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Palladium-Catalyzed Aminocarbonylation of Aliphatic Alkenes with *N,N*-Dimethylformamide as an In Situ Source of CO

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The palladium-catalyzed aminocarbonylation of aliphatic alkenes is presented for the first time without the need for external CO pressure. *N,N*-dimethylformamide (DMF) is used as an in situ source of both the required carbon monoxide and the amine substrate. The applied palladium catalytic system is well-known for a number of carbonylation reactions, including those with CO surrogates and tandem isomerizing carbonylations. The reaction pathway was investigated and proved to proceed by an acid-catalyzed DMF decomposition to CO and dimethyl amine with subsequent aminocarbonylation of the alkene. Pressure-versus-time curves gave more insight into the correlation between acid concentration and aminocarbonylation activity. Aliphatic alkenes (terminal and internal) are transformed, also in commercial glassware, into the corresponding linear *N,N*-dimethylamides with excellent selectivities. Hence, amide synthesis by aminocarbonylation moves closer to application in standard organic laboratories.

Introduction

Numerous methods exist for the preparation of amides, although their synthesis without the generation of waste and the use of toxic reagents can be challenging. Usually, amides are derived from the corresponding carboxylic derivatives (esters, anhydrides, acyl chlorides) with the respective amines, and the use of coupling reagents is often necessary.[1] Hence, the development of more atom-economic and environmentally benign strategies for amide synthesis is one of the major goals of synthetic organic chemistry.[2] Catalytic systems offer the potential to apply less activated substrates for amide synthesis, resulting in less waste production. Therefore, catalytic amide synthesis has attracted many researchers in recent years and different systems have been developed.[3] Milstein and co-workers, for instance, have developed a ruthenium catalyst yielding an amide by the coupling of an amine and an alcohol.[4] Another elegant way for the generation of amides from readily available substrates is by aminocarbonylation of olefins. This carbonylative reaction has initially been described by Reppe with nickel catalysts,[5] and among others, different palladium catalytic systems have been developed for aminocarbonylation of alkenes[6–11] and alkynes[12–23] since then. The application of CO as an active, versatile and low-cost C_1 building block for the functionalization of alkenes is nowadays an indispensable technique in the chemical industry. However, its inherent toxicity and the need for special equipment to economically and safely use this gas results in a significant inconvenience to handle it, especially in common organic laboratories. As a result, the substitution of CO in carbonylation reactions by less toxic and easier-to-handle synthetic equivalents is of considerable academic interest.[24,25] For amide formation from olefins, formamides represent ideal CO surrogates.

The reaction of olefins with formamide to amides under nickel catalysis and CO pressure was already conducted by Reppe in his initial studies on catalytic carbonylations.[5] However, first reports on other metals than nickel for this transformation have not been published until the report of Kondo and Watanabe et al. on a ruthenium-catalyzed system.[26] Later on, the drawback of external CO pressure for maintaining catalytic activity was addressed by Kondo and co-workers, and the first CO free aminocarbonylation of olefins with formamides was developed by ruthenium catalysis.[27] Since then, different catalytic systems for either inter- or intramolecular additions of formamides to olefins have been developed. Notably, a blurred taxonomy exists for this transformation (Scheme 1): The amide formation from an alkene with CO and an amine is designated aminocarbonylation, but the corresponding addition of form-

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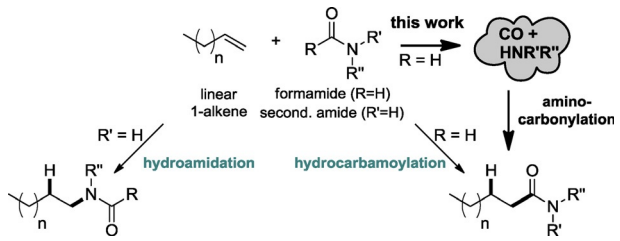


Scheme 1. Reactions of (form)amides with linear 1-alkenes.

