

Palladium-catalyzed Selective Generation of CO from Formic Acid for Carbonylation of Alkenes

Rui Sang, Peter Kucmierczyk, Kaiwu Dong, Robert Franke,
Helfried Neumann, Ralf Jackstell, and Matthias Beller

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.8b01123 • Publication Date (Web): 12 Mar 2018

Downloaded from <http://pubs.acs.org> on March 12, 2018

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.



Palladium-catalyzed Selective Generation of CO from Formic Acid for Carbonylation of Alkenes

Rui Sang,[†] Peter Kucmierczyk,^{†‡} Kaiwu Dong,[†] Robert Franke,^{‡§} Helfried Neumann,[†] Ralf Jackstell,[†] and Matthias Beller^{*†}

[†]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, Rostock, 18059, Germany

[‡]Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

[§]Evonik Performance Materials GmbH, Paul-Baumann-Str. 1, 45772 Marl, Germany

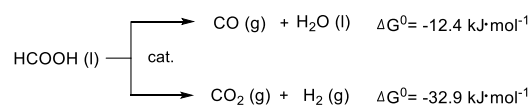
KEYWORDS: formic acid • carbonylation • CO surrogate • esters • palladium.

ABSTRACT: A general and selective palladium-catalyzed alkoxy carbonylation of all kinds of alkenes with formic acid (HCOOH, FA) is described. Terminal, di-, tri- and tetra-substituted including functionalized olefins are converted into linear esters with high yields and regioselectivity. Key-to-success is the use of specific palladium catalysts containing ligands with built-in base, e.g. **L5**. Comparison experiments demonstrate that the active catalyst system not only facilitates isomerization and carbonylation of alkenes, but also promotes the selective decomposition of HCOOH to CO under mild conditions.

INTRODUCTION

Carbonylation reactions constitute powerful tools to synthesize carboxylic acids and their derivatives both in industry and academic organic synthesis.^[1] In general, these processes make use of toxic and flammable CO under (high) pressure, which requires specific equipments and safety measures. To overcome these problems, substantial attention has been paid to the development of carbonylation reactions with so-called CO surrogates.^[2] Representative examples include transition-metal catalyzed olefin carbonylations with metal carbonyls,^[3] acyl chlorides,^[4] formic acid (HCOOH) or its derivatives,^[5] paraformaldehyde,^[6] and even CO₂.^[7] Among all of these CO substitutes, formic acid is probably the most convenient C1 source, readily available from the fermentation of bio-waste^[8] or via catalytic hydrogenation of CO₂.^[9]

Scheme 1. Formic acid decomposition pathways.

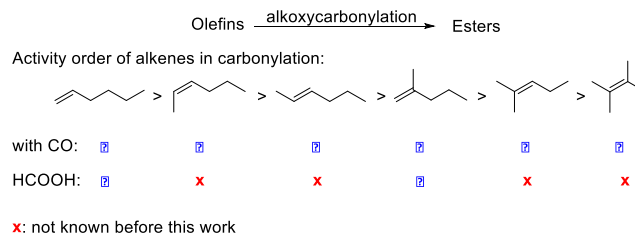


Thus, carbonylations of alkenes^[10] and alkynes^[11] as well as aryl and alkenyl (pseudo) halides using HCOOH have been investigated, albeit with moderate successes in the presence of rhodium, iridium^[12], and ruthenium^[13] complexes. A general problem for the effective use of HCOOH in these reactions is its unspecific decomposition to give both CO and water or hydrogen and CO₂ (Scheme. 1)^[9b, 14]. While numerous homogeneous catalysts are known to catalyze the latter decomposition,^[15] the former transformation is difficult to achieve selectively at low temperature. Clearly, CO can be released from

HCOOH by dehydration in the presence of strong mineral acids (e.g. sulfuric acid; Morgan reaction),^[16] but these conditions are not compatible with most carbonylation reactions.

To use HCOOH as an inexpensive and less toxic surrogate for carbonylations, acetic anhydride has been added to generate the more reactive mixed anhydride *in situ*. Following this strategy, Shi and co-workers demonstrated effective palladium-catalyzed hydroformylation^[10] and hydrocarboxylation^[17] of terminal alkenes. However, comparably high catalyst loadings (3-5 mol%) have to be employed in this case. Notably, industrially important internal alkenes did not work under these conditions. Hence, to the best of our knowledge, the selective alkoxy carbonylation of internal alkenes to give linear esters using HCOOH has not been explored yet (Scheme 2).

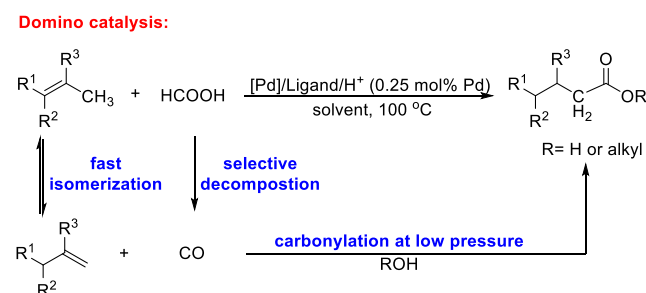
Scheme 2. Catalytic alkoxy carbonylation of olefins.



Obviously, to achieve such a transformation, the selective decomposition of formic acid to CO has to be combined with the efficient isomerization and alkoxy carbonylation of alkenes in one process (Scheme 3). Herein, we present palladium-based catalyst systems with special ligands, which for the first time are able to catalyze all these steps efficiently. Optimal

results for linear esters from sterically hindered alkenes and formic acid are obtained in the presence of the new ligand **L5**.

Scheme 3. Domino carbonylation catalysis: Hydroesterification of sterically hindered alkenes with HCOOH.



