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Adapting a Wacker-type catalyst system to the palladium-catalyzed oxidative carbonylation of aliphatic polyols[†]

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Polyols, which can be obtained readily from bio-feedstock, are converted efficiently into their corresponding cyclic carbonates by using a Wacker-type Pd/Mn catalyst system. A fine tuned redox cascade is essential in ensuring a high productivity of the Pd catalyst in the oxidative carbonylation reaction. Turnover numbers up to 784 mol_{product}/mol_{palladium} were achieved.

Converting biomass into industrially applicable chemicals will make an important contribution to the pursuit of a sustainable society.¹ Using the carbohydrate fraction of biomass (starch, cellulose, hemicellulose) as feedstock is particularly appealing, as it can be converted readily to a variety of platform chemicals such as substituted ethylene glycols, glycerol, erythritol and sorbitol.² Due to their increasing availability, these polyols attract the interest of academia and industry.³ Some polyol derivatives, such as cyclic carbonates, are applied widely in the chemical industry as emulsifiers in cosmetics, bio-lubricants, solvents and as monomers and cross-linkers for bio-based polymers. Among the most important cyclic carbonates are ethylene carbonate and propylene carbonate.4 Since the starting material ethylene stems from fossil resources, it would be highly desirable from an environmental point of view to develop alternative routes to cyclic carbonates.^{5,6} Particularly appealing is the direct oxidative carbonylation of bio-derived ethylene glycol with CO/O₂-mixtures.⁷ Oxidative carbonylation of more complex polyols can also provide access to other cyclic carbonates.

The oxidative carbonylation of aliphatic 1,2-diols using homogeneous palladium catalysts and either copper(II)chloride or oxygen as oxidant (Scheme 1) has been reported.^{7,8} During

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Scheme 1 During the oxidative carbonylation of 1,2-diols 1a-c to cyclic carbonates 2a-c two oxidation equivalents (Ox) are converted to their reduced and protonated form (HOx).

the coupling of the diol with carbon monoxide two electrons are released, whereby Pd(II) is reduced to Pd(0). While the direct re-oxidation of Pd(0) species with molecular oxygen is slow,⁹ the re-oxidation of Pd(0) with third-row transition metal co-catalysts can be a very fast reaction. The co-catalyst in turn can be re-oxidised with molecular oxygen. A Pd/Cu redox couple is, *e.g.*, at the basis of industrially relevant processes such as the Wacker oxidation of olefins.¹⁰

In the current study, we show how the application of such a coupled redox catalyst system provides a highly efficient synthetic protocol for converting polyols to cyclic carbonates. We envisaged to utilize a redox cascade (Scheme 2) similar to the one reported for the oxidative carbonylation of phenol.^{11,12} Concurrently with the transformation of the 1,2-diol to the corresponding cyclic carbonate, the Pd(II) catalyst is reduced to Pd(0). Later it is then re-oxidized by a transition metal co-catalyst, which is regenerated by reaction with molecular oxygen. Such a redox cascade has not been explored for the oxidative carbonylation of diols so far.



Scheme 2 Redox cascade for the oxidative carbonylation of 1,2-diols using a Pd/Mn catalyst system.

In this work, various co-catalysts, such as $CuCl_2$ and manganese(III)acetylacetonate (Mn(acac)₃) were evaluated in the oxidative carbonylation of **1a**. Also the role of additives and solvent was investigated and the optimized procedure applied to the oxidative carbonylation of a series of di- and triols.

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Table 1 Influence of the choice of the co-catalyst on the catalyst productivity in the oxidative carbonylation of $1a^{\alpha}$

Entry	Co-catalyst	Additive	TON
1	CuCl ₂	NaOAc	12
2	$Mn(acac)_3$	NaOAc	7
3	_ `	NaOAc	5
4 ^b	CuCl ₂	KBr	20
5 ^b	$Mn(acac)_3$	KBr	255
6 ^b		KBr	30

^{*a*} Reaction conditions: $[1a]^0 = 0.45 \text{ mM}, 1a: Pd(OAc)_2: co$ $catalyst: NaOAc = 1250: 1: 20: 1000, solvent = DME, <math>T = 60 \degree C$, 20 bar CO: $O_2: N_2$ (6: 3: 91), time = 20 h. ^{*b*} 1a: Pd(OAc)_2: co-catalyst: KBr = 1250: 1: 100: 1000.

