Palladium-Catalyzed Methoxycarbonylation of 1,3-Butadiene: Catalysis and Mechanistic Studies

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Received: November 17, 2001; Accepted: April 25, 2002

Abstract: The palladium-catalyzed methoxycarbonylation of 1,3-butadiene to methyl 3-pentenoate has been studied. Intermediates of the proposed catalytic cycle were synthesized and the elementary steps of the reaction have been investigated in detail. It is shown that the first step of the catalytic cycle, the formation of crotylpalladium complexes from 1,3-butadiene, proceeds even at room temperature. Examination of the influence of different reaction parameters on product yield and selectivity demonstrate the importance of chelating phosphine ligands and benzoic acids as additive in order to get good results.

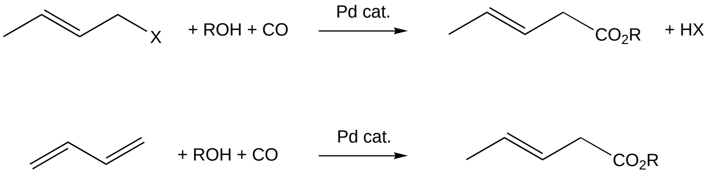
Keywords: 1,3-butadiene; carbonylation, homogenous catalysis; methyl 3-pentenoate; palladium

Introduction

The transition metal-catalyzed carbonylation of allylic compounds is of considerable importance for the synthesis of β,γ-unsaturated carboxylic acid derivatives.[1] In the past, effective carbonylation methods for the reaction of allylic carbonates,[2] esters,[3] halides,[4] amines,[5] ethers,[6] and alcohols[7] have been developed. A general drawback of these reactions is the stoichiometric formation of by-products. Interestingly, homoallylic carboxylic acid derivatives might also be synthesized by carbonylation of 1,3-dienes in the presence of a catalytic amount of acid (Scheme 1). Despite the advantage of this atom-efficient green route, the carbonylation of 1,3-dienes has scarcely been explored in academic laboratories.

Of special industrial interest is the alkoxycarbonylation of 1,3-butadiene. The resulting 3-pentenoic acid esters are of major importance as intermediates for large-scale monomers like adipic acid and ε-caprolactam.[8,9]

Up to now, catalysts based on Co (mainly studied before 1990),[9,10] Pd (more important since 1990),[8,11] Rh, and Ir have been used for this reaction. The carbonylation of butadiene was first reported by Reppe in the early 1940's, who obtained carbonylated vinylcyclohexene derivatives by using $Co_2(CO)_8$ as catalyst. Du Pont reported conversion of 1,3-butadiene to methyl pentenoate by using a Co/Cu/Th catalyst at 810 bar in 1951.[12] Fifteen years later, Tsuji[13] described the reaction of 1,3-butadiene with carbon monoxide and ethanol in the presence of a catalytic amount of palladium chloride to give ethyl 3-pentenoate. However, no detailed amounts of starting materials and product yield were given in the original paper. Later on, Tsuji et al.[13b] reported an optimized yield of *ca.* 30% of ethyl 3-pentenoate for this reaction. Matsuda demonstrated the use of cobalt catalysts in the presence of pyridines for this reaction in 1973. Here, only low turnover numbers (25 – 80) were achieved at high CO pressure. A systematic investigation of the palladium-catalyzed carbonylation of conjugated 1,3-dienes was done by Knifton.[14] Despite variation of different ligands and solvents, he observed mainly 3,8-nonadienoate esters (telomerization products). None of the catalyst systems known in the open literature is of current industrial interest due to the low product yield and catalyst performance.



Scheme 1.

