Supporting Information

A direct Synthesis of Carboxylic Acids via Platinum-catalysed Hydroxycarbonylation of Olefins

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Content

General Considerations

All manipulations were carried out under an argon atmosphere using Schlenk-techniques, unless stated otherwise. All glass devices used for synthesis were dried and cooled under vacuum before use. Chemicals were purchased from commercial sources and used as received, if not stated otherwise. Oxygen-free and dry solvents were prepared by distillation or using a solvent purification system by Innovative Technologies.

Catalytic experiments were performed either in a 25-, 100-, or 300-mL Parr autoclave. The reaction screening experiments in the 300 mL autoclave were performed in 4 mL screw cap vials, closed with a polytetrafluoroethylene (PTFE)/white rubber septum (Wheaton 13 mm Septa) and phenolic cap. The connection with the atmosphere was achieved by a needle and stirred with a magnetic stirring bar.

GC measurements were carried out on a 7890A GC-System with a HP-5 column (polydimethylsiloxane with 5% phenyl groups, length 30 m, i.d. 0.32 mm, film 0.25 µm) from Agilent Technologies.

The used Neolephos ligand is a mixture of stereoisomers. For more information see: J. Liu, J. Yang, C. Schneider, R. Franke, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.*, **2020**, *59*, 9032-9040.

Catalytic Experiments

In a typical catalytic experiment, the reactions were performed in 4 mL glass vials charged with $PtCl_2$ (1.0 mol%), Neolephos Ligand (2.2 mol%) rapidly weighed in the air. The atmosphere in the vial was then changed to argon and 1.5 mL acetic acid, 0.5 mL H_2SO_4 [0.6M] were added. Next, liquid substrates (1.0 mmol) were added, and the vials were placed in a metal plate inside a 300 mL autoclave. The reactor was closed and pressurised with nitrogen (about 10 bar), which was released again. This was carried out two times, before the same procedure was done three times with CO (about 10 bar). After the last release, the autoclave was pressurised with 40 bar CO and then heated to 80 °C for 20 h inside an aluminium block. At the end of the reaction the autoclave was placed into an ice bath to cool down and stop the reaction. Finally, the pressure was released, the reactor flushed with N_2 and opened. The reaction solution was analysed by gas chromatography (FID detector).

Catalytic Experiments with Gaseous Starting Materials

Prior to use 20 mmol gaseous starting material were condensed into a metal container with a suitable autoclave connection.

In a typical catalytic experiment with gaseous Starting Materials, the reactions were performed in a 25 mL autoclave with $[M]Cl_2$ (0.5 mol%), Neolephos Ligand (1.1 mol%) rapidly weighed in the air. The atmosphere in the autoclave was then changed to argon and 8.0 mL acetic acid, 4.0 mL H_2SO_4 [0.6M] were added. Next, the condensed substrates (20.0 mmol) were added into the autoclave. The solution was pressurized with 40 bar CO and the reaction mixture was stirred at 80 °C for 24 h inside an aluminium block. At the end of the reaction the autoclave was slowly cooled, and the pressure released. The reaction solution was analysed by gas chromatography (FID detector).

Data for the Optimization of Reaction Conditions

Tab. S1: Catalyst Loading

$PtCl_2$	yield
2.0 mol%	64 %
1.5 mol%	63 %
1 mol%	67 %
0.5 mol%	65 %
0.25 mol%	40 %

Conditions: 1.0 mmol **1a**, X mol% $PtCl_2$, 2.2 mol% **L9**, 0.5 ml H_2SO_4 [0.6 M], in 1.5 mL AcOH, 80 °C, 18 h, 40 bar (CO).

Tab. S2: Acids

acid	yield
H_2SO_4 [0.3 M]	58 %
H_2SO_4 [0.6 M]	72 %
H_2SO_4 [0.9 M]	70 %
Pyridinesulfonic acid (7.5 mol%)*	51 %
PTSA·H_2O (5 mol%) in 0.5 ml H_2O	41 %
PTSA·H_2O (10 mol%) in 0.5 ml H_2O	29 %
Aluminium triflate (5mol%)*	44 %
Aluminium triflate (10 mol%)*	43 %

Conditions: 1.0 mmol **1a**, 1 mol% $PtCl_2$, 2.2 mol% **L9**, acid, in 1.5 mL AcOH, 120 °C, 18 h, 40 bar (CO). *80 °C

Tab. S3: Solvent

Solvent (ml)	yield
Toluene (1.5)	0 %
THF (1.5)	37 %
Dioxane (1.5)	60 %
H_2SO_4 [0.6M] (2.0)	0 %
Acetic acid (1.5)	68 %

Conditions: 1.0 mmol **1a**, 1 mol% $PtCl_2$, 2.2 mol% **L9**, 0.5 ml H_2SO_4 [0.6 M], in X mL solvent, 120 °C, 18 h, 40 bar (CO).