We started our investigations by carrying out the oxidative carbonylation experiments under the conditions developed by Tam,⁷ with the variant that molecular oxygen was used as the oxidant, while CuCl₂ was employed in sub-stoichiometric amounts, in a Pd: Cu ratio of 1: 20 (Table 1, entry 1). Compared to the reference system, the loading of the palladium precursor was decreased to reduce Pd(0) aggregation. By following this new procedure, the reaction proceeded although with a low catalyst productivity (TON = 12 with respect to palladium). Under the same conditions, the use of Mn(acac)₃ instead of CuCl₂ gave an even lower TON of 7 (Table 1, entry 2). Interestingly, when the additive NaOAc was replaced by KBr, Mn(acac)₃ greatly outperformed CuCl₂ resulting in a TON of 255 (Table 1, entries 4-5), which means that every Mn ion was utilized on average 11 times. In the absence of co-catalyst much lower catalyst productivities were obtained (Table 1, entries 3 and 6).

This series of experiments clearly shows that in consistency with the concept (Scheme 2) the combination of a palladium catalyst with an appropriate co-catalyst provides a highly efficient system for the oxidative carbonylation of ethylene glycol **1a** with molecular oxygen as the oxidation agent. The higher TON obtained with $Mn(acac)_3$ compared to $CuCl_2$ indicates that it provides the right redox potential within the redox cascade. A low efficiency of $CuCl_2$ for the oxidative carbonylation of **1a** was also reported by Tam,⁷ who suggested that the substrate binds strongly to the copper ions and thus makes itself inaccessible to the Pd catalyst.

The use of KBr as an additive also seems to be essential. Even in the absence of co-catalyst, higher catalyst productivities were achieved with KBr as the additive compared to NaOAc. As the effectiveness of the two co-catalysts under study varied significantly in relation to the additive, it prompted us to evaluate several other additives such as KCl, LiCl and tetrabutylammonium bromide.^{13,14} None of these additives used in combination with Mn(acac)₃, was superior to KBr (see supplementary information†).

In order to assess the role of KBr in more detail, a series of tests at different Pd : KBr ratios was carried out. The amount of KBr barely affected the catalyst productivity in the Pd : KBr range of 1 : 5 to 1 : 500 and a constant TON between 105 and 123 was observed at a reduced reaction time of 2 h (see supplementary information†). A Pd : KBr ratio of 1 : 5 was adequate to achieve a TON of 117. This is equivalent to a catalyst activity (TOF) of 59 mol_{substrate}/mol_{palladium}/h. When KBr was omitted, a much lower TON of 14 was obtained.

Table 2 Solvent effect and substrate scope in the oxidative carbonylation of $1a-c^{\alpha}$

Entry	Substrate	Solvent	TON
1	1a	DME	255
2	1b	DME	342
3	1c	DME	91
4	1a	THF	784
5	1a	Me-THF	697
6	1a	Ethyl acetate	775
7	1b	Ethyl acetate	615
8	1c	Ethyl acetate	231

^{*a*} Reaction conditions: $[1]^0 = 0.45 \text{ mM}$, $1 : Pd(OAc)_2 : Mn(acac)_3 : KBr = 1250 : 1 : 20 : 100$, solvent (2 mL), $T = 60 \degree C$, 20 bar CO : $O_2 : N_2 (6 : 3 : 91)$, time = 20 h.

We noted that in experiments carried out in 1,2dimethoxyethane (DME) with Mn(acac)₃ as the co-catalyst a brown solid was present at the end of the reaction. Given that the mass balance of reactants and products was close to quantitative (\geq 98%), the formation of insoluble polycarbonates is excluded. Also, no side products were observed by gas chromatography. We speculate that a coordination compound containing Mn-DME units was formed. To test this hypothesis, a series of non-chelating aprotic polar solvents, namely THF, Me-THF and ethyl acetate were evaluated under the reaction conditions reported above. The transformation benefited largely from the change of reaction media, since TONs close to or higher than 700 were attained (Table 2, entries 4–6). This corresponds to catalyst activities of 35–39 mol_{substrate}/mol_{palladium}/h over a longer period of time (20 h). Clearly, non-chelating solvents are beneficial.