amides to olefins is denoted as hydrocarbamoylation[28–33] and sometimes also as hydroamidation.[34–36] Some reports also use the term hydroamidation as a synonym for aminocarbonylation.[37,38] In contrast, hydroamidation is more often referred to as the addition of an amide to an olefin under the formation of a higher substituted amide (i.e., C–N-bond formation).[39]

Low-molecular aliphatic formamides such as *N,N*-dimethylformamide (DMF) are especially interesting, as they are cheap and readily available, and hence, their application as an amide building block is an interesting alternative to the synthesis with CO, particularly in standard organic laboratories. Such a way has been reported for aryl halides,[40–44] alkynes,[28,45] and alkenes.[29] However, usually either high catalyst loadings (up to 10 mol%) are required or the system is limited to expensive aryl iodides and bromides as substrates.

In our ongoing interest in palladium-catalyzed carbonylation reactions, especially with the high-performance ligand involved in the methoxycarbonylation of aliphatic alkenes for the production of linear esters, 1,2-bis((di-*tert*-butylphosphino)methyl)benzene (1,2-DTBPMB, Figure 1),[46–56] we developed the idea of aminocarbonylation of linear aliphatic 1-alkenes with formamides using this catalytic system. Based on the reports on the alkoxycarbonylation of alkenes with formates[57] and our latest investigations in aminocarbonylation with CO applying this catalyst system,[10] we herein report the palladium-catalyzed aminocarbonylation of aliphatic alkenes with DMF as an in situ source of carbon monoxide and dimethylamine.

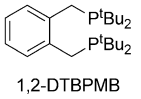


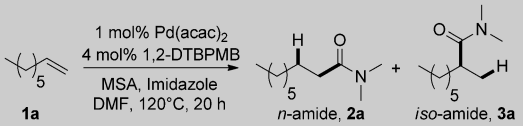
Figure 1. Ligand used in the present study (1,2-bis((di-*tert*-butylphosphino)methyl)benzene; 1,2-DTBPMB).

Results and Discussion

We first attempted the transformation of 1-octene (**1a**) with DMF at 80 °C in a glass vial sealed with a Teflon cap. $Pd(acac)_2$, methanesulfonic acid (MSA), and 1,2-DTBPMB were applied to form the catalytic system. Unfortunately, no *N,N*-dimethylnonanamide (**2a**) was formed under the chosen conditions, and only octene isomers were detected by GC analysis. However, after the reaction, an increase in pressure and a release of gas and a weight loss was noticed upon carefully opening the vial. We assumed a decomposition of DMF to CO and dimethylamine and noticed that for carbonylation reactions employing formamides, only Hallberg and co-workers reported on the decomposition of those in their investigations on microwave-assisted Pd-catalyzed aminocarbonylation of aryl bromides under basic conditions.[40,41] Notably, all other reports on carbonylations with DMF did not mention decomposition, and DMF decomposition under acidic conditions at 80 °C is also not reported.

Thus, to effectively keep carbon monoxide and dimethylamine in the condensed phase, thereby expectantly promoting aminocarbonylation, we changed the reaction vessel to a custom-made pressure-resistant autoclave. Taking inspiration from the results of Hallberg, we first raised the temperature to 120 °C. In Hallberg's investigations, imidazole was used as a co-catalyst in a ratio of 1:1 of substrate/imidazole to promote aminocarbonylation, thus we decided to add imidazole to our reaction setup. We tested different MSA/imidazole ratios on our system (Table 1) to find out whether imidazole acts as a co-catalyst in our aminocarbonylation to conclude a catalytic mechanism.

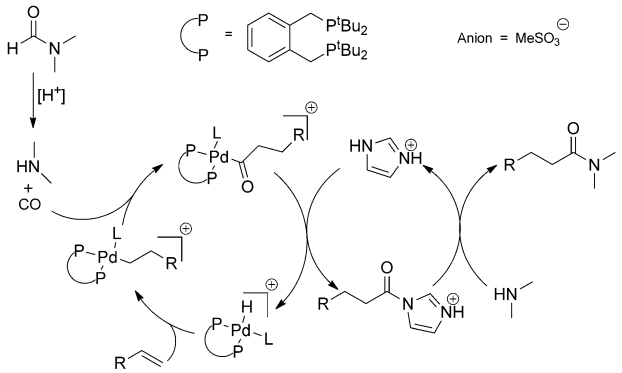
Table 1. Influence of imidazole addition on the aminocarbonylation.[a]