Tab. S4: Ratio Sulfuric Acid to Acetic Acid

H_2SO_4 / AcOH (ml)	yield
0.1 / 1.9	8 %
0.2 / 1.8	14 %
0.3 / 1.7	33 %
0.4 / 1.6	43 %
0.5 / 1.5	57 %
0.6 / 1.4	48 %

Conditions: 1.0 mmol **1a**, 1 mol% $PtCl_2$, 2.2 mol% **L9**, X ml H_2SO_4 [0.3M], X ml AcOH, 120 °C, 18 h, 40bar CO.

Tab. S5: Additives

additive	yield (n:iso)
LiCl (0.5-5 mol%)	40-50%
Acetonitrile (2.5 mol%)	48 % (85/15)
Pyridine (4 mol%)	55 % (82/17)

Conditions: 1.0 mmol 1a, 1 mol% $PtCl_2$, 2.2 mol% **L9**, 0.5 ml H_2SO_4 [0.6M], in 1.5 mL AcOH, 80 °C, 18 h, 40 bar (CO).

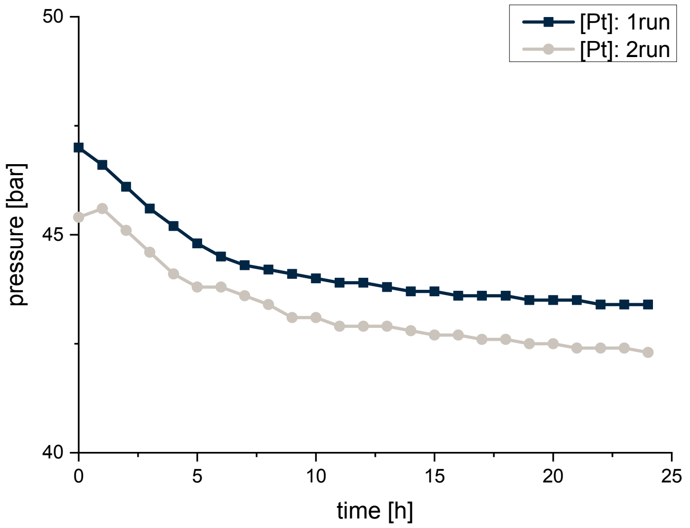
Tab. S6: Time

Time (h)	yield (n:iso)
18	65 % (90/10)
65	83 % (89/11)

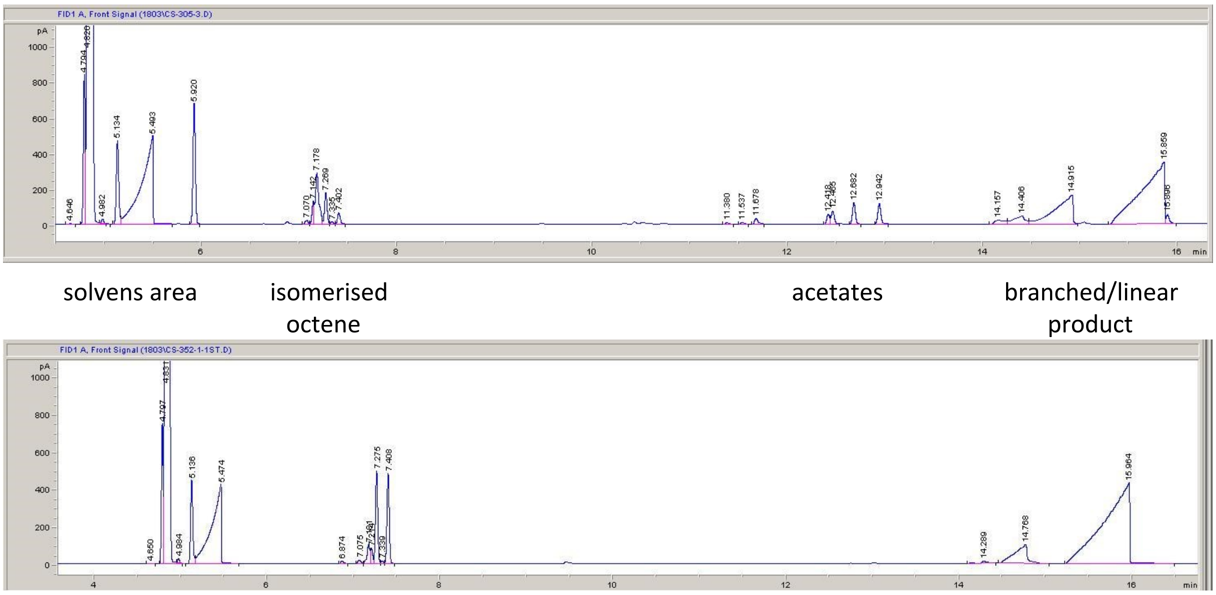
Conditions: 1.0 mmol **1a**, 1 mol% $PtCl_2$, 2.2 mol% **L9**, 0.5 ml H_2SO_4 [0.6M], in 1.5 mL AcOH, 80 °C, X h, 40 bar (CO).

