

# Palladium/tin catalyzed alkoxy carbonylation of naturally occurring bicyclic monoterpenes

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## Abstract

The alkoxy carbonylation of camphene and  $\beta$ -pinene has been studied. The following systems have been used as catalysts:  $\text{PdCl}_2(\text{PPh}_3)_2/\text{SnCl}_2/\text{PPh}_3$  and  $\text{PdCl}_2(\text{diphosphine})/\text{SnCl}_2/\text{PPh}_3$  whose diphosphines were 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane. It was observed that several concurrent transformations of monoterpenes occur in the reaction solutions. To find the optimum conditions for alkoxy carbonylation the effect of the reaction variables on the product distribution has been investigated. The reaction of  $\beta$ -pinene exclusively yields the products of the Lewis acid catalyzed skeletal rearrangement accompanied by a nucleophilic addition of chloride and methoxy groups. No products of carbon monoxide incorporation were observed. Camphene was converted to the corresponding linear ester composed of approximately equal amounts of *exo* and *endo* isomers with a selectivity of 90% and virtually 100% regioselectivity (linear/branched esters) using a  $\text{PdCl}_2(\text{PPh}_3)_2/\text{SnCl}_2/\text{PPh}_3$  system as a catalyst. Methyl bornyl ether was the only major by-product.  $\text{SnCl}_2$  and  $\text{PdCl}_2(\text{PPh}_3)_2$  exhibited a strong synergetic effect on the camphene alkoxy carbonylation.  $\text{PdCl}_2(\text{PPh}_3)_2$  alone showed a very low catalytic activity promoting the predominant formation of the thermodynamically more stable *exo* isomer (the *exo/endo* ratio is approximately 2:1). © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Alkoxy carbonylation; Palladium–tin catalysts; Camphene;  $\beta$ -pinene

## 1. Introduction

Oxygenated derivatives of abundant monoterpenes are of a considerable value for perfumery, flavor and pharmaceutical industry [1]. Previously, we have reported that allylic acetates, aldehydes and alcohols can be obtained in good yields by the oxidation [2] and hydroformylation

[3,4] of some naturally occurring monoterpenes. Metal complex catalyzed alkoxy carbonylation represents another valuable route for the functionalization of the carbon–carbon double bond of monoterpenes which provides the carboxylic acid derivatives (Scheme 1).

Alkoxy carbonylation of  $\alpha$ -olefins catalyzed by nickel and cobalt complexes results in the production of large amounts of branched ester and is accompanied by various side reactions [5]. Palladium and platinum–tin complexes operate under milder conditions and are active

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Scheme 1.

catalysts for the formation of linear products [6–11]. It has been reported that the palladium/tin catalyzed alkoxy carbonylation of limonene (**1**) and its derivatives yields the corresponding linear esters or lactones [12]. The aim of the present study was to investigate the alkoxy carbonylation of bicyclic monoterpenes, such as  $\beta$ -pinene (**2**) and camphene (**3**), in the presence of palladium/tin and platinum/tin catalytic systems. We have found that under the reaction conditions both monoterpenes undergo various concurrent transformations. Efforts have been made to study the effects of the catalyst composition and reaction variables on the product distribution in order to find the most favorable conditions for the alkoxy carbonylation.

## 2. Experimental

All chemicals were purchased from commercial sources and used as received, unless otherwise indicated.  $PtCl_2(PPh_3)_2$  and  $PtCl_2(dppb)$  were synthesized by methods described in Refs. [13] and [14], respectively. Palladium complexes  $PdCl_2P_2$  ( $P = PPh_3$  and  $P_2 = dppe, dppp, dppb$ ) were synthesized in analogy with a method described in Ref. [15] for  $P_2 = dppe$  ( $dppe$ -1,2-bis(diphenylphosphino)ethane,  $dppp$ -1,3-bis(diphenylphosphino)propane,  $dppb$ -1,4-bis(diphenylphosphino)butane). Benzene was purified under reflux with sodium wire/benzophenone for six hours and then distilled under nitrogen. R-(+)-limonene, (1S)-(-)- $\beta$ -pinene and (-)-camphene were distilled before use.

