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Rhodium catalyzed hydroformylation of β-pinene and camphene: effect of phosphorous ligands and reaction conditions on diastereoselectivity

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Abstract

The effect of phosphorus ligands on the rhodium catalyzed hydroformylation of β-pinene and camphene has been studied. In unmodified systems, β-pinene undergoes a fast isomerization to α-pinene. At longer reaction times and higher temperatures, the isomerization equilibrium is shifted resulting in the 80% chemoselectivity for β-pinene hydroformylation products (97% *trans*). The addition of various diphosphines, phosphines or phosphites improves the chemoselectivity and shifts the hydroformylation towards *cis* aldehyde **3a**. Both the rate and diastereoselectivity of the hydroformylation of β-pinene are largely influenced by the basicity of auxiliary ligands, but surprisingly no correlation between their steric characteristics and the diastereoselectivity of the catalytic system has been revealed for the ligands with cone angles of 128–165°. The systems with more basic ligands show lower activities, higher diastereoselectivities and usually higher chemoselectivities in the β-pinene hydroformylation. Camphene gives linear aldehyde 6, with virtually 100% regio- and chemoselectivity in both modified and unmodified systems. The addition of phosphorus ligands favors the formation of *endo* isomer **6b**:**6a**/**6b** ≈ 1/1.5, whereas the ratio is ca. 1/1 in unmodified systems. Neither steric nor electronic parameters of the ligands have been found to influence significantly the diastereoselectivity of the camphene hydroformylation.

Keywords: Hydroformylation; β-Pinene; Camphene; Phosphorous ligands

1. Introduction

Hydroformylation represents a versatile pathway for the production of commercially important aldehydes and alcohols, which are difficult to obtain by conventional synthetic routes. In the last decade, these catalytic reactions have become an especially attractive and flexible tool in organic synthesis, since their chemo-, regio- and stereoselectivity in many cases can be effectively controlled, e.g. by the nature of phosphorus auxiliary ligands [1,2]. Recently, we have shown that chemo- and regioselectivity of the rhodium catalyzed hydroformylation of various allyl- and propenylbenzenes strongly depends on the steric and electronic properties of ligands and developed catalytic systems for the preferential synthesis of either branched or linear aldehydes [3]. Aldehydes derived from naturally occurring monoterpenes show biological and phytosanitary activities and are also useful in flavor, perfume and pharmaceutical industries [4,5]. Optically pure terpenes containing prochiral centers are frequently easily available and their stereoselective functionalization could be useful for the production of chiral synthetic intermediates.

A number of monoterpenes including β-pinene [5–10] and camphene [10–14] have been hydroformylated in the presence of cobalt and rhodium complexes, which are most commonly used to catalyze this reaction in industrial processes. Alternative platinum–tin catalytic

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systems were also applied to the hydroformylation of both β-pinene [15] and camphene [14–16]. With unmodified cobalt, rhodium and cobalt–rhodium bimetallic systems, the isomerization of β- to α-pinene occurs about two times faster than hydroformylation, with *trans* [9] or *cis* [7] 10-formylpinane being formed as the main hydroformylation product. Rhodium systems modified with phosphorus ligands usually promote the preferable formation of *cis* 10-formylpinane [5,9,10] or corresponding acetal [8] and allow a higher chemoselectivity. On the other hand, it has been reported that some phosphite ligands favor the formation of *trans* aldehyde, but they are not efficient in suppressing substrate isomerization [5,10]. There is very little information in the literature concerning the hydroformylation of camphene and diastereoisomeric excess (d.e.) achieved in this reaction with both rhodium [10–14] and platinum complexes [14,15] bearing either achiral or chiral ligands is relatively low (15–30%).

We have recently reported the platinum–tin catalyzed hydroformylation and the related process—palladium–tin catalyzed alkoxycarbonylation—of some monoterpenes, including β-pinene and camphene [15–18]. The hydroformylation of β-pinene yielded *trans*-10-formylpinane with a 98% d.e., while for camphene the highest d.e. of 60% was shown by the systems with a BINAP ligand (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) [16]. Contrarily to most of cobalt and rhodium catalysts, chemoselectivities for platinum–tin catalyzed hydroformylation of both monoterpenes reach ca. 90%, however, the reaction times of ca. 40 h are usually necessary to achieve high conversions.

