

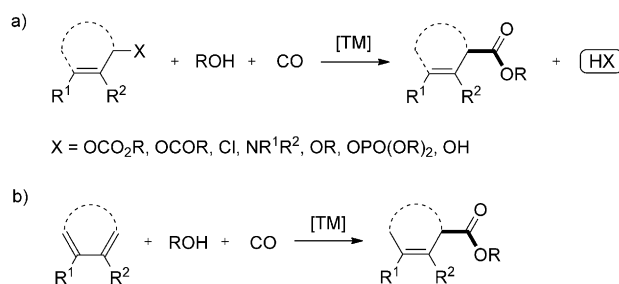
Carbonylation

# Palladium-Catalyzed Alkoxy carbonylation of Conjugated Dienes under Acid-Free Conditions: Atom-Economic Synthesis of $\beta,\gamma$ -Unsaturated Esters\*\*

Xianjie Fang, Haoquan Li, Ralf Jackstell, and Matthias Beller\*

**Abstract:** Carbonylation reactions constitute important methodologies for the synthesis of all kinds of carboxylic acid derivatives. The development of novel and better catalysts for these transformations is of interest for both academic and industrial research. Here, a benign palladium-based catalyst system for the alkoxy carbonylation of conjugated dienes under acid-free conditions has been developed. This atom-efficient transformation provides straightforward access to a variety of  $\beta,\gamma$ -unsaturated esters in good to excellent yields and often with high selectivities. As an industrially relevant example the (formal) synthesis of dimethyl adipate and  $\epsilon$ -caprolactam from 1,3-butadiene is demonstrated.

Alkene carbonylations are among the most important homogeneously catalyzed processes in industry.<sup>[1]</sup> Within this class of reactions, alkoxy carbonylations, also called hydroesterifications, represent a straightforward method for the conversion of olefins, CO, and alcohols into the corresponding esters.<sup>[2]</sup> In this respect, the transition-metal-catalyzed carbonylation of allylic compounds is of considerable interest for the synthesis of versatile  $\beta,\gamma$ -unsaturated carboxylic acid derivatives.<sup>[3]</sup> In the past, effective carbonylation methods for reactions of allylic carbonates,<sup>[4]</sup> acetates,<sup>[5]</sup> chlorides,<sup>[6]</sup> amines,<sup>[7]</sup> ethers,<sup>[8]</sup> phosphates,<sup>[5b,e,9]</sup> and alcohols<sup>[3c,6b,10]</sup> have been developed (Scheme 1a). Obviously, a general drawback of all these reactions is the stoichiometric generation of by-products. Alternatively,  $\beta,\gamma$ -unsaturated carboxylic acid derivatives can be synthesized by carbonylation of conjugated dienes (Scheme 1b). Despite the advantage of this more atom-efficient route, the carbonylation of conjugated dienes has scarcely been explored in academic laboratories. However, the selective alkoxy carbonylation of 1,3-butadiene is of major industrial interest. This substrate—produced in about  $12 \times 10^6$  metric tons annually—offers the possibility to produce bulk chemicals like adipic acid and  $\epsilon$ -caprolactam via 3-pentenoic acid esters.<sup>[11]</sup>



**Scheme 1.** Synthesis of  $\beta,\gamma$ -unsaturated esters by alkoxy carbonylation reactions. TM = transition metal.

In the early 1940s, Reppe first reported the reaction of 1,3-butadiene to carbonylated vinylcyclohexene derivatives in the presence of  $[\text{Co}_2(\text{CO})_8]$  as a catalyst.<sup>[24]</sup> Later, Du Pont reported the methoxycarbonylation of 1,3-butadiene to methyl pentenoate by using a Co/Cu/Th catalyst at very high pressure (810 bar).<sup>[12]</sup> In the late 1960s, Tsuji et al.<sup>[13]</sup> described this reaction in the presence of a catalytic amount of palladium chloride to give ethyl 3-pentenoate. While no product yield was given in the original paper, Tsuji et al.<sup>[13b]</sup> later reported an optimized yield of approximately 30% of ethyl 3-pentenoate. Matsuda and co-workers also demonstrated the use of cobalt catalysts in the presence of pyridines for this reaction.<sup>[14]</sup> However, only low catalyst turnover numbers (25–80) were achieved and high CO pressure was needed. A systematic investigation of the palladium-catalyzed carbonylation of 1,3-dienes was done by Knifton.<sup>[15]</sup> Despite variation of different ligands and solvents, mainly 3,8-nonadienoate esters (telomerization products) were obtained. A survey of the patent literature reveals significant work on the palladium-catalyzed methoxycarbonylation of 1,3-dienes by Shell,<sup>[16]</sup> Du Pont, and DSM.<sup>[11a,17]</sup> The latter companies, as well as Rhone Poulenc<sup>[18]</sup> disclosed a positive influence of added acids or quaternary onium salts on selectivity, conversion, and stability of the palladium catalyst. In addition, a Shell patent reported that by controlling the polarity of the reaction medium higher reaction rates can be achieved.<sup>[19]</sup>