The products were analyzed by gas chromatography (GC) using a Shimadzu 14B instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. NMR spectra were obtained using a Bruker CXP-400 spectrometer with tetramethylsilane as an internal standard in  $CDCl_3$ . IR spectra were recorded

on a Mattson FTIR 3000/Galaxy Series spectrophotometer. Mass spectra were obtained on a Hewlett-Packard MSD 5890/Series II instrument operating at 70 eV.

In a typical run a palladium complex (0.05 mmol),  $SnCl_2 \cdot 2H_2O$  (0.05–0.25 mmol),  $PPh_3$  (0.1 mmol), monoterpene (5 mmol), MeOH (5 mmol), and benzene (5 ml) were transferred under nitrogen into a glass lined 30 ml stainless steel reactor. The reactor was pressurized to 4 MPa total pressure of CO, placed in an oil bath, and magnetically stirred at 100°C for 16 h unless otherwise indicated. After cooling to room temperature, the excess CO was slowly vented. The solution was analyzed by GC and GC/MS. The products were separated by column chromatography (silica) using mixtures of hexane,  $CH_2Cl_2$ , and methanol as eluents; and identified by GC/MS, IR,  $^1H$ - and  $^{13}C$ -NMR spectroscopy. The ester product was isolated as a mixture of isomers **12** and **13**. The complete assignment of  $^1H$ - and  $^{13}C$ -NMR signals for products **12** and **13** was made using HMQC and DEPT NMR experiments and the stereochemistry was determined using a NOESY experiment [16]. Spectral simulations performed with the ADC/CNMR program were in agreement with the spectra observed.

## 3. New compounds

**Ester 12** (*endo*, shorter GC retention time). IR (film): 1750  $cm^{-1}$  (C=O). MS ( $m/z$ /rel.int.): 196/1 ( $M^+$ ); 153/38; 127/69; 122/100; 121/31; 107/38; 93/33; 81/44; 79/54; 69/49; 67/60; 55/44;  $^1H$ -NMR:  $\delta$  0.79 (s, 3H,  $C^{10}H_3$ ); 0.99 (s, 3H,  $C^9H_3$ ); 3.65 (s, 3H,  $OCH_3$ );  $^{13}C$ -NMR:  $\delta$  21.43 ( $C^{10}$ ); 24.04 ( $C^5$ ); 24.50 ( $C^6$ ); 31.87 ( $C^9$ ); 32.14 ( $C^8$ ); 36.82 ( $C^7$ ); 37.61 ( $C^2$ ); 42.03 ( $C^1$ ); 43.76 ( $C^4$ ); 48.97 ( $C^3$ ); 51.38 ( $C^{12}$ ); 174.50 ( $C^{11}$ ).

**Ester 13** (*exo*, longer GC retention time). IR (film): 1750  $\text{cm}^{-1}$  (C=O). MS ( $m/z$ /rel.int.): 196/1 ( $\text{M}^+$ ); 153/38; 127/69; 122/100; 121/31; 107/38; 93/33; 81/44; 79/54; 69/49; 67/60; 55/44;  $^1\text{H-NMR}$ :  $\delta$  0.85 (s, 3H,  $\text{C}^9\text{H}_3$ ); 1.02 (s, 3H,  $\text{C}^{10}\text{H}_3$ ); 3.66 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C-NMR}$ :  $\delta$  20.37 ( $\text{C}^6$ ); 24.93 ( $\text{C}^9$ ); 27.60 ( $\text{C}^{10}$ ); 29.51 ( $\text{C}^5$ ); 35.58 ( $\text{C}^7$ ); 36.10 ( $\text{C}^8$ ); 40.20 ( $\text{C}^2$ ); 42.03 ( $\text{C}^1$ ); 46.49 ( $\text{C}^4$ ); 49.35 ( $\text{C}^3$ ); 51.42 ( $\text{C}^{12}$ ); 174.55 ( $\text{C}^{11}$ ).

