Catalysis
Science &
Technology

ROYAL SOCIETY
OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Catal. Sci. Technol.*, 2021, **11**, 2026

Received 27th November 2020,
Accepted 7th March 2021

DOI: 10.1039/d0cy02283g

rsc.li/catalysis

Ruthenium-catalysed hydroxycarbonylation of olefins†

Ricarda Dühren,[a] Peter Kucmierczyk,[bc] Ralf Jackstell,[a]
Robert Franke[bc] and Matthias Beller *[a]

State-of-the-art catalyst systems for hydroxy- and alkoxycarbonylations of olefins make use of palladium complexes. In this work, we report a complementary ruthenium-catalysed hydroxycarbonylation of olefins applying an inexpensive Ru-precursor ($Ru_3(CO)_{12}$) and PCy_3 as a ligand. Crucial for the success of this transformation is the use of hexafluoroisopropanol (HFIP) as the solvent in the presence of an acid co-catalyst (PTSA). Overall, moderate to good yields are obtained using aliphatic olefins including the industrially relevant substrate di-isobutene. This atom-efficient catalytic transformation provides straightforward access to various carboxylic acids from unfunctionalized olefins.

Introduction

The transition-metal catalysed functionalization of olefins to form carbonyl-containing compounds is a powerful tool for the production of numerous fine and bulk chemicals in industry and for basic research in academia.[1,2] In fact, besides polymerizations and oxidations, carbonylation reactions using CO as a C1 building block represent the most commercially important chemical transformations. Specifically, aliphatic olefins are converted into the corresponding aldehydes on a million-ton-scale (>10 million tons per year)[3] by so-called hydroformylation. In general, these products are converted into secondary products like alcohols or carboxylic acids. In this respect, direct syntheses of carboxylic acid derivatives *via* alkoxy- or hydroxycarbonylation are also of interest due to the improved step-economy and preventing additional work up. Furthermore, they allow for 100% atom-efficient transformations.

Today's knowledge in this area is largely based on the original work of Reppe and co-workers.[4] They enabled Ni-catalysed carbonylation of acetylene to acrylic acid already in the 1930's. Since then, important catalyst developments using other metals in the presence of a variety of ligands took place and reaction conditions have been improved.[5,6] In addition, substantial research focused on the synthetic applications of transition-metal catalysed carbonylation reactions[7] as well as practical implementations. In this respect, an important example is the palladium-catalysed lucite alpha process to produce methyl methacrylate (MMA) by carbonylation of ethylene to methylpropanoate[8] in the first step followed by subsequent condensation with formaldehyde.[9] This monomer is used to produce polymethacrylates (PMMA). Apart from esters, carboxylic acids are important basic and fine chemicals, which are used to produce derivatives like carboxylate salts, anhydrides, and amides. In addition, carboxylic acids find numerous applications in daily life for instance in coatings, as food additives, disinfecting products, and pharmaceuticals.[10] Hence, there is a continuing interest in exploring more efficient and less costly routes.

For example, in the past decade several palladium-catalysed hydroxycarbonylation reactions have been disclosed.[11–13] Notably, in these reactions the price of the metal (palladium) constitutes an important factor for the overall process costs. Hence, using other less costly metals, especially ruthenium, is particularly attractive (see Fig. 1). In general, the mechanism of a ruthenium-catalysed hydroxycarbonylation should be like the state-of-the-art palladium-based transformations.[14–16] However, to the best of our knowledge only one example of a hydroxycarbonylation of olefins to acids using water in the presence of a Ru catalyst is known: in 1989, a patent by Shell International claimed the alkoxy- and hydroxycarbonylation of olefins using CO Ru/acid/additives to form esters and carboxylic acids.[17] Aside ruthenium complexes have been

---

[a] *Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany. E-mail: matthias.beller@catalysis.de*
[b] *Evonik Operations GmbH, Germany. E-mail: robert.franke@evonik.com*
[c] *Lehrstuhl für Theoretische Chemie, Ruhr-Universiät Bochum, 44780 Bochum, Germany*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cy02283g