Interestingly, in the last two decades, there have been considerable efforts from industrial researchers to develop such a process but very little basic work from the academic side has been done since 1982. A survey of the patent literature reveals significant work on the palladium-catalyzed methoxycarbonylation of 1,3-dienes by Shell,[11,15] Du Pont, and DSM.[8,16] The latter companies and also Rhone Poulenc[17] disclose a positive influence of added acids or acid sources (e.g., 1-chlorobut-2-ene as a source of hydrochloric acid) and of 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.[18]

Unfortunately, it is difficult to draw clear conclusions from most of the reported patents. Also no mechanistic work is mentioned there. Thus, we were interested in a more systematic study of this reaction in the presence of different palladium-phosphine complexes. In this manuscript we describe the influence of different reaction parameters on the palladium-catalyzed methoxycarbonylation of 1,3-butadiene. Regarding the mechanism of the reaction different crotylpalladium complexes were synthesized as proposed intermediates of the catalytic cycle (Scheme 2). Their carbonylation behavior has been studied in the presence and absence of methanol.

Results and Discussion

Influence of Different Reaction Parameters

Initial studies of the methoxycarbonylation of 1,3-butadiene to give methyl 3-pentenoate (**1**) were concerned with the influence of ligands, acids, and their concentrations on the product yield, the selectivity, and the ester/oligomer ratio. Inspired by our previous work on the telomerization of 1,3-butadiene,[19] the reactions were performed at 140 °C under 50 bar of CO with a 1,3-butadiene to methanol ratio of 1:1.5. As catalyst precursor 0.1 mol % of $Pd(OAc)_2$ was used. It is known from the methoxycarbonylation of ethene[20] and the patent literature[8] that the addition of acids is important to obtain a productive catalyst system, probably due to the formation of a Pd-hydride complex. Hence, 3 mol % of 4-*tert*-butylbenzoic acid were added to the reaction mixture. A comparison of different chelating and non-chelating phosphines under these conditions shows that most chelating phosphines gave improved selectivities of **1** compared to non-chelating phosphines (Table 1). Here, the selectivity is defined as the yield of methyl 3-pentenoate (**1**) compared to the total yield of all esters (different pentenoates and nonanoates). Among the chelating ligands, 1,4-bis(diphenylphosphino)butane (dppb) leads to a significantly better yield (69%) in comparison to similar ligands having smaller or larger bite angles. As side reactions, dimerization and telomerization of 1,3-butadiene to give C_8-olefins (1,3,7-octatriene, vinylcyclohexene, 1-methoxy-2,7-octadiene, and 3-methoxy-1,7-octadiene) are observed. The amount of these side reactions is shown in Table 1 as the ratio of esters to C_8-olefins.

Next, we studied the influence of different acids as co-catalysts (Table 2). Especially benzoic acids are useful as additives for this reaction. While the ester selectivity and the ester/C_8-olefin ratio is comparably high with all carboxylic acids, no conversion is observed in the presence of *p*-toluenesulfonic acid and tetrafluoroboric acid. As shown in Table 2 the best yield of **1** (69%) is observed using 4-*tert*-butylbenzoic acid as co-catalyst. Surprisingly, the addition of a 1:1 mixture of benzoic acid and pyridine gives similar results to the use of benzoic acid alone. This demonstrates the special role of the anion and not the amount of free acid on the product yield.

Recently, we have shown that for carbonylations of aryl halides at low catalyst concentration not the metal

Table 1. Methoxycarbonylation of 1,3-butadiene with different ligands.[a]

Entry	Ligand	L/Pd	Yield of **1**[b] [%]	Selectivity[b, c] [%]	Ester/Oligomer Ratio[b, d]
1	PPh_3[e]	12:1	5	16	2.1
2	PCy_3	12:1	13	45	5.5
3	dppe	6:1	16	85	1.3
4	dppp	6:1	18	>99	3.4
5	dppb	6:1	69	98	20.2
6	dpppe	6:1	16	77	1.8
7	dppf	6:1	5	93	0.6
8	dpppp[f]	6:1	5	43	2.1
9	dcyb[g]	6:1	0	-	-
10	Naphos[h]	6:1	7	>99	0.4

[a] 0.1 mol % $Pd(OAc)_2$, 90 mmol 1,3-butadiene, methanol/1,3-butadiene 1.5:1, 2.7 mmol 4-*tert*-butylbenzoic acid, 20 mL anisole, 140 °C, 16 h, 50 bar CO.

