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Diastereoselective hydroformylation of camphene catalyzed by platinum/tin complexes

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Abstract

The hydroformylation of camphene in the presence of platinum(II)/tin(II)/phosphine (diphosphine) catalytic systems with various achiral and chiral P-donor ligands has been studied. The reaction occurs regio-specifically to give exclusively the linear isomer of the corresponding aldehyde. With triphenylphosphine and chelating achiral diphosphines, i.e. 1,2-bis(diphenylphosphino) ethane, 1,3-bis(diphenylphosphino) propane and 1,4-bis(diphenylphosphino) butane, the chemoselectivity for hydroformylation of 90–96% and diastereoisomeric excess (d.e.) of the *exo* isomeric aldehyde of 16–30% have been achieved. The highest d.e. of 60% has been shown by the platinum/tin/(*R*)- or (*S*)-BINAP system (BINAP—2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) with ca. 90% chemoselectivity for hydroformylation products at ca. 90% camphene conversion. A new aldehyde derived from α-fenchene, which could result from the skeletal isomerization of camphene under the reaction conditions has been detected (up to 30%) at the elevated tin/platinum ratio.

Keywords: Hydroformylation; Platinum–tin catalysts; Camphene

1. Introduction

Hydroformylation represents a valuable pathway to produce aldehydes and alcohols of interest for pharmaceutical and perfume industries from inexpensive naturally occurring monoterpenes [1]. Optically pure terpenes containing prochiral centers are frequently easily available and their stereoselective functionalization could be useful for the production of chiral synthetic intermediates. Platinum/tin catalysts generally give hydroformylation products with higher asymmetric induction than cobalt and rhodium complexes [2–11]. Previously we have reported the platinum/tin catalyzed hydroformylation and the related process—palladium/tin catalyzed alkoxycarbonylation—of some monoterpenes, including β-pinene and camphene [12–15]. The hydroformylation of β-pinene yielded *trans*-10-formylpinane with 98% diastereoisomeric excess (d.e.), while camphene gave the diastereoisomers of the corresponding aldehyde with the d.e. of the thermodynamically more stable *exo* isomer of ca. 15%. There is very little information in the literature concerning the hydroformylation of camphene and the d.e.'s achieved in these reactions with both rhodium [16–19] and platinum complexes [19], bearing either achiral or chiral ligands, are relatively low. The molecular model analysis shows that both the diastereotopic faces of the camphene double bond are sterically hindered and there is a rather little steric difference between them. The aim of the present

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study was to develop the catalytic systems which were able to make a greater discrimination between the two faces of camphene double bond, thus promoting its stereoselective hydroformylation. We investigated the hydroformylation of camphene in the presence of platinum(II)/tin(II)/phosphine (diphosphine) catalytic systems with various achiral and chiral P-donor ligands.

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 a published procedure [20]. 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 [21] for $PtCl_2$(dppe). Benzene was purified under reflux with sodium wire/benzophenone for 6 h and then distilled under nitrogen. (-)-Camphene was 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), phosphorous-containing ligand (0.05–0.2 mmol), camphene (5 mmol), and benzene (5 ml) were transferred under nitrogen into a glass lined 30 ml stainless steel reactor. The reactor was pressurized to 3–9 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 products were isolated as diastereoisomeric mixtures. The assignment of ^{1}H and ^{13}C NMR signals was made using HMQC and DEPT NMR experiments and the stereochemistry of some products was determined using NOESY experiments.

3,3-Dimethyl-2-norbornaneacetaldehyde **2a** (*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^5HH); 1.58–1.62 (m, 2H, C^7HH, 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, ^2J = 16.6 Hz, ^3J = 9.3 Hz, ^3J = 2.6 Hz); 2.40 (ddd, 1H, C^8HH, ^2J = 16.6 Hz, ^3J = 6.1 Hz, ^3J = 1.6 Hz); 9.67 (dd, 1H, $C^{11}HO$, ^3J = 2.6 Hz, ^3J = 1.6 Hz). ^{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 [18] and Kollár and Bódi [19].

3,3-Dimethyl-2-norbornaneacetaldehyde **2b** (*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^5HH); 1.58–1.62 (m, 3H, C^7HH, C^4H, C^1H); 2.05–2.07 (m, 1H, C^3H); 2.31 (dd, 1H, C^8HH, ^3J = 8.3 Hz, ^3J = 2.3 Hz); 2.36 (dd, 1H, C^8HH, ^3J = 7.1 Hz, ^3J = 2.0 Hz); 9.69 (t, 1H, $C^{11}HO$, ^3J = 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 [18] and Kollár and Bódi [19].

