vs), 1462 (m), 1429 (m), 1384 (m), 1278 (m), 1227 (m), 1127(w), 1040 (w), 998 (m), 879 (w), 815 (m), 743 (s), 691 (s), 569 (m). ¹H-NMR: δ (ppm, CDCl₃) = 7.50 (dd, J = 6.9 Hz, J = 5.3 Hz, 2 H), 7.93 (dt, J = 7.8 Hz, J = 1.5 Hz, 2 H), 8.10 (s, 2 H), 8.31 (d, J = 7.9 Hz, 2 H), 8.56 (d, J = 4.7 Hz, 2 H), 10.24 (s, 2 H). ¹³C{¹H}-NMR / DEPT135: δ (ppm, CDCl₃) = 122.9 (tert., 2 C), 125.8 (tert., 2 C; quat., 2 C), 127.07 (tert., 2 C), 129.6 (quat., 2 C), 137.9 (tert., 2 C), 148.5 (tert., 2 C), 149.3 (quat, 2 C), 163.1 (quat., 2 C). MS: (EI⁺) m/z = 387 [M+H]⁺. Anal. Calcd for C₁₈Cl₂H₁₂N₄O₂: C 55.83; H 3.12; N 14.47 Found: C 54.91; H 3.08; N 14.32.

¹H-spectrum in CDCl₃ of 2:
Experimental data for 3:

The bpbNO2-ligand was prepared according to the procedure described by Vagg et al. [1]. 0.06 mol picolinic acid in 24 ml abs. pyridine was mixed with 0.03 mol 4-nitro-o-phenylenediamine in 6 ml abs. pyridine. After adding 15.72 ml (0.06 mol) triphenylphosphite the reaction solution was heated for 4 h at 120 °C and subsequently stirred at room temperature overnight. The solvent was removed under vacuum and the raw product was obtained as a brown solid. Through washing with 50 ml of ethanol and following drying under vacuum the pure product was obtained as a light yellow powder. Yield: 3.90 g (36 %).

IR (cm⁻¹): 3336 (m), 3269 (m), 3126 (w), 3052 (m), 2925 (m), 1701 (s), 1667 (vs), 1611 (m), 1592 (s), 1536 (s), 1475 (s), 1432 (m), 1344 (s), 1284 (s), 1235 (m), 1136 (w), 1109 (m), 1042 (w), 998 (m), 883 (m), 828 (w), 750 (m), 694 (m), 621 (m). ¹H-NMR: δ (ppm, CDCl₃) = 7.50 (dd, J = 7.5 Hz, J = 4.8 Hz, 1 H), 7.60 (dd, J = 7.4 Hz, J = 4.7 Hz, 1 H), 7.91 – 8.00 (m, 2 H), 8.21 (dd, J = 9.0 Hz, J = 2.3 Hz, 1 H), 8.34 (dd, J = 15.2 Hz, J = 8.0 Hz, 2 H), 8.40 (d, J = 9.0 Hz, 1 H), 8.53 (d, J = 4.6 Hz, 1 H), 8.64 (d, J = 4.8 Hz, 1 H), 8.71 (d, J = 2.4 Hz, 1 H), 10.26 (s, 1 H), 10.68 (s, 1 H). ¹³C{¹H}-NMR / DEPT135: δ (ppm, DMSO-d₆) = 121.0 (tert., 1 C), 121.2 (tert., 1 C), 122.7 (tert., 1 C), 124.4 (tert., 1 C), 127.5 (tert., 1 C), 127.6 (tert., 1 C), 130.5 (quat., 1 C), 137.5 (quart., 1 C), 138.3 (tert., 1 C), 138.5 (tert., 1 C), 143.7 (quat., 1 C), 148.7 (tert., 1 C), 148.9 (quat., 1 C), 149.6 (quat., 1 C), 150.3 (quat., 1 C), 162.8 (quat., 1 C), 163.5 (quat., 1 C). MS: (EI⁺) m/z = 364 [M+H]⁺. Anal. Calcd for C₁₈H₁₃N₅O₄: C 59.50; H 3.61; N 19.28 Found: C 59.46; H 3.72; N 19.63.

¹H-spectrum in CDCl₃ of 3:

---

Experimental data for 4:

The bppMe₂-ligand was prepared according to the procedure described by Vagg et al. [1]. 0.06 mol picolinic acid in 24 ml abs. pyridine was mixed with 0.03 mol 4,5-dimethyl-o-phenylenediamine in 6 ml abs. pyridine. After adding 15.72 ml (0.06 mol) triphenylphosphite the reaction solution was heated for 4 h at 120 °C and subsequently stirred at room temperature overnight. The solvent was removed under vacuum and the raw product was obtained as a brown solid. Through washing with 50 ml of ethanol and following drying under vacuum the pure product was obtained as a white powder. Yield: 8.09 g (78 %).

IR (cm⁻¹): 3055 (w), 2923 (m), 2856 (w), 1669 (vs), 1592 (m), 1433 (m), 1316 (m), 1282 (w), 1238 (m), 1126(m), 1041 (w), 997 (m), 875 (w), 820 (m), 748 (s), 690 (s), 553 (m). ¹H-NMR: δ (ppm, CDCl₃) = 2.30 (s, 6 H), 7.44 (ddd, J = 7.6 Hz, J = 4.8 Hz, J = 1.2 Hz, 1 H), 7.62 (s, 2 H), 7.89 (dt, J = 7.7 Hz, J = 1.7 Hz, 2 H), 8.29 – 8.32 (m, 2 H), 8.54 – 8.57 (m, 2 H), 10.15 (s, 2 H). ¹³C{¹H}-NMR / DEPT135: δ (ppm, CDCl₃) = 19.5 (prim., 2 C), 122.5 (tert., 2 C), 125.6 (tert., 2 C), 126.3 (tert., 2 C), 127.7 (quat., 2 C), 134.8 (quat., 2 C), 137.4 (tert., 2 C), 148.1 (tert., 2 C), 149.8 (quat., 2 C), 162.8 (quat., 2 C), 164.3 (quat., 2 C). MS: (EI⁺) m/z = 347 [M+H]⁺. Anal. Calcd for C₂₀H₁₈N₄O₂: C 69.35; H 5.24; N 16.17 Found: C 69.69; H 5.41; N 16.42.

