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Platinum/tin catalyzed hydroformylation of naturally occurring monoterpenes

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Abstract

(−)-β-Pinene, *R*-(+)-limonene, and (−)-camphene have been hydroformylated regiospecifically to give exclusively the linear isomers of corresponding aldehydes. The following systems were used as catalysts: $PtCl_2(PPh_3)_2/SnCl_2/PPh_3$, and $PtCl_2$(diphosphine)$/SnCl_2/PPh_3$ whose diphosphines were 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino) butane. The hydroformylation of β-pinene yields *trans*-10-formylpinane with a 98% diastereoisomeric excess (d.e.), while limonene and camphene give the diastereoisomers of the corresponding aldehydes in approximately equal amounts (d.e. of ca. 10 and 15%, respectively). Differently from most of the rhodium and cobalt catalysts, the undesirable isomerization of β- to α-pinene is rather slow (1–5% based on reacted β-pinene). The primarily formed aldehyde of limonene undergoes the highly diasteroselective intramolecular cyclization (d.e. of virtually 100%) catalyzed by the platinum/tin active species yielding 4,8-dimethyl-bicyclo[3.3.1]non-7-en-2-ol. The effects of the catalyst composition and ligand nature on the product distribution have been studied. The use of PPh_3 as the only phosphorous-containing ligand, as well as the excess of $SnCl_2$ ($Sn/Pt > 1$) promote the isomerizations of monoterpenes. The system with 1,3-bis(diphenylphosphino)propane causes excessive hydrogenation of the olefinic double bonds. Under optimized conditions, chemoselectivities for aldehyde formation of near 90% have been attained for all monoterpenes studied.

Keywords: Platinum; Tin; Monoterpenes

1. Introduction

Naturally occurring monoterpenes are a useful source of inexpensive olefins. Functionalization of these olefins can provide oxygenated derivatives which are important to the perfume, flavor, and pharmaceutical industries as well as useful synthetic intermediates and chiral building blocks [1,2]. Previously we have reported that allylic acetates, alcohols, and carboxylic acid derivatives can be obtained in good yields by the metal complex catalyzed oxidation [3,4], hydroformylation [5], and alkoxycarbonylation [6] of some monoterpenes. Hydroformylation represents a valuable pathway to produce com-

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mercially important aldehydes and alcohols from olefins. A number of monoterpenes including limonene [2,7–10], β-pinene [2,9–13], and camphene [10,14–16] have been hydroformylated in the presence of cobalt and rhodium complexes, which are most commonly used to catalyze this reaction in industrial processes. Among the alternative catalytic systems, those based on platinum/tin compositions are probably the most promising ones.

Hydroformylation catalyzed by platinum(II) complexes in the presence of $SnCl_2$ has been extensively studied because these systems allow high regioselectivity for the formation of linear aldehydes and are especially efficient in asymmetric reactions providing high stereoselectivity [17–28]. However, their applications to monoterpenes (such as limonene and camphene) are scarcer [5,29,30]. To the best of our knowledge, there have been no attempts to perform a stereoselective hydroformylation of β-pinene using platinum/tin catalysts. It should be mentioned that most of the cobalt and rhodium catalysts promote the undesirable isomerization of β- to α-pinene in significant amounts under the reaction conditions.

This work describes the hydroformylation of (−)-β-pinene, *R*-(+)-limonene, and (−)-camphene catalyzed by the platinum(II)/tin(II)/phosphine(diphosphine) catalytic systems. We have found that under the reaction conditions all monoterpenes studied, as well as the primarily formed aldehydes undergo various concurrent transformations such as isomerization, hydrogenation, cyclization. Efforts have been made to investigate the effects of the catalyst composition and ligand nature on the product distribution in order to find the most favorable conditions for hydroformylation.