## 4. Results and discussion

### 4.1. Alkoxy carbonylation of limonene

Before starting to work with the bicyclic monoterpenes, such as  $\beta$ -pinene and camphene, we have studied the alkoxy carbonylation of limonene under the conditions similar to those reported in Ref. [12] (Table 1). Limonene reacts with CO and methanol, in the presence of catalytic amounts of  $\text{PdCl}_2(\text{PPh}_3)_2$  (**I**) and  $\text{SnCl}_2$ , to give mainly the linear ester **4** (Scheme 2) with high regioselectivity (runs 1 and 3). In the absence of  $\text{SnCl}_2$ , the reaction proceeds slower and the branched ester **5** is formed in larger amounts (runs 2 and 4). The product of the addition of methanol to the exocyclic double bond of limonene, i.e.,  $\alpha$ -terpenyl methyl ether **6**, is detected in small amounts (up to 4%).  $\text{SnCl}_2$  acting as a Lewis acid also promotes the

isomerization of limonene double bond to give  $\alpha$ -terpinolene (**7**) and  $\gamma$ -terpinene (**8**), which contain no terminal double bonds. High concentrations of **7** and **8** are detected at low conversion of limonene (up to 50% based on reacted limonene, run 3), however, no products of their alkoxy carbonylation are detected after the reaction. The alkoxy carbonylation of internal olefins is known to proceed much slower than that of terminal olefins due to steric factors [7]. With the increase in limonene conversion the isomerization equilibrium is shifted towards the formation of limonene and the concentrations of **7** and **8** decrease. At 85% limonene conversion the final amounts of **7** and **8** do not exceed 4% based on reacted limonene (run 1).

### 4.2. Reactions of $\beta$ -pinene under the alkoxy carbonylation conditions

We tried to extend this alkoxy carbonylation methodology to the bicyclic monoterpenes, such as  $\beta$ -pinene (**2**) and camphene (**3**), containing disubstituted terminal double bonds. Table 2 shows the distribution of the products formed from  $\beta$ -pinene in benzene–methanol solutions containing palladium or platinum complex,  $\text{SnCl}_2$  and  $\text{PPh}_3$  at a carbon monoxide pressure of 4–8 MPa and 100–120°C. As catalysts were used  $\text{PdCl}_2(\text{PPh}_3)_2$  (**I**),  $\text{PtCl}_2(\text{PPh}_3)_2$  (**II**) and  $\text{PtCl}_2(\text{dppb})$  (**III**).  $\beta$ -Pinene undergoes skeletal rearrangements accompanied with a nucleophilic addition of chloride and methoxy groups

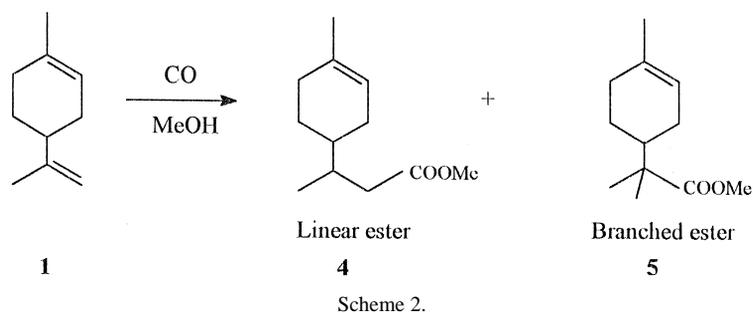
Table 1  
Alkoxy carbonylation of limonene catalyzed by  $\text{PdCl}_2(\text{PPh}_3)_2$  and  $\text{PdCl}_2(\text{PPh}_3)_2/\text{SnCl}_2$

| Run | Catalyst (method)                                   | Conversion <sup>a</sup> (%) | Selectivity <sup>a,b</sup> for esters <b>4</b> and <b>5</b> (%) | Ester distribution (%) |          |
|-----|-----------------------------------------------------|-----------------------------|-----------------------------------------------------------------|------------------------|----------|
|     |                                                     |                             |                                                                 | <b>4</b>               | <b>5</b> |
| 1   | $\text{PdCl}_2(\text{PPh}_3)_2 + \text{SnCl}_2$ (A) | 85                          | 91                                                              | 99                     | 1        |
| 2   | $\text{PdCl}_2(\text{PPh}_3)_2$ (A)                 | 45                          | 92                                                              | 90                     | 10       |
| 3   | $\text{PdCl}_2(\text{PPh}_3)_2 + \text{SnCl}_2$ (B) | 42                          | 41                                                              | 99                     | 1        |
| 4   | $\text{PdCl}_2(\text{PPh}_3)_2$ (B)                 | 33                          | 79                                                              | 87                     | 13       |