Entry	Imidazole (eq./**1a**)[c]	MSA (eq./**1a**)[c]	S_{2a+3a} (**2a**:**3a**)	Y_{2a+3a}[b]
1.1	1.0	0.7	0	0
1.2	1.0	0.5	0	0
1.3	1.0	0.2	0	0
1.4	0.75	0.7	0	0
1.5	0.5	0.7	94±1 (21:1)	36±5
1.6	0.25	0.7	91±1 (22:1)	47±5
1.7	0	0.7	0	0

[a] Conditions: 7 mL stainless steel autoclave, **1a** (1 mL, 6.33 mmol), $Pd(acac)_2$ (19.3 mg, 0.063 mmol), 1,2-DTBPMB (4 equiv./Pd: 100 mg, 0.25 mmol), DMF (5 mL), 120 °C, 20 h. [b] Entries 5, 6: all reactions were repeated 2–4 times. Yield (Y) is given as sum of both amide isomers (**2a**+**3a**) and reported in % based on GC–FID analysis [c] eq.: equivalent to **1a**.

As imidazole acts as a base and captures all protons, no active palladium hydride species is formed in this nonacidic environment. Hence, no activity was observed in entries 1.1 to 1.4 (Table 1). We therefore assume a palladium hydride mechanism, in accordance with preliminary carbonylations applying this catalytic system. The amount of MSA has thus to be higher than the amount of imidazole in oncoming optimization. However, as soon as the imidazole amount dropped below the one from MSA, aminocarbonylation of **1a** with DMF was successful and the chosen catalytic system selectively yielded the desired amide **2a** with very high linear-to-branched ratios exceeding 20:1 (entry 1.5 and 1.6). In the absence of imidazole as a promoter, no activity was observed (entry 1.7). Thus, based on our work in methoxy- and aminocarbonylation and Hallberg's proposed mechanism, we suggest the full catalytic cycle of the reaction in Scheme 2, in which



Scheme 2. Proposed catalytic cycle.

imidazole acts as co-catalyst for the formation of aliphatic amides by transamidation of the corresponding aromatic imidazoylamide intermediate.

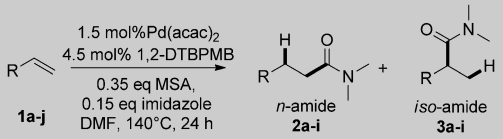
Encouraged by the promising results and findings from our initial screening, we were further interested in the decomposition reaction of DMF under the chosen conditions. To gain more insight into this important part of the reaction, we first optimized the decomposition temperature. As a compromise between the tolerated temperature of the applied palladium catalyst and the decomposition reaction, we found 140 °C to be purposeful. In time-dependent pressure curves, the individual components' influence on the decomposition of DMF was investigated in detail and the nature of the gaseous products was characterized (see the Supporting Information). It was revealed that the palladium precursor and imidazole only negligibly cause decarbonylation, and MSA is responsible for the formation of CO and dimethylamine. The amount of MSA is reduced by the application of imidazole, resulting in lower decarbonylation activity. CO and dimethylamine are the predominant species in the gas phase, proving aminocarbonylation with CO and dimethylamine occurs. Additionally, we assume that the pressure increase is limited, which might be caused by the loss of acidity owing to the liberation of dimethylamine.