2. Experimental

All chemicals were purchased from commercial sources and used as received, unless otherwise indicated. *cis*-$[PtCl_2(PPh_3)_2]$ was prepared by published procedure [31]. The $PtCl_2$(diphosphine) complexes (diphosphine: 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane (dppb)) were synthesized by analogy with a method described in [32] for $PtCl_2$(dppe). Benzene was purified under reflux with sodium wire/benzophenone for 6 h and then distilled under nitrogen. *R*-(+)-Limonene, (−)-β-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 Brucker 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 platinum complex (0.05 mmol), $SnCl_2 \cdot 2H_2O$ (0.05–0.25 mmol), PPh_3 (0.1 mmol), monoterpene (5 mmol), and benzene (5 ml) were transferred under nitrogen into a glass lined 30 ml stainless steel reactor. The reactor was pressurized to 9 MPa total pressure ($CO/H_2 = 1/1$), placed in an oil bath, and stirred with a magnetic stirrer. After carrying out the reaction and cooling to room temperature, the excess CO and H_2 were 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, ^{1}H, and ^{13}C-NMR spectroscopy. The aldehyde and alcohol products were isolated as the diasteroisomeric mixtures. The assignment of ^{1}H and ^{13}C-NMR signals was made using HMQC and DEPT NMR experiments and the stereochemistry was determined using NOESY experiments. Spectral simulations performed with the ADC/CNMR program were in agreement with the spectra observed.

*2.1. 3-(4-Methylcyclohex-3-enyl)butanal **4***

Compound described by Kollár et al. [29].

*2.1.1. 4,8-Dimethylbicyclo[3.3.1]non-7-en-2-ol **5a / 5b***

IR ν_{max}(film)/cm^{-1}: 3400 (ν (O–H)), 1370 (δ (O–H)), 1030(ν (C–O)). MS (*m/z*/rel.int.): 166/13 (M^+); 148/30; 133/20; 121/12; 106/26; 93/100. ^{1}H NMR: δ 0.92 (d, 3H, CH_3, $J = 6.5$Hz); 1.03 (d, 3H, CH_3, $J = 7.4$ Hz); 1.21–1.25 (m, 2H); 1.49–1.53 (m, 4H); 1.63–1.68 (m, 6H); 1.78 (s, 3H, CH_3); 1.79 (s, 3H,CH_3); 1.98–2.01 (m, 3H); 2,32–2.34 (m, 3H); 3.84–3.88 (m, 1H, C*H*OH); 3.98–4.09 (m, 1H, C*H*OH); 5.55–5.58 (m, 2H, C*H*=(**5a**), C*H*=(**5b**)). ^{13}C NMR: δ 69.67 (C–OH); 74.46 (C–OH); 123.68 (C=C); 124.33 (C=C); 133.69 (C=C); 134.21 (C=C).

*2.2. 10-Formylpinane (10-pinanecarbaldehyde) **8a** (cis, longer GC retention time) and **8b** (trans, shorter GC retention time)*

Compounds described by Azzaroni et al. [13] and Sirol and Kalck [10].

*2.3. 3,3-Dimethyl-2-norbornaneacetaldehyde **14a** (exo, shorter GC retention time)*

IR (film): 1720 cm^{-1} (C=O). MS (*m/z*/rel.int.): 166/3 (M^+); 122/36; 109/25; 107/43; 97/100; 83/25; 81/35; 79/48; 69/59; 67/64; 55/60. ^{1}H NMR: 0.79 (s, 3H, C$^{10}H_3$); 0.96 (s, 3H, C$^9H_3$); 1.03–1.05 (m, 1H, C^7HH); 1.13–1.16 (m, 1H, C^5HH); 1.44–1.52 (m, 1H, C^{5}H*H*); 1.58–1.62 (m, 2H, C^{7}H*H*, C^4H); 1.63–1.65 (m, 2H, C$^6H_2$); 1.69–1.71 (m, 1H, C^1H); 1.86–1.88 (m, 1H, C^3H); 2.15 (ddd, 1H, C^8HH, ^{2}J = 16.6Hz, ^{3}J = 9.3 Hz, ^{3}J = 2.6 Hz); 2.40 (ddd, 1H, C^{8}H*H*, ^{2}J = 16.6 Hz, ^{3}J = 6.1 Hz, ^{3}J = 1.6 Hz); 9.67 (dd, 1H, C^{11}HO, ^{3}J = 2.6 Hz, ^{3}J = 1.6Hz). ^{13}C NMR: δ 23.01 (C^6); 24.39 (C^{10}); 26.59 (C^9); 28.42 (C^5); 34.64 (C^7); 39.25 (C^2); 42.79 (C^3); 45.12 (C^8); 46.79 (C^4); 48.08 (C^1); 202.28 (C^{11}). Compound described by Sirol and Kalck [10] and Kollár and Bódi [30].