The aim of the present work was a systematic study of ligand effects on the chemo- and diastereoselectivity of the rhodium catalyzed hydroformylation of β-pinene (**1**) and camphene (**2**). The discrimination between the two diastereotopic faces of these monoterpenes is not trivial, especially for camphene. We investigated rhodium catalytic systems both unmodified and modified with various phosphine, diphosphine and phosphite ligands and discussed the influence of their electronic and steric properties on the rate and selectivity of hydroformylation.

2. Experimental

All chemicals were purchased from Aldrich and used as received, unless otherwise indicated. Bis[(μ-acetate)(1,5 - ciclooctadiene)rhodium(I)] — [Rh(COD)-(OAc)]$_2$—was prepared by published procedure [19]. Tri-*p*-methoxyphenylphosphine (P(*p*-$OCH_3Ph)_3$) and 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphtyl (naphos) were kindly donated by Professor B. Hanson (Virginiatech, US) and tri-*o*-*terc*-butylphenylphosphite (P(O-*o*-^{t}BuPh)$_3$) by Professor J.C. Bayón (Universidad Autónoma de Barcelona). Benzene was purified under reflux with sodium wire/benzophenone for 6 h and then distilled under nitrogen. β-Pinene and camphene were distilled before use.

The products were analyzed by gas chromatography (GC) using a Shimadzu 17B 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 Me_4Si as an internal standard in $CDCl_3$. Mass spectra were obtained on a Hewlett–Packard MSD 5890/Series II instrument operating at 70 eV.

In a typical run a mixture of [Rh(COD)(OAc)]$_2$ (0.014 mmol), phosphine, phosphite or diphosphine, if any, (0.028–0.140 mmol), substrate (3.7 mmol) and benzene (18 ml) was transferred from a Schlenck tube under nitrogen into a stainless steel magnetic stirred autoclave. The reactor was pressurized to 4.4–9.0 MPa total pressure ($CO–H_2 = 1/1$), placed in an oil bath and stirred. Reactions were followed by a gas–liquid chromatography using a sampling system. 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 and CH_2Cl_2 as eluents and identified by GC–MS, ^{1}H- and ^{13}C-NMR spectroscopy.

2.1. 10-Formylpinane *3a* (cis, longer GC retention time) and *3b* (trans, shorter GC retention time)

Compounds described by Azzaroni et al. [9] and Kalck et al. [10].

2.2. 10-Pinanemethanol *4a* (cis, longer GC retention time)

MS (*m*/*z*/rel.int.): 150/12 ($[M]^+ - H_2O$); 135/16 ($[M]^+ - H_2O - CH_3$); 107/71; 95/65; 94/34; 93/46; 82/55; 81/54; 79/92; 69/68; 67/100; 55/88; 53/31.

2.3. 10-Pinanemethanol *4b* (trans, shorter GC retention time)

MS (*m*/*z*/rel.int.): 168/0.3 ($[M]^+$); 150/5 ($[M]^+ - H_2O$); 135/10 ($[M]^+ - H_2O - CH_3$); 123/34; 107/58; 95/40; 83/36; 82/72; 81/66; 79/74; 69/100; 67/88; 55/96.

2.4. 3-Formylpinane (*5*)

Compound described by Himmele et al. [20] and Kalck et al. [10].

2.5. 3,3-Dimethyl-2-norbornaneacetaldehyde **6a** (exo, shorter GC retention time) and **6b** (endo, longer GC retention time)

Compounds described by Kalck et al. [10], Kollár et al. [14] and Gusevskaya et al. [15].

3. Results and discussion

3.1. Hydroformylation of β-pinene

Hydroformylation of β-pinene (**1**) occurs smoothly with $[Rh(COD)(OAc)]_2$ used as the catalyst precursor (60–120 °C, 9.0 MPa), giving rise to a high conversion of the substrate within 1–4 h (Table 1). Several transformations occur under the reaction conditions: hydroformylation of **1** yielding the diastereomeric mixture of aldehydes **3a** and **3b**, double bond isomerization of β- to α-pinene and hydrogenation of both pinenes to pinane (Scheme 1). Under certain conditions, alcohols **4a** and **4b** resulting from the hydrogenation of **3** and the product of the hydroformylation of α-pinene, i.e. aldehyde **5**, are also detected. In all systems studied, β-pinene has been hydroformylated regiospecifically to give exclusively linear aldehyde **3**, with chemo- and diastereoselectivity being strongly dependent on the presence of phosphorus auxiliary ligands and their nature, as well as on the reaction conditions.