¹H-spectrum in CDCl₃ of 4:
According to literature procedure [2] 2.0 mmol of Co(OAc)\textsubscript{2} x 4H\textsubscript{2}O and 2.0 mmol of ligand 1 were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 2.88 mmol of NEt\textsubscript{4}Cl H\textsubscript{2}O was added and the solution was stirred at RT for additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile and filtered. Through adding 20 ml of diethyl ether to the solution and cooling down to 2 °C a green precipitate was formed. After filtering, washing with 20 ml of 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as green crystals. Yield 885 mg (71 %).

IR (cm\textsuperscript{-1}): 3058 (w), 2978 (m), 2940 (m), 2655 (w), 1621 (s), 1595 (s), 1567 (s), 1478 (s), 1399 (s), 1371 (m), 1173 (w), 1096 (w), 1032 (w), 961 (w), 784 (m), 681 (m). \textsuperscript{1}H-NMR: δ (ppm, dmso-d\textsubscript{6}) = 0.98 (s, 6 H), 1.09 (tr, J = 7.2 Hz, 12 H), 3.14 (q, J = 7.2 Hz, 8 H), 6.87 (dd, J = 5.9 Hz, J = 3.5 Hz, 2 H), 7.61 (tr, J = 7.1 Hz, 2 H), 7.81 (d, J = 7.7 Hz, 2 H), 8.03 (tr, J = 7.6 Hz, 2 H), 8.77 (dd, J = 6.0 Hz, J = 3.5 Hz, 2 H), 10.13 (d, J = 5.5 Hz, 2 H). \textsuperscript{13}C\textsubscript{1}H-NMR / DEPT135: δ (ppm, dmso-d\textsubscript{6}) = 7.7 (prim., 4 C), 24.7 (prim., 2 C), 52.0 (sec., 4 C), 122.0 (tert., 2 C), 122.7 (tert., 2 C), 122.9 (tert., 2 C), 124.2 (tert., 2 C), 139.7 (tert., 2 C), 144.5 (quat., 2 C), 157.5 (tert., 2 C), 160.5 (quat., 2 C), 166.5 (quat., 2 C), 176.4 (quat., 2 C). MS: (ESI−) m/z = 375 [M-2*(OAc)-NEt\textsubscript{4}]\textsuperscript{−}. Anal. Calcd for C\textsubscript{30}H\textsubscript{38}CoN\textsubscript{5}O\textsubscript{6}: C, 57.78; H, 6.14; N, 11.23. Found: C, 57.26; H, 6.35; N, 10.82.

\textsuperscript{1}H-spectrum in DMSO-d\textsubscript{6} of 5:
Experimental data for 6:

2.0 mmol of Co(OAc)₂ 4 H₂O, 2.0 mmol of ligand 2 were dissolved in 15 ml of DMF and stirred at RT under air for 10 min. Then 2.88 mmol of NEt₄OAc 4 H₂O were added and the solution stirred at 70 °C for 12 h. After cooling, the solution was stirred for additional 6 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile. A precipitate was formed on adding 20 ml of diethyl ether to the solution and cooling down to 2 °C. The product was isolated after filtering, washing two times with 20 ml of a 1:1 acetonitrile/diethyl ether mixture and drying under vacuo. The product was isolated as green powder/crystals. For complex 6 green crystals were obtained by slowly adding a small excess of diethyl ether into an acetonitrile solution of 6 and subsequently cooling down to 2 °C. After 2 days small green crystals were formed. Yield 885 mg (71%).

IR (cm⁻¹): 2985 (w), 2924 (w), 2853 (w), 1625 (s), 1598 (s), 1557 (m), 1470 (s), 1400 (m), 1314 (m), 1229 (w), 1102 (w), 1002 (w), 977 (w), 926 (w), 764 (w), 683 (m), 670 (m), 548 (w).

¹H-NMR δ (ppm, dmsod-6) = 1.01 (s, 6 H), 1.10 (t, J = 7.3 Hz, 12 H), 3.15 (q, J = 7.3 Hz, 8 H), 7.65 – 7.69 (m, 2H), 7.84 (dd, J = 7.6 Hz, J = 1.5 Hz, 2 H), 8.07 (t, J = 7.3 Hz, 2 H), 8.88 (d, J = 0.6 Hz, 2 H), 10.09 (d, J = 5.8 Hz, 2 H).

¹³C{¹H}NMR / DEPT135: δ (ppm, dmsod-6) = 7.1 (prim., 4 C), 24.1 (prim, 2 C), 51.4 (sec., 4 C), 121.0 (tert., 2 C), 122.5 (tert., 2 C; quat., 2 C), 124.3 (tert., 2 C), 139.5 (tert., 2 C), 143.7 (quat., 2 C), 156.8 (tert., 2 C), 158.8 (quat., 2 C), 166.5 (quat., 2 C), 175.9 (quat., 2 C). MS: (ESI–) m/z = 561 [M-NEt₄]. Anal. Calcld for C₃₀H₃₆Cl₂CoN₅O₆: C, 52.03; H, 5.24; N, 10.11. Found: C, 51.27; H, 5.49; N, 10.05.

¹H-spectrum in DMSO-d6 of 6:
Experimental data for 7:

\[
\text{NH}_2\text{N} + \text{Co(OAc)}_2\cdot 4\text{H}_2\text{O} \xrightarrow{\text{DMF, CH}_3\text{CN, rt, 12 h}} \text{C}_{30}\text{H}_{37}\text{CoN}_6\text{O}_8\cdot \text{H}_2\text{O} \quad 668.58 \text{ g/mol}
\]

A 2.0 mmol of CoOAc\textsubscript{2} 4 H\textsubscript{2}O, 2.0 mmol of ligand 3 were dissolved in 15 ml of DMF and stirred at RT under air for 10 min. Then 2.88 mmol of NEt\textsubscript{4}OAc 4 H\textsubscript{2}O were added and the solution stirred at 70 °C for 12 h. After cooling, the solution was stirred for additional 6 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile. A precipitate was formed on adding 20 ml of diethyl ether and cooling down to 2 °C. The product was isolated after filtering, washing two times with 20 ml of a 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as brown powder. Yield 839 mg (63 %).