In line with our interest in industrially relevant carbonylation reactions, we performed a systematic study on the methoxycarbonylation of 1,3-butadiene.<sup>[20]</sup> Examination of the influence of different reaction parameters on product yield and selectivity demonstrated the importance of chelating phosphine ligands and benzoic acids as additives to get good results. Until today, basically all of the published catalyst systems for carbonylation of dienes suffer from drawbacks such as the need for harsh reaction conditions and/or

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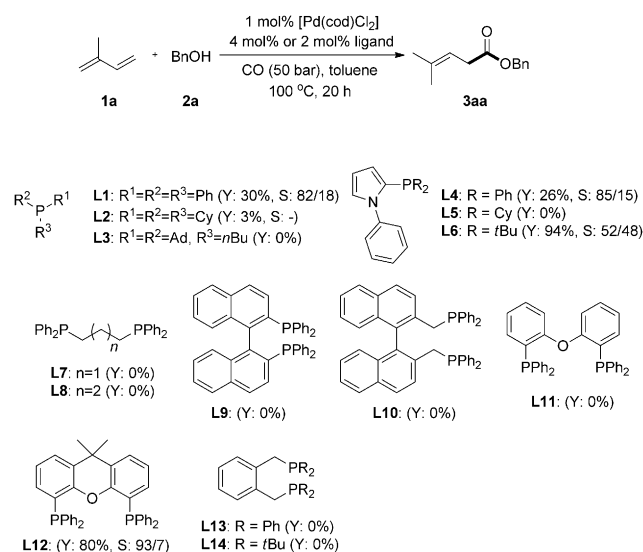


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additives, for example, acids, narrow substrate scope, relatively low product yield, and limited selectivity. In this regard, the development of improved and acid-free catalyst systems for this reaction is of high importance and constitutes a challenging and relevant topic for academic and industrial research.

Herein, we present an efficient palladium-based catalyst system for the selective alkoxycarbonylation of conjugated dienes under relatively mild reaction conditions. Notably, the various mono-, di-, and tri- $\beta,\gamma$ -unsaturated esters were obtained in high yield with good selectivity under acid-free conditions.

At the start of this study, we investigated the alkoxycarbonylation of isoprene (**1a**) and benzyl alcohol (**2a**) as a model reaction in the presence of [Pd(cod)Cl<sub>2</sub>] and different phosphine ligands (**L1–L14**; Scheme 2). The application of



**Scheme 2.** Palladium-catalyzed alkoxycarbonylation of isoprene (**1a**) with benzyl alcohol (**2a**): Influence of the ligand. Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), [Pd(cod)Cl<sub>2</sub>] (1.0 mol %), monodentate Ligand (4.0 mol %), bidentate ligand (2.0 mol %), CO (50 bar), toluene (2 mL), 100 °C, 20 h. Yield (Y) determined by GC analysis using isooctane as the internal standard. The ratios of isomers were determined by GC analysis. S=selectivity. Ad=adamantyl, cod=1,5-cyclooctadiene; Cy=cyclohexyl.

the monodentate ligands **L3** and **L5**, did not lead to any conversion. Notably, using **L1**, **L2**, and **L4** provided the desired product **3aa** without acid, albeit in low yields. When commercially available cataCXium PtB **L6** was used, the desired product **3aa** was obtained in good yield, however with low selectivity. Then, commercially available bidentate ligands were tested. Interestingly, all of bidentate ligands exhibited no activity in the formation of the desired product except Xantphos (**L12**), which was identified as the most promising ligand to afford the desired product **3aa** in good yield with high selectivity.