[b] Detected by gas chromatography.

[c] Methyl 3-pentenoate yield as a function of total $C_5 + C_9$ acid ester.

[d] Total $C_5 + C_9$ acid ester/total C_8-oligomer.

[e] Methyl nonadienoate is the major product.

[f] 2,2′-Bis(diphenylphosphino)-1-phenylpyrrole.

[g] 1,4-Bis(dicyclohexylphosphino)butane.

[h] 2,2′-Bis(diphenylphosphinomethyl)-1,1′-binaphthyl.

concentration is important for optimal catalyst productivity but rather the actual ligand concentration.[21] Therefore, we investigated the influence of ligand and acid concentration on the yield of **1**. Applying 0.1 mol % of $Pd(OAc)_2$, the use of 0.6 mol % of dppb leads to optimal results (Table 2, entry 7). If a ligand concentration of 0.4 mol % or 1.0 mol %, respectively, is used the product yield and the ester to C_8-olefin ratio decrease, while the selectivity is almost constant between 97% and 98%. Regarding the amount of acid, the use of 3.0 mol % 4-*tert*-butylbenzoic acid gives the best result.

Due to the high price of palladium (currently 10 – 20 US $/g), it is important to minimize the catalyst amount in order to apply this reaction on a larger scale. Unfortunately, in the presence of 0.025 mol % $Pd(OAc)_2$, 6 equiv. dppb, and 30 equiv. acid, only 9% of methyl 3-pentenoate is obtained. However, using 24 equiv. dppb and 120 equiv. acid 30% methyl 3-pentenoate is produced (Table 3, entry 3). This corre-

Table 2. Methoxycarbonylation of 1,3-butadiene with different acids.[a]

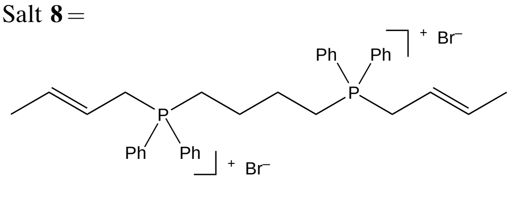
Entry	Acid	dppb [mol %]	Yield of **1**[b] [%]	Ester Selectivity[b, c] [%]	Ester/C_8-Olefin Ratio[b, d]
1	HOAc	0.6	49	97	13.8
2	Benzoic acid	0.6	57	98	14.7
3	2,4,6-Trimethylbenzoic acid	0.6	58	>99	27.6
4	2- Phenylbenzoic acid	0.6	64	>99	51.6
5	4-*tert*-Butylbenzoic acid	0.4	53	97	13.6
6	4-*tert*-Butylbenzoic acid[e]	0.6	36	98	8.1
7	4-*tert*-Butylbenzoic acid	0.6	69	98	20.2
8	4-*tert*-Butylbenzoic acid[f]	0.6	62	98	21.4
9	4-*tert*-Butylbenzoic acid	1.0	52	98	12.7
10	*p*-TsOH	0.6	0	0	0
11	HBF_4	0.6	0	0	0
12	Benzoic acid/Pyridine 1:1	0.6	62	96	8.6

[a] 0.1 mol % $Pd(OAc)_2$, 90 mmol 1,3-butadiene, methanol/1,3-butadiene 1.5:1, 3.0 mol % acid, dppb, 20 mL anisole, 140 °C, 16 h, 50 bar CO.
[b] Detected by gas chromatography.
[c] Methyl 3-pentenoate yield as a function of total $C_5 + C_9$ acid ester.
[d] Total $C_5 + C_9$ acid ester/total C_8-olefins.
[e] 1.5 mol % acid.
[f] 5.0 mol % acid.