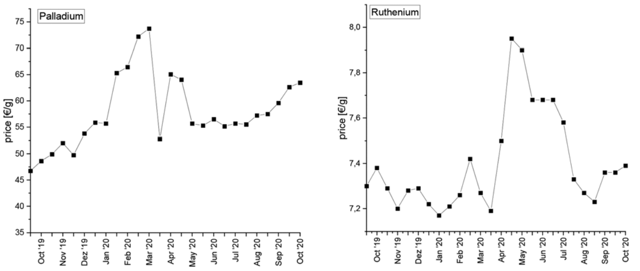


Fig. 1 Prices of ruthenium and palladium for May 2019 until May 2020 according to https://www.gold.de/kurse/palladiumpreis/ and https://www.gold.de/kurse/rutheniumpreis/ (status October 2020).

successfully applied in related reactions of olefins such as hydroesterification using formates,[18–20] the alkoxycarbonylation with CO_2 as CO surrogate,[21] and CH-carbonylations of (hetero)arenes.[22]

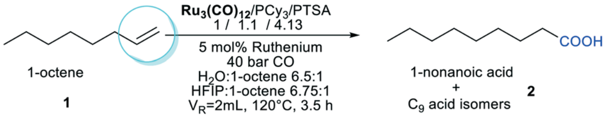
Herein, we report that commercially available ruthenium salts and carbonyl complexes in the presence of basic monophosphines catalyse the carbonylation of olefins in fluorinated solvents to give the corresponding carboxylic acids in a chemoselective manner. We believe these findings will stimulate the use of alternative (less expensive) catalyst metals in carbonylation reactions in general.

Results and discussion

At the start of this project, we studied the influence of different solvents, metal precursors and ligands on the ruthenium-catalysed hydroxycarbonylation of 1-octene. This benchmark reaction was chosen due to the industrial interest in the carbonylation of long chain aliphatic olefins. In fact, the resulting linear product nonanoic acid (pelargonic acid), is used in the preparation of plasticizers and lacquers. Moreover, the corresponding esters are applied as flavorings and ammonium nonanoate is a known herbicide.[23] It should be noted that due to the possibility of olefin isomerization reactions, this model system is also demanding. Inspired by previous work on palladium-catalysed hydroxycarbonylation including a design of experiments study,[24] a mixture of 1-octene/water/solvent (1 : 6.5 : 6.75) was used in the presence of an acid co-catalyst (*p*-toluenesulfonic acid; PTSA) at 120 °C for 3.5 h. To find a suitable reaction environment, we tested a broad range of solvents (Tables 1 and S1† for all tested solvents). Surprisingly, only in fluorinated solvents, *e.g.* hexafluoroisopropanol (HFIP) and trifluoro acetic acid (TFA) the desired product is obtained in moderate to high yield (38–70%). To exclude the involvement of fluoride ions in this transformation additionally some of the non-fluorinated solvents were tested in the presence of additional CsF. However, no desired products were observed. At this point it is interesting to note that positive solvent effects using fluorinated alcohols like HFIP are well-known. Often it is supposed that the strong H-donor ability is the cause for enhanced reactivity.[25,26]

Based on these results, we chose to use HFIP as the solvent for all following reactions. Interestingly, under these conditions no significant amounts of the corresponding aldehydes or alcohols are observed. In order to identify the optimal catalyst more efficiently, potentially active ruthenium phosphine complexes were generated *in situ*. To recognize the best metal precursor, eight different ruthenium salts and complexes were compared (Table S2†). Among these only $Ru_3(CO)_{12}$ and $Ru(acac)_3$ led to the desired C_9-acids **2** as a mixture of linear and branched isomers in moderate to high yields (63–70%). According to GC-measurements the internal carboxylic acid isomers were detected as a 1 : 1 : 1 mixture. In contrast to palladium-catalysed alkoxy-carbonylations of olefins, halide-containing precursors do not favor this reaction (Table S2,† entries 2–4, 6 and 7). Thus, further catalytic tests were carried out with 5 mol% $Ru_3(CO)_{12}$ and different ligands (Ru : L = 1 : 1.1 for monodentate ligands and 1 : 0.55 for bidentate ligands to keep the ratio of Ru : P in solution constant) (Fig. 2). In the presence of bidentate phosphines including the industrially important ligand **L2** as well as Xantphos **L5**, lower yields (49–62%) of **2** were obtained.