Next, to improve the reaction, we evaluated the influence of critical reaction parameters such as the molar ratio of **1a** to **2a**, catalyst loading, palladium precursors, temperature, and

gas pressure for the model reaction using Xantphos as the ligand of choice. As shown in Table 1, the yield of **3aa** was significantly affected by the molar ratio of **1a** to **2a**. Consequently, as the molar ratio of **1a** to **2a** increased to 1.2:1, the yield of **3aa** increased to 94% (entries 1 and 2). Lowering the catalyst loading revealed an optimal loading of

**Table 1:** Palladium-catalyzed alkoxycarbonylation of isoprene (**1a**) with benzyl alcohol (**2a**): Investigation of reaction conditions.<sup>[a]</sup>

| Entry            | Catalyst                                               | $p_{CO}$ [bar] | $T$ [°C] | Yield [%] <sup>[b]</sup> | Selectivity <sup>[c]</sup> |
|------------------|--------------------------------------------------------|----------------|----------|--------------------------|----------------------------|
| 1 <sup>[d]</sup> | [Pd(cod)Cl <sub>2</sub> ]                              | 50             | 100      | 80                       | 93:7                       |
| 2                | [Pd(cod)Cl <sub>2</sub> ]                              | 50             | 100      | 94                       | 93:7                       |
| 3 <sup>[e]</sup> | [Pd(cod)Cl <sub>2</sub> ]                              | 50             | 100      | 71                       | 94:6                       |
| 4                | Pd(OAc) <sub>2</sub>                                   | 50             | 100      | 0                        | –                          |
| 5                | [Pd(acac) <sub>2</sub> ]                               | 50             | 100      | 0                        | –                          |
| 6                | PdCl <sub>2</sub>                                      | 50             | 100      | 87                       | 94:6                       |
| 7                | [Pd(dba) <sub>2</sub> ]                                | 50             | 100      | 0                        | –                          |
| 8                | [Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub> ] | 50             | 100      | 91                       | 94:6                       |
| 9                | [{Pd(cinnamyl)Cl} <sub>2</sub> ]                       | 50             | 100      | 87                       | 93:7                       |
| 10               | [Pd(cod)Cl <sub>2</sub> ]                              | 50             | 80       | 64                       | 97:3                       |
| 11               | [Pd(cod)Cl <sub>2</sub> ]                              | 40             | 100      | 92                       | 93:7                       |
| 12               | [Pd(cod)Cl <sub>2</sub> ]                              | 20             | 100      | 80                       | 88:12                      |

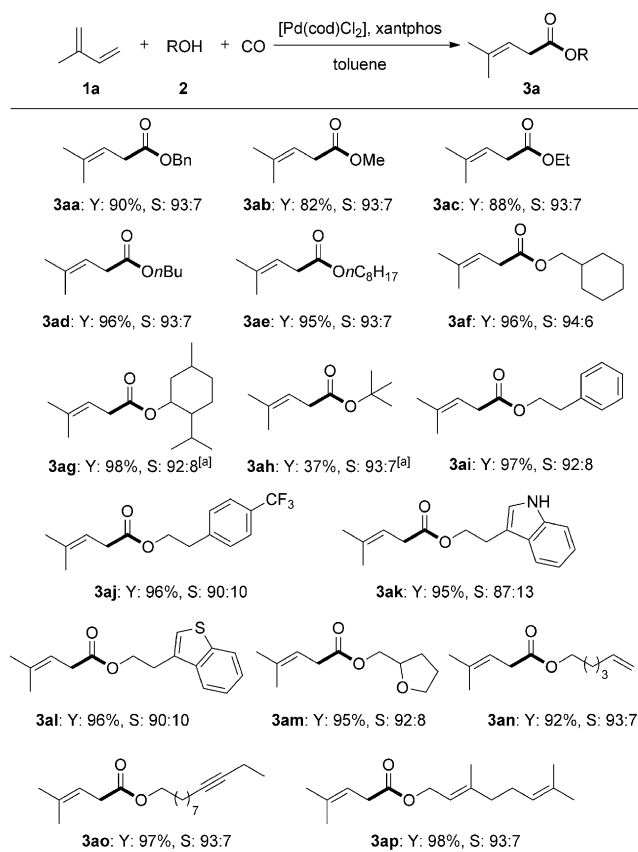
[a] Reaction conditions: **1a** (1.2 mmol), **2a** (1.0 mmol), [Pd] (1.0 mol %), Xantphos (2.0 mol %), CO (50 bar), toluene (2 mL), 100 °C, 20 h.