*2.4. 3,3-Dimethyl-2-norbornaneacetaldehyde **14b** (endo, longer GC retention time)*

IR (film): 1720 cm^{-1} (C=O). MS (*m/z*/rel.int.): 166/4 (M^+); 122/27; 109/20; 107/35; 97/100; 83/23; 79/43; 69/48; 67/55; 55/52. ^{1}H NMR: 0.72 (s, 3H, C$^9H_3$); 0.93 (s, 3H, C$^{10}H_3$); 1.11–1.13 (m, 1H, C^7HH); 1.19–1.21 (m, 1H, C^5HH); 1.21–1.23 (m, 2H, C$^6H_2$); 1.44–1.52 (m, 1H, C^{5}H*H*); 1.58–1.62 (m, 3H, C^{7}H*H*, C^4H, C^1H); 2.05–2.07 (m, 1H, C^3H); 2.31 (dd, 1H, C^8HH, ^{3}J = 8.3 Hz, ^{3}J = 2.3 Hz); 2.36 (dd, 1H, C^{8}H*H*, ^{3}J = 7.1 Hz, ^{3}J = 2.0 Hz); 9.69 (t, 1H, C^{11}HO, ^{3}J = 2.2 Hz). ^{13}C NMR: δ 19.39 (C^6); 20.81 (C^9); 23.49 (C^5); 30.96 (C^{10}); 36.64 (C^7); 35.94 (C^2); 41.01 (C^3); 41.17 (C^8); 43.49 (C^4); 47.78 (C^1); 202.32 (C^{11}). Compound described by Sirol and Kalck [10] and Kollár and Bódi. [30].

3. Results and discussion

The reactions of limonene (**1**), β-pinene (**2**), and camphene (**3**) with CO and H_2 were investigated using the following catalytic systems: $PtCl_2(PPh_3)_2/SnCl_2/PPh_3$ and $PtCl_2$(diphosphine)/$SnCl_2/PPh_3$ with different chelating diphosphines: dppe, dppp and dppb. Benzene was employed as the solvent. The results are given in Tables 1–3. All monoterpenes have been hydroformylated regiospecifically to give exclusively the linear aldehydes. No traces of the branched aldehydes, which might be formed in a typical Markovnikov fashion, have been detected. Sterical hindrance of **1**, **2**, and **3**, which have the exocyclic 2,2-disubstituted double bonds, and the steric bulk of both the phosphine (diphosphine) and $SnCl_3^-$ ligands in the platinum complex should favor an anti-Markovnikov H addition, with the formation of less sterically crowded straight-chain σ-alkyl

Table 1
Hydroformylation of limonene (**1**) catalyzed by $PtCl_2L_2/SnCl_2$[a]

Run	Ligand	Temperature (°C)	Time (h)	Conversion[b] (%)	Product distribution[b] (%)			
					Hydrogenation[c]	Isomerization[d]	**4**	**5 (5a / 5b)**[e]
1	dppp	100	4	11	7	3	90	traces
2	dppb	100	4	10	7	3	89	traces
3	dppb	100	20	19	6	4	52	38 (48/52)
4	dppb	130	24	85	13	3	21	63 (47/53)
5	PPh_3	130	50	83	1	70	–	29 (50/50)
6	dppp	130	50	93	22	4	7	67 (44/56)
7	dppb	130	50	95	11	4	3	82 (47/53)
8[g]	dppb	130	50	85	traces	80	–	20 (45/55)

[a] Reaction conditions: substrate (5 mmol), $PtCl_2L_2$ (0.05 mmol), $SnCl_2 \cdot 2H_2O$ (0.05 mmol), PPh_3 (0.1 mmol), benzene (5 ml), 9 MPa ($CO/H_2 = 1/1$).
[b] Determined by gas chromatography.
[c] The product of limonene hydrogenation — carvomenthene.
[d] The products of limonene isomerization, mainly, α-terpinolene (**6**) and γ-terpinene (**7**).
[e] The ratio of 1*R*,2*R*,4*S*,5*R* (**5a**) and 1*R*,2*R*,4*R*,5*R* (**5b**) (may be reversed).
[g] $SnCl_2 \cdot 2H_2O$ — 0.25 mmol.