Table 1 Investigation of influence of different solvents on the hydroxycarbonylation of 1-octene



Entry	Solvent	Additive	Yield (**2**) [%]	*n*/iso [%]
1	HOAc	—	0	—
2	HFIP	—	70	19/81
3	TFA	—	38	25/75
4	Trifluoroethanol	—	0	—
5	Dioxane	—	0	—
6	Dioxane	5 mol% CsF	0	—
7	Anisole	—	0	—
8	Anisole	5 mol% CsF	0	—

Reaction conditions: **1** (2 mmol), Ru-precursor (5 mol% Ru), $PTSA \cdot H_2O : PCy_3$ (3.75 : 1, 20.6 mol%), $PCy_3 : Ru$ (1.1 : 1, 5.5 mol%), H_2O : 1-octene (6.5 : 1), HFIP : 1-octene (6.75 : 1), CO (40 bar), 120 °C, 3.5 h, V_R = 2 mL. Yield of **2** was determined by GC analysis using hexadecane as internal standard. *n*/iso describes the ratio of the linear nonanoic acid to all other C_9 acid isomers.

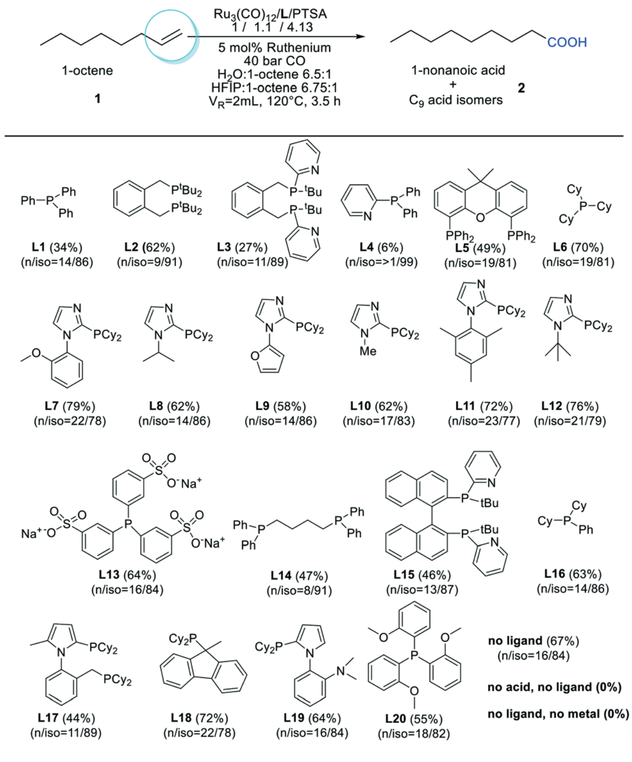


Fig. 2 Effect of different ligands on the ruthenium-catalysed hydroxycarbonylation of 1-octene. General conditions: **1** (2 mmol), $Ru_3(CO)_{12}$ (5 mol% Ru), monodentate ligands **L1**, **L4**, **L6–L13**, **L16**, **L18–L20** (5.5 mol%) or bidentate ligands **L2**, **L3**, **L5**, **L14–L15**, **L17** (2.75 mol%), $PTSA{\cdot}H_2O$: L (3.75 : 1), H_2O : 1-octene (6.5 : 1), HFIP : 1-octene (6.75 : 1), CO (40 bar), 120 °C, 3.5 h, V_R = 2 mL. Yield of **2** was determined by GC analysis using hexadecane as internal standard. *n*/iso describes the ratio of the linear nonanoic acid to all other C_9 acid isomers.