With unmodified rhodium catalyst (Table 1), hydroformylation is seriously complicated by the excessive terminal C=C bond isomerization resulting in ca. 50% of α-pinene based on converted β-pinene (run 1). At 60 °C, *cis* (**3a**) and *trans* (**3b**) isomers of 10-formylpinane are formed in approximately equal amounts, with not even traces of aldehyde **5** being observed because of the well known low reactivity of internal olefins in hydroformylation. We have observed the extremely strong effect of temperature on diastereoselectivity: at 100 (run 2) and 120 °C (run 3), a 90 and 97% of the hydroformylation products, respectively, have a *trans* configuration. At 120 °C, a 96% conversion of **1** occurs within 1 h, but a chemoselectivity for hydroformylation is only 30%, with the β to α-pinene ratio reaching the composition of the isomerization equilibrium (ca. 4% β/ca. 96% α) [7]. At longer reaction times, the amounts of α-pinene considerably decrease at the expense of the β-pinene hydroformylation, which shifts the isomerization equilibrium. Within 20 h, the chemoselectivity for hydroformylation products as high as ca. 80% has been obtained, with only 6% of aldehyde **5** being formed. It should be mentioned that a significant hydrogenation of aldehyde **3**, at a much faster rate than that of the substrate itself, occurs under such conditions: ca. 50% of aldehyde **3** formed (97% *trans*) is converted into corresponding alcohol **4** (also ca. 97% *trans*) (run 3).

The formation of *trans* aldehyde **3b** requires the catalyst coordination to the more sterically hindered face of olefin, *syn* to the isopropylidene bridge ('*exo*' coordination). It is, therefore, surprising the extremely high preference for this pathway for the unmodified catalyst at higher temperatures. The addition of a rhodium(I) hydride to the '*exo*' coordinated β-pinene results in a thermodynamically more stable (less hindered) rhodium alkyl intermediate. On the other hand, the thermodynamically more stable '*endo*' π-complex gives more hindered rhodium alkyl and acyl intermediates and then originates thermodynamically less stable *cis* aldehyde **3a**. The *trans*/*cis* ratio is considerably increased with raising the temperature, in both unmodified (Table 1, runs 2 and 3 vs. run 1) and modified (discussed below) systems. Higher temperature favors much stronger the formation of *trans* isomer **3b** imply-

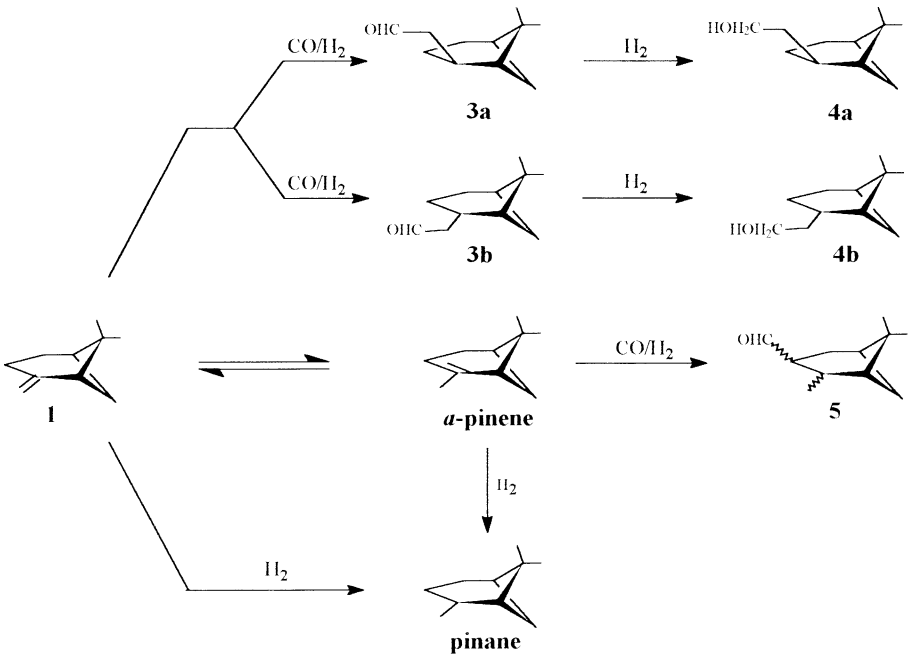
Table 1
Hydroformylation of β-pinene (**1**) catalyzed by unmodified $[Rh(COD)(OAc)]_2$: effect of temperature