7,7-Dimethyl-2-norbornaneacetaldehyde **3a** (*exo*, shorter GC retention time). MS (*m*/*z*/rel. int.): 166/3 (M^+); 122/71; 110(26); 109/21; 107/26; 81/35; 80/35; 79/50; 67/40; 66/100; 55/31. ^{1}H NMR: 0.89 (s, 3H, C^9H_3); 0.90 (s, 3H, $C^{10}H_3$); 2.23 (dd, 1H, C^8HH, ^3J = 7.2 Hz, ^3J = 2.0 Hz); 2.29 (dd, 1H, C^8HH, ^3J = 7.2 Hz, ^3J = 2.0 Hz); 9.65 (t, 1H, $C^{11}HO$, ^3J = 2.0 Hz). ^{13}C NMR: δ 21.68; 25.67 (C^9); 30.06 (C^{10}); 30.62; 32.04; 33.71; 39.27; 42.36; 45.53 (C^8); 47.14; 202.30 (C^{11}).

7,7-Dimethyl-2-norbornaneacetaldehyde **3b** (*endo*, longer GC retention time). MS (*m*/*z*/rel. int.): 166/3 (M^+); 122/71; 110(26); 109/21; 107/26; 81/35; 80/35; 79/50; 67/40; 66/100; 55/31. ^{1}H NMR: 0.96 (s, 3H, C^9H_3); 1.01 (s, 3H, $C^{10}H_3$); 2.20 (dd, 1H, C^8HH, $^3J = 7.3$ Hz, $^3J = 2.1$ Hz); 2.26 (dd, 1H, C^8HH, $^3J = 7.3$ Hz, $^3J = 2.1$ Hz); 9.64 (t, 1H, $C^{11}HO$, $^3J = 2.1$ Hz). ^{13}C NMR: δ 19.80, 20.61, 20.73; 28.53; 31.22; 35.96; 39.37; 43.21; 46.42; 46.84 (C^8); 202.30 (C^{11}).

3. Results and discussion

The hydroformylation of camphene (**1**) was investigated using the following catalytic systems: $PtCl_2(PPh_3)_2/SnCl_2/PPh_3$, $PtCl_2$(diphosphine)/$SnCl_2/PPh_3$ with different chelating achiral diphosphines such as dppe, dppp and dppb, and $PtCl_2(PhCN)_2/SnCl_2$/diphosphine containing chiral diphosphines: (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((*S*,*S*)-DIOP), (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((*R*,*R*)-DIOP), (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP), and (*S*)-(-)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*S*)-BINAP). Benzene was employed as a solvent. The results are given in Tables 1 and 2. In the absence of $SnCl_2$, all platinum complexes studied show no activity in the hydroformylation of camphene. A synergetic effect of $SnCl_2$ and Pt(II) on hydroformylation has been thoroughly investigated [22–27] and discussed in our previous work [14]. It has been recently shown in a theoretical study [28] on the olefin insertion in the $Pt(H)(PH_3)(SnCl_3)(C_2H_4)$ complex that the most important effect of the $SnCl_3^-$ ligand is to stabilize the pentacoordinated Pt(II) intermediates and facilitate the olefin insertion due to the weakening of the Pt–H bond *trans* to this ligand.

Camphene 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 linear aldehyde **2** with virtually 100% regioselectivity (linear/branched aldehydes) (Scheme 1, Table 1). No traces of branched aldehydes, which might be formed in a typical Markovnikov fashion have been detected.

Table 1
Hydroformylation of camphene (**1**) catalyzed by the $PtCl_2L_2/SnCl_2/PPh_3$ systems containing achiral ligands (L)[a]