IR (cm\textsuperscript{-1}): 3081 (w), 2985 (w), 2926 (w), 1629 (vs), 1601 (s), 1557 (m), 1482 (s), 1427 (m), 1386 (s), 1315 (vs), 1297 (s), 1146 (m), 1062 (w), 1002 (w), 957 (w), 898 (w), 756 (w), 683 (m), 616 (m), 505 (w), 464 (w). \textsuperscript{1}H-NMR δ (ppm, CD\textsubscript{3}CN) = 1.01 (s, 6 H), 1.09 (tt, J = 7.3 Hz, J = 1.7 Hz, 12 H), 3.13 (q, J = 7.2 Hz, 8 H), 7.65 – 7.73 (m, 2H), 7.88 (dt, J = 8.6 Hz, J = 1.6 Hz, 3 H), 8.06 – 8.12 (m, 2 H), 8.82 (d, J = 9.0 Hz, 1 H), 9.54 (d, J = 2.6 Hz, 2 H), 10.10 (dd, J = 12.2 Hz, J = 5.3 Hz, 2 H).

\textsuperscript{13}C{\textsuperscript{1}H}-NMR / DEPT135: δ (ppm, CD\textsubscript{3}CN) = 7.5 (prim., 4 C), 24.5 (prim., 2 C), 51.8 (sec., 4 C), 116.0 (tert., 1 C), 119.5 (tert., 1 C), 120.1 (tert., 1 C), 123.0 (tert., 1 C), 123.3 (tert., 1 C), 124.8 (tert., 1 C), 125.1 (tert., 1 C), 140.0 (tert., 2 C), 141.8 (quat., 1 C), 144.2 (quat., 1 C), 151.3 (quat., 1 C), 157.1 (quat., 1 C), 157.2 (quat., 1 C), 158.7 (quat., 1 C), 159.2 (quat., 1 C), 167.2 (quat., 1 C), 167.7 (quat., 1 C), 176.4 (quat., 2 C). MS: (ESI–) m/z = 538 [M–NEt\textsubscript{4}]\textsuperscript{–}. Anal. Calcd for C\textsubscript{30}H\textsubscript{37}CoN\textsubscript{6}O\textsubscript{8}: C, 53.89; H, 5.73; N, 12.24. Found: C, 52.48; H, 5.72; N, 12.49.
Experimental data for 8:

\[
\text{O} \quad \text{NH} \quad \text{HN} \quad \text{O} \quad + \quad \text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O} \\
\text{DMF, CH}_3\text{CN, rt, 12 h}
\]

2.0 mmol of CoOAc\(_2\) \cdot 4\text{H}_2\text{O}, 2.0 mmol of ligand 4 were dissolved in 15 ml of DMF and stirred at RT under air for 10 min. Then 2.88 mmol of NEt\(_4\)OAc 4\text{H}_2\text{O} were added and the solution stirred at 70 °C for 12 h. After cooling, the solution was stirred for additional 6 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile. A precipitate was formed on adding 20 ml of diethyl ether to the solution and cooling down to 2 °C. The product was isolated after filtering, washing two times with 20 ml of a 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as green powder. Yield 660 mg (51 %).

IR (cm\(^{-1}\)): 3087 (w), 2978 (w), 2921 (w), 2857 (w), 1621 (s), 1596 (vs), 1485 (s), 1456 (m), 1405 (s), 1371 (s), 1316 (m), 1172 (w), 1095 (w), 1001 (m), 886 (w), 759 (m), 681 (m), 619 (w), 509 (w).

\(^{1}\text{H-NMR}\) δ (ppm, dmso-d\(_6\)) = 1.02 (s, 6 H), 1.15 (t, J = 7.3 Hz, 12 H), 2.24 (s, 6 H), 3.20 (q, J = 7.2 Hz, 8 H), 7.64 (ddd, J = 7.4 Hz, J = 5.6 Hz, J = 1.6 Hz, 2H), 7.83 (dd, J = 7.7 Hz, J = 1.2 Hz, 2 H), 8.07 (dt, J = 7.6 Hz, J = 1.3 Hz, 2 H), 8.62 (s, 2 H), 10.16 (d, J = 5.5 Hz, 2 H).

\(^{13}\text{C}\{(^{1}\text{H})\}-\text{NMR / DEPT135}\) δ (ppm, dmso-d\(_6\)) = 7.1 (prim., 4 C), 19.8 (prim., 2 C), 24.2 (prim., 2 C), 51.4 (sec., 4 C), 122.1 (tert., 2 C), 122.4 (tert., 2 C), 123.5 (tert., 2 C), 129.5 (quat., 2 C), 139.1 (quat., 2 C), 141.7 (quat., 2 C), 156.8 (quat., 2 C), 160.2 (quat., 2 C), 165.3 (quat., 2 C), 175.8 (quat., 2 C). MS: (ESI –) m/z = 521 [M–NEt\(_4\)]\(^-\). Anal. Calcd for C\(_{32}\)H\(_{42}\)CoN\(_5\)O\(_6\) \cdot \text{H}_2\text{O}: C, 57.39; H, 6.62; N, 10.46. Found: C, 56.22; H, 6.89; N, 10.34.
According to literature procedure [2] 2.0 mmol of CoCl₂, 2.0 mmol of ligand 1 and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 4.42 mmol of [NEt₄]Cl H₂O was added and the solution was stirred at RT an additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 30 ml of acetonitrile and filtered. Through adding 30 ml of diethyl ether to the solution and cooling down to 2 °C a brown precipitate was formed. After filtering, washing with 20 ml of 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as an orange-brown powder. Yield 991 mg (86 %).

IR (cm⁻¹): 3058 (w), 2979 (m), 2677 (m), 2494 (w), 1621 (s), 1595 (s), 1563 (s), 1474 (s), 1393 (s), 1291 (m), 1183 (w), 1091 (w), 1032 (m), 949 (w), 762 (m), 680 (m). 

¹H-NMR: δ (ppm, CD₃CN) = 1.19 (tr, J = 7.5 Hz, 12 H), 3.15 (q, J = 7.3 Hz, 8 H), 6.94 - 7.04 (m, 2 H), 7.76 - 7.86 (m, 2 H), 8.06- 8.20 (m, 4 H), 8.89 (dd, J = 5.9 Hz, J = 3.6 Hz, 2 H), 9.65 (d, J = 5.6 Hz, 2 H). 