Run	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%) [a]	**3a/3b**	Product distribution (%)					
						α-Pinene	Pinane	**3a**	**3b**	**4** [b]	**5**
1	60	1	35	23	1.1/1	56	21	12	11		
		4	54	35	1/1.1	55	10	17	18		
		20	90	41	1/1.2	53	7	19	22		
2	100	1	65	39	1/5.5	55	6	6	33		
		4	98	46	1/8.2	52	2	5	41		
		20	99	54	1/8.8	43	3	5	44		5
3	120	1	96	30	1/27.0	65	5	1	27	1	1
		4	97	40	1/32.0	52	8	1	32	4	3
		20	98	76	1/30.0	13	11	1	30	39	6

Reaction conditions; β-pinene (3.7 mmol), $[Rh(COD)(OAc)]_2$ (0.014 mmol), benzene (18 ml), 9.0 MPa ($CO-H_2 = 1/1$). Conversion and selectivity were determined by GC.

[a] Selectivity for hydroformylation products.

[b] Approximately the same ratio of diastereomers as for aldehydes **3**.



Scheme 1.

ing that *cis* isomer **3a** is kinetically preferred and seems to be formed with a lower activation energy in a rate-limiting step, which is, more probably, the coordination of β-pinene or its migratory insertion into the Rh–H bond. A related discussion of the rate determining step in olefin hydroformylation has been recently presented by van Leeuwen et al. [21].

In the presence of triphenylphosphine, which is a more basic ligand than CO, the coordination of the substrate is disfavored and the rate of hydroformylation decreases. The addition of triphenylphosphine, as expected from previous reports [5,9], also improves the chemoselectivity of hydroformylation and orients the diastereoselectivity towards *cis* aldehyde **3a** (Table 2, *cis*/*trans* ca. 4/1 in runs 2 and 3 vs. ca. 1/8 in run 1). The effect on chemoselectivity is completely consistent with the expected mechanism of β-pinene hydroformylation and isomerization. The addition of the rhodium(I) hydride to the coordinated olefin, which is more likely a reversible process [21], results in linear and branched rhodium alkyl intermediates. The former then originates linear aldehyde **3**, while the latter could give either α-pinene via a rhodium hydride elimination or a branched aldehyde via carbonylation. Since the branched aldehyde has never been detected in appreciable amounts, the chemoselectivity is determined by the concentrations of the corresponding linear and branched alkyl intermediates as well as the relative reactivity of the former towards carbonylation and of the latter towards the β-hydride elimination. The steric bulk of the phosphine ligand in the rhodium complex should favor the formation of the less sterically crowded linear alkyl inter-

Table 2
Hydroformylation of β-pinene (**1**) catalyzed by $[Rh(COD)(OAc)]_2$: effect of triphenylphosphine and diphosphine addition

Run	Ligand	P–Rh [a]	Conversion (%)	Selectivity (%) [b]	**3a/3b**	Product distribution (%)			
						α-Pinene	Pinane	**3a**	**3b**
1	None	–	98	46	1/8.2	52	2	5	41
2	PPh_3	5	68	87	3.8/1	10	3	69	18
3	PPh_3	10	68	89	4.6/1	6	5	73	16
4	dppe [c]	10	9	90	17.0/1	9	1	85	5
5	dppb [c]	10	12	93	12.3/1	7		86	7
6	naphos [c]	10	10	91	8.1/1	9		81	10

Reaction conditions; β-pinene (3.7 mmol), $[Rh(COD)(OAc)]_2$ (0.014 mmol), benzene (18 ml), 9.0 MPa ($CO–H_2 = 1/1$), 100 °C, 4 h. Conversion and selectivity were determined by GC.

[a] Phosphorous–rhodium atomic ratio.