Run	Ligand	[Pt]/[Sn]	Pressure (MPa)	Conversion[b] (%)	Selectivity[c] (%)	Product distribution[b] (%)				
						Hydroformylation products		Other products		
						2 (**2a**/**2b**)	**3** (**3a**/**3b**)	**6**	**7**	**8**
1	PPh_3	1/1	9	40	94	89 (58/42)	5 (n.d.)[d]	2	3	1
2	dppe	1/1	9	52	96	96 (58/42)	Tr.[e]	1	1	1
3	dppp	1/1	9	53	92	89 (55/45)	3 (n.d.)	2	1	5
4	dppb	1/1	9	49	96	92 (57/43)	4 (n.d.)	2	Tr.	2
5	PPh_3	1/5	9	49	85	65 (56/44)	20 (90/10)	2	12	1
6	dppe	1/5	9	51	88	70 (56/44)	18 (93/7)	1	10	1
7	dppp	1/5	9	44	76	58 (54/46)	18 (94/6)	3	13	8
8	dppp	1/1	5	28	85	63 (55/45)	22 (93/7)	1	9	5
9	dppp	1/5	5	43	71	54 (55/45)	17 (95/5)	3	17	9
10	dppp	1/5	3	65	63	46 (52/48)	17 (87/13)	3	26	8
11[f]	dppp	1/1	9	71	88	86 (66/34)	2 (n.d.)	Tr.	Tr.	12
12[g]	dppb	1/1	9	81	87	82 (62/38)	5 (n.d.)	Tr.	2	11

[a] Reaction conditions: substrate (5 mmol), $PtCl_2L_2$ (0.05 mmol), $SnCl_2 \cdot 2H_2O$ (0.05–0.25 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 hydroformylation products **2** and **3**; corresponding alcohols **4** and **5** were detected in trace amounts.
[d] Not determined.
[e] Trace amounts.
[f] Reaction time: 92 h.
[g] 130 °C.

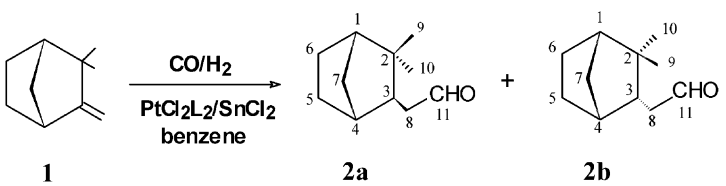
Table 2
Hydroformylation of camphene (**1**) catalyzed by $PtCl_2(PhCN)_2/SnCl_2$/diphosphine systems containing chiral diphosphines[a]

Run	Diphosphine	[Pt]/[P]	Conversion[b] (%)	Selectivity[c] (%)	Product distribution[b] (%)					
					Hydroformylation products			Other products		
					2 (2a/2b)	**3a**	**4 + 5 (4/5)**	**6**	**7**	**8**
1	None		65	11	4 (n.d.)[d]	7	Tr.[e]	15	65	9
2	(*R*)-BINAP	1/2	92	91	84 (80/20)	1	6 (100/tr.)	Tr.	Tr.	9
3	(*S*)-BINAP	1/2	88	92	80 (74/26)	2	10 (100/tr.)	Tr.	Tr.	8
4[f]	(*R*)-BINAP	1/4	100	88	76 (82/18)	2	10 (86/14)	Tr.	Tr.	12
5	(*S*,*S*)-DIOP	1/2	100	90	33 (70/30)	3	54 (90/10)	Tr.	Tr.	10
6	(*R*,*R*)-DIOP	1/2	100	89	34 (62/38)	3	52 (100/tr.)	Tr.	Tr.	11
7	(*S*,*S*)-DIOP	1/4	18	93	75 (72/28)	18	Tr.	4	Tr.	4
8[f]	(*S*,*S*)-DIOP	1/8	<3	n.d.	Tr.	Tr.				

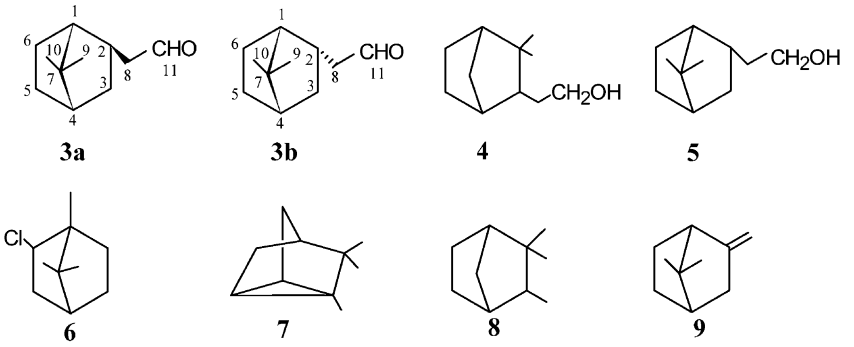
[a] Reaction conditions: substrate (5 mmol), $PtCl_2(PhCN)_2$ (0.05 mmol), $SnCl_2 \cdot 2H_2O$ (0.05 mmol), diphosphine (0.05–0.20 mmol), benzene (5 ml), 9 MPa ($CO/H_2 = 1/1$), 100 °C, reaction time: 45 h.
[b] Determined by gas chromatography.
[c] Selectivity for the hydroformylation products **2**–**5**.
[d] Not determined.
[e] Trace amounts.
[f] Reaction time: 85 h.