With the aim to further increase the yield and to gain more insight into the reaction system, we screened different reaction temperatures under the conditions of Table 1, entry 1.6 (see the Supporting Information). As anticipated, after the reaction at 160 °C, we noticed the presence of black particles in suspension, suggesting a decomposition of the catalytic species. Fortunately, the optimum temperature was found to be 140 °C, yielding up to 57±5% at high selectivity of 95±1%. The screening of different amounts of MSA, imidazole, DMF, and concentrations and ratios of the catalyst system can be found in the Supporting Information. Highest yields of **2a** of 73% were achieved at 140 °C for 24 h reaction time, using 0.35 equivalents of MSA, 0.15 equivalents of imidazole, a precursor concentration of 1.5 mol% at a palladium-to-ligand ratio [Pd]:L of 3 in 1 mL DMF. The selectivity to the linear amide was high with 94%, although already a [Pd]:L ratio of 2 provided selectivities to the linear amide of approximately 90%. To the best of our knowledge, it is the first time only two equivalents of the 1,2-DTBPMB ligand are used in a carbonylation reaction providing such high *n*:*iso* ratios. Usually four, five equivalents or more are used.[46–56]

With the optimized conditions in hand, we decided to apply the developed catalytic system to a range of alkenes **1a–j** with varying the chain length from 3 to 16 carbon atoms, to prove the general usability of our system for the synthesis of linear amides.

First of all, the substrate scope proves that the chemo- as well as regioselectivities of the developed catalytic system are independent from the applied substrate at high to very high values of 92–96% and 21–32:1, respectively (Table 2). Indeed,

Table 2. Substrate scope of the developed protocol.[a]



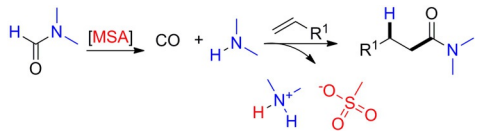
Entry	Substrate	S_{2+3} (**2**:**3**)	Y_{2+3}[b]
2.1	propene **1b**, R = methyl	96 (30:1)	96
2.2	1-pentene **1c**, R = *n*-propyl	93 (25:1)	85
2.3	1-hexene **1d**, R = *n*-ethyl	92 (22:1)	81
2.4	1-octene **1a**, R = *n*-hexyl	94 (21:1)	73
2.5	1-decene **1e**, R = *n*-octyl	93 (23:1)	43
2.6	1-dodecene **1f**, R = *n*-decyl	92 (21:1)	31
2.7	1-tetradecene **1g**, R = *n*-dodecyl	93 (21:1)	24
2.8	1-hexadecene **1h**, R = *n*-tetradecyl	94 (23:1)	12
2.9	4,4-dimethyl-1-pentene **1i**, R = *tert*-butyl	96 (32:1)	77
2.10	4-octene **1j**	94 (21:1)	62

[a] Conditions: 7 mL stainless steel autoclave, **1a–j** (2.21 mmol), $Pd(acac)_2$ (1.5 mol%: 10.1 mg, 0.033 mmol), 1,2-DTBPMB (4.5 mol%: 26.2 mg, 0.07 mmol), MSA (0.35 equiv.: 0.05 mL, 0.78 mmol), imidazole (0.15 equiv.: 22.6 mg, 0.33 mmol), 1 mL DMF, 140 °C, 24 h. [b] Yield (Y) is given as sum of both amide isomers and reported in % based on GC–FID analysis.

the catalytic system used is well-known for its ability to isomerize the double bond all over the chain but selectively operating the carbonylation at the very end of the chain. In all examples in Table 2 (except entries 2.1 and 2.9), only isomers of the starting alkene were found in the GC–FID trace, indicating that isomerization is much faster than carbonylation, but only 1-alkenes react regioselectively. This was proven in the reaction of 4-octene **1j** under the optimized conditions. Besides the lower yield of the amides of 62% than for 1-octene **1a**, the selectivity is evenly high (entry 2.10). Whereas selectivity is untouched by the chain length of the starting alkene, the yield for the amide significantly decreases with increasing chain length from propene **1b** (96%) to 1-hexadecene **1h** (12%, entries 2.1–2.8) The sterically more demanding 4,4-dimethyl-1-pentene **1i** achieves a yield of 77%, although highest selectivities were observed, presumably caused by the sterically demanding *tert*-butyl group, which protects the internal position from carbonylation (entry 2.9).