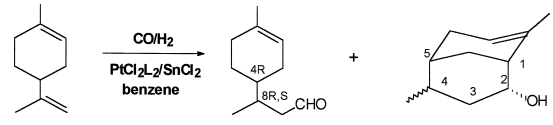
platinum intermediates leading to the linear products. Under certain reaction conditions these systems show a marked acidic behavior promoting product and/or substrate isomerizations. The nature of the phosphorus-containing ligands exerts a strong effect on the activity of the catalytic system in the conversion of monoterpenes and the product distribution.

In the absence of $SnCl_2$, all platinum complexes studied show no activity in the hydroformylation of **1**, **2**, and **3**. A strong synergetic effect of $SnCl_2$ and Pt(II) on the hydroformylation has been observed for various olefins. Previous studies [17,18,27] suggest that complexes containing the [Pt–$SnCl_3$] fragment, such as hydride, alkyl, and acyl intermediates formed from the $PtCl(SnCl_3)(PPh_3)_2$ precursor, are involved in these catalytic reactions. The $SnCl_3^-$ ligand due to its high π-acceptor ability removes electron density from the Pt atom which enhances olefin coordination and prevents the reduction of Pt [33]. The strong *trans*-activation effect of the $SnCl_3^-$ ligand plays an important role in the catalytic activity favoring the ligand-exchange reactions [33,35]. In addition, the $SnCl_3^-$ ligand is known to stabilize the pentacoordinated Pt(II) species [27,34] which facilitates the olefin insertion into a Pt–H bond via trigonal bipyramidal intermediates. The presence of $SnCl_2$ decreases the activation energies of both the olefin insertion and hydrogenolysis reactions [27].

3.1. Hydroformylation of limonene

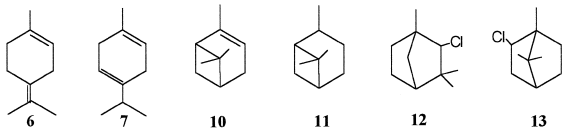
The hydroformylation of limonene gives a mixture of two diasteroisomers of the linear aldehyde **4** in approximately equal amounts with a 90% chemoselectivity (Scheme 1; Table 1, runs 1 and 2). Only the terminal double bond is selectively transformed and no traces of the branched aldehyde have been observed. The major competing reactions are the isomerization of the terminal ethylenic double bond resulting mainly in α-terpinolene (**6**) and γ-terpinene (**7**) (Scheme 2) as well as the hydrogenation of **1**.

The isomeric bicyclic alcohols **5a** and **5b**, described in our previous work [5] and useful as



1 **4** **5a** - (1R, 2R, 4S, 5R)
5b - (1R, 2R, 4R, 5R)

Scheme 1.



6 7 10 11 12 13

Scheme 2.