Employing platinum complexes containing either PPh_3 or any of the achiral diphosphines (dppe, dppp, dppb) as P-donor ligands with equimolar amounts of $SnC1_2$, 89–96% selectivities for **2** have been achieved at the conversions of near 50% (runs 1–4). While the chemoselectivity for the formation of **2** reaches the value of 96% (run 2), the extent of diastereoselectivity is low in all runs: the d.e. of thermodynamically more stable *exo* isomer **2a** is nearly 15%. In an attempt to improve the stereoselectivity of hydroformylation, we have studied the effect of reaction variables and catalyst composition on the product distribution (runs 5–12).

It has been found that several concomitant transformations occur under the reaction conditions: hydroformylation yielding the diastereoisomeric mixtures of aldehydes **2a** and **2b** as well as **3a** and **3b**; hydrogenation of aldehydes **2** and **3** resulting into corresponding alcohols **4** (a mixture of *endo* and *exo* isomers in approximately equal amounts) and **5**; skeletal isomerization of **1** accompanied by a chloride addition yielding bornyl chloride **6** (a mixture of *endo* and *exo* isomers); skeletal isomerization of **1** to tricyclene **7**; and finally hydrogenation of **1** to isocamphane **8** (a mixture of *endo* and *exo* isomers in approximately equal amounts) (Scheme 2). The relative amounts of the products depend on the tin/platinum ratio, the pressure of the CO/H_2 mixture, the reaction temperature and time. Unexpectedly, there is only a slight difference between the activities and selectivities of all platinum complexes bearing the achiral ligands (runs 1–4 and 5–7). However, the higher activity of the $PtCl_2$(dppp) complex in the hydrogenation of the camphene olefinic double bond compared to other



Scheme 1.



Scheme 2.

systems has been noted (runs 3 and 7). Similar trend was also observed for this system in the hydroformylation of limonene and β-pinene [14].

The selectivity for hydroformylation products **2** and **3** is dependent on the tin/platinum ratio and decreases to 76–88% at Sn/Pt = 5 (runs 5–7) from the 92–96% level at Sn/Pt = 1 (runs 1–4). The major competing reaction is the skeletal isomerization of camphene resulting in tricyclene **7**. The acid-catalyzed formation of tricyclene from camphene is a well-documented reaction [29], which may proceed via a carbonium ion mechanism [30]. Bornyl chloride **6** is the product of the skeletal isomerization of camphene accompanied by a chloride addition to the intermediate carbonium ion. It should be mentioned that **6** is formed in very small amounts even at Sn/Pt = 5, different from β-pinene which gives up to 20% (based on reacted substrate) of bornyl and fenchyl chlorides under the conditions similar to those used for the hydroformylation of camphene [14]. The formation of chlorinated products might cause a catalyst deactivation due to the loss of chloride ligands.

It is noteworthy that the composition of the hydroformylation products is also strongly influenced by the tin/platinum ratio. At Sn/Pt = 5, the formation of new aldehydes **3a** and **3b** in amounts of up to 30% of total aldehyde product (runs 5–7 and 10) has been detected. Using GC/MS, ^{1}H, and ^{13}C NMR spectroscopy, products **3a** and **3b** have been identified as *exo* and *endo* isomers of 7,7-dimethyl-2-norbornaneacetaldehyde (Scheme 2). Judging from the structure, their formation could be explained by the hydroformylation of α-fenchene **9** which might be formed by the isomerization of camphene promoted by the Lewis acidic stannous chloride. α-Fenchene itself has not been detected in the reaction solutions, so it seems to be more reactive towards hydroformylation than camphene due to the less steric constraints of its double bond. As can be seen from Table 1 (runs 5–7 and 10), the formation of **3** is always accompanied by larger amounts of tricyclene. So, the excess of stannous chloride in the reaction solutions causes the skeletal isomerizations of camphene, with both tricyclene and α-fenchene as well as borneol derivatives (bornyl chloride **6**) being originated from common carbonium ions [30]. It is important to note the high diastereoselectivity of the hydroformylation of α-fenchene. Almost exclusive (up to 95%) formation of the thermodynamically less stable *exo* isomer of aldehyde **3**, which is kinetically preferred since it is derived from the 'bottom'-type platinum coordination and the H attack on the less sterically hindered 'bottom' face of the double bond, was observed. The steric constraints in the particularly hindered platinum/tin catalysts with the combined steric bulk of the phosphine/diphosphine and $SnCl_3^-$ ligands favor the catalyst coordination to the less crowded face of olefin. Owing to a more pronounced steric difference between the two faces of the α-fenchene double bond compared to that of camphene, a stereoselective hydroformylation should be easily achievable for α-fenchene. It is interesting to note that the hydroformylation of β-pinene, whose structure looks more similar to that of α-fenchene than of camphene, under the same conditions is also highly diastereoselective (98% d.e.) [14].