Bearing in mind that isomerization is much faster than carbonylation, the explanation to the trend in yield might be that back-isomerization of linear alkenes to the terminal position

takes longer the further the double bond is buried in the chain. However, no significant increase in yield was observed if the reaction of 1-dodecene **1 f** was conducted for 96 h. Thus, we anticipated that another, not yet considered, parallel reaction takes place, which is responsible for the reaction to "fall asleep". It was proven that the decomposition of DMF depends on the amount of MSA (Scheme 3). Hence, if the concentration



Scheme 3. Reaction of dimethylamine with MSA in the acid-catalyzed decomposition of DMF.

of MSA decreases in situ by the liberation of dimethylamine, the decomposition will stop at one point and no further carbonylation will occur. This happens earlier the slower the carbonylation is, and thus, the longer the applied alkene.

The pH of the reaction mixture after the aminocarbonylation was tested with a pH test strip to be approximately 5 whereas in the reaction setup it was approximately 1. A test decomposition of DMF at a pH adjusted to 5 before the reaction showed no significant increase in pressure, demonstrating that an acidic environment is crucial for decomposition.

We then performed two standard reactions (according to the conditions in Table 2, entry 2.6) in which 1-dodecene **1 f** was converted over a longer reaction period. In the first reaction, we vented the autoclave, withdrew aliquots for GC analysis, and added additional portions of MSA after certain periods of time (light gray graphs, Figure 2). In the second reaction, the reactor was opened, the pressure released, and only aliquots were withdrawn from the reactor (gray graphs, Figure 2).

We assumed, based on the hypothesis of the in situ loss of acidity in our reaction setup, that with regularly refreshing

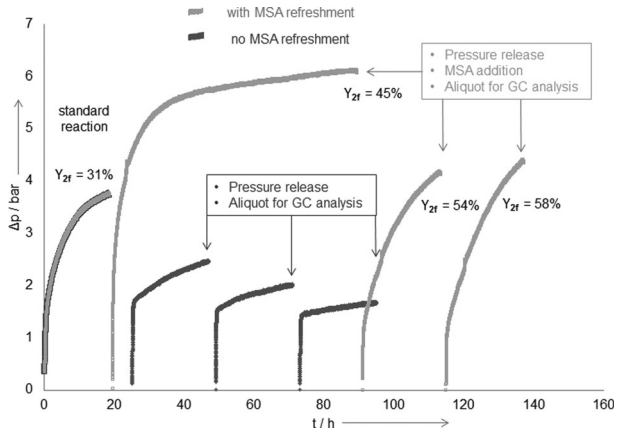


Figure 2. Pressure curves of the aminocarbonylation of 1-dodecene **1 f** with (light gray) and without (gray) refreshment of MSA. Conditions: 7 mL stainless steel autoclave, **1 f** (0.49 mL, 2.21 mmol), $Pd(acac)_2$ (1.5 mol%: 10.1 mg, 0.033 mmol), 1,2-DTBPMB (4.5 mol%: 26.2 mg, 0.07 mmol), MSA (0.35 equiv.: 0.05 mL, 0.78 mmol), imidazole (0.15 equiv.: 22.6 mg, 0.33 mmol), 140 °C. Refreshment of MSA equals the initial amount (0.35 equiv.).

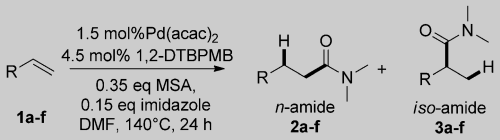
MSA, the decomposition of DMF can be performed over a longer period of time, thereby enabling higher yields for the desired linear amide **2 f** than for the one-step reaction setup in Table 2, entry 2.6. In contrast, with no MSA refreshment, the decomposition activity, and hence the pressure increase, should be less after each pressure release, resulting in no additional yield for the linear amide **2 f**. As seen in Figure 2, after releasing the pressure from the autoclave without MSA refreshment, the pressure increase flattens significantly after already four reactions. No increase in yield for the linear amide was detected in the absence of additional MSA. If MSA was refreshed after 19 h reaction time, the pressure increased to approximately 6 bar within 72 h, a value higher than that under standard conditions. It seems as if MSA was not fully consumed after 19 h and the addition of another 0.35 equivalents of MSA caused a higher overall concentration of MSA leading to an increased pressure. The following runs with MSA refreshment after 91 and 115 h showed a parallel pressure curve to the standard reaction. As a consequence of the successive refreshment of MSA, the yield for the desired amide product **2 f** was expectedly increased to 45% in the second, 54% in the third and 58% in the fourth run, respectively. Hence, the limited yield in the aminocarbonylation of longer chained alkenes can be attributed to two effects:

