Experimental section

General Remarks

All reactions were performed using 10 mL window equipped stainless steel autoclaves. THF was dried and distilled according to standard methods.[i] Reagents were purchased from Aldrich Chemical Co. and were used as received. PEG was purchased from Fluka. ^{1}H - ^{13}C NMR spectra were measured on a Bruker DPX 300 or Bruker AV 600 spectrometer. GC-MS analyses were carried out with a Varian CP3800–1220L Quadrupol instrument. HRMS measurements were realised on a Finnigan MAT 95 spectrometer. IR spectra were measured on a Thermo Nicolet Avatas 380 FT-IR and a Perkin Elmer 1760 FT spectrometer. ICP measurements were carried out in the group of Prof. Dr. A. Behr at the University of Dortmund, TEM measurements at the Max Planck Institute of coal Research in the group of Dr. Bernd Tesche.

Preparation of the PEG_{1000}-stabilized cobalt nanoparticles

After degassing $PEG_{1000}(OMe)_2$ (1.1 g, 1.1 mmol) for 3 h at 80°C, a solution of $[Co_2(CO)_8]$ (170.0 mg, 0.5 mmol) in 10 mL toluene was injected to the molten PEG under counter current flow of argon. The reaction solution was heated to 100°C for 20 min under rigorous shaking and was concentrated afterwards over 1h under reaction conditions leading to a green black waxy precipitate. The PEG_{1000}-stabilized cobalt nanoparticles were analysed by IR spectroscopy on an impregnated KBr pastille. For the TEM measurements a sample was prepared by placing a drop of a solution of the catalyst in dichloromethane (CH_2Cl_2) on a carbon coated copper grid.

Preparation of the PEG_{5000}-stabilized cobalt nanoparticles

After degassing $PEG_{5000}(OMe)_2$ (1.8 g, 0.4 mmol) for 3 h at 80°C, a solution of $[Co_2(CO)_8]$ (58.3 mg, 0.2 mmol) in 10 mL toluene was injected to the molten PEG under counter current flow of argon. Under rigorous shaking the reaction solution was heated to 100°C for 20 min. The toluene was evaporated over 1h under reaction conditions leading to a green black precipitate which is solid at room temperature. The catalyst was analysed by IR and TEM as described.

Intra- and Intermolecular Pauson-Khand reactions catalyzed by PEG-stabilized cobalt nanoparticles

General procedure for the intramolecular PKR using PEG_{1000}-stabilized cobalt nanoparticles (entries 1-3 Table 2). A solution of PEG_{1000}-stabilized cobalt nanoparticles (7.0 mg, 0.7 10^{-2} mmol) in CH_2Cl_2 was added to a dry and degassed window equipped 10 mL stainless steel autoclave under counter current flow of argon. The solvent was evaporated under vacuum at room temperature. A solution of enyne (19.8 10^{-2} mmol) in 4 mL THF was added. The reactor was charged with 15 bar of CO at room temperature and heated under stirring at 130 °C for 16 h. Under reaction conditions the pressure in the autoclave increased to 23 bar. After the reaction the reactor was cooled to room temperature and vented carefully to the exhaust line. The remaining solution was analysed by GC-MS.

General procedure for the intramolecular PKR using PEG_{5000}-stabilized cobalt nanoparticles (entries 1-3 Table 2).

A solution of PEG_{5000}-stabilized cobalt nanoparticles (20.0 mg, 0.4 10^{-2} mmol) in CH_2Cl_2 was added to a stainless steel autoclave as described above. After evaporation of the solvent a solution of enyne (12.0 10^{-2} mmol) in 4 mL THF was added. The reactor was charged with 15 bar of CO at room temperature and heated under stirring at 130 °C for 16 h. Under reaction conditions the pressure in the autoclave increased to 23 bar. After the reaction the reactor was cooled to room temperature and vented carefully to the exhaust line. The remaining solution was analysed by GC-MS. Additional the reaction solution was evaporated remaining the crude product and the catalyst. Extraction of the product with diethyl ether (Et_2O) leads to the pure product which was analysed by NMR.

General procedure for the intermolecular PKR using PEG_{1000}-stabilized cobalt nanoparticles (entries 4-7 Table 2).

A solution of PEG_{1000}-stabilized cobalt nanoparticles (12 mg, 1.1 10^{-2} mmol) in CH_2Cl_2 was added to a dry and degassed window equipped 10 mL stainless steel autoclave under counter current flow of argon. The solvent was evaporated under vacuum at room temperature. A solution of alkyne (22.7 10^{-2} mmol) (except for substrat **8**, 34.0 10^{-2} mmol were used) and norbonene **7** (34.0 10^{-2} mmol, 1.5 eq.) was added. The reactor was charged with 25 bar of CO at room temperature and heated under stirring to 130 °C for 16 h. Under reaction conditions the pressure in the autoclave increased to 35 bar. After the reaction, the reactor was cooled to room temperature and worked up as described above.

General procedure for the intermolecular PKR using PEG_{5000}-stabilized cobalt nanoparticles (entries 4-7 Table 2).