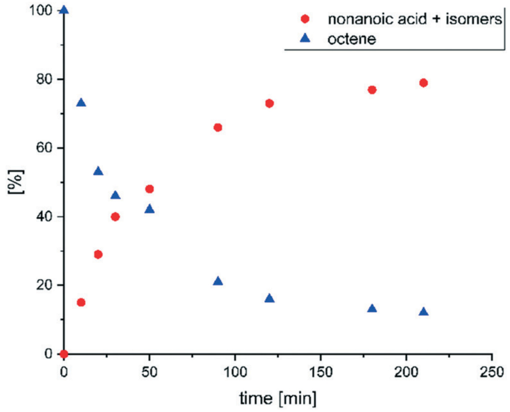


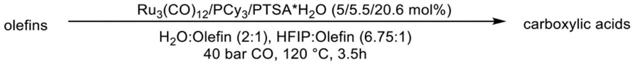
Fig. 3 Conversion and product yields for the ruthenium-catalysed hydroxycarbonylation of 1-octene in course of the time. Reaction conditions: 1-octene (33 mmol), Ru-precursor (5 mol% Ru), $PTSA{\cdot}H_2O$: PCy_3 (3.75 : 1, 20.6 mol%), PCy_3 : Ru (1.1 : 1, 5.5 mol%), H_2O : 1-octene (2 : 1), HFIP : 1-octene (6.75 : 1), CO (40 bar), V_R = 30 mL. Yields are given as the sum of all four isomers.

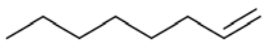
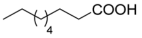
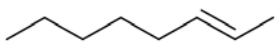
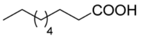
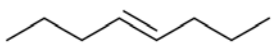
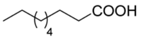
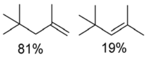
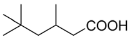
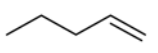
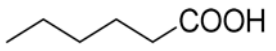
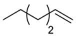
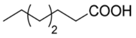
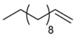
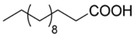
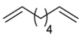
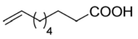
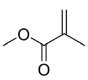
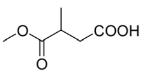
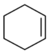
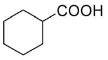
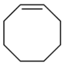
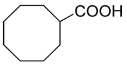
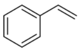
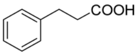
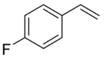
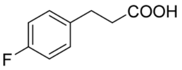
Triphenylphosphine **L1** and the water-soluble triphenylphosphine trisulfonate (TPPTS) ligand **L13** also gave the desired product in moderate yields (34–64%). In contrast to PPh_3, 2-pyridyl-diphenyl-phosphine **L4** gave a lower yield (6%). Interestingly, using cyclohexyl-substituted phosphines such as easily accessible **L6** and **L16** gave improved yield (63–70%) of **2**. Because of this positive effect, several easily accessible heterocyclic monodentate phosphorous ligands containing dicyclohexyl-phosphino groups **L7–L12** and **L19** were tested. In general, they led to **2** in moderate to good yields (58–79%). None of the tested ligands gave improved *n* : iso ratios compared to the reaction without ligand. Hence, the terminal and different internal acids were achieved in similar amounts. Based on the availability and price of PCy_3, this ligand was used in the following experiments to find out the optimal concentration of ruthenium, ratio of ligand : metal and water : substrate (see ESI† Table S3).

