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Electronic Supplementary Information

Synthesis of carbonates by catalytic reaction of phenol and methyl formate as alternative to the use of carbon monoxide

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S1. Experimental details for the oxidative carbonylation of phenol with MF

All the reagents and solvents were purchased from commercial suppliers and were used as received.

Reagents used in the study

Chemical	**Supplier**	**Purity (%)**
Phenol	Sigma-Aldrich	99
$NaOCH_3$	Fluka	97
$KOCH_3$	Sigma-Aldrich	95
Methyl formate	Sigma-Aldrich	99
Tetrabutyl ammonium bromide	Sigma-Aldrich	99
Benzoquinone	Sigma-Aldrich	98
$PdBr_2$	Sigma-Aldrich	99
$Mn(acac)_3$	Sigma-Aldrich	Technical grade
CH_2Cl_2	Sigma-Aldrich	99.8
Methanol	Carl Roth	99.8
Molecular Sieves 3Å	Sigma-Aldrich	-
$Pd(OAc)_2$	Sigma-Aldrich	99.9
Pd on Carbon	Sigma-Aldrich	10
Pd on Carbon	Sigma-Aldrich	5
$PdCl_2(CH_3CN)_2$	Sigma-Aldrich	99
$Ce(OAc)_2$	Sigma-Aldrich	99.9
$CuCl_2$	Sigma-Aldrich	99
$Cu(OAc)_2$	Sigma-Aldrich	98
N,N'-bis(salicylidene)-ethylenediamine	Sigma-Aldrich	98
Ethanol	Sigma-Aldrich	99
Methyl Phenyl Carbonate	Alfa Aesar	97
Lithium methoxide	Sigma-Aldrich	98
Dimethyl oxalate	Sigma-Aldrich	99
Phenyl acetate	Sigma-Aldrich	99

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The protocol for the carbonylation of phenol by MF was as follows: a 160 mL Parr autoclave reactor was charged with MF (45 mL), $NaOCH_3$ (4.68-9.36 mmol), Pd(II) catalyst (0.11 mmol), co-catalyst (0.688mmol), tetrabutyl ammonium bromide (TBAB, 0.55 g, 1.7 mmol), benzoquinone (BQ, 27 mg, 0.25 mmol) and molecular sieves 3Å (MS, 1 g). The reaction mixture was heated to 373 K. After the temperature had stabilized and the internal pressure (P_{in}) became almost constant, the reactor was pressurized with O_2 (7% of P_{in} at 373 K). Immediately thereafter phenol (0.854 g, 9.09 mmol) dissolved in CH_2Cl_2 (10 mL) was injected into the reactor (3.5 mL/min) using a high pressure HPLC pump. The injection of phenol was considered as start of the reaction (t = 0). After 3h the reaction was terminated by cooling the reactor with ice-water. The autoclave was opened and the reaction products were analysed by Gas Chromatography (GC)and Gas Chromatography–Mass Spectrometry (GC-MS).

Synthesis of the Pd(salen) catalyst: $PdCl_2(CH_3CN)_2$ (85.5 mg, 0.33 mmol) and salen (*N*,*N*′-bis(salicylidene)-ethylenediamine, 88.5 mg, 0.33 mmol) were dissolved in ethanol (30 mL). The solution was stirred for 16 h at room temperature (25±2 °C). After 16 h, a yellow precipitate was obtained, which was dried in a partial vacuum.

The method used for GC analysis was as follows:
Instrument: Thermo SCIENTIFIC TRACE GC Ultra, column: OV1-IVA (50 m × 0.25 mm × 0.5 μm); 50-250 °C, 5 min isothermal, 8 °C/min, 30 min isothermal; FID 250 °C; t_{PhOH}: 14.26 min, t_{MPC}: 17.71, t_{DMO}: 10.08 min.
The method used for GC-MS analysis was as follows:
Instrument: VARIAN CP3800 gas chromatograph - VARIAN 1200L Quadrupole MS/MS; column: SE34 (30m × 0.32 mm);50-250 °C, 5 min isothermal, 8 °C/min, 30 min isothermal; FID 250 °C.

The details for the experiments listed in Table 1 of the main text are given in Table S2

Table S1. Carbonylation of phenol by MF using different redox catalysts

No.	Catalyst	Co-catalyst	P_{CO} at 100 °C (bar)	Solvent	Phenol Conversion (mmol)	Phenol Conversion (%)	Amount of MPC (mmol)	Selectivity to MPC (%)
1	$PdBr_2$	$Mn(acac)_3$	67-69	DCM[a]	0.145	1.6	0.137	94.5
10	$PdBr_2$	$Mn(acac)_3$	67-69	DMF[b]	0.127	1.4	0.119	93.6
11	$PdBr_2$	$Mn(acac)_3$	67-69	THF[c]	0.099	1.1	0.093	94.4
2	$Pd(OAc)_2$	$Mn(acac)_3$	67-69	DCM	0.154	1.7	0.146	95.2
3	Pd(salen)[c]	$Mn(acac)_3$	67-69	DCM	0.154	1.7	0.140	91.3
4	Pd(10%)/C	$Mn(acac)_3$	67-69	DCM	0.099	1.1	0.093	83.7
5	Pd(5%)/C	$Mn(acac)_3$	67-69	DCM	0.154	1.7	0.116	75.4
6	$Pd(OAc)_2$	$Ce(OAc)_2$	67-69	DCM	0.163	1.8	0.138	85.0
7	$PdBr_2$	$CuCl_2$	67-69	DCM	0.118	1.3	0.114	97.0
8	$Pd(OAc)_2$	$Cu(OAc)_2$	67-69	DCM	0.327	3.6	0.189	57.9
9	$PdCl_2(CH_3CN)_2$	$Cu(OAc)_2$	67-69	DCM	0.209	2.3	0.124	59.7

