Supplementary information

Adapting a Wacker-Type Catalyst System to the Palladium-Catalyzed Oxidative Carbonylation of Aliphatic Polyols

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Experimental

Materials and instrumentation: All reagents and solvents were purchased from commercial suppliers (Table 1) and used as received.

Table 1. Source and purity of reagents obtained from commercial suppliers

Chemical	Supplier	Purity [a] / %
Dimethyl ethylene glycol (DME)	Sigma Aldrich	99.9
Ethylene glycol (EG)	Sigma Aldrich	99.8
Propylene glycol (PG)	Sigma Aldrich	99.5
Phenylethylene glycol (PEG)	Sigma Aldrich	97
Ethylene carbonate (EC)	Sigma Aldrich	>99.0
Propylene carbonate (PC)	Fluka	99.7
Palladium(II)acetate	Sigma Aldrich	>99.9
Palladium(II)bromide	Sigma Aldrich	99
Palladium(II)chloride	Alfa Aesar	99.9
Copper(II)chloride	Sigma Aldrich	>99.9
Sodium acetate	Sigma Aldrich	>99.0
Potassium bromide	ABCR	>99.9
Manganese(III)acetylacetonate	Sigma Aldrich	tech.
Potassium chloride	Fisher Scientific	>99
Lithium chloride	Sigma Aldrich	>99.0
Triethylamine	Fluka	>99.5
Gas mixture $CO/O_2/N_2$	Air Products	5.99:2.99:91.02
Tetrabutylammonium bromide (TBAB)	Fluka	>99.0
Diethylene glycol dimethyl ether	Sigma Aldrich	99.5

[a] minimum purity as stated by the manufacturer

Gas chromatographic analyses were performed on a Focus GC-Thermo Scientific or Siemens SiChromat 1-4 gas chromatograph. For HPLC analysis, a Jasco instrument was used (pump = PU-2080*Plus;* degaser = DG-2080-54; gradient = LG-2080-04S; autosampler = AS-2055*Plus;* Diode-Array-Detector = MD-2010*Plus;* RI-Detector = RI-2031*Plus)*

Oxidative carbonylation of diols: The experiments were performed in 20 mL stainless steel autoclaves equipped with thermocouple, glass liner and magnetic stirring bar. In a typical experiment, the glass liner was charged with ethylene glycol (56 mg, 0.9 mmol), KBr (10.7 mg, 0.09 mmol), $Pd(OAc)_2$ (0.71 μmol, 200 μL, 3.56 mM in DME), $Mn(acac)_3$ (5.0 mg, 14.3 μmol) and DME (2 mL). The autoclave was purged three times with argon (4 bar) and subsequently pressurized with 20 bar of a gas mixture $CO:O_2:N_2$ (6:3:91). The reaction mixture was stirred with 300 rpm at 60 °C. After 20 h, the autoclave was cooled down and the pressure released. Diethylene glycol dimethyl ether (DiglyMe) (0.70 mmol, 100 μL) was added as internal standard for gas chromatography and the solution filtered through a polyamide filter with a pore size of 0.20 μm.

The conditions for gas chromatographic analysis of ethylene glycol (EG), propylene glycol (PG), 3-methoxypropane-1,2-diol (MG) were as follows: CP-Wax-58-CB column, inlet temperature = 250 °C, initial temperature = 50 °C (5 min), 50-180 °C with a ΔT (10 °C/min) and 180 °C (27 min), FID temperature = 250 °C; t_{EG} = 14.97 min, t_{PG} = 14.42 min, t_{MG} = 16.91 min, $t_{EG\text{-}carbonate}$ = 18.82 min, $t_{PG\text{-}carbonate}$ = 17.69 min, $t_{MG\text{-}carbonate}$ = 21.39 min, $t_{DiglyMe}$ = 10.58 min.

Phenyl ethylene glycol (PEG) was analysed at the following conditions: Rtx-5-Sil-MS column, inlet temperature = 250 °C, initial temperature = 80 °C (5 min), 80-300 °C with a ΔT (12 °C/min) and 180 °C (27 min), FID temperature = 300 °C; t_{PEG} = 10.74 min, $t_{PEG\text{-}carbonate}$ = 13.10 min, $t_{DiglyMe}$ = 3.76 min.

Oxidative carbonylation of glycerol: The experiments were performed in 200 mL stainless steel autoclaves equipped with thermocouple and magnetic stirring bar. In a

typical experiment, the autoclave was charged with glycerol (492 mg, 5.34 mmol), KBr (212 mg, 1.78 mmol), $Pd(OAc)_2$ (4.0 mg, 17.8 μmol), $Mn(acac)_3$ (126 mg, 360 μmol), and ethyl acetate (100 mL). The autoclave was purged three times with argon (4 bar) and subsequently pressurized with 20 bar of a gas mixture $CO:O_2:N_2$ (6.3:91). The reaction mixture was stirred with 300 rpm at 60 °C. After 20 h, the autoclave was cooled down and the pressure released. The solution was filtered trough a polyamide filter with a pore size of 0.20 μm.

Selectivity and conversion were determined by HPLC (Showa Denko - Sugar SH1011 column, oven temperature = 20 °C, flow = 1.0 mL/min, eluent: 0.01% acetic acid in water, $t_{glycerol}$ = 9.91 min, $t_{glycerol\text{-}carbonate}$ = 14.39 min).

Results and additional data

In order to assess the role of KBr, a series of tests at different Pd:KBr ratios was carried out. The catalyst productivity significantly increased, when KBr was used as additive in a Pd:KBr ratio of 1:5. Surprisingly, further increase in the KBr concentration hardly affected the catalyst productivity in the Pd:KBr range of 1:5 to 1:500 (Table 2).

Table 2. Effect of the Pd/KBr ratio on the oxidative carbonylation of **1a**[a]

Entry	Pd/KBr	TON
1	1/0	13.6
2	1/5	117
3	1/10	109
4	1/50	105
5	1/100	123
6	1/500	113

[a] *Reaction conditions*: $[\mathbf{1a}]^0$ = 0.45 mM, **1a**:$Pd(OAc)_2$:$Mn(acac)_3$ = 1250:1:20, solvent = DME (2 mL), T = 60 °C, 20 bar $CO:O_2$: N_2 (6:3:91), reaction time = 2 h.

The effect of various additives such as KCl, LiCl and tetrabutylammonium bromide (TBAB) on the performance of the catalyst in the oxidative carbonylation of **1a** was also explored (Table 3). Potassium bromide provided the highest turnover numbers.

Table 3. Effect of different additives on the oxidative carbonylation of **1a**[a]

Entry	Additive	TON
1	-	17
2	NaOAc[b]	17.4
3	TBAB	23
4	KBr	123
5	KCl	32
6	LiCl	45

[a] *Reaction conditions*: $[\mathbf{1a}]_0$ = 0.45 mM; **1a**:$Pd(OAc)_2$:$Mn(acac)_3$:additive = 1250:1:20:100; solvent = DME (2 mL); T = 60 °C, 20 bar $CO:O_2:N_2$ (6:3:91); time = 2 h.
[b] $Pd(OAc)_2$:additive = 1/1000, reaction time = 20 h