Substituted ethylene glycols such as methyl ethylene glycol 1b and phenyl ethylene glycol 1c were also evaluated. While in ethyl acetate the productivity decreased in the sequence 1a > 1b > 1c (Table 2, entries 6–8), the trends were not as clear in DME (Table 2, entries 1–3). The steric requirement of the substituent R apparently plays an important role.

Several Pd salts were evaluated in the absence of additives (Table 3). Also in this case, $PdBr_2$ was most efficient (Table 3, entry 3) indicating that the presence of bromide ions is essential to achieve a good catalyst performance. Note that the combination of $Pd(OAc)_2$ and KBr (Table 3, entry 4) clearly outperformed $PdBr_2$. A similar, PdI_2 -KI catalyst system had been reported by Gabriele *et al.* for the oxidative carbonylation of various aliphatic diols with oxygen as the sole oxidant.⁸ However, when we used KI as additive under our conditions, the results remained inconclusive.

Table 3 Influence of the palladium precursor on the conversion obtained in the oxidative carbonylation of $1a^{\alpha}$

Entry	Catalyst	Additive	TON
1	Pd(OAc) ₂	_	13
2	PdCl ₂	_	5
3	$PdBr_2$	_	91
4 ^b	$Pd(OAc)_2$	KBr	123

^{*a*} Reaction conditions: $[1a]^0 = 0.45 \text{ mM}$, $1a : Pd(OAc)_2 : Mn(acac)_3 = 1250 : 1 : 20$, solvent = DME (2 mL), $T = 60 \, ^\circ C$, 20 bar $CO : O_2 : N_2 \ (6 : 3 : 91)$, time = 2 h. ^{*b*} $1a : Pd(OAc)_2 : Mn(acac)_3 : KBr = 1250 : 1 : 20 : 100$.

As the combination of Pd(OAc)₂ and KBr provided the best productivities, we assume that a palladium salt with mixed anions forms the active species (Scheme 3). In the first step, the diol coordinates to the palladium,⁸ whereby HBr is released concurrently. Insertion of carbon monoxide into the Pd-O bond provides a (2-hydroxyethoxy)carbonyl ligand, which reductively eliminates with the neighbouring bromide ligand. The eliminated 2-hydroxyethyl carbonobromidate undergoes a rapid intramolecular nucleophilic attack,¹⁵ whereby the cyclic carbonate is formed thereby releasing HBr. During the reductive elimination step,¹¹ the Pd(II) centre is reduced to Pd(0) and is subsequently re-oxidised with two Mn(III) to the active palladium salt with a mixed ligand sphere. The Mn(II) in turn is re-oxidised with molecular oxygen.



Scheme 3 Catalytic cycle proposed for the oxidative carbonylation of ethylene glycol with a Pd/Mn redox couple.

To expand the substrate scope, other polyols such as glycerol 3a and 3-methoxypropane-1,2-diol 3b were evaluated as substrates (Scheme 4). The direct oxidative carbonylation of 3a (Table 4, entry 1) in ethyl acetate as the solvent resulted in a low TON. Note that 3a is poorly soluble in ethyl acetate and the formation of a two phase system might be the origin of the low catalyst productivity. When the solvent was changed to acetone (Table 4, entry 2), the TON improved significantly. No side products were observed. In comparison to Li et al.,¹⁶ who reported the catalytic oxidative carbonylation of 3a at 140 °C in DMF as a high boiling solvent, our protocol allows for the conversion of 3a at much milder conditions. In a reference experiment, whereby the Pd catalyst was omitted, no glycerol carbonate was formed, confirming that manganese salts do not induce glycerol carbonate formation. For 3b, the catalyst productivity was similar in the two solvents ethyl acetate and acetone (Table 4, entries 3-4).



bR=Me

Scheme 4 Oxidative carbonylation of glycerol 3a and 3-methoxypropane-1,2-diol 3b.