[b] Yield determined by GC analysis using isooctane as the internal standard. [c] The ratios of isomers were determined by GC analysis.

[d] **1a** (1.0 mmol). [e] [Pd] (0.5 mol %), Xantphos (1.0 mol %). acac = acetylacetonate

1 mol % of [Pd] (entry 3). Several palladium(II) and palladium(0) precursors were also investigated. Interestingly, when standard palladium precatalysts such as Pd(OAc)<sub>2</sub>, [Pd(acac)<sub>2</sub>], and [Pd(dba)<sub>2</sub>] were used, no conversion was observed (entries 4, 5, and 7). However, the use of other palladium chloride precursors resulted in desired product **3aa** in 87–91% yield with high selectivity (entries 6, 8, and 9). This crucial effect of chloride ions for the successful alkoxycarbonylation is not yet completely understood. The yield of the desired ester **3aa** significantly decreased when lowering the reaction temperature (entry 10). Furthermore, lowering the CO pressure to 40 bar resulted in a similar yield and selectivity compared to 50 bar of CO, but at 20 bar CO the product yield and selectivity decreased (entries 11 and 12).

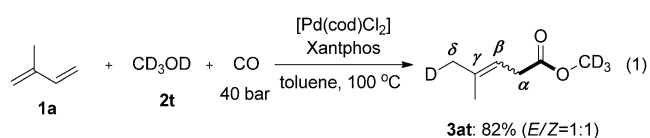
With optimized reaction conditions established (Table 1, entry 10), we examined the general scope of this acid-free alkoxycarbonylation process with respect to aliphatic alcohols (Scheme 3). A variety of substituted primary aliphatic alcohols gave the corresponding carbonylative products in excellent yields with high selectivity. Interestingly, menthol and heterocyclic alcohols proved to be efficient coupling partners and gave the corresponding esters (**3ag**, **3ak**, **3al**, and **3am**) in excellent yields with good selectivities, too. A broad range of functional groups is tolerated, including reactive alkene (**3an**), alkyne (**3ao**), and benzyl (**3aa**) groups, which provide useful handles for further synthetic



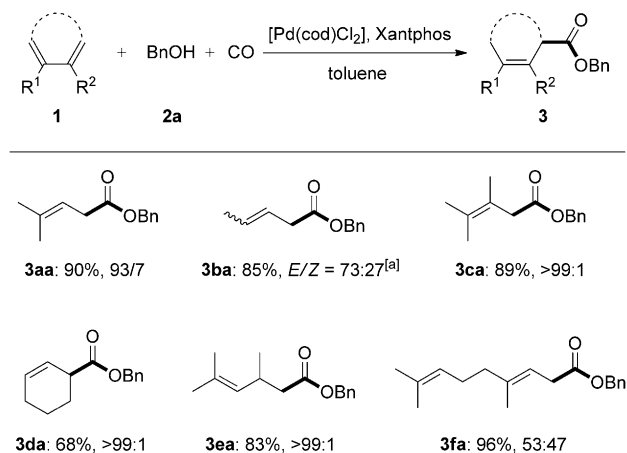
**Scheme 3.** Palladium-catalyzed alkoxy carbonylation of isoprene (**1a**) with aliphatic alcohols (**2**). Reaction conditions: **1a** (1.2 mmol), **2a** (1.0 mmol), [Pd(cod)Cl<sub>2</sub>] (1.0 mol %), Xantphos (2.0 mol %), CO (40 bar), toluene (2 mL), 100 °C, 20 h. Yield is that of the isolated product. The ratios of isomers were determined by GC analysis. [a] Used [Pd(cod)Cl<sub>2</sub>] (2.5 mol %), Xantphos (5.0 mol %), 120 °C.

transformations. Notably, we demonstrated the utility of our carbonylation protocol in the reaction of the allylic alcohol geraniol (**2p**), an ingredient commonly used in perfumes and flavors (**3ap**). Even tertiary alcohols underwent this transformation, although in lower yields, probably because of the increased steric effect (**3ah**).