Table 3. Catalytic runs with less $Pd(OAc)_2$, different MeOH/butadiene ratios and halides as additives.[a]

Entry	MeOH [mmol]	dppb [equiv.]	Acid [equiv.]	Halides	Yield[b] of **1** [%]	Ratio MeOH/Butadiene/Pd
1	135	6	30	–	8	6000:4000:1
2[c]	135	6	30	–	9	6000:4000:1
3[c]	135	24	120	–	30	6000:4000:1
4	90	6	30	–	10	4000:4000:1
5	45	6	30	–	18	2000:4000:1
6	34	6	30	–	23 (61)[d]	1500:4000:1
7	34	6	30	NBu_4Br (1 equiv. to Pd)	12	1500:4000:1
8	34	6	30	NBu_4Br (0.5 mmol)	n.d. polymer	1500:4000:1
9	34	6	30	LiCl (0.3 mmol)	n.d. polymer	1500:4000:1
10	34	6	30	salt **8** (1 equiv. to Pd)[e]	9	1500:4000:1
11	23	6	30	–	16 (64)[d]	1000:4000:1

[a] 90 mmol butadiene, 0.025 mol % $Pd(OAc)_2$ (based on butadiene), 6 equiv. dppb, 4-*tert*-butylbenzoic acid, 140 °C, 50 bar CO, 5 mL anisole.
[b] Based on 1,3-butadiene.
[c] 20 mL anisole.
[d] Based on MeOH.
[e] Salt **8** =



sponds to a catalyst turnover number (TON) of 1200, which is the highest number reported for the methoxycarbonylation of 1,3-butadiene. Apart from the aforementioned reaction parameters, the methanol/butadiene ratio is also an important factor influencing the catalyst productivity. By switching from a methanol to 1,3-butadiene ratio of 1.5:1 to 1:4 a total yield of methyl 3-pentenoate of 64% (TON = 640) is obtained in the presence of 0.1 mol % of $Pd(OAc)_2$.[22] Further variation of reaction conditions as well as the addition of halide additives such as tetra-*n*-butylammonium bromide, lithium chloride and the phosphonium salt **8**[23] do not give any better yields and catalyst turnover numbers (Table 3, entries 7 – 10).

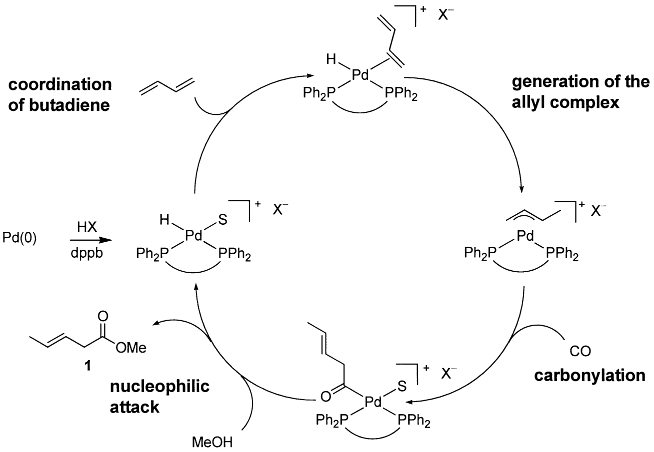
Mechanistic Investigations

After considerable screening of ligands and reaction conditions, **1** was obtained in 69% yield and high selectivity in the presence of 0.1 mol % of palladium catalyst containing dppb as ligand (Table 1). In order to further improve these results we were interested in mechanistic studies. Scheme 2 shows the generally accepted mechanism for the alkoxycarbonylation of 1,3-butadiene.