¹³C{¹H}-NMR / DEPT135: δ (ppm, dmso-d₆) = 7.8 (prim., 4 C), 52.0 (sec., 4 C), 122.5 (tert., 2 C), 123.2 (tert., 2 C), 124.0 (tert., 2 C), 127.7 (tert., 2 C), 139.8 (tert., 2 C), 143.8 (quat., 2 C), 152.0 (quat., 2 C), 152.4 (quat., 2 C), 161.3 (quat., 2 C).

¹H-spectrum in CD₃CN of 9:

Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2013
Experimental data for 10:

![Chemical Diagram]

According to literature procedure [2] 2.0 mmol of CoCl₂, 2.0 mmol of ligand 2 and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 4.42 mmol of NET₄Cl H₂O was added and the solution was stirred at RT an additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile and filtered. Through adding 20 ml of diethyl ether to the solution and cooling down to 2 °C a brown precipitate was formed. After filtering, washing with 40 ml of 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as a red-brown powder. Yield 857 mg (66%).

IR (cm⁻¹): 3070 (w), 2980 (w), 2948 (w), 1631 (s), 1598 (s), 1553 (m), 1471 (vs), 1388 (vs), 1286 (m), 1174 (w), 1095 (m), 997 (w), 976 (w), 880 (w), 760 (m), 544 (w), 479 (w). ¹H-NMR: δ (ppm, CD₃CN) = 1.17 (tr, J = 7.1 Hz, 12 H), 3.12 (q, J = 7.2 Hz, 8 H), 7.81 (tr, J = 5.6 Hz, 2 H), 8.05-8.20 (m, 4 H), 8.96 (s, 2 H), 9.61 (d, J = 5.1 Hz, 2 H). ¹³C ¹H-NMR / DEPT135: δ (ppm, dmoso-d6) = 7.6 (prim., 4 C), 53.0 (sec., 4 C), 122.9 (tert., 2 C), 124.9 (tert., 2 C; quat., 2 C), 128.2 (tert., 2 C), 140.4 (tert., 2 C), 144.1 (quat., 2 C), 152.0 (tert., 2 C), 161.0 (quat., 2 C), 167.6 (quat., 2C).

¹H-spectrum in CD₂CN of 10:
Experimental data for 11:

2.0 mmol of CoCl₂, 2.0 mmol of ligand 3, 4.0 mmol triethylamine and 4.42 mmol of NEt₄Cl H₂O were dissolved in 15 ml of DMF and stirred at RT under normal atmosphere for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red-brown powder. Yield 1134 mg (91%).

IR (cm⁻¹): 3070 (w), 2986 (w), 2949 (w), 1632 (vs), 1600 (s), 1558 (s), 1481 (vs), 1426 (m), 1390 (s), 1319 (vs), 1296 (s), 1142 (m), 1062 (m), 999 (w), 958 (w), 758 (m), 684 (m), 615 (w), 508 (w), 465 (w), 352 (w).

¹H-NMR δ (ppm, CD₃CN) = 1.12 – 1.19 (m, 12 H), 3.11 (q, J = 7.3 Hz, 8 H), 7.80 – 7.86 (m, 2H), 7.94 (dd, J = 9.0 Hz, J = 2.6 Hz, 1 H), 8.10 – 8.21 (m, 4 H), 8.93 (d, J = 8.8 Hz, 1 H), 9.60 – 9.67 (m, 3 H).

¹³C{¹H}-NMR / DEPT135: δ (ppm, CD₃CN) = 7.5 (prim., 4 C), 52.9 (sec., 4 C), 117.5 (tert., 1 C), 120.4 (tert., 1 C), 121.4 (tert., 1 C), 125.0 (tert., 1 C), 125.3 (tert., 1 C), 128.4 (tert., 1 C), 128.7 (tert., 1 C), 140.5 (tert., 2 C), 143.5 (quat., 1 C), 144.3 (quat., 1 C), 151.0 (quat., 1 C), 152.0 (tert., 1 C), 152.1 (tert., 1 C), 160.5 (quat., 1 C), 161.0 (quat., 1 C), 168.0 (quat., 1 C), 168.4 (quat., 1 C).

MS: (ESI–) m/z = 490 [M-NEt₄⁻]. Anal. Calcd for C₂₆H₃₁Cl₂CoN₆O₄: C, 50.25; H, 5.03; N, 13.52. Found: C, 50.05; H, 4.96; N, 13.67.
Experimental data for 12:

2.0 mmol of CoCl₂, 2.0 mmol of ligand 4, 4.0 mmol triethylamine and 4.42 mmol of NEt₄Cl H₂O were dissolved in 15 ml of DMF and stirred at RT under normal atmosphere for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red powder. Yield 1060 mg (88 %).

IR (cm⁻¹): 3077 (w), 2984 (w), 2924 (w), 2856 (w), 1625 (vs), 1595 (s), 1577 (s), 1486 (m), 1456 (m), 1404 (s), 1290 (m), 1251 (m), 1178 (m), 1092 (w), 1003 (w), 889 (w), 765 (m), 681 (m), 651 (w), 406 (w). ¹H-NMR δ (ppm, CD₃CN) = 1.16 (t, J = 7.3 Hz, 12 H), 2.29 (s, 6 H), 3.10 (q, J = 7.3 Hz, 8 H), 7.76 (t, J = 6.4 Hz, 2 H), 8.05-8.16 (m, 4 H), 8.68 (s, 2 H), 9.64 (d, J = 5.5 Hz, 2 H). ¹³C{¹H}-NMR / DEPT135: δ (ppm, CD₃CN) = 7.6 (prim., 4 C), 20.0 (prim., 4 C), 52.9 (sec., 4 C), 123.9 (tert., 2 C), 124.4 (tert., 2 C), 127.5 (tert., 2 C), 131.9 (quat., 2 C), 140.0 (tert., 2 C), 142.1 (quat., 2 C), 151.7 (tert., 2 C), 162.4 (quat., 2 C). MS: (ESI-) m/z = 473 [M-NEt₄]-. Anal. Calcd for C₂₈H₃₆Cl₂CoN₅O₂.H₂O: C, 54.03; H, 6.15; N, 11.25. Found: C, 54.26; H, 6.39; N, 11.38.