Table 4 Direct oxidative carbonylation of glycerol 3a and 3methoxypropane-1,2-diol 3ba

thyl acetate 12
cetone 75
thyl acetate 219
cetone 220

^{*a*} Reaction conditions: $[3]_0 = 0.45 \text{ mM}; 3: Pd(OAc)_2: Mn(acac)_3: KBr =$ 300: 1: 20: 100; solvent (2 mL); $T = 60 \degree C$, 20 bar CO: $O_2: N_2 (6: 3: 91)$; time = 20 h

In conclusion, the use of a Wacker-type Pd/Mn redox catalyst system provides an efficient and mild protocol for the oxidative carbonylation of di- and triols. A high catalyst productivity (TON up to 784 mol_{substrate}/mol_{palladium}) and activity (TOF up to 61 mol_{substrate}/mol_{palladium}/h) were achieved. We demonstrated that molecular oxygen can be used as the oxidation agent. A transition metal-based co-catalyst is essential in ensuring high catalyst productivities in this transformation. The choice of environmentally more benign solvents such as Me-THF and ethyl acetate provided the base for excellent catalyst performance.

These results are a step forward towards the development of an industrial route alternative to the existing fossil-based production of cyclic carbonates. Currently, ethylene carbonate is produced in a two-step process involving first the oxidation of ethylene to the corresponding epoxide, which is then reacted with CO₂.⁴ Likewise, glycerol carbonate is produced conventionally by condensation of phosgene with glycerol.⁵ Also established is the transesterification of glycerol with dimethylcarbonate or urea.5 The direct oxidative carbonylation of polyols represents a promising and more direct alternative to these routes.

Currently, we are investigating the application of this protocol to the oxidative carbonylation of higher polyols such as erythritol and sorbitol.

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Notes and references

- 1 J. J. Bozell and G. R. Petersen, Green Chem., 2010, 12, 539-554.
- 2 A. L. Marshall and P. J. Alaimo, Chem.-Eur. J., 2010, 16, 4970-4980.
- 3 A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, Green Chem., 2008, 10, 13-30.
- 4 H. A. Wittcoff, B. G. Reuben and J. S. Plotkin, Industrial Organic Chemistry, Wiley-Interscience, New Jersey. 2004, Ch. 3.
- 5 M. Aresta, A. Dibenedetto, F. Nocito and C. Ferragina, J. Catal., 2009, 268, 106-114
- 6 K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. T. Li and K. Kunimori, Green Chem., 2004, 6, 206-214.
- 7 W. Tam, J. Org. Chem., 1986, 51, 2977-2981.
- 8 B. Gabriele, R. Mancuso, G. Salerno, G. Ruffolo, M. Costa and A. Dibenedetto, Tetrahedron Lett., 2009, 50, 7330-7332 and references therein.
- 9 S. S. Stahl, Angew. Chem., Int. Ed., 2004, 43, 3400-3420.

- 10 J. A. Keith and P. M. Henry, Angew. Chem., Int. Ed., 2009, 48, 9038– 9049.
- 11 H. Yasuda, J. C. Choi, S. C. Lee and T. Sakakura, *Organometallics*, 2002, **21**, 1216–1220.
- 12 A. Vavasori and L. Toniolo, J. Mol. Catal. A: Chem., 1999, 139, 109–119.
- 13 J. Gong, X. Ma and S. Wang, Appl. Catal. A, 2006, 316, 1–21.
- 14 L. Ronchin, A. Vavasori, E. Amadio, G. Cavinato and L. Toniolo, J. Mol. Catal. A: Chem., 2009, 298, 23–30.
- 15 For acyliodides as corresponding reaction intermediates, refer to the mechanism of methanol carbonylation; see, e.g., D. Forster, J. Chem. Soc., Dalton Trans., 1979, 1639.
- 16 J. Hu, J. Li, Y. Gu, Z. Guan, W. Mo, Y. Ni, T. Li and G. Li, *Appl. Catal.*, A, 2010, **386**, 188–193.