Reaction conditions:  $[\text{limonene}]/[\text{MeOH}]/[\text{catalyst}]/[\text{SnCl}_2 \cdot 2\text{H}_2\text{O}]$ (if any)/ $[\text{PPh}_3] = 100/100/1/2.5/2$ ; benzene (5 ml), 100°C, CO (4 MPa), reaction time 16 h; method A: 20 mmol of limonene. Method B: 5 mmol of limonene.

<sup>a</sup>Determined by gas chromatography.

<sup>b</sup>Main by-products are  $\alpha$ -terpinolene and  $\gamma$ -terpinene.  $\alpha$ -Terpenyl methyl ether **6** is detected in small amounts (up to 4%).



resulting in the formation of limonene (**1**),  $\alpha$ -terpenyl methyl ether (**6**),  $\alpha$ -terpinolene (**7**),  $\gamma$ -terpinene (**8**), bornyl chloride (**9**), fenchyl chloride (**10**), and  $\alpha$ -pinene (**11**) (Scheme 3). No products of carbon monoxide incorporation are observed.

Varying the catalyst (runs 1–3), component concentrations (run 4), temperature (run 5) and carbon monoxide pressure (run 6) results in some changes in the product distribution but not in the product nature. As can be seen from the run 7,  $\text{SnCl}_2$  alone, in the absence of Pd or Pt complexes, acts as a Lewis acid and catalyzes the undesirable transformations of  $\beta$ -pinene. It is noteworthy that these transformations (isomerization and nucleophilic addition) are fully suppressed by decreasing the tin/palladium

atomic ratio from 2.5 to 1 (run 8) and only the starting material was recovered after 50 h. It can be suggested that  $\text{SnCl}_2$  forms a stable 1:1 complex with Pd(II) under the reaction conditions, however, this complex shows no activity in alkoxy-carbonylation of  $\beta$ -pinene.

#### 4.3. Alkoxy-carbonylation of camphene

The reaction of camphene (**3**) with CO and methanol was investigated using the following catalytic systems:  $\text{PdCl}_2(\text{PPh}_3)_2/\text{PPh}_3/\text{SnCl}_2$  and  $\text{PdCl}_2(\text{diphosphine})/\text{PPh}_3/\text{SnCl}_2$  with different chelating diphosphines: 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane (dppb). Benzene was employed as

Table 2

Distribution of the products formed from  $\beta$ -pinene under the alkoxy-carbonylation conditions Catalysts:  $\text{PdCl}_2(\text{PPh}_3)_2$  (I),  $\text{PtCl}_2(\text{PPh}_3)_2$  (II), and  $\text{PtCl}_2(\text{dppb})$  (III)

| Run            | Catalyst | $\beta$ -pinene (mmol) | Conversion <sup>a</sup> (%) | Product distribution <sup>a</sup> (%) |          |              |          |           |           |
|----------------|----------|------------------------|-----------------------------|---------------------------------------|----------|--------------|----------|-----------|-----------|
|                |          |                        |                             | <b>1</b>                              | <b>6</b> | <b>7 + 8</b> | <b>9</b> | <b>10</b> | <b>11</b> |
| 1              | I        | 20                     | 8                           | 8                                     | 28       | 7            | 29       | 14        | 14        |
| 2              | II       | 20                     | 12                          | 10                                    | 24       | 7            | 24       | 12        | 23        |
| 3              | III      | 20                     | 16                          | 14                                    | 14       | 4            | 17       | 7         | 44        |
| 4              | I        | 5                      | 10                          | 16                                    | traces   | 7            | 28       | 11        | 38        |
| 5 <sup>b</sup> | I        | 5                      | 11                          | 14                                    | 9        | 10           | 30       | 12        | 25        |
| 6 <sup>c</sup> | I        | 20                     | 15                          | 10                                    | 27       | 7            | 23       | 13        | 20        |
| 7 <sup>d</sup> | —        | 5                      | 15                          | 26                                    | 22       | 5            | 11       | 4         | 32        |
| 8 <sup>e</sup> | I        | 5                      | < 3                         |                                       | traces   |              |          |           | traces    |

Reaction conditions: [  $\beta$ -pinene ]/[MeOH]/[catalyst]/[ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ]/[ $\text{PPh}_3$ ] = 100/100/1/2.5/2; benzene (5 ml), 100°C, CO (4 MPa), reaction time 16 h.