By using the deuterated alcohol **2t** instead of MeOH, a similar yield and selectivity of the desired product was obtained under optimal reaction conditions [Eq. (1)]. Here,



the deuterium atom was found to be incorporated only at the  $\delta$ -carbon atom of the product **3at**, which makes a cyclo-metallation mechanism more possible. However, we can exclude a selective insertion of the more sterically hindered double bond of the 1,3-diene into the Pd–D bond, which would also result in **3at**.



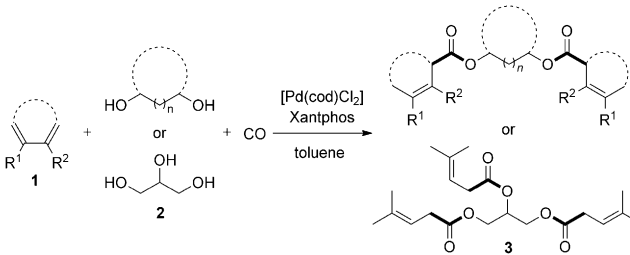
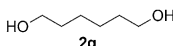
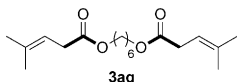
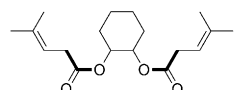
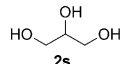
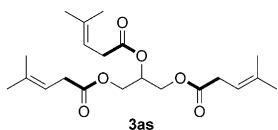
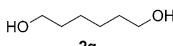
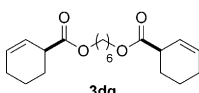
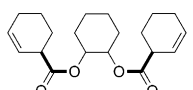
**Scheme 4.** Palladium-catalyzed alkoxy carbonylation of conjugated dienes (**1**) benzyl alcohol (**2a**). Reaction conditions: **1a** (1.2 mmol), **2a** (1.0 mmol), [Pd(cod)Cl<sub>2</sub>] (1.0 mol %), Xantphos (2.0 mol %), CO (40 bar), toluene (2 mL), 100 °C, 20 h. Yield is that of the isolated product. The ratios of isomers were determined by GC analysis. [a] **1b** (12 mmol), **2a** (10 mmol).

Next, we evaluated the scope of conjugated 1,3-dienes using benzyl alcohol (**2a**) as a standard coupling partner (Scheme 4). From an industrial point of view it is important that 1,3-butadiene furnish the corresponding product (**3ba**) in good yield. Furthermore, sterically crowded conjugated dienes **1c** and **1e** were smoothly transformed into the corresponding  $\beta,\gamma$ -unsaturated esters in good yields and with excellent selectivities (**3ca** and **3ea**). The cyclic conjugated diene **1d** was also efficiently transformed into the corresponding cyclic  $\beta,\gamma$ -unsaturated ester in good yield and with excellent selectivity (**3da**). Notably, the use of the renewable diene myrcene (**1f**) led to the desired functionalized  $\beta,\gamma$ -unsaturated ester in excellent yield though low selectivity (**3fa**).

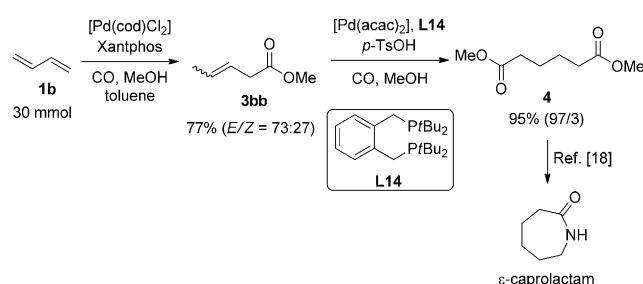
Considering the importance of diesters and triesters, which are widely applied in industry as alternative plasticizers,<sup>[21]</sup> we turned our attention to this class of compounds by using diols and glycerol as coupling reagents. As shown in Table 2, the reactions of isoprene (**1a**) with the open-chain diol **2q** and cyclic diol **2r** gave the corresponding products in very good yields (entries 1 and 2). Even the triester **3as** was obtained in good yield by triple carbonylation of **1a** with glycerol **2s** (entry 3). Moreover, the cyclic diene **1d** also proved to be an efficient coupling partner for this dialkoxy-carbonylation reaction and smoothly transformed into corresponding diesters in good yields (entries 4 and 5).