[a] Dichloromethane, [b] dimethyl formamide, [c] tetrahydrofuran

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S2. Experimental details for the oxidative carbonylation of phenol with CO/CH_3OH

Similar to the reactions with MF, a 160 mL Parr autoclave reactor was charged with MeOH (45 ml), $NaOCH_3$ (0.253 g, 4.68 mmol), Pd(II) catalyst (0.11 mmol), co-catalyst ($Mn(acac)_3$, 0.688 mmol), tetrabutyl ammonium bromide (TBAB, 0.55 g, 1.7 mmol), benzoquinone (BQ, 27 mg, 0.25 mmol) and molecular sieves 3Å (1 g). The reaction mixture was heated to 373 K. After the temperature had stabilized, the reactor was pressurized first with CO and then O_2 to the desired pressure ($P_{(O_2)}$ was 7% of $P_{(CO)}$). Immediately thereafter, phenol (0.854 g, 9.09 mmol) dissolved in CH_2Cl_2 (10 mL) was injected into the reactor (3.5 mL/min) using a high pressure HPLC pump. The injection of phenol was considered as start of the reaction (t = 0). After 3 h, the reaction was terminated by cooling the reactor with ice-water. The autoclave was opened and the reaction products were analysed by GC and GC-MS.

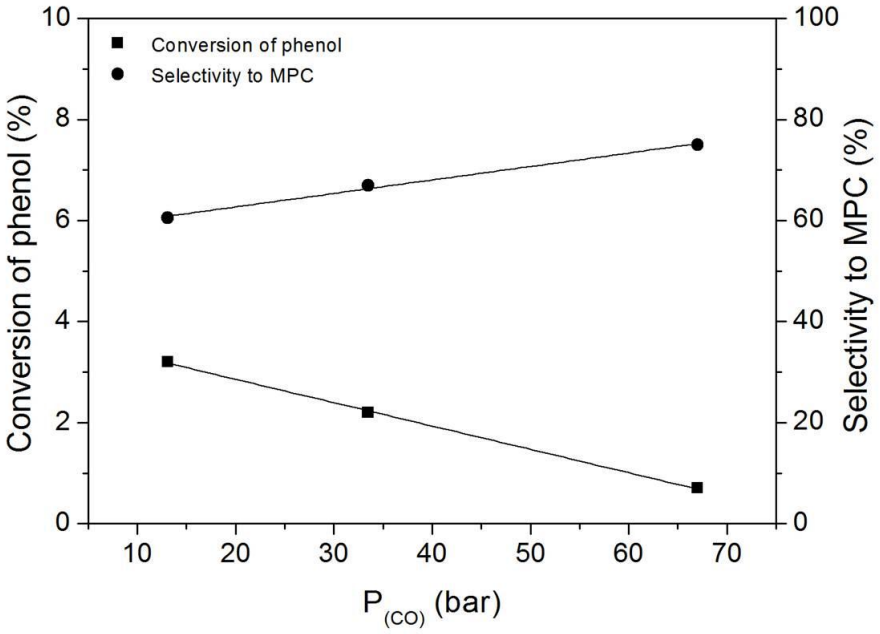
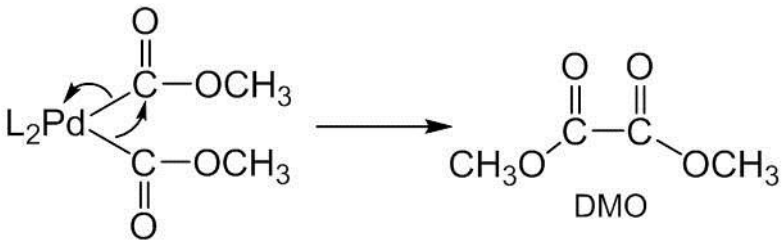


Fig. S1 Oxidative carbonylation of phenol with MF using $KOCH_3$ as catalyst for the activation of MF.



Scheme S1. Proposed structure of the $L_2Pd(COOCH_3)_2$ complex and formation of DMO as by-product in the oxidative carbonylation of phenol with MF

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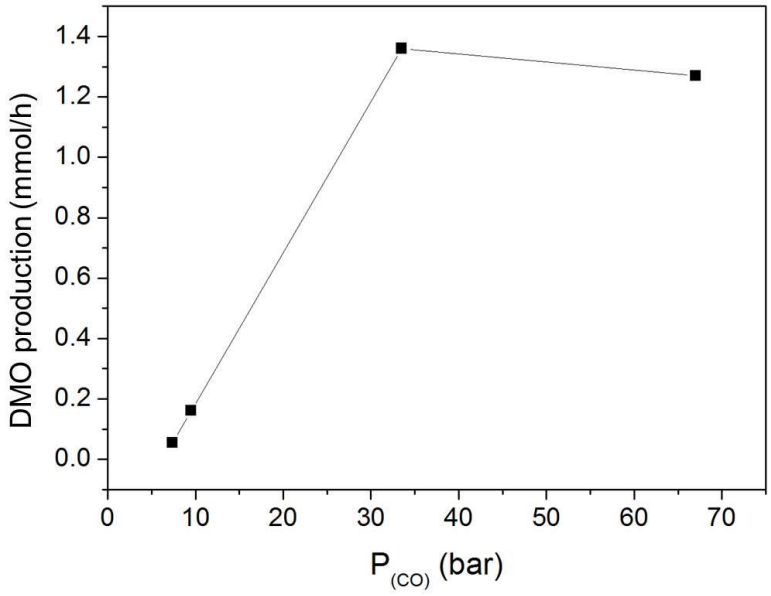

Fig S2 DMO production *vs.*the initial CO pressure during the oxidative carbonylation of phenol with MF