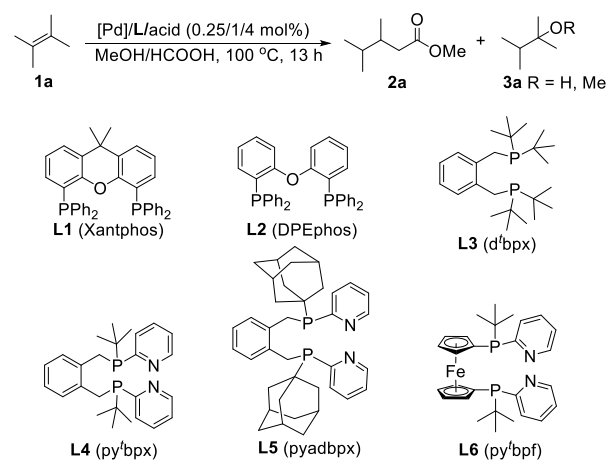
RESULTS AND DISCUSSION

Initially, the Pd-catalyzed methoxycarbonylation of *tetra*-methylene **1a** using HCOOH was investigated in the presence of different ligands. Typically, reactions were carried out with Pd/ligand/PTSA ratio of 0.25/1/4 mol% at 100 °C for 13 h in a sealed tube. As depicted in Table 1, regular ligands Xantphos **L1** and DPEphos **L2**, which are known to catalyze the hydrocarboxylation of olefins using HCOOH in the presence of acetic anhydride, gave no desired ester **2a** and substantial amounts of byproducts **3a** were formed in both cases (Table 1, entries 1 and 2). Notably, 2-methoxy-2,3-dimethylbutane results from the simple acid-catalyzed etherification of the olefin, while 2,3-dimethylbutan-2-ol is a result of the subsequent hydrolysis. On the other hand, **L3** (d**4**bpx), which is currently used in industry for alkene alkoxy carbonylation,^[18] afforded the desired product in moderate yield (32%; Table 1, entry 3). Recently, we modified this type of ligand by introducing basic heterocycles on the P-atom (e.g. **L4**, **L5** and **L6**), which led to improved catalysts.^[19] Indeed, when the benchmark reaction was performed with **L4**, the linear ester was obtained in 62% yield (Table 1, entry 4). Even better results were observed using the new ligand **L5** and **2a** was obtained in 67% yield (Table 1, entry 5). The low yield (10%) of **2a** in the presence of **L6** revealed the importance of the backbone in the ligand (Table, entry 6). Other well-known mono- and bidentate phosphine ligands such as PPh₃, dppf, Naphos, etc. (**L7-L14**) were also explored, but in no case any product was observed under identical reaction conditions (see Table S1 in the supporting information).

Further investigations of the reaction conditions applying the optimal ligand **L5** revealed a substantial effect of the palladium precursor, the ratio of MeOH/HCOOH, and the type of acid co-catalyst. Specifically, a similar yield (65%) of **2a** was got by using Pd(acac)₂, other palladium salts including PdCl₂, Pd₂(dba)₃ did not catalyze this transformation efficiently and less than 7% yield of **2a** was detected (Table 1, entries 7-9). Reducing the amount of HCOOH (MeOH/HCOOH, 1.8/0.2 mL), the yield of the desired product also decreased to 36% (Table 1, entry 10), which might be explained by the slower generation of CO. On the other hand, carrying out the benchmark reaction in MeOH/HCOOH (1.0/1.0 mL), the yield of the desired ester dropped to 48% (Table 1, entry 11). The necessity of the acid co-catalyst, which is responsible for

the generation of the active palladium hydride complex, is ascertained by the control experiment without PTSA (Table 1, entry 12).

Table 1. Alkoxy carbonylation of 2,3-dimethyl-2-butene **1a with HCOOH: Effect of ligands, palladium precursors and acids.^[a]**



Entry	L	Pd source	Acid	2a /Yield% ^[b]	3a /Yield% ^[b]
1	L1	Pd(OAc) ₂	PTSA	0	30
2	L2	Pd(OAc) ₂	PTSA	0	34
3	L3	Pd(OAc) ₂	PTSA	32	22
4	L4	Pd(OAc) ₂	PTSA	62	13
5	L5	Pd(OAc) ₂	PTSA	67	13
6	L6	Pd(OAc) ₂	PTSA	10	27
7	L5	Pd(acac) ₂	PTSA	65	13
8	L5	PdCl ₂	PTSA	0	29
9	L5	Pd ₂ (dba) ₃	PTSA	7	27
10 ^[c]	L5	Pd(OAc) ₂	PTSA	36	24
11 ^[d]	L5	Pd(OAc) ₂	PTSA	48	10
12	L5	Pd(OAc) ₂	0	6	1
13	L5	Pd(OAc) ₂	CF ₃ SO ₃ H	60	13
14	L5	Pd(OAc) ₂	CH ₃ SO ₃ H	65	12
15	L5	Pd(OAc) ₂	H ₂ SO ₄	59	14
16 ^[e]	L5	Pd(OAc) ₂	PTSA	81	9
17 ^[e, f]	L5	Pd(OAc) ₂	PTSA	93	1
18 ^[e, g]	L5	Pd(OAc) ₂	PTSA	97	trace

[a] Reaction conditions: **1a** (2.0 mmol), [Pd] (0.25 mol%), **L** (1.0 mol%), acid co-catalyst (4.0 mol%), MeOH/HCOOH (1.5/0.5 mL), 100 °C, 13h; by-products **3a** is a mixture of 2-methoxy-2,3-dimethylbutane and 2,3-dimethylbutan-2-ol. [b] Determined by GC analysis using *iso*-octane as internal standard. [c] MeOH/HCOOH (1.8/0.2 mL). [d] MeOH/HCOOH (1.0/1.0 mL). [e] 20 h [f] [Pd]/L/acid (0.5/2/8 mol%). [g] **1a**

(1mmol), [Pd]/L/acid (1/4/16 mol%). PTSA: *p*-toluenesulfonic acid (monohydrate).