¹H-spectrum in CD₃CN of 12:
Experimental data for 13:

According to literature procedure [3] 2.0 mmol of FeCl₂ x 4H₂O, 2.0 mmol of H₂bpb (I) and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 4.42 mmol of NEt₄Cl H₂O was added and the solution was stirred at RT for additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 30 ml of acetonitrile and filtered. Adding 30 ml of diethyl ether to the solution and cooling down to 2 °C yielded a green precipitate. After filtering, washing with 20 ml of 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as a green powder. Yield 957 mg (83 %).

IR (cm⁻¹): 2982 (m), 2942 (m), 2739 (w), 2677 (m), 2491 (w), 1619 (s), 1591 (s), 1563 (s), 1472 (m), 1349 (s), 1292 (m), 1173 (m), 1096 (w), 1003 (m), 942 (w), 750 (m), 668 (m). MS: (EI⁺) m/z = 372 [M-2Cl-NEt₄]⁺. Anal. Calcd for C₂₆H₃₂Cl₂FeN₅O₂: C, 54.47; H, 5.63; N, 12.22. Found: C, 53.55; H, 5.78; N, 11.69.

IR-spectrum of 13:
Experimental data for 14:

According to literature procedure [4] 2.0 mmol of FeCl₃, 2.0 mmol of ligand 2 and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 4.42 mmol of NEt₄Cl H₂O was added and the solution was stirred at RT for additional 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a green powder. Yield 957 mg (83 %).

IR (cm⁻¹): 3110 (w), 3054 (w), 2983 (m), 2947 (w), 1619 (s), 1593 (vs), 1559 (s), 1457 (s), 1373 (vs), 1343 (s), 1283 (m), 1235 (w), 1173 (w), 1109 (m), 1044 (w), 1021 (w), 951 (m), 886 (w), 816 (w), 762 (m), 697 (m), 642 (w), 542 (w). MS: (EI⁻) m/z = 512 (100 %), 510 (81 %) [M-NEt₄]⁻.

Anal. Caled for C₂₆H₃₀Cl₄FeN₅O₂: C, 48.63; H, 4.71; N, 10.91. Found: C, 48.51; H, 4.53; N, 10.89.
IR-spectrum of 14:

![Agilent Resolution Pro](image)


Experimental data for 15:

\[
\begin{align*}
\text{NO}_2 & \quad + \quad \text{FeCl}_3 \\
\text{O} & \quad \text{NH} & \quad \text{H} & \quad \text{N} & \quad \text{O} \\
\text{N} & \quad \text{O} & \quad \text{N} & \quad \text{C}_{26}H_{31}Cl_{2}FeN_{6}O_{4}
\end{align*}
\]

2.0 mmol of FeCl₃, 2.0 mmol of ligand, 4.0 mmol triethylamine and 4.42 mmol of NEt₄Cl H₂O were dissolved in 15 ml of DMF and stirred at RT and air for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. The resulting precipitate was filtered and washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a green powder. Yield 992 mg (80%).

IR (cm⁻¹): (cm⁻¹): 3122 (w), 3068 (w), 2983 (w), 2925 (w), 1625 (vs), 1594 (s), 1559 (s), 1506 (m), 1471 (m), 1421 (w), 1346 (s), 1323 (vs), 1296 (s), 1136 (m), 1045 (w), 969 (w), 924 (w), 827 (w), 760 (m), 647 (w), 488 (m). MS: (ESI –) m/z = 487 (100 %), 489 (65 %) [M-NEt₄]⁻. Anal. Calcd for C_{26}H_{31}Cl_{2}FeN_{6}O_{4}.H₂O: C, 49.08; H, 5.23; N, 13.21. Found: C, 49.18; H, 4.95; N, 13.40.
Experimental data for 16:

2.0 mmol of FeCl₃, 2.0 mmol of ligand 4, 4.0 mmol triethylamine and 4.42 mmol of NEt₄Cl H₂O were dissolved in 15 ml of DMF and stirred at RT and air for 12 hours. DMF was removed in vacuo and 20 ml of a 1:1 acetonitrile/diethyl ether mixture was added to the residue. The resulting precipitate was filtered and washed thrice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a green powder. Yield 818 mg (68%).

IR (cm⁻¹): 3045 (w), 2985 (w), 2915 (w), 2865 (w), 1615 (s), 1582 (vs), 1563 (s), 1478 (s), 1455 (m), 1401 (m), 1354 (s), 1287 (m), 1254 (w), 1182 (w), 1093 (w), 1044 (m), 1002 (w), 954 (w), 893 (w), 764 (m), 695 (m), 648 (w), 504 (w), 470 (w). MS: (ESI–) m/z = 470 [M-NEt₄]⁻. Anal. Calcd for C₂₈H₃₆Cl₂FeN₅O₂·2H₂O: C, 52.76; H, 6.33; N, 10.99. Found: C, 53.03; H, 6.62; N, 11.19.

IR-spectrum of 16:
Experimental data for 17:

\[
\begin{align*}
\text{N} & \text{H} & \text{N} & \text{O} \\
\text{O} & \text{N} & \text{1} & \text{Cr} \\
\text{Cl} & \text{CrCl}_3 \text{6H}_2\text{O} \\
\text{C}_{26}\text{H}_{32}\text{Cl}_2\text{CrN}_5\text{O}_2 \\
\text{569.47 g/mol}
\end{align*}
\]

2.0 mmol of CrCl\textsubscript{3} 6H\textsubscript{2}O, 2.0 mmol of ligand 1, 4.0 mmol triethylamine and 4.42 mmol of NEt\textsubscript{4}Cl H\textsubscript{2}O were dissolved in 15 ml of DMF and stirred at 120°C for 12 hours. After cooling the solution was stirred at RT and under air for additional 6 hours. DMF was removed in vacuo and 20 ml of a 1:1 acetonitrile/diethyl ether mixture was added to the residue yielding a precipitate, which was filtered, washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red powder. Yield 1005 mg (88%).

IR (cm\textsuperscript{-1}): 3055 (w), 2987 (w), 2946 (w), 1620 (s), 1592 (vs), 1565 (vs), 1471 (s), 1363 (s), 1289 (m), 1183 (w), 1146 (w), 1094 (w), 1036 (m), 961 (w), 906 (w), 764 (m), 690 (m), 511 (m), 328 (m).