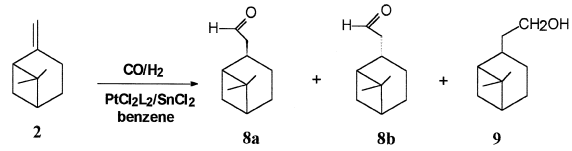
perfumes, have been detected in only trace amounts under the conditions used. The temperature and reaction time have been increased in an attempt to improve the limonene conversion (runs 3 and 4). This has led to the formation of the significant amounts of **5** which becomes the dominant product at 130°C. Product distribution depends on the phosphine used as a ligand in the platinum complex, the tin/platinum ratio, and the reaction time. The system with PPh_3 as the only phosphorus-containing ligand promotes the isomerization of **1** in a great extent (run 5), but shows the lowest hydrogenation activity compared to the other ones. On the other hand, considerable amounts (22%) of the limonene hydrogenation product, i.e., carvomenthene, and only 4% of the isomerization products are formed when the $PtCl_2$(dppp) complex is used (run 6). When a platinum complex containing dppb with equimolar amounts of $SnC1_2$ is used, a 82% selectivity for **5** has been achieved at a 95% conversion (run 7). The formation of hydroformylation products **4** and **5** is strongly influenced by the tin/platinum atomic ratio and drastically decreases to 20% at $Sn/Pt = 5$ (run 8). Thus, the undesirable isomerization of the terminal double bond of **1** to an unreactive internal position is also catalyzed by the excess $SnCl_2$ which acts as a Lewis acid. It has been found that, in the absence of the additional amounts of PPh_3, both $PtCl_2$(diphosphine)/$SnCl_2$ and $PtCl_2(PPh_3)/SnCl_2$ systems are not stable under the reaction conditions for time required to reach the good yields. Even within 4 h of the reaction the black precipitate (most likely, the metallic Pt) and decrease in catalyst activity were observed. To stabilize the catalytic systems in most of the runs we used the excess PPh_3.

A stepwise mechanism of the formation of the alcohol **5** from **1**, via the intermediate formation of **4**, followed by its cyclization into **5a** and **5b** can be suggested. Menthene **4** undergoes a complete conversion into **5a** and **5b**, in the presence of the $PtCl_2$(dppb)/$SnCl_2/PPh_3$ system, under the same reaction conditions. It should be mentioned that the intramolecular cyclization of **4** is highly diasteroselective, differently from the hydroformylation of **1**, which gives a mixture of diasteroisomers of **4** (4*R*,8*S* and 4*R*,8*R*) in approximately equal amounts. A stereospecific interaction of the carbonyl group with the endocyclic double bond in each of two diasteroisomers of **4** results in the formation of only one diasteroisomer of **5**. It is worthwhile noting that no cyclization of **4** is observed in the absence of either a platinum complex or $SnCl_2$. It seems unlikely that $SnCl_2$ alone acts as a Lewis acid catalyzing the transformation of **4** into **5**. Most probably, the Pt–Sn species are involved in this cyclization reaction. The $SnCl_3^-$ ligand maintains a Lewis acid character to coordinate to Lewis bases by exchanging with the Cl^- ligand [33], which may allow extra interaction with the carbonyl group of aldehyde **4** coordinated to the adjacent Pt atom via olefinic bond.

Thus, the $PtCl_2$(dppb)/$SnCl_2/PPh_3$ combination represents a selective bifunctional catalyst that promotes both the hydroformylation of limonene and then the diasterospecific intramolecular cyclization of the aldehyde formed. At low limonene conversions and lower temperatures high selectivities for the formation of aldehyde **4** can be attained.

3.2. Hydroformylation of β-pinene

β-Pinene (**2**) reacts with CO and H_2, in the presence of catalytic amounts of $PtCl_2L_2$/$SnCl_2/PPh_3$ ($L_2 = 2PPh_3$, dppe, dppp, dppb), to give mainly the linear aldehyde **8** (Scheme 3) with high diastereoselectivity (Table 2). Several transformations of **2** occur under the reaction conditions: hydroformylation yielding the di-



Scheme 3.

astereomeric mixture of **8a** and **8b**, hydrogenation of aldehyde **8** resulting into the corresponding alcohol **9**, skeletal isomerization mainly to α-terpinolene (**6**) and γ-terpinene (**7**), double bond isomerization to α-pinene (**10**), hydrogenation of **2** to pinane (**11**), and, finally, skeletal isomerization accompanied by a chloride addition yielding fenchyl (**12**) and bornyl (**13**) chlorides. Relative amounts of the products depend on the nature of the ligands used, the tin/platinum ratio, and the reaction temperature. In contrast with most of the rhodium and cobalt systems, the undesirable isomerization of **2** to α-pinene is rather slow (1–5% based on reacted β-pinene) even with a large excess of $SnCl_2$. As expected, no products of the hydroformylation of α-pinene could be detected because of the lower reactivity of internal olefins in hydroformylation compared to that of terminal olefins due to steric factors.