Apart from PTSA, other types of strong acids are also suitable (Table 1, entries 13-15). Finally, the yield of **2a** could be increased to 97% with PTSA by optimization of the catalyst, substrate concentration and extension of the reaction time (Table 1, entry 18).

To understand the significant difference in reactivity of our special ligands (**L4**, **L5**) with “built-in base” compared to other well-known phosphines, we performed control experiments for the decomposition of HCOOH to CO in MeOH/HCOOH (6.5/1.5 mL, 40 mmol FA) at 100 °C for 18 h. As shown in Figure 1, no or very little conversion (less than 0.5 bar of pressure generated) was observed using Pd(OAc)₂, PTSA or a mixture of these reagents. Surprisingly, in the presence of Pd(OAc)₂ and **L3** strong gas formation occurred resulting in 8.6 bar pressure. However, gas chromatographic measurements showed that similar amounts of carbon dioxide and carbon monoxide (58:42) were formed. Notably, using ligand **L4** instead of **L3**, in which a tertiary butyl substituent on every phosphorous atom is replaced by pyridine base, selective formation of CO took place and 2.2 bar of pressure was generated (CO vs CO₂ = 82:18). When Pd(OAc)₂/**L4** was applied together with PTSA (0.05/0.2/1 mol%) both high activity and selectivity was detected by GC analysis (5.5 bar, CO vs CO₂ = 95:5). Apparently, the catalyst containing the built-in base ligand allows for faster and more selective CO generation from HCOOH. In agreement with this assumption, using a related ligand **L5** (Pd(OAc)₂/**L5**/PTSA), 6.0 bar of gas with 92% selectivity of CO (CO vs CO₂) was produced in the autoclave. To the best of our knowledge, [Pd]/**L4**/PTSA or [Pd]/**L5**/PTSA constitute the first homogeneous metal catalysts allowing such selective formation of CO directly from FA under comparably mild conditions.

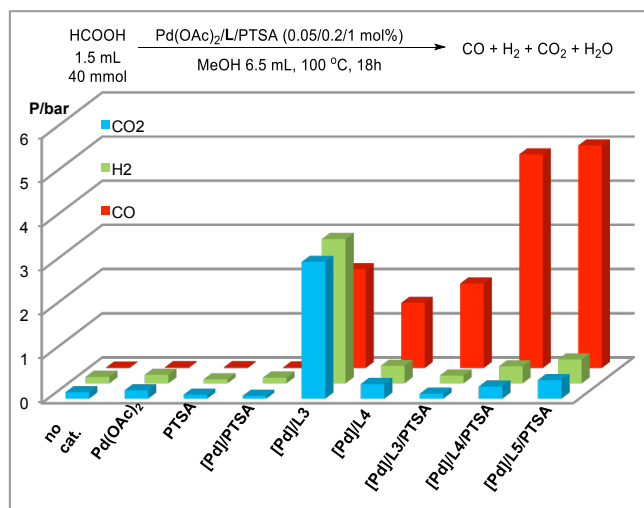


Figure 1. Control experiments on the catalytic decomposition of HCOOH to CO, H₂, and CO₂. Reaction conditions: 25 mL autoclave, Pd(OAc)₂ (0.02 mmol), **L5** (0.08 mmol), PTSA (0.4 mmol), HCOOH (1.5 mL), MeOH (6.5 mL), 100 °C, 18 h.

To gain further mechanistic information on the rate of the individual steps of this domino transformation, the methoxycarbonylation of 2,3-dimethyl-2-butene **1a** using formic acid was investigated in more detail. As shown in Figure 2, 92% of

1a was converted within 7 hours. After that time, the turnover number for CO gas formation is TON_{CO} = 279 (see SI). In the first 20 minutes, almost all the consumed **1a** is transformed into internal alkene **1ab** and the corresponding ether or alcohol **3a** and only traces of the desired product **2a** are formed. Performing the reaction for 20 minutes in a sealed glass tube gas formation can be already observed (Figure 3). After that time, gas formation in the autoclave increased in a linear manner. In contrast, the yield of the internal alkene **1ab**, reached a maximum after 20 minutes (6%) and then is reduced due to the relatively faster methoxycarbonylation. Hence, after 5 hours only traces of this intermediate are detected. Similarly, the yield of **3a** increased in the initial phase of the reaction and after 90 minutes, started decreasing again to the end. The yield of the desired product **2a** constantly increased after the initial first 20 minutes. Notably, comparing concentrations of substrate **1a** and the undesired by-product **3a**, the later compound is always the less. Hence, we conclude the isomerization of the notoriously unreactive internal olefin **1a** to the more reactive terminal alkene **1ab** is the slow (key) step in this process.