Lowering the amount of Ru to 1 mol% resulted in a significant change of the *n*/iso ratio towards the iso-products. Anyways, best results were achieved with 5 mol% of Ru. The ratio of water : substrate could be lowered to 2 : 1 using PCy_3 which leads to an improved space–time-yield. In comparison, the yield without ligand decreased by lowering the amount of water (75 *vs.* 60%). Those results clearly show that the ligand stabilizes the reaction system. Next, the influence of CO pressure was investigated in between 15 and 60 bars. To keep the absolute pressure at a minimum of 40 bars either pure CO or mixtures of CO and N_2 were used. Previous work on ruthenium-catalysed hydroformylations and hydroaminomethylations showed the positive effect of hydrogen or *in situ* generated hydrogen on the performance of the active ruthenium catalyst.[27,28] Inspired by that work, we also performed experiments with 40 bar of CO and additional 5 bar of H_2 and with 35 bar of CO and 5 bar of H_2. However, in this case no significant effect of H_2 on the reaction system could be observed (64 and 57% yield). Applying the optimal conditions (1.7 mol% Ru-precursor, 5.5 mol% $PTSA{\cdot}H_2O$, 5.5 mol% PCy_3, olefin : HFIP : water = 1 : 6.75 : 2, 40 bar CO) **2** was achieved in 75% yield. With these general conditions in hand, we measured the concentration of substrates and products over time (Fig. 3).

Finally, we tested the reactivity of other aliphatic olefins under the optimized reaction conditions. As shown in Table 2, internal olefins such as 2- and 4-octene reacted in a comparable manner to 1-octene (Table 2, entries 2–3). Applying the industrial mixture of di-isobutene gave regioselectively the desired linear acid, albeit in lower yield (Table 2, entry 4). Shorter and longer chain substrates gave the corresponding acids in 56–84% yield (Table 2, entries 5–7). In case of 1,7-octadiene the reactivity dropped and only traces of products could be obtained (Table 2, entry 8). In a similar manner, methyl methacrylate (MMA) proved to be unreactive (Table 2, entry 9). In contrast, cyclohexene, as an example for cyclic olefins, reacted well and provided cyclohexanecarboxylic acid in 63% yield (Table 2, entry 10). Lastly, aromatic olefins (styrene, 4-fluorostyrene) were tested but did not underwent the desired transformation, probably because a polymerization took place instead.

Table 2 Ruthenium-catalysed hydroxycarbonylation of various olefins



Entry	Olefin	Linear acid	Yield [%, *n*/iso]
1			75 (22/78)
2			73 (18/82)
3			63 (17/83)
4			29
5			56 (29/71)
6			67 (20/80)
7			84 (22/78)
8			Traces
9			0
10			63
11			41
11			0
12			0

General conditions: olefin, $Ru_3(CO)_{12}$ (5 mol% Ru), $PTSA·H_2O:PCy_3$ (3.75 : 1, 20.6 mol%), PCy_3 : Ru (1.1 : 1, 5.5 mol%), H_2O : olefin (2 : 1), HFIP : olefin (6.75 : 1), CO (40 bar), V_R = 2 mL. Yields and ratios of isomers were determined *via* GC analysis using hexadecane as the internal standard. *n*/iso describes the ratio of the linear acid to all other acid isomers.

Conclusions

In conclusion, we have developed a ruthenium-catalysed hydroxycarbonylation of olefins. Crucial for this transformation is the use of hexafluoroisopropanol as the solvent. Best results are achieved with the convenient combination of $Ru_3(CO)_{12}/PCy_3$ in the presence of PTSA as co-catalyst. Various aliphatic olefins (terminal, internal, and cyclic) provided the corresponding carboxylic acids in moderate to good yields.

Experimental

General considerations

All air- and moisture-sensitive syntheses were performed under argon atmosphere in heating gun dried glassware using Schlenk techniques. Chemicals were purchased from commercial sources and used as received unless the purity was less than 98%. O_2-Free and dry solvents were prepared by distillation.

Standard catalytic experiment

In a typical experiment, the vial was charged with $Ru_3(CO)_{12}$ (1.7 mol%), **L6** (5.5 mol%), $PTSA·H_2O$ (20.6 mol%) and a stirring bar. The vial was closed by PTFE septum and phenolic cap, fixed in an alloy plate, and connected to atmosphere with a needle. The vial was evacuated and recharged with argon for three times. HFIP (1.44 mL), H_2O (0.35 mL) and olefin (2 mmol) were injected and under argon atmosphere, the vial was transferred into the autoclave. After the autoclave was flushed three times with 10 bar CO at room temperature, it was charged with 40 bar CO, and heated to 120 °C for 3.5 hours. Afterwards, the autoclave was cooled to room temperature and the pressure was released carefully. The yield was determined by GC analysis with hexadecane (100 μL) as internal standard.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work has been funded in part by Evonik Industries, and the State of Mecklenburg-Western Pomerania and the German Federal State (BMBF). We thank the analytical team of LIKAT for their support.