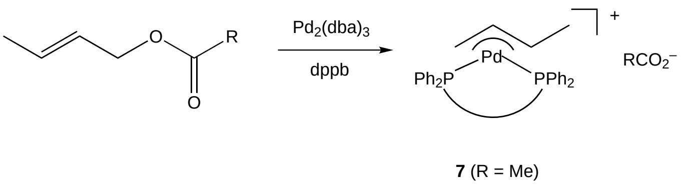
The first step of the reaction is the coordination of the 1,3-diene to a palladium hydride complex formed by oxidative addition of an acid to Pd(0). After generation of the crotylpalladium complex, CO insertion leads to the corresponding acylpalladium complex. Subsequent attack by the alcohol forms the product and the palladium hydride complex is regenerated. It is important to note that efficient catalysis proceeds only at relatively high reaction temperatures (>120 °C). We aimed to investigate why these high reaction temperatures are needed and which of the reaction steps is the rate-determining step. In order to examine the mechanism of the methoxycarbonylation, more closely defined intermediates of the catalytic cycle were prepared and the elementary steps of the reaction were separately investigated. First, the cationic crotylpalladium complexes **5** and **6** were synthesized by reacting $AgBF_4$ with π-crotylpalladium(II) chloride dimer in the presence of 1,4-bis(diphenylphosphino)butane and 1,2-bis(diphenylphosphino)ethane at room temperature (**5**: 55% yield, **6**: 61% yield).

Encouraged by the work of Amatore et al.,[24] we also tried to synthesize crotylpalladium complexes by oxidative addition of different crotyl esters, e.g., crotyl acetate, crotyl benzoate, crotyl 4-*tert*-butylbenzoate, to Pd(0) (Scheme 4). This strategy has the advantage to obtain directly palladium complexes having the same counterions compared to the intermediates of the catalytic cycle. Unfortunately, a general problem of this route is the purity of the isolated complexes. Except for (π-crotyl)-1,4-bis(diphenylphosphino)butanepalladium(II) acetate **7** (purity > 95%), the corresponding palladium complexes were obtained in 50 – 70% purity. According to ^{31}P NMR there are apart from the desired complex always other phosphine species, mainly phosphonium salts present.

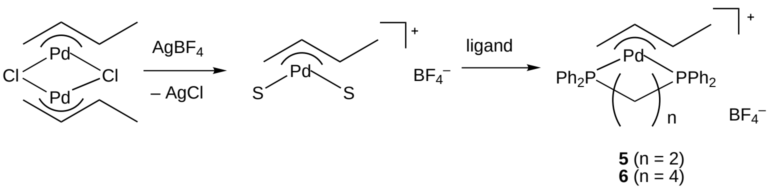
With respect to the proposed catalytic cycle it should be possible to synthesize crotylpalladium complexes directly by reaction of 1,3-butadiene and a Pd(0) complex in the presence of acid. Indeed, the reaction of $Pd_2(dba)_3$, dppb, HBF_4 and butadiene in a 1:1:5:100 ratio (Scheme 5) yielded **6** in 58% after 16 h. ^{31}P NMR studies at different temperatures showed that **6** is



Scheme 2.



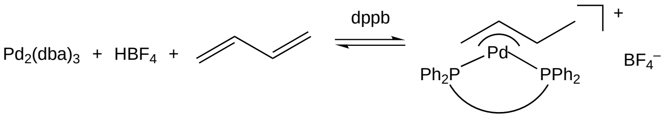
Scheme 4.



Scheme 3.

Table 4. ^{31}P NMR of different crotylpalladium complexes.

Pd(crotyl)dppb$^+$ RCOO$^-$	δ [ppm]	*J* [Hz]
R = trimethylphenyl	18.5, 20.1	48.6
R = Me (**7**)	20.0, 20.6	48.6
R = *t*-Bu	18.2, 20.1	48.6
R = biphenyl	20.0, 21.0	47.2
R = *t*-butylphenyl	20.2, 21.5	48.8
Pd(crotyl)dppb$^+$ BF_4^- (**6**)	19.6, 20.2	47.2
Pd(crotyl)dppe$^+$ BF_4^- (**5**)	48.3, 49.3	34.0



Scheme 5.