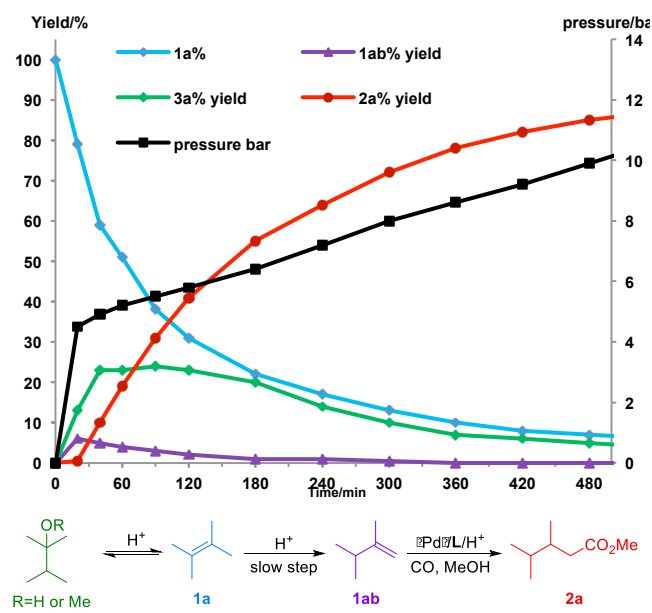


Figure 2. Reaction pathways of the methoxycarbonylation of **1a** using formic acid as CO surrogate. Reaction conditions: 25 mL autoclave, Pd(OAc)₂ (0.7 mol%), **L5** (2.8 mol%), PTSA (11.2 mol%), **1a** (1.0 mL, 8.5 mmol), *iso*-octane (0.5 mL), HCOOH (3.0 mL), MeOH (9.0 mL), 100 °C.

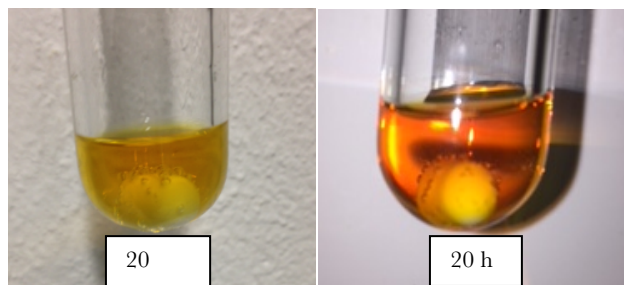
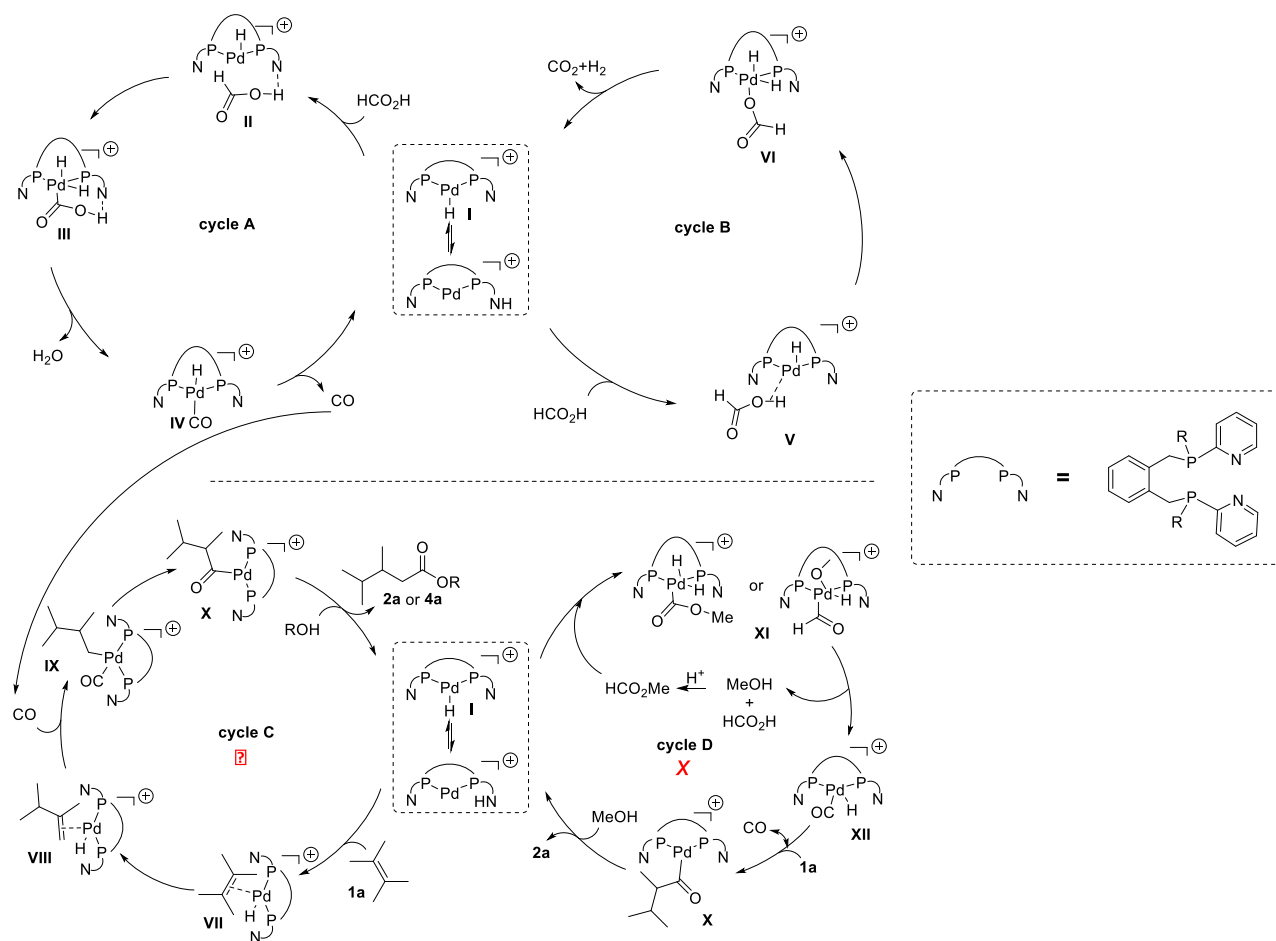


Figure 3. Methoxycarbonylation of **1a** using formic acid in a sealed glass tube. Reaction conditions: 35 mL glass tube, Pd(OAc)₂ (1.0 mol%), **L5** (4.0 mol%), PTSA (16.0 mol%), **1a** (1.0 mmol), *iso*-octane (0.1 mL), HCOOH (0.5 mL), MeOH (1.5 mL), 100 °C.