A solution of PEG_{5000}-stabilized cobalt nanoparticles (60 mg, 1.2 10^{-2} mmol) in CH_2Cl_2 was added to a stainless steel autoclave as described above. The solvent was evaporated under vacuum. A solution of alkyne (23.7 10^{-2} mmol) (except for substrat **8**, 35.6 10^{-2} mmol were used) and norbonene **7** (35.6 10^{-2} mmol, 1.5 eq.) was added. The reactor was charged with 25 bar of CO at room temperature and heated under stirring to 130 °C for 16 h. Under reaction conditions the pressure in the autoclave increased to 35 bar. After the reaction, the reactor was cooled to room temperature and worked up as described above. Extraction with Et_2O leads to the pure product which was analysed by NMR.

General procedure for the PKR in water using $PEG_{1000}(OMe)_2$ stabilized cobalt nanoparticles (Scheme 2).

A solution of PEG_{1000}-stabilized cobalt nanoparticles (125.0 mg, 11.8 10^{-2} mmol) and **1** (80.0 mg, 33.6 10^{-2} mmol) in 2 mL CH_2Cl_2 was added to a dry and degassed window equipped 10 mL stainless steel autoclave under counter current flow of argon. After evaporation of the solvent 2.5 mL H_2O were added. The reactor was charged with 15 bar of CO at room temperature and heated under stirring at 130 °C for 16 h. Under reaction conditions the pressure in the autoclave increased to 25 bar. After the reaction the reactor was cooled to room temperature and vented carefully to the exhaust line. The remaining aqueous phase was extracted three times with 4 mL Et_2O. The combined organic phases were dried over $MgSO_4$, concentrated and analysed by GC-MS. The separation of the side product **16** from the product mixture was achieved by preparative thin layer chromatography (Pentane/CH_2Cl_2; 1/10). **16** was characterised by NMR.

Characterisation of the products

Diethyl-3,3a,4,5-tetrahydro-5-oxopentalene-2,2(1H)-dicarboxylate **2**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (q, 6 H), 1.67 (t, 1 H), 2.10 (m, 2 H), 2.53-2.77 (m, 2 H), 3.24 (q, 2 H), 4.17 (m, 4 H), 5.87 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0, 34.1, 37.9, 41.1, 44.0, 59.8, 61.1, 124.6, 170.5, 184.7, 208.7. MS (EI) m/z (%): 266 (4.7 %, M^+), 244 (27.0 %), 221 (4.7 %, M^+-C_2H_5O), 215 (B), 192 (8.8 %, M^+-C_2H_6), 119 (20.0 %, M^+-147), 93 (61.2 %), 65 (25.3 %), 55 (24.7 %).

Diethyl-3,3a,4,5-tetrahydro-6-methyl-5-oxopentalene-2,2(1H)-dicarboxylate **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (q, 6 H), 1.58 (m, 1 H), 1.65 (s, 3 H), 2.05 (d, 2 H), 2.53-2.75

(m, 2 H), 3.13 (m, 2 H), 4.16 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.5, 14.0, 34.0, 39.7, 41.39, 42.7, 61.0, 61.9, 126.1, 171.0, 177.8, 209.4. MS (EI) m/z (%): 280 (22.0 %, M^+), 235 (10.8 %, M^+-C_2H_5O), 206 (70.8%, M^+-$C_4H_{10}O$), 178 (21.7 %, M^+-$C_5H_{11}O_2$), 133 (B, M^+-$C_6H_{10}O_4$), 105 (40.4 %), 91 (25.0 %).

4,5,6,6a-tetrahydro-5,5-bis(hydroxymethyl)pentalen-2(1H)-one **6** : ^{1}H NMR (300 MHz, DMSO): δ = 1.02 (t, 2 H), 1.93 (m, 2 H), 2.47 (d, 2 H), 3.28 (m, 1 H), 3.42 (m, 4 H), 4.63 (t, 1 H), 4.74 (t, 1H), 5.79 (s, 1 H). ^{13}C NMR (75 MHz, DMSO): δ = 32.8, 35.8, 42.3, 44.0, 51.4, 65.3, 123.63, 191.0, 209.7. MS (EI) m/z (%): 182 (32.5 %, M^+), 164 (10 %, M^+-H_2O), 136 (37.5 %, M^+- C_2H_5O), 134 (50.0%, M^+-CH_4O_2), 133 (B) , 117 (32.5 %), 108 (30.0 %, M^+-$C_3H_6O_2$), 107 (37.5 %), 105 (77.5 %), 95 (43.7 %, M^+-$C_4H_9O_2$), 92 (26.2 %), 91 (99.0 %), 82 (31.5 %), 79 (53.7 %), 77 (50.0 %), 67 (24.8 %, M^+-$C_6H_{11}O_2$), 66 (40,0 %), 65 (30.0 %), 55 (40.0 %). HRMS (EI): calcd. for $C_{10}H_{14}O_3$: 182.0937, found: 182.0942. IR (KBr): n = 3393 (s), 3009 (m), 2924 (m), 2873 (m), 1694 (s, -CO), 1628 (s, -C=C-), 1414 (m), 1264 (w), 1218 (w), 1178 (m), 1032 (s), 890 (w), 834 (w), 757 (s), 667 (w) cm^{-1}.