Finally, we were interested in demonstrating the usefulness of our procedure for the synthesis of adipic acid esters and caprolactam. Hence, the synthesis of **3bb** was scaled up to 30 mmol of 1,3-butadiene (**1b**; Scheme 5). Indeed, 77 % yield of the corresponding  $\beta,\gamma$ -unsaturated ester was obtained. Subsequent transformation of **3bb** gave dimethyl adipate (**4**) in high yield with excellent regioselectivity.<sup>[22]</sup> It should be noted that this sequence also allows a straightforward prep-

**Table 2:** Palladium-catalyzed di- and trialkoxycarbonylation of 1,3-dienes (**1**) with diols and glycerol (**2**).<sup>[a]</sup>

|  |    |                                                                                          |                                                                                           |           |
|-----------------------------------------------------------------------------------|----|------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|-----------|
| Entry                                                                             | 1  | 2                                                                                        | 3                                                                                         | Yield [%] |
| 1                                                                                 | 1a | <br>2q  | <br>3aq  | 95        |
| 2 <sup>[b]</sup>                                                                  | 1a | <br>2r  | <br>3ar  | 98        |
| 3 <sup>[c]</sup>                                                                  | 1a | <br>2s  | <br>3as  | 81        |
| 4 <sup>[d]</sup>                                                                  | 1d | <br>2q  | <br>3dq  | 93        |
| 5 <sup>[b]</sup>                                                                  | 1d | <br>2r | <br>3dr | 77        |

[a] Reaction conditions: **1a** (2.4 mmol), **2a** (1.0 mmol), [Pd(cod)Cl<sub>2</sub>] (1.0 mol %), Xantphos (2.0 mol %), CO (40 bar), toluene (2 mL), 100 °C, 20 h. Yield is that of isolated product. The ratios of isomers were determined by GC analysis. [b] [Pd(cod)Cl<sub>2</sub>] (5.0 mol %), Xantphos (10.0 mol %), 120 °C. [c] **1a** (3.6 mmol), [Pd(cod)Cl<sub>2</sub>] (5.0 mol %), Xantphos (10.0 mol %), 120 °C. [d] Reaction temperature: 120 °C.



**Scheme 5.** Straightforward synthesis of dimethyl adipate (**4**) and  $\epsilon$ -caprolactam from 1,3-butadiene (**1b**). Ts = 4-toluenesulfonyl.

aration of  $\epsilon$ -caprolactam, which is primarily used in the production of nylon 6 fibers and resins.<sup>[23]</sup>

In summary, we developed a novel protocol for the palladium-catalyzed alkoxy carbonylation of conjugated 1,3-dienes to produce a variety of synthetically useful  $\beta,\gamma$ -

unsaturated esters in good yields with often high selectivity. Compared to previously known procedures the substrate scope is enhanced and no additives such as acids, which might cause corrosion problems are needed. Furthermore, we reported the first catalytic di- and trialkoxycarbonylations of 1,3-dienes utilizing easily accessible diols and glycerol. These products are of interest as alternative plasticizers. Combining the presented procedure with established carbonylation reactions allows an efficient preparation of adipates and  $\epsilon$ -caprolactam. We believe these procedures will inspire chemists to use carbonylation reactions more frequently in organic synthesis.

## Experimental Section

Typical procedure for the preparation of **3**: A vial (4 mL) was charged with [Pd(cod)Cl<sub>2</sub>] (2.85 mg, 1 mol %), Xantphos (11.6 mg, 2 mol %), and a stirring bar was added. Then, toluene (2 mL), the conjugated diene **1** (1.2 mmol) and alcohol **2** (1 mmol) were injected by syringe. The vial was placed in an alloy plate, which was transferred into an autoclave (300 mL) of the 4560 series from Parr Instruments under argon atmosphere. At room temperature, the autoclave was flushed with CO three times, pressurized with CO to 40 bar, and finally the pressure was increased to 90 bar by adding nitrogen. The reaction was performed for 20 h at 100 °C. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released and isooctane (150  $\mu$ L) (internal standard) was added to the solution. The yield and selectivity were measured by GC analysis. After removing the solvent by vacuum, the residue was directly purified by flash chromatography on silica gel (eluent: heptane/ethyl acetate = 20:1) to give the desired product **3**.