Scheme 5. Proposed mechanism.

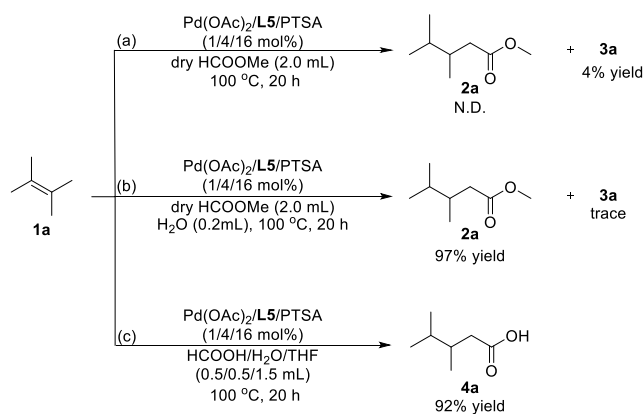


Under acidic conditions formic acid and methanol easily form methyl formate (MF), which might also act as a CO-releasing agent. To better understand the influence of MF in our reaction, comparison experiments using MF and FA were investigated (see SI, Scheme S1). In the presence of FA the desired product **2a** was obtained in 64% yield under standard conditions, while using the same amount of MF only the unwanted ether **3a** was observed. Notably, adding MF and water, which allows hydrolysis to FA, **2a** was formed again. As shown in Scheme 4, the reaction using MF as solvent without water gave no desired product even after 20h, while in the presence of only 0.2 mL water **2a** is obtained in 97% yield (Scheme 4, a and b). Interestingly, using FA and water without any methanol present, hydroxycarbonylation occurred with similar efficiency to give **4a** in 92% yield (Scheme 4, c).

On the basis of these studies and previous mechanistic investigations^[19(a),20] we propose the following mechanism (Scheme 5): Initially, formation of the cationic complex **I** [L₂PdH]⁺ takes place, which after formic acid coordination and activa-

tion leads mainly to CO and H₂O (Scheme 5, cycle A). As shown in Figure 1 *vide supra* CO₂ and H₂ are formed to a minor extent in the presence of [Pd]/**L3**/PTSA, or [Pd]/**L4** and [Pd]/**L4**/PTSA (Scheme 5, cycle B). Apparently, under acidic conditions the cationic [L₂PdH]⁺ complex **I** will more easily activate the C-H bond compared to the

Scheme 4. Comparison of Pd-catalyzed carbonylation of 2,3-dimethylbutene with HCO₂Me and FA.

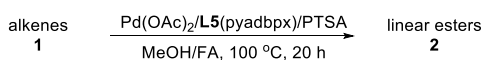


Reaction condition: 35 mL glass tube, Pd(OAc)₂ (1.0 mol%), **L5** (4.0 mol%), PTSA (16.0 mol%), **1a** (1.0 mmol), solvent, 100 °C, 20h.

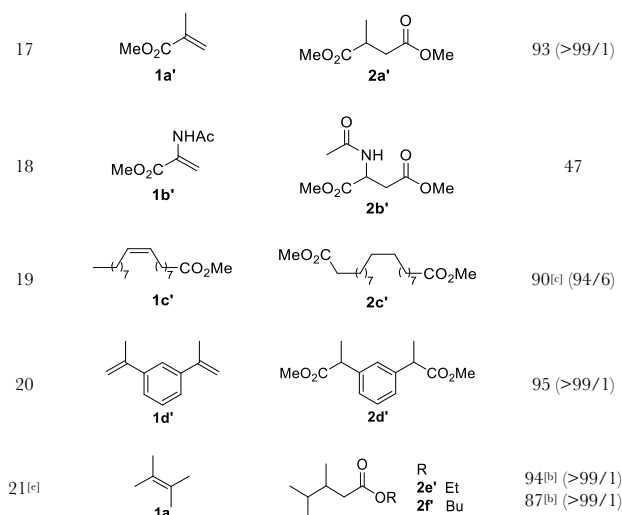
more electropositive O-H bond in formic acid. After *in situ* generation of CO and parallel isomerization of the internal olefin **1a** to the more reactive terminal alkene **1ab** (Scheme 5, cycle C), olefin coordination and insertion leads to the corresponding alkyl complex **IX**. Subsequent CO insertion and final nucleophilic attack by methanol or water gives the product and regenerates the active catalyst. It should be noted that comparison experiments in Scheme 4 and Scheme S1 clearly prove that the previously reported mechanism for Ru- and Pd-catalyzed carbonylations of olefins using alkyl formates is not operating here (Scheme 5, cycle D)^[5].