Notes and references

1 L. Wu, Q. Liu, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, 2014, **53**, 6310–6320.

2 A. Brennführer, H. Neumann and M. Beller, *ChemCatChem*, 2009, **1**, 28–41.

3 R. Franke, D. Selent and A. Börner, *Chem. Rev.*, 2012, **112**, 5675–5732.

4 W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Justus Liebigs Ann. Chem.*, 1948, **560**, 1–92.

5 M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpaintner, *J. Mol. Catal. A: Chem.*, 1995, **104**, 17–85.

6 G. Kiss, *Chem. Rev.*, 2001, **101**, 3435–3456.

7 C. Torborg and M. Beller, *Adv. Synth. Catal.*, 2009, **351**, 3027–3043.

8 W. Clegg, G. R. Eastham, M. R. J. Elsegood, R. P. Tooze, X. L. Wang and K. Whiston, *Chem. Commun.*, 1999, 1877–1878.

9 J. M. Pearson and R. A. Hadden, US20010051745A1, Lucite International UK Ltd, 2001.

10 Y. Wang, W. Ren and Y. Shi, *Org. Biomol. Chem.*, 2015, **13**, 8416–8419.

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

12 V. Goldbach, L. Falivene, L. Caporaso, L. Cavallo and S. Mecking, *ACS Catal.*, 2016, **6**, 8229–8238.

13 T. M. Konrad, J. T. Durrani, C. J. Cobley and M. L. Clarke, *Chem. Commun.*, 2013, **49**, 3306–3308.

14 K. Dong, R. Sang, X. Fang, R. Franke, A. Spannenberg, H. Neumann, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, 2017, **56**, 5267–5271.

15 I. del Rio, N. Ruiz, C. Claver, L. A. van der Veen and P. W. N. M. van Leeuwen, *J. Mol. Catal. A: Chem.*, 2000, **161**, 39–48.

16 I. del Rio, C. Claver and P. W. N. M. Van Leeuwen, *Eur. J. Inorg. Chem.*, 2001, 2719–2738.

17 E. Drent and A. J. M. Breed, EP0329252B1, Shell International Research, 1989.

18 H. Konishi, T. Ueda, T. Muto and K. Manabe, *Org. Lett.*, 2012, **14**, 4722–4725.

19 S. Ko, Y. Na and S. Chang, *J. Am. Chem. Soc.*, 2002, **124**, 750–751.

20 H. Konishi, T. Muto, T. Ueda, Y. Yamada, M. Yamaguchi and K. Manabe, *ChemCatChem*, 2015, **7**, 836–845.

21 L. Wu, Q. Liu, I. Fleischer, R. Jackstell and M. Beller, *Nat. Commun.*, 2014, **5**, 3091.

22 A. Tlili, J. Schranck, J. Pospech, H. Neumann and M. Beller, *ChemCatChem*, 2014, **6**, 1562–1566.

23 R. A. Smiley, US6323156B1, Falcon Lab LLC, 2000.

24 R. Dühren, P. Kucmierczyk, R. Jackstell, R. Franke and M. Beller, unpublished work.

25 A. Berkessel, J. A. Adrio, D. Hüttenhain and J. M. Neudörfl, *J. Am. Chem. Soc.*, 2006, **128**, 8421–8426.

26 J. Wencel-Delord and F. Colobert, *Org. Chem. Front.*, 2016, **3**, 394–400.

27 L. Wu, I. Fleischer, R. Jackstell and M. Beller, *J. Am. Chem. Soc.*, 2013, **135**, 3989–3996.

28 I. Fleischer, L. Wu, I. Profir, R. Jackstell, R. Franke and M. Beller, *Chem. – Eur. J.*, 2013, **19**, 10589–10594.