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[1] For recent reviews and compendia on carbonylation, see: a) X.-F. Wu, H. Neumann, M. Beller, *Chem. Rev.* **2013**, *113*, 1; b) X.-F. Wu, H. Neumann, M. Beller, *Chem. Soc. Rev.* **2011**, *40*, 4986; c) J. Hartwig in *Organotransition Metal Chemistry*, University Science Books, Sausalito, CA, **2010**, pp. 745–824; d) *Modern Carbonylation Methods* (Ed.: L. Kollár), Wiley-VCH, Weinheim, **2008**; e) *Catalytic Carbonylation Reactions* (Ed.: M. Beller), Springer, Berlin, **2006**; f) *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2002**; g) X.-F. Wu, X. Fang, L. Wu, R. Jackstell, H. Neumann, M. Beller, *Acc. Chem. Res.* **2014**, *47*, 1041.

[2] For reviews, see: a) B. ElAli, H. Alper, M. Beller, C. Bolm in *Transition Metals for Organic Synthesis* Wiley-VCH, Weinheim, **2008**, pp. 49–67; b) G. Kiss, *Chem. Rev.* **2001**, *101*, 3435; c) A. Brennfürer, H. Neumann, M. Beller, *ChemCatChem* **2009**, *1*, 28; d) Q. Liu, H. Zhang, A. Lei, *Angew. Chem.* **2011**, *123*, 10978; *Angew. Chem. Int. Ed.* **2011**, *50*, 10788.

[3] a) M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, Wiley-VCH, Weinheim, **1998**; b) J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, **1995**; c) W.-J. Xiao, G. Vasapollo, H. Alper, *J. Org. Chem.* **2000**, *65*, 4138; d) Y. S. Lin, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 723; e) T. Satoh, M. Ikeda, Y. Kushino, M. Miura, M. Nomura, *J. Org. Chem.* **1997**, *62*, 2662.