1) The slower overall carbonylation activity owing to isomerization of the starting 1-alkene. The longer the applied 1-alkene is, the more possible internal alkenes result, which leads to a lower probability of linear palladium–alkyl species. As it was already proven for other carbonylations applying our catalytic system, only the linear palladium–alkyl species readily react to form the carbonylation product,[50,52] resulting in high *n*:branched ratios as also found here.
2) The loss of acidity owing to the in situ neutralization of MSA by the release of dimethylamine during DMF decomposition leads to a loss of decomposition activity and lower concentration of palladium hydride species and thus to lower carbonylation activity.

We demonstrated the general usability of our hitherto developed protocol for the conversion of short- to medium-chained alkenes to linear amides with good yields and excellent selectivities. However, long-chained alkenes only lead to poor yields in our one-step protocol. With successive MSA refreshment, the yield for linear amides from longer chained 1-alkenes can be increased. Nonetheless, this approach suffers from long reaction times, the necessity of high MSA amounts, inconvenient handling, and still seems to be limited in yield. To develop a one-step protocol that allows for the useful, preparative isolation with higher yield of the respective linear amides also from longer chained alkenes, we increased the scale of the reaction by the factor four. This allowed for a further increase in concentration, (25% more concentrated than in Table 2) by using only a 3 mL volume of DMF.

With the scale-up, the yield for the respective amides from the C3–C6 alkenes remained almost constant (Table 3). However, for the longer chained alkenes **1 e** and **1 f**, the yield in-

Table 3. Upscaling of aminocarbonylation for preparative isolation.[a]



Entry	Substrate	S_{2+3} (2:3)	Y_{2+3}[b] (GC)	Y_2[c] (isolated)
3.1	propene **1b**, R = methyl	95 (29:1)	94	85
3.2	1-pentene **1c**, R = *n*-propyl	90 (22:1)	85	82
3.3	1-hexene **1d**, R = *n*-ethyl	92 (21:1)	80	78
3.4	1-octene **1a**, R = *n*-hexyl	90 (21:1)	72	69
3.5	1-decene **1e**, R = *n*-octyl	91 (22:1)	68	61
3.6	1-dodecene **1f**, R = *n*-decyl	92 (22:1)	67	58
3.7[d]	1-octene **1a**, R = *n*-hexyl	91 (20:1)	63	60
3.8[e]	1-octene **1a**, R = *n*-hexyl	92 (23:1)	55	50

[a] Conditions: 7 mL stainless steel autoclave, **1a–f** (8.8 mmol), $Pd(acac)_2$ (1.5 mol%: 40 mg, 0.133 mmol), 1,2-DTBPMB (4.5 mol%: 105 mg, 0.27 mmol), MSA (0.35 equiv.: 0.2 mL, 3.1 mmol), imidazole (0.15 equiv.: 90 mg, 1.33 mmol), 3 mL DMF, 140 °C, 24 h. [b] Yield (Y) is given as sum of both amide isomers (**2** + **3**) and reported in % based on GC-FID analysis. [c] isolated yield after chromatographic workup [d] 300 mL stainless steel autoclave, **1a** (14 mL, 88.6 mmol), $Pd(acac)_2$ (1.5 mol%: 405.8 mg, 1.33 mmol), 1,2-DTBPMB (1048.5 mg, 2.66 mmol), MSA (2 mL, 31 mmol), imidazole (904.5 mg, 13.29 mmol), DMF (40 mL 140 °C, 24 h. [e] 8 mL pressure tube, **1a** (8.8 mmol), $Pd(acac)_2$ (1.5 mol%: 40 mg, 0.133 mmol), 1,2-DTBPMB (4.5 mol%: 105 mg, 0.27 mmol), MSA (0.35 equiv.: 0.2 mL, 3.1 mmol), imidazole (0.15 equiv.: 90 mg, 1.33 mmol), 3 mL DMF, 140 °C, 24 h.