2-Phenyl-3a,4,5,6,7,7a-hexahydro-4,7-methano-inden-1-on **9**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (m, 2 H), 1.23 (m, 2 H), 1.53 (m, 2 H), 2.15 (m, 1 H), 2.25 (m, 1 H), 2.39 (m, 1 H), 2.57 (m, 1 H), 7.27 (m, 3 H), 7.52 (d, 1 H), 7.61 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ =28.4, 29.2, 31.3, 38.4, 39.5, 47.7, 55.0, 127.1, 128.4, 131.6, 146.1, 160.3, 209.0. MS (EI) m/z (%): 225 (15.0%), 224 (B, M^+), 196 (17.5 %), 167 (17.5 %), 158 (91.7 %), 156 (67.5 %), 129 (18.6 %), 128 (47.5 %), 115 (37.0 %), 103 (13.45 %), 102 (33.5 %), 91 (27.5 %), 77 (35.0 %), 67 (78.5 %), 66 (25,0 %), 51 (20.0 %).

2-(3-Hydroxy-propyl)-3a,4,5,6,7,7a-hexahydro-4,7-methano-inden-1-on **11**: ^{1}H NMR (300 MHz, DMSO): δ = 0.91 (m, 2 H), 1.26 (m, 2 H), 1.58 (m, 4 H), 2.11 (m, 5 H), 2.57 (s, 1 H), 3.36 (m, 2 H), 4.44 (t, 1 H), 7.27 (s, 1 H). ^{13}C NMR (75 MHz, DMSO): δ = 20.8, 27.8, 28.5, 30.57, 30.63, 37.4, 38.4, 47.4, 52.9, 60.2, 148.1, 159.1, 209.8. MS (EI) m/z (%): 206 (36.5 %, M^+), 188 (93.6 %, M^+-H_2O), 173 (33.33 %, M^+-H_2O_2), 150 (39.7 %), 145 (30.15 %), 131 (21.0 %, M^+-$C_3H_7O_2$), 122 (77.8 %, M^+- C_5H_8O), 105 (30.16 %), 91 (B), 77 (58.7 %), 67 (71.4 %), 53 (23.8 %), 41 (42.8 %), 31 (22.7 %).

2-Propyl-3a,4,5,6,7,7a-hexahydro-4,7-methano-inden-1-on **13**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (m, 5 H), 1.27 (m, 2 H), 1.42 (m, 2 H), 1.59 (m, 2 H), 2.11 (m, 4 H), 2.36 (m, 1 H), 2.55 (m, 1 H), 7.09 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 21.1, 26.7, 28.4, 29.1, 31.0, 38.0, 40.0, 48.1, 53.9, 149.2, 158.9, 211.3. MS (EI) m/z (%): 190 (B, M^+); 175 (32.5 %, M^+-CH_3); 162 (55%, M^+-CO), 161 (62.5%, M^+-C_2H_5); 147 (31%, M^+-C_3H_7), 124 (56%), 95 (50%, M^+-C_6H_8O), 91 (67.5%), 79 (60%), 67 (31%).

2-Hexyl-3a,4,5,6,7,7a-hexahydro-4,7-methano-inden-1-on **15**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (m, 5 H), 1.19 (m, 8 H), 1.36 (m, 2 H), 1.52 (m, 2 H), 2.05 (m, 4 H), 2.30 (m, 1 H), 2.49 (m, 1 H), 7.03 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.5, 24.7, 27.8, 28.4, 29.1, 31.0, 31.6, 38.0, 39.0, 48.1, 53.9, 149.5, 158.7, 211.3. MS (EI) m/z (%): 232 (34.8 % M^+), 203 (19.6 %, M^+-C_2H_5), 189 (12.7 %, M^+-C_3H_7) 175 (15.2%, M^+-C_4H_5), 163 (B), 91 (34.2 %), 67 (34.3 %), 41 (21.0%).

1,2,4,5,6,6a-Hexahydro-2-oxopentalen-5-yl propionat **16**:

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.30 (q, 3H), 1.45 (ddd, 1H), 2.65 (dd, 1H), 2.52 (m, 1H), 2.65 (m, 1H), 2.95 (m, 1H), 3.02 (m, 1H), 3.28 (m, 1H), 4.2 (q, 2H), 5.95 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 18.0, 30.1, 35.0, 35.3, 42.1, 44,2, 61.0, 125.6, 174.3, 187,5, 210,1. MS (EI) m/z (%): 194 (9.5 %, M^+), 166 (18.9 %, M^+-CO), 149 (17.6 %, M^+-CO_2), 137 (4.0 %, M^+-C_2H_5O), 121 (79.0 %, M^+-$C_2H_5O_2$), 93 (B), 91 (63.5 %), 77 (29.7 %), 65 (14.2 %), 51 (8.1 %), 39 (20.9 %). HRMS (EI): calcd. for $C_{11}H_{14}O_3$: 194.0937, found: 194.0943.

([i]) D. D. Perrin, W. L. F. Armarego, *Purification of Labroatory Chemicals*, Pergamon Press 1988.