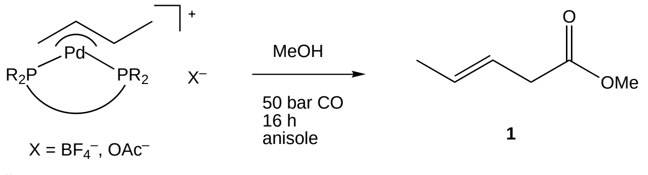
Table 5. Methoxycarbonylation of crotylpalladium complexes.[a]

Entry	Complex	Temperature	Yield of **1** [%]
1	**6**	rt	12
2	**6**	80 °C	20
3	**6**	140 °C	< 5
4	**7**	rt	0
5	**7**	80 °C	40
6	**7**	140 °C	34
7	**5**	rt	0
8	**5**	80 °C	10
9	**5**	140 °C	< 5

[a] 30 mg of the complexes were used, 16 h, 50 bar CO, 2 mL anisole, 10 equiv. MeOH.

formed already at room temperature under these conditions. To prove if there is an influence of the CO pressure on the crotylpalladium complex formation, we also performed the reaction under 50 bar of CO. In the presence of CO the formation of the crotylpalladium complex is retarded. Also the purity of the isolated complex is low (60%). Nevertheless, **6** is formed at 50 bar CO even at room temperature in 34% yield. This demonstrates that the generation of the crotylpalladium complex proceeds under much milder conditions compared to the overall catalytic cycle. Most likely, the formation of the crotylpalladium complex is not the rate-determining step under catalytic reaction conditions.

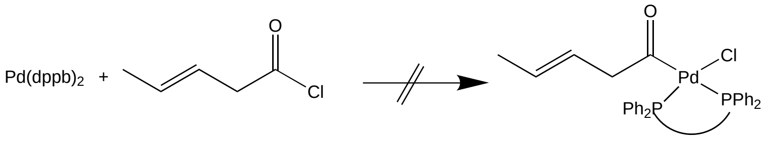
With the isolated crotylpalladium complexes **5**, **6**, and **7** in hand, we were able to study the carbonylation step in the absence and presence of MeOH at different temperatures (rt, 80 °C, 140 °C, Scheme 6, Table 5). Under standard reaction conditions (30 mg complex, 10 equiv. MeOH, 16 h, 50 bar CO, 2 mL anisole), only the cationic dppb palladium complex **6** did react at room temperature to give **1**, albeit in low yield (12%). Using the cationic palladium dppe complex **1** was obtained in low yields (< 10%) at all three reaction temperatures. Applying the crotylpalladium acetate complex **7**, which resembles the actual intermediate of the catalytic cycle the best yield (40%) of the desired ester **1** was obtained at 80 °C. The ^{31}P NMR showed no **6** or **7** left after reactions at 80 and 140 °C. At room temperature there is always some crotylpalladium complex present after the reaction; in the case of the dppe-palladium complex **5** even after the reaction at 80 °C. We explain the relatively low yield of **1** at full conversion of the crotyl complexes by the formation of 1,3-butadiene as side reaction. β-Hydride elimination of the crotylpalladium complex forms directly 1,3-butadiene, which undergoes further transformations. Not surprisingly, these side reactions are more pronounced at 140 °C compared to 80 °C.



Scheme 6.

Apparently the "real" mechanism of the alkoxycarbonylation of 1,3-butadiene is much more complicated compared to the mechanism shown in Scheme 2. It is noteworthy that the formation of the crotylpalladium complex is reversible. In addition, a transfer of the crotyl moiety from the palladium center to phosphorus atoms leading to phosphonium salts (e.g., **8**) is occurring.

Because of the fact that complex **6** could be carbonylated at room temperature, we wondered if it is possible to observe the corresponding acylpalladium complex[25] by reaction of **6** with CO. Hence, 30 mg of **6** were stirred in 2 mL anisole in the presence of 50 bar of CO for 45 h. The mixture was cooled to –10 °C and analyzed by ^{31}P NMR. Apart from the crotylpalladium complex **6** there were no other phosphine species present. Also the preparation of the acylpalladium complex by oxidative addition of 3-pentenoyl chloride to Pd(dppb)$_2$ (Scheme 7)[26,27] was not successful. Here, we observed



Scheme 7.