It is important to note a high diasteroselectivity of the hydroformylation of **2**. It has been observed almost exclusive formation of the thermodynamically more stable *trans* isomer of 10-formylpinane **8b**, which is usually obtained with the rhodium and cobalt systems only in minor amounts. There is a rather small difference in the steric hindrance of the two enantiotopic faces of β-pinene. In our experiments carried out with the achiral phosphines, however, the **8a/8b** ratio was usually 2/98. The formation of *trans* aldehyde **8b** requires the catalyst coordination to the more sterically hindered face of olefin. The steric constraints in the particularly hindered platinum/tin catalysts with the combined steric bulk of the phosphine(diphosphine) and $SnCl_3^-$ ligands should favor the

Table 2
Hydroformylation of β-pinene (**2**) catalyzed by $PtCl_2L_2/SnCl_2$[a]

Run	Ligand	Time (h)	Conversion[b] (%)	Selectivity[c] (%)	Ratio of diastereomers	Product distribution[b] (%)					
						Hydroformylation products		Other products			
					8a/8b	**8**	**9**	**6 + 7**	**10**	**11**	**12 + 13**
1	PPh_3	14	9	81	1/99	61	20	tr.	1	tr.[d]	18
2	dppp	14	11	75	1/99	75	tr.	tr.	5	16	4
3	dppb	14	19	87	3/97	87	tr.	1	3	4	5
4	dppb	45	31	90	3/97	85	5	1	1	5	3
5[e]	dppb	45	70	84	3/97	81	3	tr.	3	8	5
6[f]	dppb	45	28	85	2/98	81	4	2	tr.	4	9
7[g]	dppb	45	25	39	3/97	33	6	18	3	2	38
8	PPh_3	45	25	81	3/97	51	30	3	4	1	11
9	dppe	45	17	74	3/97	70	4	3	5	7	11
10	dppp	45	45	81	2/98	75	6	1	tr.	14	4
11	dppp	70	43	83	2/98	78	5	1	tr.	13	3
12[h]	dppb	45	16	81	2/98	71	10	1	3	4	11

[a] Reaction conditions: substrate (5 mmol), $PtCl_2L_2$ (0.05 mmol), $SnCl_2 \cdot 2H_2O$ (0.05 mmol), PPh_3 (0.1 mmol), benzene (5 ml), 9 MPa ($CO/H_2 = 1/1$), 100°C.
[b] Determined by gas chromatography.
[c] Selectivity for the hydroformylation products **8** and **9**.
[d] Trace amounts.
[e] 130°C.
[f] $SnCl_2 \cdot 2H_2O$ — 0.10 mmol.
[g] $SnCl_2 \cdot 2H_2O$ — 0.25 mmol.
[h] Anhydrous $SnCl_2$ was used.

formation of the *cis* isomer **8a**, which is kinetically preferred since it derived from the 'bottom'-type coordination and the H attack on the less crowded 'bottom' face of the double bond. It is surprising that the formation of *cis* isomer **8a** becomes so disfavourable. It seems reasonable to explain the diastereomeric distribution of aldehyde products by the suggestion that not only a difference in steric hindrance but also a difference in electron density and/or in the relative energies of the transition states contribute to the discrimination between the two faces of β-pinene made by the platinum/tin active species. A related discussion of the stereoselective hydroformylation of β-pinene catalyzed by rhodium complexes has been recently presented by Azzaroni et al. [13].