- [4] a) J. Tsuji, K. Sato, H. Okumoto, *J. Org. Chem.* **1984**, *49*, 1341; b) T.-a. Mitsudo, N. Suzuki, T. Kondo, Y. Watanabe, *J. Org. Chem.* **1994**, *59*, 7759.
- [5] a) Y. Koyasu, H. Matsuzaka, Y. Hiroe, Y. Uchida, M. Hidai, *J. Chem. Soc. Chem. Commun.* **1987**, 575; b) S. Murahashi, Y. Imada, Y. Taniguchi, S. Higashiura, *Tetrahedron Lett.* **1988**, 29, 4945; c) H. Matsuzaka, Y. Hiroe, M. Iwasaki, Y. Ishii, Y. Koyasu, M. Hidai, *J. Org. Chem.* **1988**, *53*, 3832; d) M. Iwasaki, Y. Kobayashi, J. P. Li, H. Matsuzaka, Y. Ishii, M. Hidai, *J. Org. Chem.* **1991**, *56*, 1922; e) S. Murahashi, Y. Imada, Y. Taniguchi, S. Higashiura, *J. Org. Chem.* **1993**, *58*, 1538.
- [6] a) W. T. Dent, R. Long, G. H. Whitfield, *J. Chem. Soc.* **1964**, 1588; b) J. Tsuji, J. Kiji, S. Imamura, M. Morikawa, *J. Am. Chem. Soc.* **1964**, *86*, 4350; c) T. Okano, N. Okabe, J. Kiji, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2589; d) A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433; e) J. Kiji, T. Okano, Y. Higashimae, Y. Fukui, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1029; f) S. Tommasi, S. Perrone, F. Rosato, A. Salomone, L. Troisi, *Synthesis* **2012**, 423.
- [7] S.-I. Murahashi, Y. Imada, K. Nishimura, *Tetrahedron* **1994**, *50*, 453.
- [8] a) D. Neibecker, J. Poirier, I. Tkatchenko, *J. Org. Chem.* **1989**, *54*, 2459; b) M. C. Bonnet, J. Coombes, B. Manzano, D. Neibecker, I. Tkatchenko, *J. Mol. Catal.* **1989**, *52*, 263.
- [9] R. Takeuchi, Y. Akiyama, *J. Organomet. Chem.* **2002**, *651*, 137.
- [10] a) J. F. Knifton, *J. Organomet. Chem.* **1980**, *188*, 223; b) M. Sakamoto, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1065; c) R. Naigre, H. Alper, *J. Mol. Catal. A* **1996**, *111*, 11; d) Q. Liu, L. Wu, H. Jiao, X. Fang, R. Jackstell, M. Beller, *Angew. Chem.* **2013**, *125*, 8222; *Angew. Chem. Int. Ed.* **2013**, *52*, 8064.
- [11] a) O. Sielcken, F. Agterberg, N. Haasen (DSM, Du Pont), EP 728733, **1996**; [*Chem. Abstr.* 124, 342675 P]; b) W. Bertleff, R. Maerkl, G. Kuehn, P. Panitz, R. Kummer (BASF AG), EP 0267497, **1988**; [*Chem. Abstr.* 109, 057058 Y]; c) R. Maerkl, W. Bertleff, H. J. Wilfinger, G. Schuch, W. Harder, G. Kuehn, P. Panitz (BASF AG), US Patent 4,894,474, **1990**; [*Chem. Abstr.* 110, 192257 Y].
- [12] W. F. Gresham, R. E. Brooks (Du Pont), US Patent 2,542,767, **1951**.
- [13] a) J. Tsuji, J. Kiji, S. Hosaka, *Tetrahedron Lett.* **1964**, *5*, 605; b) S. Hosaka, J. Tsuji, *Tetrahedron* **1971**, *27*, 3821; c) J. Tsuji, Y. Mori, M. Hara, *Tetrahedron* **1972**, *28*, 3721.
- [14] A. Matsuda, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 524.
- [15] J. F. Knifton, *J. Catal.* **1979**, *60*, 27.
- [16] a) E. Drent, W. Jager (Shell), US Patent 5,350,876, **1994**; b) E. Drent (Shell), EP 235864, **1986**; [*Chem. Abstr.* 125, 238907 D].
- [17] F. Agterberg, O. Sielcken, M. D'Amore, H. Bruner (DSM, Du Pont), EP 728732, **1996**; [*Chem. Abstr.* 125, 221199 Y].
- [18] J. Jenck (Rhône Poulenc), US Patent 4,454,333, **1984**; [*Chem. Abstr.* 99, 070228Y].
- [19] E. Drent (Shell), EP 577205, **1992**; [*Chem. Abstr.* 121, 05700 W].
- [20] M. Beller, A. Krotz, W. Baumann, *Adv. Synth. Catal.* **2002**, *344*, 517.
- [21] a) H. Bengs, J. Grande (Hoechst AG), DE 19729306, **1997**; b) B. Mehta, M. Kathalewar, A. Sabnis, *J. Appl. Polym. Sci.* **2014**, *131*, 40354.
- [22] a) C. J. Moulton, B. L. Shaw, *J. Chem. Soc. Chem. Commun.* **1976**, 365; b) R. P. Tooze, G. R. Eastham, K. Whiston, X. L. Wang, WO96/19434, **1996**; c) C. Jiménez-Rodríguez, D. F. Foster, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Commun.* **2004**, 1720; d) C. Jiménez-Rodríguez, G. R. Eastham, D. J. Cole-Hamilton, *Inorg. Chem. Commun.* **2005**, *8*, 878; e) C. Jiménez-Rodríguez, G. R. Eastham, D. J. Cole-Hamilton, *Dalton Trans.* **2005**, 1826; f) I. Fleischer, R. Jennerjahn, D. Cozzula, R. Jackstell, R. Franke, M. Beller, *ChemSusChem* **2013**, *6*, 417; g) M. Roeper, M. Schäfer, M. Slany (BASF AG), WO2002064249, **2002**.
- [23] E. L. Dias, V. J. Murphy, J. Longmire, H. Jiang (Rennovia), WO2013126250, **2013**.
- [24] W. Reppe, H. Kröper, *Liebigs Ann. Chem.* **1953**, 582, 38.