Decreasing the total pressure from 9 to 5 MPa and then to 3 MPa (compare runs 3 and 8; runs 7, 9, and 10) leads to the changes in product distribution similar

to those observed in tin/platinum ratio rising. Due to the decrease in the hydroformylation rate at lower pressures, the contribution of the skeletal isomerizations of camphene becomes greater which increases the relative amounts of products **7** and **3**, with the latter probably being derived from isomeric monoterpene **9** as mentioned above.

To achieve higher substrate conversions we varied the reaction time (run 11) and temperature (run 12). Increasing the reaction time from 45 to 92 h results in rising the conversion from 53 (run 3) up to 71% (run 11) with the selectivity being almost maintained. The 80% conversion can be attained at the temperature of 130 °C but the selectivity slightly decreases from 96 to 87% (compare runs 4 and 12).

As can be seen from Table 1, the tin/platinum ratio and the reaction conditions results in significant changes in the chemoselectivity but not in the diastereoselectivity for the formation of main aldehydes **2a** and **2b**. The highest d.e.'s (ca. 30%) in the hydroformylation of camphene with platinum complexes bearing achiral ligands were achieved when the reaction was run for longer time (run 11) and higher temperature (run 12).

Diastereoselective hydroformylation of camphene up to 60% d.e. has been achieved with $PtCl_2(PhCN)_2/SnCl_2$/diphosphine catalysts containing chiral diphosphines such as (*S*,*S*)-DIOP, (*R*,*R*)-DIOP, (*R*)-BINAP and (*S*)-BINAP (Table 2). In the absence of diphosphine, the $PtCl_2(PhCN)_2/SnCl_2$ system shows a very low catalytic activity in the hydroformylation. At 65% conversion of camphene, as low as 11% combined selectivity for hydroformylation products **2**–**5** has been detected, with the remaining being isomerization (**6**, **7**) and hydrogenation (**8**) products (run 1). In the presence of equimolar amounts of the chiral diphosphine and under the conditions listed in Table 2, all the four catalysts give virtually complete substrate conversion (88–100%), with the camphene hydrogenation resulting in a mixture of *endo* and *exo* isocamphanes (**8**) (nearly 1:1), being the only significant competing reaction (runs 2, 3, 5 and 6). Although the selectivities for the hydroformylation are rather high in all the runs (ca. 90%), the systems with BINAP show higher diastereoselectivity. Interestingly, the compositions of the hydroformylation products are quite different for these two ligands: the systems with DIOP show higher activity in the hydrogenation of primarily formed aldehydes, but not in the hydrogenation of camphene itself (runs 5 and 6). With the $PtCl_2(PhCN)_2/SnCl_2$/DIOP catalysts, alcohol **4** becomes the main hydroformylation product. As can be seen (run 2 vs. run 3 and run 5 vs. run 6), both isomers of chiral ligands favor the preferential formation of *exo* aldehyde **2a**. Thus the steric and electronic characteristics of these diphosphine ligands rather than their chirality seem to be important for the discrimination made by the catalyst between the two faces of the camphene double bond. As expected, the addition of diphosphine in more than equimolar amounts ([P]/[Pt] > 2) leads to the reduction in catalytic activity; however it does not improve diastereoselectivity (runs 4, 7 and 8).

4. Conclusions

The hydroformylation of camphene in the presence of platinum(II)/tin(II)/phosphine (diphosphine) catalytic systems with various achiral and chiral P-donor ligands has been studied aiming to promote a stereoselective reaction. The highest diastereoisomeric excess of 60% of the *exo* isomeric aldehyde is achieved with the platinum/tin/(*R*)- or (*S*)-BINAP system which shows ca. 85% chemoselectivity for the linear aldehyde at ca. 90% camphene conversion.

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