With optimized reaction conditions in hand, we investigated the substrate scope for the Pd-catalyzed alkoxy carbonylation reaction with formic acid and methanol (Table 2). Reactions of terminal aliphatic alkenes such as 1-octene (**1b**), *tert*-butyl ethylene (**1c**), and styrene (**1d**) proceeded efficiently with no less than 80% yields and up to 99% linear selectivity (Table 2, entries 1-3). Internal alkenes as well as mixtures of internal and terminal olefins are preferred for the industrial manufacture of bulk chemicals due to their lower price. Therefore, olefin isomerization followed by carbonylation is of significant interest. Hence, we were pleased to see that this catalytic system is able to convert aliphatic internal olefins, including 2-octene (**1e**), 4-octene (**1f**) as well as the mixture of octenes (**1g**), into the corresponding linear methyl nonanoate with high yields and *n*-selectivity (Table 2, entries 4-6). Cyclic olefins such as cyclopentene (**1h**), cyclohexene (**1i**), cycloheptene (**1j**), cyclooctene (**1k**) as well as indene (**1l**) and 1,2-dihydronaphthalene (**1m**) were also transformed into the desired esters in good yields and selectivities (Table 2, entries 7-8). The reactions of α -methylstyrene derivatives with various substituents on the phenyl ring (**1n-1s**) as well as α -phenylstyrene (**1t**) and stilbene (**1u**) afforded a series of terminal araliphatic esters in no less than 94% yields again with excellent selectivities (Table 2, entries 9-11).

Table 2. Pd-catalyzed alkoxy carbonylation of alkenes 1a-1d' with HCOOH.^a



Entry	Alkene	Linear ester	Yield/% (<i>n</i> / <i>iso</i>)
1 ^[b]	1b (n-C ₆ H ₁₃)	2b (n-C ₆ H ₁₃)	95 ^[c] (94/6)
2	1c	2c	95 ^[c] (>99/1)
3	1d (Ph)	2d (Ph)	80 ^[c] (75/25)
4	1e (n-C ₅ H ₁₁)	2b (n-C ₆ H ₁₃)	93 ^[c] (94/6)
5	1f (n-C ₃ H ₇)	2b (n-C ₆ H ₁₃)	87 ^[c] (92/8)
6	1g (mixture of 1b , 1e , 1f)	2b (n-C ₆ H ₁₃)	91 ^[c] (94/6)
7	1h n = 0 1i n = 1 1j n = 2 1k n = 3	2h n = 0 2i n = 1 2j n = 2 2k n = 3	90 93 94 96
8	1l n = 1 1m n = 2	2l n = 1 2m n = 2	94 (1/2 = 90/10) 88 ^[b] (2/1 = 87/13)
9	1n R = C ₆ H ₅ 1o R = 4-FC ₆ H ₄ 1p R = 4-ClC ₆ H ₄ 1q R = 2-MeC ₆ H ₄ 1r R = 4-MeC ₆ H ₄ 1s R = 2-naphthyl	2n R = C ₆ H ₅ 2o R = 4-FC ₆ H ₄ 2p R = 4-ClC ₆ H ₄ 2q R = 2-MeC ₆ H ₄ 2r R = 4-MeC ₆ H ₄ 2s R = 2-naphthyl	94 (>99/1) 96 (>99/1) 94 (>99/1) 96 (>99/1) 95 (>99/1) 94 (>99/1)
10	1t (Ph)	2t (Ph)	96 (>99/1)
11 ^[b]	1u (Ph)	2u (Ph)	97 ^[c]
12 ^[b]	1v diisobutylene (81% + 19%)	2v	95 (>99/1)
13	1w (n-C ₈ F ₁₇)	2w (n-C ₈ F ₁₇)	24 (>99/1)
14	1x (Et ₃ Si)	2x (Et ₃ Si)	90 (>99/1)
15	1y	2y	32 (>99/1)
16	1z (MeO ₂ C)	2z (MeO ₂ C)	90 ^[c] (90/10)

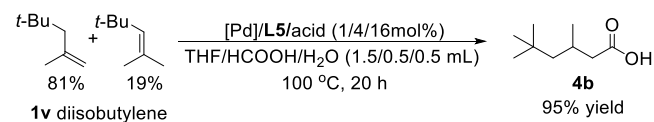


[a] Reaction conditions: **1** (1.0 mmol), Pd(OAc)₂ (1.0 mol%), **L5** (4.0 mol%), PTSA (16.0 mol%), MeOH/HCOOH (1.5/0.5 mL), 100 °C, 20 h. GC yields using *iso*-octane as internal standard. [b] isolated yields. [c] **L3** instead of **L5**. [d] 40 h. [e] solvent: ROH instead of MeOH, ROH/HCOOH (1.5/0.5 mL).

Furthermore, methoxycarbonylation of the industrial feedstock diisobutene^[21] (**1v**) proceeded via double-bond isomerization and consecutive carbonylation to produce selectively the desired ester **2v** in very good yield (Table 2, entries 12). From a synthetic point of view it is important that various functionalized olefins containing fluoride, silyl, imide, and ester groups (**1w-1a'**) were tolerated. The desired esters were achieved in up to 93% yields with high linear selectivities (Table 2, entries 13-17). Furthermore, methyl 2-acetamidoacrylate (**1b'**) - an example of a notoriously unreactive push-pull olefin - produced the corresponding amino acid derivative in 47% yield (Table 2, entries 18).

The renewable internal ester **1c'** underwent the same isomerization/methoxycarbonylation transformation to provide the diester in 90% yield and 94% *n*-selectivity (Table 2, entry 19). Additionally, the dimethoxycarbonylated compound **2d'** was obtained in 95% yield by carbonylation of **1d'** (Table 2, entry 20). Notably, carbonylation of **1a** with EtOH or BuOH afforded the corresponding esters (**2e'** and **2f'**) in high yields and selectivities (Table 2, entry 21). Finally, hydroxycarbonylation product **4a** (Scheme 4) and **4b** (Scheme 6) can be obtained separately in 92% and 95% isolated yield. This process demonstrates the possibility to obtain useful carboxylic acids in a 100% atom-efficient way using formic acid!

Scheme 6. Domino catalysis: Hydroxycarbonylation of sterically hindered alkenes with HCOOH.