several signals in the ^{31}P NMR, but no acylpalladium-phosphine species. The different signals are explained by oligomeric dppb-palladium species as described previously.[28]

Conclusion

Among the combinations of phosphine ligands and acid co-catalysts investigated, 1,4-bis(diphenylphosphino)-butane (dppb) and substituted benzoic acids such 4-*tert*-butylbenzoic acid give the highest yield and selectivity to methyl 3-pentenoate in the Pd-catalyzed methoxycarbonylation of 1,3-butadiene. By using this catalyst system, the telomerization reaction to the 3,8-nonadienoate ester is almost completely suppressed under carbonylation conditions. Comparably high catalyst productivity (TON up to 1200) is achieved at low catalyst concentration. Mechanistic studies revealed that a cationic crotylpalladium complex is formed by reaction of $Pd_2(dba)_3$, dppb, HBF_4, and 1,3-butadiene already at room temperature (58%). Hence, the first half of the catalytic cycle appears to be occurring without difficulty, although there is a negative influence of the CO pressure on the yield of the crotylpalladium complex. Furthermore, carbonylation experiments of different crotylpalladium complexes showed that the yield of **1** depends on the counterion and on the ligand. In all reactions, an acylpalladium complex could neither be observed nor be isolated. The formation of these complexes might be the most difficult step under our reaction conditions. Further progress of this industrially important reaction is expected by specifically improving the alkoxycarbonylation of allylpalladium complexes.

Experimental Section

General Remarks

All reactions were carried out under an atmosphere of argon with the use of Schlenk techniques. Chemicals and dry solvents were purchased from Aldrich. ^{31}P NMR spectra were obtained on a Bruker ARX 400 spectrometer. Gas chromatographic analyses were run on a Hewlett-Packard GC 6890 series, HP 5, 5% phenyl-methyl-siloxane, capillary (30 m, 250 μm, 0.25 μm). Methoxycarbonylations were carried out in 25-mL (stoichiometric experiments) and 100-mL (catalytic experiments) stainless steel autoclaves.

Methoxycarbonylation Experiments

A typical experiment was performed in the following manner: a 100-mL stainless steel autoclave was filled under an argon atmosphere with 20.2 mg (0.09 mmol) palladium acetate, 230.3 mg (0.54 mmol) dppb, 481.2 mg (2.70 mmol) 4-*tert*-butylbenzoic acid, 20 mL anisole and 5.5 mL methanol. After cooling with dry ice 4.87 g (90 mmol) of 1,3-butadiene were condensed into the autoclave. The reactor was pressured with carbon monoxide to 50 bar and heated to 140 °C. After 16 h of stirring at this temperature, the autoclave was allowed to cool to room temperature. The reaction mixture was analyzed by gas chromatography. Product **1** isolation was performed by distillation. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 5.58-5.53$ (m, 2H, CH), 3.66 (s, 3H, OCH_3), 3.01 (d, $J = 5.9$ Hz, 2H, CH_2), 1.69 (d, $J = 4.9$ Hz, 3H, CH_3); MS (70 eV): $m/z = 114$ [M^+], 99 [$M^+ - CH_3$], 82, 72, 59, 55.

Stoichiometric Experiments

For the separate investigation of the carbonylation step a 25-mL stainless steel autoclave was filled under an argon atmosphere with 30 mg of the corresponding crotylpalladium complex, 10 equiv. of methanol and 2 mL of anisole. The reactor was pressured with carbon monoxide to 50 bar. The resulting mixture was stirred for 16 h at the desired temperatures (room temperature, 80 °C, 140 °C), allowed to cool to room temperature and analyzed by gas chromatography.