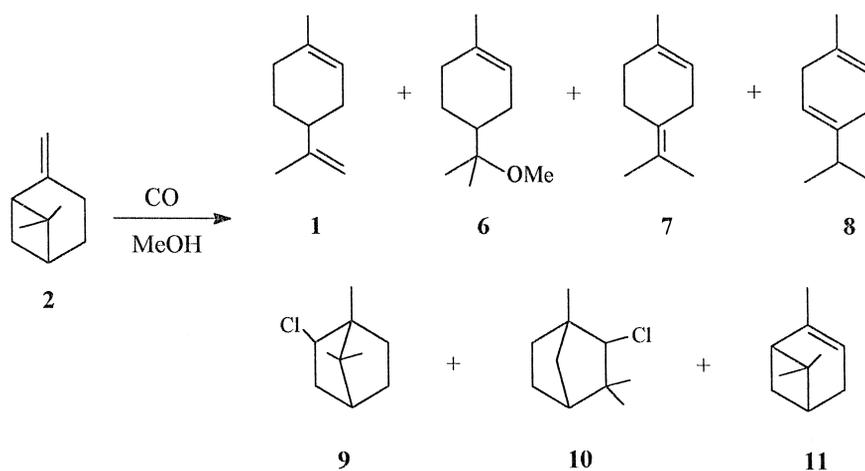
<sup>a</sup>Determined by gas chromatography.

<sup>b</sup>[Catalyst]/[ $\text{PPh}_3$ ] = 1/4; 120°C, reaction time 25 h.

<sup>c</sup>8 MPa.

<sup>d</sup>In the absence of the catalyst.

<sup>e</sup>[Catalyst]/[ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ] = 1/1, reaction time 50 h.



Scheme 3.

a solvent. The results are given in Table 3. The formation of the two isomers of the correspond- ing linear ester (**12** and **13**) is observed under

the conditions similar to those used for the alkoxycarbonylation of limonene (Table 3, run 1), however, with a rather low selectivity (30%).

Table 3  
Alkoxycarbonylation of camphene catalyzed by PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (I), PdCl<sub>2</sub>(dppf) (IV), PdCl<sub>2</sub>(dppp) (V), and PdCl<sub>2</sub>(dppb) (VI)

| Run             | Catalyst | [Sn]/[Pd] | Conversion <sup>a</sup> (%) | Selectivity <sup>a</sup> for esters (%) | Ester distribution (%)    |                          |
|-----------------|----------|-----------|-----------------------------|-----------------------------------------|---------------------------|--------------------------|
|                 |          |           |                             |                                         | <b>12</b> ( <i>endo</i> ) | <b>13</b> ( <i>exo</i> ) |
| 1               | I        | 2.5       | 79                          | 30                                      | 55                        | 45                       |
| 2               | I        | 5         | 79                          | 20                                      | 56                        | 44                       |
| 3               | I        | 1         | 61                          | 90                                      | 52                        | 48                       |
| 4 <sup>b</sup>  | —        | —         | 18                          | 0                                       | —                         | —                        |
| 5 <sup>c</sup>  | —        | —         | 0                           | 0                                       | —                         | —                        |
| 6 <sup>d</sup>  | I        | 1         | 37                          | 87                                      | 51                        | 49                       |
| 7 <sup>e</sup>  | I        | 1         | 60                          | 90                                      | 50                        | 50                       |
| 8 <sup>f</sup>  | I        | 1         | 71                          | 65                                      | 56                        | 44                       |
| 9 <sup>g</sup>  | I        | 1         | 54                          | 68                                      | 52                        | 48                       |
| 10              | IV       | 1         | < 3                         | —                                       | —                         | —                        |
| 11              | V        | 1         | < 3                         | —                                       | —                         | —                        |
| 12              | VI       | 1         | 14                          | 45                                      | 61                        | 39                       |
| 13 <sup>h</sup> | I        | 0         | 9                           | 88                                      | 35                        | 65                       |
| 14 <sup>i</sup> | I        | 1         | 37                          | 72                                      | 42                        | 58                       |