Stability of the Catalyst

In a catalytic experiment for investigating the stability, the reactions were performed in a 25 mL autoclave with $PtCl_2$ (1.0 mol%), Neolephos Ligand (2.2 mol%) rapidly weighed in the air. The atmosphere in the autoclave was then changed to argon and 7.5 mL acetic acid, 2.5 mL H_2SO_4 [0.6M], and 1-octene (10.0 mmol were added. The solution was pressurized with 40 bar CO and the reaction mixture was stirred at 80 °C for 24 h inside an aluminium block. At the end of the reaction the autoclave was slowly cooled, and the pressure released. Under an argon flow the autoclave was charged with another 10.0 mmol of 1-octene, closed, pressurized with 40 bar CO, and stirred at 80°C for 24h.
For the whole reaction, the pressure lines were measured.



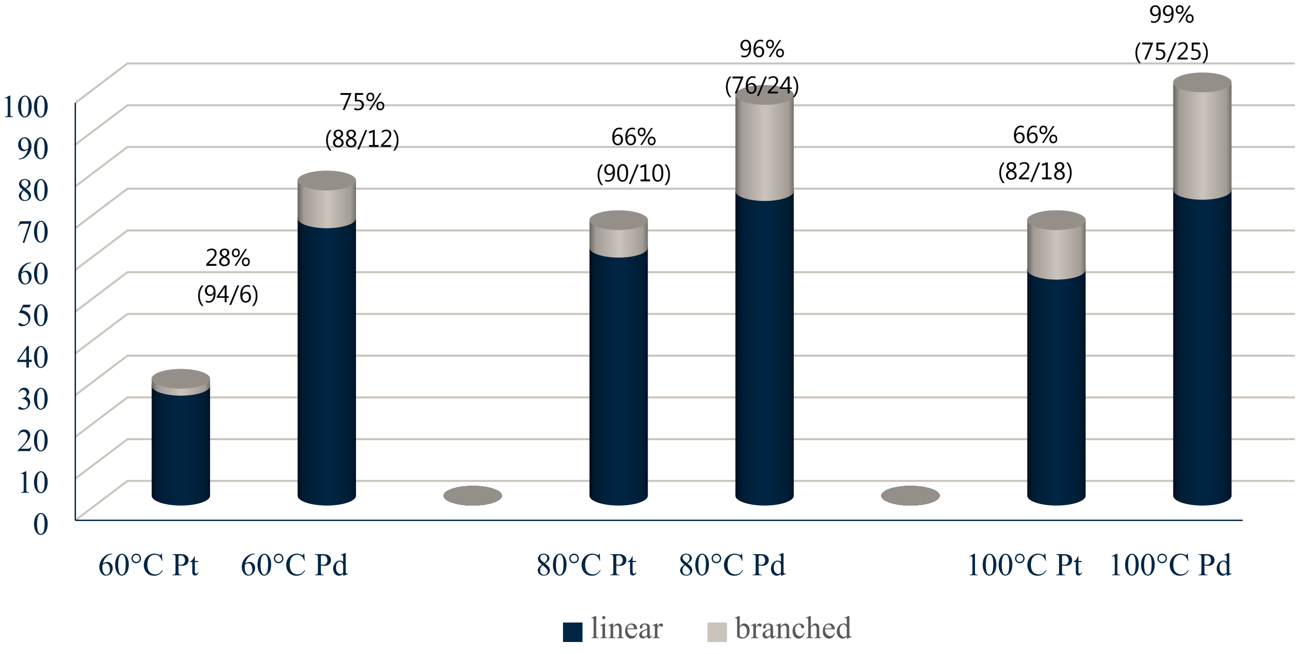
GC spectra example



TOP: Reaction conditions: 1.0 mmol 1a, 1.0 mol% $PtCl_2$, 2.2 mol% L9, 0.5 mL 0.3M H_2SO_4, 1.5 ml acetic acid, 40 bar CO, 120 °C, 18 h.

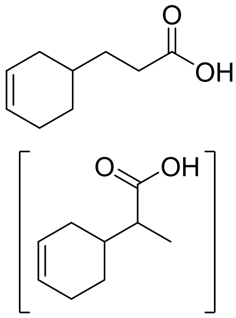
Bottom: Reaction conditions: 1.0 mmol 1a, 1.0 mol% $PtCl_2$, 2.2 mol% L9, 0.5 mL 0.6 M H_2SO_4, 1.5 ml acetic acid, 40 bar CO, 80 °C, 20 h.