MS: (ESI–) m/z = 438 [M–NEt\textsubscript{4}]\textsuperscript{−}. Anal. Calcd for C\textsubscript{26}H\textsubscript{32}Cl\textsubscript{2}CrN\textsubscript{5}O\textsubscript{2}.H\textsubscript{2}O: C, 53.16; H, 5.83; N, 11.92. Found: C, 52.48; H, 5.57; N, 11.86.

**IR-spectrum of 17:**
According to literature procedure [5] 2.0 mmol of CrCl₃ 6H₂O, 2.0 mmol of ligand 2, 4.0 mmol triethylamine and 4.42 mmol of NEt₄Cl H₂O were dissolved in 15 ml of DMF and stirred at 120°C for 12 hours. After cooling the solution was stirred at RT and under air for additional 6 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. The resulting precipitate was filtered and washed with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red-brown powder. Yield 906 mg (71%).

IR (cm⁻¹): 3062 (w), 2982 (m), 2947 (w), 1630 (vs), 1595 (s), 1557 (s), 1466 (s), 1376 (s), 1285 (m), 1228 (w), 1199 (w), 1174 (w), 1094 (m), 1048 (w), 1027 (w), 974 (m), 885 (w), 810 (w), 761 (m), 691 (m), 652 (w), 540 (w), 448 (m). MS: (ESI−) m/z = 506 [M-NEt₄]. Anal. Calcd for C₂₆H₆₀Cl₄CrN₅O₂·H₂O: C, 53.16; H, 5.83; N, 11.92. Found: C, 52.48; H, 5.57; N, 11.86.
IR-spectrum of 18:

Experimental data for 19:

2.0 mmol of CrCl_3·6H_2O, 2.0 mmol of ligand 4, 4.0 mmol triethylamine and 4.42 mmol of NEt_4Cl H_2O were dissolved in 15 ml of DMF and stirred at 120°C for 12 hours. After cooling the solution was stirred at RT and under air for additional 6 hours. DMF was removed in vacuo and 20 ml of a 1:1 acetonitrile/diethyl ether mixture was added to the residue yielding a precipitate, which was filtered, washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red-brown powder. Yield 1035 mg (87%).

IR (cm⁻¹): 3067 (w), 2981 (w), 2924 (w), 1629 (s), 1562 (vs), 1514 (m), 1482 (s), 1366 (s), 1291 (m), 1238 (w), 1178 (m), 1095 (w), 1048 (w), 1003 (w), 892 (w), 764 (w), 695 (m), 663 (w), 510 (w), 422 (w). MS: (ESI−) m/z = 466 [M-NEt_4]. Anal. Calcd for C_{28}H_{36}Cl_2CrN_5O_2·2H_2O: C, 53.08; H, 6.36; N, 11.05. Found: C, 52.76; H, 6.33; N, 11.42.
According to literature procedure [6] 2.0 mmol of CoBr$_2$ xH$_2$O, 2.0 mmol of ligand 1 and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT and air for 20 min. Then 4.42 mmol of NEt$_4$Br was added and the solution was stirred at RT under normal atmosphere for additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 30 ml of acetonitrile and filtered. Through adding 30 ml of diethyl ether to the solution and cooling down to 2 °C a brown precipitate was formed. After filtering, washing with diethyl ether and drying under vacuo the product was separated as a brown powder. Yield 745 mg (56 %).

IR (cm$^{-1}$): 3058 (w), 2984 (w), 2924 (m), 2853(w), 1620 (s), 1595 (vs), 1564 (s), 1475 (s), 1393 (s), 1291 (m), 1183 (w), 1092 (w), 1031 (m), 950 (w), 760 (s), 678 (m), 516 (m).

$^1$H-NMR: δ (ppm, dms-o-d6) = 1.16 (tr, $J = 5.5$ Hz, 12 H), 3.20 (q, $J = 7.0$ Hz, 8 H), 7.00-7.07 (m, 2 H), 7.94-8.04 (m, 2 H), 8.16 (d, $J = 7.7$ Hz, 2 H), 8.34 (tr, $J = 7.4$ Hz, 2 H), 8.85-8.95 (m, 2 H), 9.85-9.95 (m, 2 H).

$^{13}$C($^1$H)NMR / DEPT135: δ (ppm, dms-o-d6) = 7.8 (prim., 4 C), 52.0 (sec., 4 C), 122.7 (tert., 2 C).
124.2 (tert., 2 C), 124.8 (tert., 2 C), 128.9 (tert., 2 C), 141.2 (tert., 2 C), 143.0 (quat., 2 C), 152.8 (tert., 2 C), 160.6 (quat., 2 C), 167.5 (quat., 2 C). MS: (ESI–) m/z = 375 [M-2Br-NEt₄]. Anal. Calcd for C₂₆H₃₂Br₂CoN₅O₂·H₂O: C, 45.70; H, 5.02; N, 10.25. Found: C, 45.47; H, 4.93; N, 9.97.

^1^H-spectrum in DMSO-d₆ of 20:

1H-NMR δ (ppm, CD₃CN) = 1.18 (t, J = 7.2 Hz, 12 H), 3.13 (q, J = 7.2 Hz, 8 H), 7.83 (tr, J = 6.3 Hz, 2 H), 8.07-8.17 (m, 4 H), 9.00 (s, 2 H), 9.70 (d, J = 5.3 Hz, 2 H). 13C{¹H}-NMR / DEPT135: δ (ppm, CD₃CN) = 7.6 (prim., 4 C), 52.9 (sec., 4 C), 123.3 (tert., 2 C), 124.9 (tert., 2 C), 125.1 (quat., 2 C), 128.4 (tert., 2 C), 140.3 (tert., 2 C), 144.1 (quat., 2 C), 153.0 (quat., 2 C), 161.6 (quat., 2 C), 167.5 (quat., 2 C).

Experimental data for 21:

\[
\text{ClCl} \quad \text{NH} \quad \text{HN} \quad \text{O} \quad \text{O} \quad \text{N}^2+ \\
\text{O} \quad \text{N} \quad \text{Cl} \quad \text{Cl} \quad \text{CoBr}_2 \cdot x \text{H}_2 \text{O} \\
\text{TEA, } [\text{NEt}_4] \text{Br, O}_2, - \text{HNEt}_3 \text{Br, - H}_2 \text{O} \\
\text{DMF, CH}_3 \text{CN, rt, 12 h} \\
\]

2.0 mmol of CoBr₂-xH₂O, 2.0 mmol of ligand 2, 4.0 mmol triethylamine and 4.42 mmol of NEt₄Br were dissolved in 15 ml of DMF and stirred under air at RT for 12 hours. DMF was removed in vacuo and 20 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was obtained as a brown powder. Yield 961 mg (65 %).