Reaction conditions: monoterpene (5 mmol), catalyst (0.05 mmol), SnCl<sub>2</sub> · 2H<sub>2</sub>O (atomic Sn/Pd ratio is indicated), PPh<sub>3</sub> (0.1 mmol), MeOH (5 mmol), benzene (5 ml), 100°C, CO (4 MPa), reaction time 16 h.

<sup>a</sup>Selectivity for the formation of esters **12** and **13** determined by gas chromatography.

<sup>b</sup>In the absence of the Pd complex.

<sup>c</sup>In the absence of both the Pd complex and SnCl<sub>2</sub>.

<sup>d</sup>Reaction time 8 h.

<sup>e</sup>Reaction time 28 h.

<sup>f</sup>Anhydrous SnCl<sub>2</sub> was used.

<sup>g</sup>H<sub>2</sub>O (0.05 mmol) was added, along with methyl bornyl ether **14**, the formation of borneol (ca 10%) was observed.

<sup>h</sup>In the absence of SnCl<sub>2</sub>.

<sup>i</sup>8 MPa.

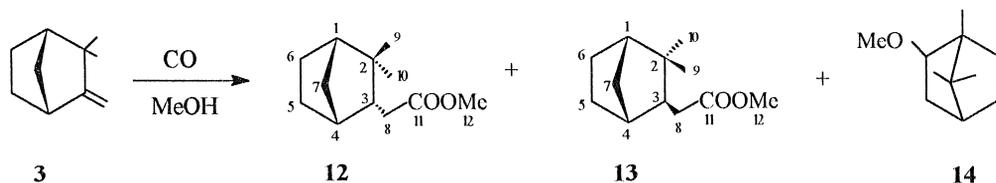
A skeletal isomerization accompanied by a methanol addition resulting in methyl bornyl ether **14** is the only major competing reaction (Scheme 4), differently from  $\beta$ -pinene which gives a wide variety of the isomerization and addition products (Scheme 3).

Camphene is alkoxy-carbonylated regioselectively to give exclusively the linear ester. No traces of the branched ester, which might be formed in a typical Markovnikov fashion, are detected even in the absence of  $\text{SnCl}_2$ . Sterical hindrance of camphene should favor anti-Markovnikov H addition with the formation of less sterically crowded straight-chain  $\sigma$ -alkyl Pd intermediate leading to the linear product. The linear ester product is composed of 45% of the thermodynamically more stable *exo* isomer **13** and 55% of *endo* isomer **12**. In the absence of Pd complex (run 4), the formation of **14** becomes virtually the exclusive reaction. In the absence of both  $\text{SnCl}_2$  and Pd complex, only the starting material was recovered after reaction (run 5). Hence, the undesirable transformations of camphene are promoted by  $\text{SnCl}_2$  which exhibits a Lewis-acid character.

As expected, the selectivity for ester formation is strongly influenced by the Sn/Pd ratio (runs 1–3) and reaches the value of 90% at Sn/Pd = 1 (run 3).  $\text{SnCl}_2$  seems to form a stable 1:1 complex with Pd(II),  $[\text{PdCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ , which effectively catalyzes alkoxy-carbonylation of camphene. As it can be seen, the skeletal rearrangement of camphene promoted by free  $\text{SnCl}_2$  is almost suppressed (a 90% selectivity in ester), therefore, the equilibrium is essentially shifted towards the formation of the complex mentioned above. It is worthwhile noting a strong synergetic effect of