CONCLUSIONS

In summary, an operationally simple and general applicable protocol for the carbonylation of alkenes was developed. Terminal, internal, tri- and even tetra-substituted as well as functionalized olefins were converted efficiently into the desired esters in high yields with good to excellent linear selectivity. This advanced catalytic process relies: 1. on the selective catalytic decomposition of HCOOH to CO and 2. the fast alkene isomerization and regioselective alkoxy-carbonylation or hydroxycarbonylation in the presence of our palladium-phosphine complexes with ligands **L4** and **L5**. Considering the readily availability of HCOOH, this powerful method provides an alternative for alkene carbonylation in both industry and laboratory.

ASSOCIATED CONTENT

Supporting Information

Additional experimental results and procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* Matthias.Beller@catalysis.de

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENT

We thank for financial support from Evonik Performance Materials GmbH and the State of Mecklenburg-Vorpommern. The support of the analytical team of LIKAT is appreciated.

ABBREVIATIONS

FA, formic acid; MF methyl formate; Ad, adamantyl; PTSA, *p*-toluenesulfonic acid monohydrate; TON, turnover numbers.

REFERENCES

- (a) Kiss, G. *Chem. Rev.* **2001**, *101*, 3435-3456. (b) Kollár, L. *Modern Carbonylation Methods*, Wiley-VCH, Weinheim, **2008**. (c) Beller, M. *Catalytic Carbonylation Reactions*, Springer, Berlin, **2006**.
- (a) Gautam, P.; Bhanage, B. M. *Catal. Sci. Technol.* **2015**, *5*, 4663-4702. (b) Cao, J.; Zheng, Z. J.; Xu, Z.; Xu, L. W. *Coord. Chem. Rev.* **2017**, *336*, 43-53.
- Odell, L. R.; Russo, F.; Larhed, M. *Synlett.* **2012**, *23*, 685-698.
- Hermange, P.; Lindhardt, A. T.; Taaning, R. H.; Bjerglund, K.; Lupp, D.; Skrydstrup, T. *J. Am. Chem. Soc.* **2011**, *133*, 6061-6071.
- (a) Lin, I. J. B.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1989**, 248-249. (b) Keim, W.; Becker, J. *J. Mol. Catal.* **1989**, *54*, 95-101. (c) Isnard, P.; Denise, B.; Sneed, R. P. A.; Cognion, J. M.; Durual, P. *J. Organomet. Chem.* **1983**, *256*, 135-139. (d) Lavigne, G.; Lugan, N.; Kalck, P.; Soulie, J. M.; Lerouge, O.; Saillard, J. Y.; Halet, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 10669-10670. (e) Ko, S.; Na, Y.; Chang, S. *J. Am. Chem. Soc.* **2002**, *124*, 750-751. (f) Wu, L.; Liu, Q.; Jackstell, R.; Beller, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 6310-6320.

(6) Liu, Q.; Yuan, K.; Arockiam, P.-B.; Franke, R.; Doucet, H.; Jackstell, R.; Beller, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 4493-4497.

(7) (a) Friis, S. D.; Taaning, R. H.; Lindhardt, A. T.; Skrydstrup, T. *J. Am. Chem. Soc.* **2011**, *133*, 18114-18117. (b) Ren, X.; Zheng, Z.; Zhang, L.; Wang, Z.; Xia, C.; Ding, K. *Angew. Chem. Int. Ed.* **2017**, *56*, 310-313. (c) Lian, Z.; Nielsen, D. U.; Lindhardt, A. T.; Daasbjerg, K.; Skrydstrup, T. *Nat. Commun.* **2016**, *7*, 13782-13788.

(8) (a) Jin, F.; Yun, J.; Li, G.; Kishita, A.; Tohji, K.; Enomoto, H. *Green Chem.* **2008**, *10*, 612-615. (b) Wölfel, R.; Taccardi, N.; Bösmanna, A.; Wasserscheid, P. *Green Chem.* **2011**, *13*, 2759-2763. (c) Albert, J.; Wölfel, R.; Bösmann, A.; Wasserscheid, P. *Energy Environ. Sci.* **2012**, *5*, 7956-7962.

(9) (a) Moret, S.; Dyson, P. J.; Laurenczy, G. *Nat. Comm.* **2014**, *5*, 4017-4021. (b) Sordakis, K.; Tang C.; Vogt L. K.; Junge, H.; Dyson P. J.; Beller, M.; Laurenczy, G. *Chem. Rev.* **2018**, *118*, 372-433.

(10) Ren, W.; Chang, W.; Dai, J.; Shi, Y.; Li, J.; Shi, Y. *J. Am. Chem. Soc.* **2016**, *138*, 14864-14867.

(11) (a) Hou, J.; Xie, J. -H.; Zhou, Q. -L. *Angew. Chem. Int. Ed.* **2015**, *54*, 6302-6305. (b) Fu, M. -C.; Shang, R.; Cheng, W. -M.; Fu, Y. *ACS Catal.* **2016**, *6*, 2501-2505. (c) Hou, J.; Yuan, M. -L.; Xie, J.-H.; Zhou, Q. -L. *Green Chem.* **2016**, *18*, 2981-2984.

(12) Simonato, J. -P.; Walter, T.; Métivier, P. *J. Mol. Catal. A: Chem.* **2001**, *171*, 91-94.

(13) Braca, G.; Guainai, G.; Raspolli, A. M.; Sbrana, G.; Valentini, G. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 409-417.

(14) (a) *CRC Handbook of Chemistry and Physics*, 95th ed. (Ed.: W. M. Haynes), CRC Press/Taylor and Francis, Boca Raton, FL, **2015**. (b) Kuehnel, M. F.; Wakerley, D. W.; Orchard, K. L.; Reisner, E. *Angew. Chem. Int. Ed.* **2015**, *54*, 9627-9631.