IR (cm⁻¹): 3086 (w), 3051 (w), 2982 (w), 2945 (w), 1626 (vs), 1598 (s), 1589 (s), 1468 (s), 1395 (s), 1285 (m), 1200 (w), 1097 (m), 1049 (w), 975 (m), 925 (w), 887 (w), 760 (m), 680 (m), 546 (m), 482 (w). ^1^H-NMR δ (ppm, CD₃CN) = 1.18 (t, J = 7.2 Hz, 12 H), 3.13 (q, J = 7.2 Hz, 8 H), 7.83 (tr, J = 6.3 Hz, 2 H), 8.07-8.17 (m, 4 H), 9.00 (s, 2 H), 9.70 (d, J = 5.3 Hz, 2 H). ^1^C{¹H}-NMR / DEPT135: δ (ppm, CD₃CN) = 7.6 (prim., 4 C), 52.9 (sec., 4 C), 123.3 (tert., 2 C), 124.9 (tert., 2 C), 125.1 (quat., 2 C), 128.4 (tert., 2 C), 140.3 (tert., 2 C), 144.1 (quat., 2 C), 153.0 (quat., 2 C), 161.6 (quat., 2 C), 167.5 (quat., 2 C).
Experimental data for 22:

2.0 mmol of CoBr₂ · H₂O, 2.0 mmol of ligand 3, 4.0 mmol triethylamine and 4.42 mmol of NEt₄Br were dissolved in 15 ml of DMF and stirred under air at RT for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was obtained as a red-brown powder/crystal. For complex 22 red-brown crystals were obtained by slowly adding a small excess of diethyl ether into an acetonitrile solution of 22 and subsequently cooling down to 2 °C. After 2 days small red-brown crystals were formed. Yield 887 mg (62 %).

IR (cm⁻¹): 3124 (w), 3054 (w), 2987 (w), 2925 (w), 1631 (vs), 1598 (s), 1558 (vs), 1493 (s), 1478 (s), 1422 (m), 1389 (s), 1318 (s), 1293 (s), 1140 (m), 1094 (w), 1058 (m), 998 (w), 985 (w), 897 (w), 759 (m), 682 (m), 506 (w), 459 (w). ¹H-NMR δ (ppm, CD₃CN) = 1.15 – 1.21 (m, 12 H), 3.14 (q, J = 7.2 Hz, 8 H), 7.83 – 7.90 (m, 2H), 7.95 (dd, J = 8.9 Hz, J = 2.5 Hz, 1 H), 8.14 – 8.20 (m, 4 H), 8.96 (d, J = 9.0 Hz, 1 H), 9.65 – 9.74 (m, 3 H). ¹³C{¹H}-NMR / DEPT135: δ (ppm, CD₃CN) = 7.6 (prim., 4 C), 52.9 (sec., 4 C), 117.9 (tert., 1 C), 120.5 (tert., 1 C), 121.8 (tert., 1 C), 125.0 (tert., 1 C),
125.3 (tert., 1 C), 128.5 (tert., 1 C), 128.8 (tert., 1 C), 140.4 (tert., 1 C), 140.5 (tert., 1 C), 143.6 (quat., 1 C), 143.7 (quat., 1 C), 151.1 (quat., 1 C), 153.0 (tert., 1 C), 153.1 (tert., 1 C), 161.2 (quat., 1 C), 161.7 (quat., 1 C), 167.5 (quat., 1 C), 167.7 (quat., 1 C). MS: (ESI−) m/z = 580 [M-NEt4]. Anal. Calcd for C26H31Br2CoN6O4: C, 43.96; H, 4.40; N, 11.83. Found: C, 43.68; H, 4.41; N, 12.25.

1H-spectrum in CD3CN of 22:

Experimental data for 23:

2.0 mmol of CoBr2·xH2O, 2.0 mmol of ligand 4, 4.0 mmol triethylamine and 4.42 mmol of NEt4Br were dissolved in 15 ml of DMF and stirred under air at RT for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was obtained as a brown powder/crystal. For complex 23 brown crystals were obtained by slowly adding a small excess of diethyl ether into an acetonitrile solution of 23 and subsequently cooling down to 2 °C. After 2 days small brown crystals were formed. Yield 1025 mg (74 %).

IR (cm−1): 3077 (w), 2984 (w), 2923 (w), 2858 (w), 1625 (s), 1594 (vs), 1485 (s), 1456 (m), 1404 (s), 1290 (w), 1251 (w), 1178 (w), 1093 (w), 1003 (m), 889 (w), 764 (m), 680 (m), 588 (w), 509 (w), 406 (w). 1H-NMR δ (ppm, CD3CN) = 1.15 – 1.20 (m, 12 H), 2.29 (s, 6 H), 3.13 (q, J = 7.3 Hz, 8 H), 7.72 – 7.90 (m, 2H), 8.02 – 8.28 (m, 4 H), 8.68 (s, 2 H), 9.56 – 9.70 (m, 2 H). 13C{1H}-NMR /
DEPT135: $\delta$ (ppm, CD$_3$CN) = 7.6 (prim., 4 C), 20.0 (prim., 2 C), 53.0 (sec., 4 C), 124.3 (tert., 2 C), 124.4 (tert., 2 C), 127.7 (tert., 2 C), 127.7 (quat., 2 C), 132.2 (quat., 2 C), 140.0 (tert., 2 C), 142.0 (quat., 2 C), 152.7 (tert., 2 C), 163.1 (quat., 2 C). MS: (ESI−) m/z = 561 [M-NEt$_4$]. Anal. Calcd for C$_{28}$H$_{36}$CoN$_5$O$_2$.H$_2$O: C, 47.27; H, 5.38; N, 9.84. Found: C, 46.28; H, 5.34; N, 9.71.