$\text{SnCl}_2$  and palladium(II) on the camphene alkoxy-carbonylation.  $\text{PdCl}_2(\text{PPh}_3)_2$  alone shows a very low catalytic activity. We observed a 9% conversion of camphene for 16 h and a selectivity in ester of 88% using  $\text{PdCl}_2(\text{PPh}_3)_2$  alone as a catalyst (run 13), while in the presence of equimolar amounts of  $\text{SnCl}_2$ , the conversion increases up to 60% with approximately the same selectivity (run 3). It is remarkable the change in the ester isomer distribution in the absence of  $\text{SnCl}_2$  with the formation of *exo* isomer as the major product (the *exo/endo* ratio is approximately 2/1). To achieve higher conversions we varied the reaction time and carbon monoxide pressure. Increasing the reaction time from 8 to 16 h results in rising the camphene conversion from 37% (run 6) up to 61% (run 3). However, with reaction time increased up to 28 h no further improvement in ester yield is observed (run 7) which can indicate a catalyst deactivation. It should be noted that no further increase in the concentration of **14**, which is the product of the competing reaction, has been also detected at longer reaction times. Hence, there is no free  $\text{SnCl}_2$  in the solution containing deactivated catalyst after the reaction. The studies of the reasons for the catalyst deactivation are in progress.

At carbon monoxide pressure of 8 MPa (run 14) the camphene conversion drops to 37% from the 61% level found at 4 MPa (run 3). The reduction in activity of palladium chloride complexes toward the olefin alkoxy-carbonylation at high carbon monoxide pressures was earlier reported by Bittler et al. [9]. The inhibitive coordination of CO results also in the decrease in the ester selectivity from 90% (run 3) to 72% (run 14). Interestingly, the ester isomers distribution



Scheme 4.

in run 14 (predominant formation of *exo* isomer) is close to that found for  $\text{PdCl}_2(\text{PPh}_3)_2$  alone, in the absence of  $\text{SnCl}_2$  (compare runs 13 and 14). The data obtained indicate that at higher CO pressure, the  $\text{SnCl}_2$  is partially displaced from the coordination sphere of Pd by another strong back-bonding ligand, which is CO. Free  $\text{SnCl}_2$  catalyzes the skeletal rearrangement of camphene accompanied by a nucleophilic addition of methanol resulting in the formation of **14** and lowering the ester selectivity. As mentioned above  $\text{PdCl}_2(\text{PPh}_3)_2$  shows a lower activity in camphene alkoxy carbonylation compared with  $\text{Pd}(\text{SnCl}_3)\text{Cl}(\text{PPh}_3)_2$  and promotes the preferable formation of the *exo* isomer **13**.

We have found that water favors the alkoxy-carboxylation activity of the  $\text{PdCl}_2(\text{PPh}_3)_2/\text{SnCl}_2$  catalyst (runs 3 and 8). This water requirement is satisfied by the water of hydration present on the  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The further increase in water concentration (run 9) leads to a significant decrease in ester selectivity (from 90%, run 3, to 68%, run 9). The use of anhydrous  $\text{SnCl}_2$  inhibits the ester formation (compare runs 3 and 8). In a related system for alkoxy carbonylation using a platinum–tin chloride complex as a catalyst the authors showed that small amounts of water were necessary for the reaction [10]. Knifton also observed that  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  replacement by anhydrous  $\text{SnCl}_2$  resulted in a loss in the rate of 1-heptene alkoxy carbonylation catalyzed by  $\text{PdCl}_2(\text{PPh}_3)_2/\text{SnCl}_2$  [7]. Probably, the palladium hydride, which is supposed to be an intermediate in the catalytic alkoxy carbonylation, is formed more easily by the interaction of the Pd–Sn complex with water via reduction of Pd(II) by CO and further protonation of the resulting Pd(0) species. The formation of Pt(II) and Pd(II) hydrides from water via similar route was previously reported [7,17]. On the other hand, the lowering of the reactivity of methanol as a nucleophile in the presence of water due to the formation of hydrogen bonds [18] results in a decrease in ester yield at higher water levels

( $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1/1$ , run 9). Earlier Knifton [7,11] studied the effect of nucleophile nature on the carbonylation of 1-heptene catalyzed by palladium–tin and platinum–tin chlorides and also observed that increased nucleophilicity led to improved yields of ester. We detected no trace of the corresponding carboxylic acid at the  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  molar ratio of 1 (run 9), so, water itself is a poorer nucleophile compared to methanol under the reaction conditions.