The hydroformylation activity of the platinum/tin/phosphine(diphosphine) catalytic systems and the product distribution are strongly dependent on the nature of the ligands and the chain-length of the diphosphine (runs 1–3 and 4, 8–10). The best result is achieved employing a platinum complex containing dppb as a ligand. The selectivity for hydroformylation products **8** and **9** reaches the value of 90% (85% of **8** and 5% of **9**) at 30% conversion of **2** and Sn/Pt = 1 (run 4). A 70% substrate conversion can be attained with rising temperature up to 130°C, but the selectivity slightly decreases to 84% (run 5). The use of PPh_3 as the only phosphorous-containing ligand (runs 1 and 8) favors the hydrogenation of the aldehyde **8** with the formation of the alcohol **9** in significant amounts: up to 40% of both hydroformylation products. Interestingly, this system, as in limonene hydroformylation (run 5, Table 1), shows the lowest activity in olefin hydrogenation compared with the other catalytic systems and only small amounts of **11** have been detected after the runs. Thus, the $PtCl_2$-$(PPh_3)_2/SnCl_2/PPh_3$ system effectively catalyzes the hydrogenation of the carbonylic double bond of the aldehyde **8**, but not the olefinic double bond in β-pinene. The total selectivity for the hydroformylation products is lower than that for the $PtCl_2$(dppb) complex because of the concomitant skeletal isomerization of **2** accompanied by a chloride addition which results in fenchyl (**12**) and bornyl (**13**) chlorides.

On the other hand, the skeletal isomerization of **2** to the products **6**, **7**, **12**, and **13** is practically negligible when we use the system with the $PtCl_2$(dppp) complex, but this catalyst causes the substantial hydrogenation of **2** giving up to 16% of pinane **11** (runs 2, 10, 11). The highest activity of the $PtCl_2$(dppp)/$SnCl_2$ system in the hydrogenation of the ethylenic bond, compared to the other systems, has been also observed in the hydroformylation of limonene (Table 1). As has been shown by Gómez et al. [27] the products of alkene hydrogenation under hydroformylation conditions are, most likely, produced from the platinum alkyl intermediates containing $SnCl_3^-$ ligand by hydrogenolysis, rather than from the acyl complexes via decarbonylation, which is completely inhibited in the presence of CO. Thus, the amounts of hydrogenation vs. hydroformylation products should be determined by the relative reactivity of the corresponding platinum alkyl intermediates towards the hydrogenolysis vs. carbon monoxide insertion reactions, which appears to depend on the nature of the phosphine or diphosphine coordinated to Pt(II), as shown by the results obtained in the present work.

The combination with dppe, which can make up a strong chelate ring, shows the lowest activity and selectivity in the hydroformylation of **2** (run 9).

As expected, the selectivity for hydroformylation is strongly influenced by the tin/platinum ratio and drastically decreases to near 40% at Sn/Pt = 5 (run 7) from the 90% level at Sn/Pt = 1 (run 4). The major competing reaction is a skeletal isomerization of β-pinene resulting in α-terpinolene (**6**) and γ-terpinene (**7**) (18%) and fenchyl (**12**) and bornyl (**13**) chlorides (38%). The formation of the products **12** and **13** should cause the catalyst destruction by consuming chloride groups. So, the undesirable skeletal rearrangements of β-pinene are promoted by the

Table 3
Hydroformylation of camphene (**3**) catalyzed by $PtCl_2L_2/SnCl_2$[a]

Run	Ligand	Conversion[b] (%)	Selectivity[c] (%)	Ratio of diastereomers **14a**/**14b**
1	PPh_3	40	89	58/42
2	dppe	52	96	58/42
3	dppp	53	89	55/45
4	dppb	49	92	57/43
5[d]	dppp	44	58	54/46

[a] Reaction conditions: substrate (5 mmol), $PtCl_2L_2$ (0.05 mmol), $SnCl_2 \cdot 2H_2O$ (0.05 mmol), PPh_3 (0.1 mmol), benzene (5 ml), 9 MPa ($CO/H_2 = 1/1$), 100°C, reaction time 45 h.
[b] Determined by gas chromatography.
[c] Selectivity for the aldehydes **14a** and **14b**.
[d] $SnCl_2 \cdot 2H_2O$ — 0.25 mmol. The products of camphene hydrogenation (*endo* and *exo* camphanes) and isomerization (tricyclene) along with some unidentified products were observed.