$^1$H-spectrum in CD$_3$CN of 23:

TGA of complex 23: [(LMe$_2$)CoBr$_2$]NEt$_4$ (TGA recorded for the purpose of the recycling study)
Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2013
X-ray structure determination of 6, 22 and 23:  

Molecular structure of 6:
Molecular structure of 22
Molecular structure structure of 23:
Quick evaluation of the operating conditions for the screening tests (propylene oxide with catalyst 10)

Table 1 Setting tests for propylene oxide with catalyst 10 (Co/LCl₂/Cl₂)⁹

<table>
<thead>
<tr>
<th>Entry</th>
<th>Mol % catalyst</th>
<th>p (bar)</th>
<th>T (°C)</th>
<th>Conversion (%) ³</th>
<th>Selectivity of the coupling ³ ⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>35</td>
<td>60</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>35</td>
<td>80</td>
<td>78</td>
<td>0 / 100</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>35</td>
<td>100</td>
<td>94</td>
<td>0 / 100</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>50</td>
<td>80</td>
<td>3</td>
<td>0 / 100</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>35</td>
<td>80</td>
<td>86</td>
<td>0 / 100</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>35</td>
<td>80</td>
<td>71</td>
<td>0 / 100</td>
</tr>
</tbody>
</table>

a Standard reaction conditions: 10 ml of Epoxide, 20 h, 80 °C

b Conversion = n(Monomer units in isolated product)/n(epoxide)*100

² Mass of isolated long chain polymers / mass of isolated cyclic monomer

Considering the different reaction parameters for complex 10 (Table 1), three parameters were firstly investigated. Studying the influence of temperature (Entry 1-3, from 60°C to 100 °C in 20 °C steps) revealed that higher temperatures increased the overall conversion up to 94 %. 80 °C seems to be the lowest temperature necessary to achieve an acceptable conversion.

The second parameter was the amount of carbon dioxide i.e. the epoxide: CO₂ molar ratio. Two ratio were tested 1:1 (entry 2: 35 bar, 7 g CO₂) and 1:2 (entry 4: 50, 10 g CO₂), showing that higher CO₂ concentration induces a markedly decreased conversion. This suggests that an excess of CO₂ inhibits the coupling reaction via either a dilution effect of the reaction medium or a decrease of the catalyst solubility in this CO₂-expanded mixture.

The last parameter studied was the influence of the substrate-to-catalyst molar ratio (Entry 5: 0.5 Mol% catalyst; Entry 2: 0.2 Mol% catalyst and Entry 6: 0.1 Mol% catalyst) which showed that a lower substrate-to-catalyst molar ratio leads only two a slightly decreased conversion.
PCHC characterization:

$^1$H-spectrum in benzene-d$_6$ of PCHC (with traces of dichloromethane: 4.26 ppm) obtained from Table 8 Entry 1:

$^{13}$C-spectrum in chloroform-d$_1$ of PCHC obtained from Table 5 Entry 2:
IR-spectrum of PCHC obtained from Table 5 Entry 2:

*Agilent Resolutions Pro*
PC characterization:

$^1$H-spectrum in benzene-d$_6$ of PC obtained from Table 5 Entry 14:

![$^1$H-spectrum in benzene-d$_6$ of PC](image)

IR-spectrum of PC obtained from Table 4 Entry 8:

**Agilent Resolutions Pro**

![IR-spectrum of PC](image)
Characterization of products summarized in table 7:

Characterization of 4-phenyl-1,3-dioxolan-2-one (Entry 3):

$^1$H-NMR $\delta$ (ppm, C$_6$D$_6$) = 3.33 (t, J = 8.2 Hz, 1H), 3.50 (t, J = 8.3 Hz, 1H), 4.50 (t, J = 8.9 Hz, 1H), 6.73 (dd, J = 7.6 Hz, J = 1.4 Hz, 2H), 6.92 – 7.00 (m, 3H).

Characterization of 4-butyl-dioxolan-2-one (Entry 4):

$^1$H-NMR $\delta$ (ppm, C$_6$D$_6$) = 0.77 – 0.82 (m, 3H), 1.15 - 1.30 (m, 6H), 2.07 (td, J = 5.3 Hz, J = 2.6 Hz, 1H), 2.32 – 2.34 (m, 1H), 2.53 – 2.59 (m, 1H).
Characterization of 4-chloromethyl-1,3-dioxolan-2-one (Entry 5):

$^1$H-NMR $\delta$ (ppm, C$_6$D$_6$) = 2.42 (dd, $J = 11.9$ Hz, $J = 4.1$ Hz, 1H), 2.54 (dd, $J = 12.0$ Hz, $J = 5.4$ Hz, 1H), 3.16 – 3.23 (m, 2H), 3.46 – 3.54 (m, 1H).

Characterization of 4-phenyloxymethyl-1,3-dioxolan-2-one (Entry 6):

$^1$H-NMR $\delta$ (ppm, C$_6$D$_6$) = 2.99 (dd, $J = 10.4$ Hz, $J = 3.2$ Hz, 1H), 3.14 (dd, $J = 10.4$ Hz, $J = 3.5$ Hz, 1H), 3.27 (t, $J = 8.4$ Hz, 1H), 3.38 (t, $J = 6.9$ Hz, 1H), 3.69 – 3.75 (m, 1H), 6.55 (d, $J = 7.8$ Hz, 2 H), 6.82 (t, $J = 7.3$ Hz, 1 H), 7.04 (t, $J = 7.3$ Hz, 2 H).
Characterization of **4-Allyloxymethyl-1,3-dioxolan-2-one** (Entry 7):

\[ ^1H\text{-NMR } \delta (\text{ppm, C}_6\text{D}_6) = 2.69 \text{ (dd, } J = 10.8 \text{ Hz, } J = 3.8 \text{ Hz, 1H)}, 2.86 \text{ (dd, } J = 10.9 \text{ Hz, } J = 3.7 \text{ Hz, 1H)}, 3.36 \text{ (t, } J = 8.3 \text{ Hz, 1H)}, 3.50 - 3.55 \text{ (m, 3H)}, 3.71 - 3.77 \text{ (m, 1H)}, 4.95 \text{ (dd, } J = 10.4 \text{ Hz, } J = 1.3 \text{ Hz, 1H)}, 5.05 \text{ (dd, } J = 17.3 \text{ Hz, } J = 1.5 \text{ Hz, 1H)}, 5.55 - 5.65 \text{ (m, 1H)}. \]
Recycle experiments for 23: $^1$H-spectrum of 23 in CD$_3$CN:

Typical $^1$H-spectrum of 23 in CD$_3$CN (end of recycling, with traces of propylene carbonate):