(15) (a) Gao, Y.; Kuncheria, J.; Puddephatt, R. J.; Yap, G. P. A. *Chem. Commun.* **1998**, 2365-2366. (b) Fellay, C.; Dyson, P. J.; Laurenczy, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 3966-3968. (c) Loges, B.; Boddien, A.; Junge, H.; Beller, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 3962-3965. (d) Himeda Y., *Green Chem.* **2009**, *11*, 2018-2022; (e) Morris, D. J.; Clarkson, G. J.; Wills, M.; *Organometallics* **2009**, *28*, 4133-4140. (f) Boddien, A.; Mellmann, D.; Gartner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. *Science* **2011**, *333*, 1733-1736. (g) Hull, J. F.; Himeda, Y.; Wang, W. -H.; Hashiguchi, B.; Periana, R.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. *Nat. Chem.* **2012**, *4*, 383-388. (h) Barnard, J. H.; Wang, C.; Berry, N. G.; Xiao, J. *Chem. Sci.* **2013**, *4*, 1234-1244. (i) Mellone, I.; Peruzzini, M.; Rosi, L.; Mellmann, D.; Junge, H.; Beller, M.; Gonsalvi, L. *Dalton Trans.* **2013**, *42*, 2495-2501. (j) Oldenhof, S.; de Bruin, B.; Lutz, M.; Siegler, M. A.; Patureau, F. W.; van der Vlugt, J. I.; Reek, J. N. H. *Chem.-Eur. J.* **2013**, *19*, 11507-11511. (k) Zell, T.; Butschke, B.; Ben-David, Y.; Milstein, D. *Chem.-Eur. J.* **2013**, *19*, 8068-8072. (l) Sponholz, P.; Mellmann, D.; Junge, H.; Beller, M. *ChemSusChem* **2013**, *6*, 1172-1176. (m) Manaka, Y.; Wang, W. -H.; Suna, Y.; Kambayashi, H.; Muckerman, J. T.; Fujita, E.; Himeda, Y. *Catal. Sci. Technol.* **2014**, *4*, 34-37. (n) Myers, T. W.; Berben, L. A. *Chem. Sci.* **2014**, *5*, 2771-2777. (o) Bielinski, E. A.; Lagaditis, P. O.; Zhang, Y.; Mercado, B. Q.; Würtele, C.; Bernskoetter, W. H.; Hazari, N.; Schneider, S. *J. Am. Chem. Soc.* **2014**, *136*, 10234-10237.

(16) (a) Mars, P.; Scholten, J. J. F.; Zwietering, P. in *Adv. Catal., Vol. 14*; Eley, H. P. D. D.; Paul, B. W. Eds.; Academic

Press, San Diego, **1963**. (b) Morgan, J. S. *J. Chem. Soc., Trans.* **1916**, *109*, 274-283.

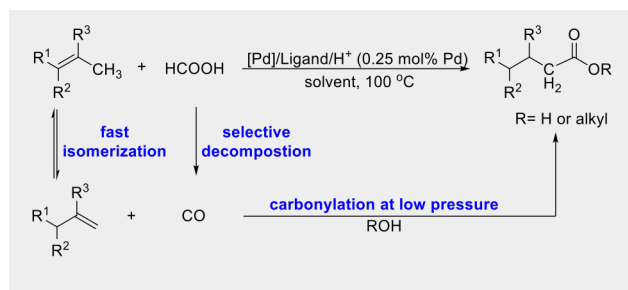
(17) (a) Liu, W.; Ren, W.; Li, J.; Shi, Y.; Chang, W.; Shi, Y. *Org. Lett.* **2017**, *19*, 1748-1751. (b) Dai, J.; Ren, W.; Wang, H.; Shi, Y. *Org. Biomol. Chem.* **2015**, *13*, 8429-8432. (c) Wang, Y.; Ren, W.; Shi, Y. *Org. Biomol. Chem.* **2015**, *13*, 8416-8419.

(18) (a) Rodriguez, C. J.; Foster, ; Eastham, D. F. G. R.; Cole-Hamilton, D. J. *Chem. Commun.* **2004**, 1720-1721. (b) Clegg, W.; Elsegood, M. R. J.; Eastham, G. R.; Tooze, R. P.; Wang, X. Lan; Whiston, K. *Chem. Commun.* **1999**, 1877-1878.

(19) (a) Dong, K.; Fang, X.; Gülak, S.; Franke, R.; Spannenberg, A.; Neumann, H.; Jackstell, R.; Beller, M. *Nat. Commun.* **2017**, *8*, 14117-14123. (b) Dong, K.; Sang, R.; Franke, R.; Spannenberg, A.; Neumann, H.; Jackstell, R.; Beller, M. *Angew. Chem. Int. Ed.* **2017**, *56*, 5267-5271.

(20) Dong, H. Li, K.; Jiao, H.; Neumann, H.; Jackstell, R.; Beller, M. *Nat. Chem.* **2016**, *8*, 1159-1166.

(21) An industrial mixture of C8 alkenes, known as “diisobutene” from the dimerization of isobutene, consisting of two trimethylpentene isomers.



Rui Sang, Peter Kucmierczyk, Kaiwu Dong, Robert Franke, Helfried Neumann, Ralf Jackstell, and Matthias Beller*

Page No. – Page No.

Palladium-catalyzed Selective Generation of CO from Formic Acid for Carbonylation of Alkenes

10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Let's play domino. Palladium-catalyzed carbonylations of olefins with formic acid proceeds in high yields and regioselectivities using phosphines with "built-in" base.