creased significantly from 43% and 31% (Table 2, entries 2.5 and 2.6) to 68% and 67%, respectively (Table 3, entries 3.5 and 3.6). Despite the observation of a general loss of selectivity of 1 to 2%, the up-scaled protocol allowed for the preparative isolation of the respective linear amides from a range of linear 1-alkenes with fair to very good isolated yields. Additionally, a factor 10 upscale with 1-octene **1a** (entry 3.7) gives 60% isolated yield of the desired linear amide **2a**. Finally, to further move our developed protocol towards potential application in common organic laboratories, we tested the reaction of **1a** in a commercially available pressure-resistant glass tube ("pressure tube", entry 3.8). Besides the high selectivity, the yield was slightly lower than in the autoclave, presumably caused by the higher internal volume of the pressure tube. Nevertheless, 50% of the respective linear amide **2a** were isolated.

Conclusions

We have developed a new method for the synthesis of *N,N*-dimethyl-substituted amides from aliphatic alkenes by aminocarbonylation, involving the [Pd]/H^+/1,2-DTBPMB (DTBPMB = 1,2-bis((di-*tert*-butylphosphino)methyl)benzene) system in an environment free from initial pressure of carbon monoxide. *N,N*-dimethylformamide (DMF) was used as an in situ source of both carbon monoxide and dimethylamine. The reaction path was investigated, and evidence was found for the reaction to proceed through DMF decomposition with subsequent aminocarbonylation. Obtained yields, up to 96% in the optimized conditions, are linked to the chain length of the alkene: the longer the alkene, the lower the yield. It was shown that the in situ loss of acidity by the liberation of dimethylamine is almost certainly responsible for the limited yields if long-chained alkenes are employed. With successive acid refreshments, the yield for long-chain amides was significantly improved. Moreover, the well-known regioselectivity of the applied catalytic system as well as its ability to convert internal alkenes to linear products by preliminary isomerization were confirmed and transferred to our system. Indeed, a maximum selectivity of 96% was obtained, and an average selectivity of 90% to the linear amides was usually observed. On a preparative scale, isolated yields of the respective linear amides were fair to very high up to 85%. Additionally, up-scaling of the reaction and the operation in commercial glassware was also successful. Therefore we hope that this work encourages other researchers to apply, extend, and improve carbonylations with DMF as a convenient CO substitute.

Experimental Section

General procedure for aminocarbonylation with DMF

In a 7 mL stainless steel autoclave equipped with a magnetic stirring bar, $Pd(acac)_2$ (10.0 mg, 0.033 mmol), imidazole (22.4 mg, 0.33 mmol), and 1,2-DTBPMB (26.0 mg, 0.07 mmol) were introduced. The autoclave was sealed and purged three times with argon. Degassed DMF (1 mL), alkene (2.19 mmol), and methanesulfonic acid (0.05 mL, 0.77 mmol) were introduced in the autoclave by a cannula. The autoclave was placed in a preheated oil bath and magnetically stirred at 140 °C for 24 h. After the desired reaction time, the autoclave was cooled down to RT in a water/ice bath, carefully opened, and an aliquot was taken for GC analysis, by using dibutyl ether as an internal standard and dichloromethane as a diluter.

General procedure for the isolation of the products

The reaction mixture from the up-scaled reaction under the conditions of Table 3 was extracted with dichloromethane and filtered through a plug of celite on a Büchner funnel. The celite was washed with dichloromethane. The filtrate was concentrated under reduced pressure on a rotary evaporator. Hexane and water were added to the flask, and the biphasic system was decanted in a decantation funnel. The organic phase was dried with magnesium sulfate and filtered on a Büchner funnel and concentrated under reduced pressure on a rotary evaporator. The residues were purified by flash chromatography by using ethyl acetate and cyclohexane (EtOAc/cyclohexane, 2:3).

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