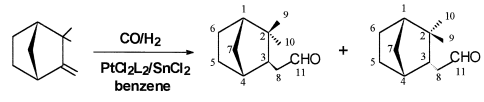
excess of the Lewis acidic stannous chloride and catalyst deactivation could be due to the lost of chloride ligands which act as nucleophiles and attack the intermediate carbonium ions. As can be seen, in most of the runs at $Sn/Pt = 1$ the isomerization of β-pinene is almost suppressed indicating that there is almost no free $SnCl_2$ in the solution. $SnCl_2$ seems to form a stable 1:1 complex with Pt(II) under the reaction conditions and the equilibrium depends on the nature of the phosphorous containing ligands coordinated to Pt(II). For diphosphines (dppe, dppp and dppb) the equilibrium is essentially shifted towards the formation of the Pt–Sn complexes. However, for the PPh_3 it seems to present some free $SnCl_2$ in the solution, which can explain the elevated amounts of the isomerization products at the hydroformylation of both limonene and β-pinene catalyzed by $PtCl_2(PPh_3)_2/SnCl_2/PPh_3$ system.

To achieve higher conversions we varied the reaction time. Increasing the reaction time from 14 to 45 h results in rising the β-pinene conversion from 11% (run 2) up to 45% (run 10). However, when the reaction time was increased up to 70 h, no further improvement in the aldehyde yield was observed (run 11) which can indicate catalyst deactivation. It should be noted that no further increase in the concentration of the products of the competing reactions has been detected at longer reaction times. Hence, there is no free $SnCl_2$ in the solution containing deactivated catalyst after the reaction. The studies of the reasons for the catalyst deactivation are in progress.

The use of anhydrous $SnCl_2$ instead of $SnCl_2 \cdot 2H_2O$ inhibits hydroformylation (compare runs 4 and 12). In previous work we observed that water favored the activity of the $PdCl_2(PPh_3)_2/SnCl_2$ catalyst in the alkoxycarboxylation of camphene and this water requirement was satisfied by the water of hydration present on the $SnCl_2 \cdot 2H_2O$ [6]. The further increase in water concentration led to a significant decrease in ester selectivity, on the other hand, the use of anhydrous $SnCl_2$ decelerated the ester formation markedly. In related systems for alkoxycarbonylation using a platinum/tin and palladium/tin chloride complexes as catalysts the authors also observed that $SnCl_2 \cdot 2H_2O$ replacement by anhydrous $SnCl_2$ resulted in a loss in the reaction rate [36,37]. Probably, the platinum hydride, which is supposed to be an intermediate in both hydroformylation and alkoxycarbonylation of olefins, is formed more easily by the interaction of the platinum/tin complex with water via reduction of Pt(II) and further protonation of the resulting Pt(0) species. The formation of Pt(II) hydrides from water via similar route was previously reported [38].

3.3. Hydroformylation of camphene

The hydroformylation of camphene (**3**) under the conditions similar to those used for limenene and β-pinene proceeds rather smoothly to give the linear aldehyde **14** with virtually 100% regioselectivity (linear/branched aldehydes) (Table 3, Scheme 4). Employing platinum complexes containing either PPh_3 or any of diphosphines (dppe, dppp, dppb) as ligands with



Scheme 4.

equimolar amounts of $SnCl_2$, 89–96% selectivities have been achieved at the conversions of near 50%. The selectivity drops to near 60% at $Sn/Pt = 5$ (run 5), as with the other studied monoterpenes. The hydrogenation of **3** resulting in *endo* and *exo* camphanes and isomerization of **3** into tricyclene are the main side reactions. In addition, traces of the corresponding alcohols and some unidentified products have been detected. Unexpectedly, there is only a slight difference between the activities and selectivities of all platinum complexes studied. However, the higher activity of the $PtCl_2(PPh_3)_2$ complex in the skeletal isomerization of monoterpene and of the $PtCl_2$(dppp) complex in the hydrogenation of the olefinic double bond compared with the other systems have also been noted, as with limonene and β-pinene.

While the chemoselectivity for the formation of **14** reaches the value of 96% (run 2), the extent of diastereoselectivity is low in all runs: a diastereoisomeric excess of the thermodynamically more stable *exo* isomer **14a** is near 15%. The molecular model analysis shows that both faces of the camphene double bond are sterically hindered and there is a rather little steric difference between them. The studies aimed to develop the catalytic systems able to make a greater discrimination between the two enantiotopic faces of camphene and achieve its stereospecific hydroformylation are in progress in our laboratory.

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