Temperature Studies for Pt- and Pd-based Catalyst Systems



Conditions: 1.0 mmol 1a, 1.0 mol% [M], 2.2 mol% **L9**, 0.5 mL H_2SO_4 [0.6 M], in 1.5 mL acetic acid, X °C, 18 h. Results are obtained by GC analysis.

Product Characterization

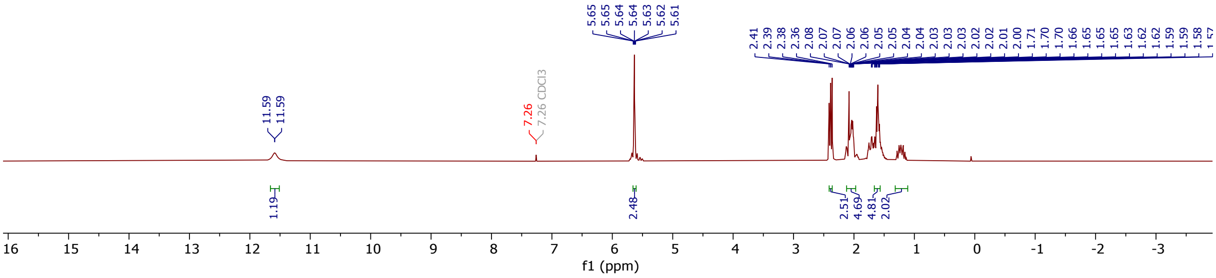


3-(cyclohex-3-en-1-yl)propionic acid (**2c**) and **2-(cyclohex-3-en-1-yl)propanoic acid**: ^{1}H NMR (300 MHz, $CDCl_3$):): δ = 11.59 (s), 5.65-5,61 (m), 2.41-2.36 (m), 2.13-2.00 (m), 1.77-1.51 (m), 1.29-1.14 (m) ppm.

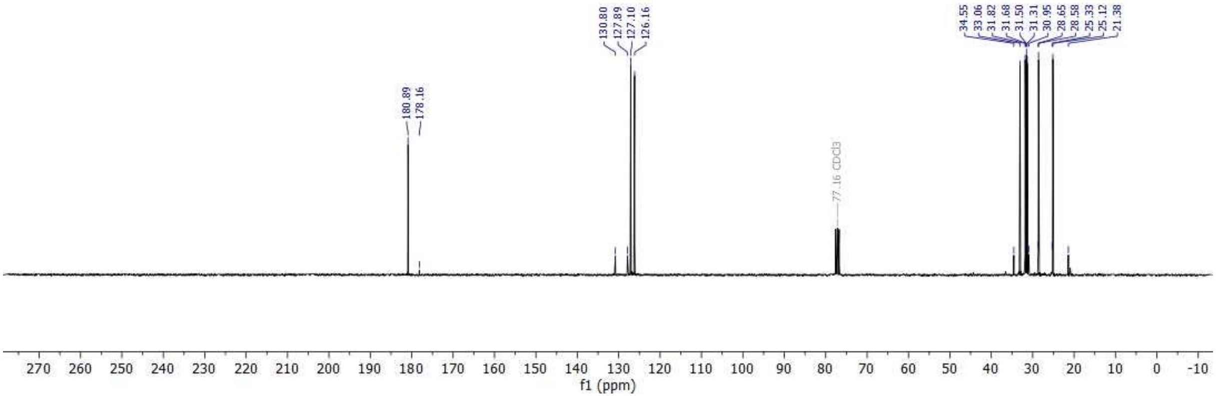
^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.89 (l), 178.16 (b), 130.80 (b), 127.89 (b), 127.10 (l), 126.16 (l), 34.55 (b), 33.06 (l), 31.82 (l), 31.68 (b), 31.50 (l), 31.31 (l), 30.95 (b), 28.65 (b), 28.58 (l), 25,33 (b), 25.12 (l), 21.38 (b) ppm.

- b = branched and l = linear

HR-MS (EI) calculated for $C_9H_{14}O_2$: 154.0988
Found for for $C_9H_{14}O_2$: 154.0984



^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 2c.



^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 2c.

4-phenylbutanoic acid[1] (**2f**): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.11 (s, 1H), 7.28-7.32 (m, 2H), 7.18 -7.24 (m, 3H), 2.69 (t, J = 8.0 Hz. 2H), 2.39 (t, J = 8.0 Hz, 2H), 1.93 -2.04 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl3): δ = 179.99, 141.31, 128.62, 128.56, 126.19, 35.12, 33.44, 26.34 ppm.

Reference:

1) R. Sang, P. Kucmierczyk, R. Dühren, R. Razzaq, K. Dong, J. Liu, R. Franke, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.*, 2019, **58**, 14365-14373.