(π-Crotyl)-1,4-bis(diphenylphosphino)-ethanepalladium(II) Tetrafluoroborate (5)

191.1 mg (0.485 mmol) crotylpalladium chloride dimer was dissolved in 5 mL THF and 188.9 mg (0.97 mmol) $AgBF_4$ in 2 mL THF were added. A white precipitate occurred immediately. The reaction mixture was stirred at room temperature for 15 min and filtered. 386.5 mg (0.97 mmol) dppe in 4 mL THF were added. The reaction mixture was stirred again for 2 h and filtered. The product was washed with small amounts of THF, dried in vacuum and crystallized from $CHCl_3$/diethyl ether; yield: 348 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta =$ 7.61 – 7.33 (m, 20H, Ar-H), 5.68 – 5.66 (m, 1H, H-2), 4.54 – 4.47 (m, 1H, H-1_{syn}), 4.32 – 4.21 (m, 1H, H-3_{anti}), 3.11 – 3.02 (m, 1H, H-1_{anti}), 2.74 – 2.31 [m, 4H, $(CH_2)_2$], 1.66 – 1.58 (m, 3H, CH_3); ^{31}P NMR (C_6D_6, 161 MHz, 25 °C): $\delta = 48.3$ (d, $J = 34.0$ Hz, 1P), 49.3 (d, $J = 34.0$ Hz, 1P).

(π-Crotyl)-1,4-bis(diphenylphosphino)-butanepalladium(II) Tetrafluoroborate (6)

197.0 mg (0.50 mmol) crotylpalladium chloride dimer was dissolved in 5 mL THF and 194.7 mg (1.00 mmol) $AgBF_4$ in 2 mL THF were added. A white precipitate occurred immediately. The reaction mixture was stirred at room temperature for 15 min and filtered. 426.5 mg (1.00 mmol) dppb in 4 mL THF were added. The reaction mixture was stirred again for 2 h and the solvent evaporated. The product **6** was crystallized from CH_2Cl_2/diethyl ether; yield: 413 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.56 - 7.30$ (m, 20H, Ar-H), 5.52 – 5.40 (m, 1H, H-2), 4.11 – 4.00 (m, 1H, H-3_{anti}), 3.69 – 3.60 (m, 1H, H-1_{syn}), 2.89 – 2.81 (m, 1H, H-1_{anti}), 2.74 – 2.35 (m, 4H, CH_2), 1.99 – 1.59 (m, 4H, CH_2), 1.11 – 1.01 (m, 3H, CH_3); ^{31}P NMR (C_6D_6, 161 MHz, 25 °C): $\delta = 19.6$ (d, $J = 47.2$ Hz, 1P), 20.2 (d, $J = 47.2$ Hz, 1P).

(π-Crotyl)-1,4-bis(diphenylphosphino)-butanepalladium(II) Acetate (7)

A mixture of 208 mg (0.227 mmol) $Pd_2(dba)_3$ and 194 mg (0.455 mmol) dppb in 4 mL THF was stirred at room temperature for 15 min. 5.19 g (45.5 mmol) but-2-enyl acetate were added. The mixture was stirred for another 1.5 h, filtered and the solvent removed in vacuum. After addition of hexane, the product formed a second phase at the bottom of the Schlenk tube. The mixture was cooled to –70 °C, the hexane phase decanted and the product dried in vacuum; yield: 220 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.52-7.25$ (m, 20H, Ar-H), 5.47–5.36 (m, 1H, H-2), 4.08–3.94 (m, 1H, H-3_{anti}), 3.78–3.58 (m, 1H, H-1_{syn}), 2.74–2.43 (m, 5H, H-1_{anti}, CH_2), 1.95 (s, 3H, CH_3). 1.93–1.56 (m, 4H, CH_2), 1.14–1.05 (m, 3H, CH_3); ^{31}P NMR (C_6D_6, 161 MHz, 25 °C): $\delta = 20.1$ (d, $J = 48.6$ Hz, 1P), 20.6 (d, $J = 48.6$ Hz, 1P).

Acknowledgements

We thank Mrs. S. Buchholz (IfOK) for excellent technical support. Dr. Ralf Jackstell (IfOK) is thanked for providing the ligand dpppp. We are also indebted to Dr. Heike Schaffrath and Dr. Imre Tóth (both from DSM Research) for stimulating discussions. This work was supported by DSM and the State Mecklenburg-West Pomerania.

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