We have found that the nature of the phosphorus-containing ligands exerts a strong effect on the activity of the catalytic system in the conversion of camphene and the product distribution. The complexes with dppe and dppp, which can make up strong chelate rings, are completely inactive in the alkoxy carbonylation of **3** (runs 10 and 11). A palladium complex containing dppb, which forms an easier opening seven-membered chelate ring, shows rather low activity and selectivity in ester formation (run 12). The alkoxy carbonylation results in a preferable formation of the thermodynamically less stable *endo* isomer (*endo/exo* = 3:2).

The catalytic system  $\text{PdCl}_2(\text{PPh}_3)_2/\text{PPh}_3/\text{SnCl}_2$  showed satisfactory results in the alkoxy carbonylation of camphene while no activity in the alkoxy carbonylation of the other bicyclic monoterpene, i.e.,  $\beta$ -pinene. Both olefins contain an exocyclic disubstituted double bond and we suppose that the surprising difference in their reactivity could be related with the facility of  $\beta$ -pinene for the formation of the  $\pi$ -allyl complexes with Pd(II) [19]. Although the carbonylation of  $\pi$ -allyl palladium species is known [20,21], the structural factors in the allylic compound were found to have a strong influence on the carbonylation rate which was rather low for cyclic allylic derivatives [20]. It seems reasonable to explain the inactivity of  $\beta$ -pinene in alkoxy carbonylation by the formation of the  $\pi$ -allyl complexes with Pd(II) but the additional experiments are needed to support this suggestion. The study of the reasons for the difference in the reactivity of camphene and  $\beta$ -pinene is in progress. The only allylic hydro-

gen in the molecule of camphene is at a tertiary carbon atom and not easily abstractable. The interaction of camphene with a Pd(II) hydride leads to the formation of a  $\pi$ -olefin complex followed by the H addition. The stereochemistry of the resulted ester is determined by the mode of camphene coordination to the Pd atom: ‘bottom’ or ‘top’. The molecular model analysis shows that both faces of the camphene double bond are sterically hindered and rather difficult to access for the Pd(II) complex containing bulky phosphine ligands. The formation of the thermodynamically more stable *exo* isomer **13** implicates the camphene coordination and the further hydrogen attack on the more crowded face of the camphene double bond (‘bottom’). The *exo* isomer is predominantly formed when PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> alone is used as a catalyst. Replacement of Cl<sup>-</sup> by SnCl<sub>3</sub><sup>-</sup> in the Pd complex provides a particularly sterically hindered catalyst with the combined steric bulk of the phosphine and SnCl<sub>3</sub><sup>-</sup> ligands. The steric constraints favor the formation of the thermodynamically less stable *endo* isomer **12** which is derived from the ‘top’-type coordination and the H attack on the less crowded ‘top’ face of the camphene double bond.

It is remarkable that SnCl<sub>2</sub> and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> exhibit a strong synergetic effect on the camphene alkoxy-carbonylation. With less crowded olefins the addition of SnCl<sub>2</sub> into the palladium–phosphine catalyst produces a beneficial effect on the linearity of ester products and no effect (for 1-heptene [7]) or much poorer effect (for limonene [13]) on the catalyst activity in alkoxy-carbonylation. The steric hindrance seems to be the crucial factor in determining the camphene low reactivity in a palladium–phosphine system. PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> alone shows a very low catalytic activity in camphene alkoxy-carbonylation. The SnCl<sub>3</sub><sup>-</sup> ligand due to its high  $\pi$ -acceptor ability removes electron density from the Pd atom and enhances olefin coordination. In addition, the SnCl<sub>3</sub><sup>-</sup> ligand is known to stabilize the five-coordinated Pt(II) species [22,23] which facilitates the olefin insertion into a Pt–H bond

via trigonal bipyramidal intermediates [24,25]. We believe that this ability of SnCl<sub>3</sub><sup>-</sup> should be also important in the palladium chemistry.

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