[b] Selectivity for hydroformylation products.

[c] dppe, 1,2-bis(diphenylphosphino)ethane; dppb, 1,4-bis(diphenylphosphino) butane; naphos, 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphtyl.

mediate. Moreover, the presence of PPh_3, which is a stronger electron donor ligand than CO, should disfavor the hydride transfer because the rhodium atom bears now higher electron density and also because of blocking the coordination site, which appears after the olefin migratory insertion. Finally, it was found [22] that the more nucleophilic the incoming ligand at the migration of the alkyl group to a *cis* CO, the faster the carbonylation step. Thus, in the presence of triphenylphosphine, the relative concentration of the linear alkyl intermediate is increased and its carbonylation is strongly favored.

In modified systems (in the presence of auxiliary ligands), rhodium complexes with none, one or more phosphorus ligand, linked by multiple equilibria under the reaction conditions, can be involved in hydroformylation and should show different catalytic activities and selectivities. We have found that diphosphines, which usually give an enhanced preference for bis(phosphine)rhodium complexes, offer a better control over the diastereoselectivity of the β-pinene hydroformylation compared with PPh_3 (Table 2, runs 4–6 vs. run 3). Diastereoselectivity of ca. 95% for *cis* isomer **3a** (> 90% chemoselectivity) has been achieved, however, at the expense of activity—only ca. 10% of the substrate has been converted for 4 h. Thus, bisligand species seem to be much less active, whereas more selective in the hydroformylation of β-pinene than those containing the single coordinated phosphine or only CO ligands. Although the reasons for the increased diastereoselectivity seen for diphosphines are not yet fully understood, both the combined electron donating effect of two phosphine groups bound to rhodium and their increased steric bulk can contribute to the preference of these chelate complexes to coordinate β-pinene almost exclusively via the less sterically demanding '*endo*' face.

In an attempt to clarify the effect of phosphorus ligand on diastereoselectivity, we have studied the hydroformylation of β-pinene in the presence of a series of phosphines and phosphites exerting different steric and electronic effects (Table 3): triphenylphosphine, PPh_3; tribenzylphosphine, $P(CH_2Ph)_3$; tri(*n*-butyl)phosphine, $P(n\text{-Bu})_3$; tricyclohexylphosphine, $P(Cy)_3$; tri-*p*-methoxyphenylphosphine, $P(p\text{-}OCH_3Ph)_3$; tripentafluorophenylphosphine, $P(C_6F_5)_3$; tri-*o*-tolylphosphine, $P(o\text{-}CH_3Ph)_3$; triphenylphosphite, $P(OPh)_3$, and tri-*o*-*tert*-butylphenylphosphite, $P(O\text{-}o\text{-}^t BuPh)_3$. The ligand cone angles, θ, and χ-value were taken as the quantitative measures of steric and electronic effects, respectively, as proposed by Tolman [23]. The higher the cone angle is, the greater steric crowding the phosphorus ligand introduces to the metal center. The χ-value is determined by IR spectroscopy and becomes lower with increase in the ligand basicity. To facilitate the analysis of the ligand effect, data obtained are also presented in a simplified way in Table 4.

It is clearly seen from Table 4, that the ligands with highest cone angles, $P(o\text{-}CH_3Ph)_3$ ($\theta = 194°$) and $P(C_6F_5)_3$ ($\theta = 184°$) show almost the same activity, chemo- and diastereoselectivity in the hydroformylation of β-pinene as the unmodified system, promoting the preferential formation of *trans* aldehyde **3b** as well as a fast substrate isomerization (40–50% chemoselectivity) (Table 3, runs 6 and 7 vs. Table 1, runs 1 and 2; also

Table 3
Hydroformylation of β-pinene (**1**) catalyzed by $[Rh(COD)(OAc)]_2$–L systems: steric and electronic effects of auxiliary phosphorus ligand (L)

Run	Ligand [a]	χ-value [b]	Cone angle [b] (°)	Temperature (°C)	Conversion (%)	Selectivity [c] (%)	**3a/3b**	Product distribution (%)			
								α-Pinene	Pinane	**3a**	**3b**
1	PPh_3	13.25	145	100	68	87	3.8/1	10	3	69	18
				60	55	80	15.0/1	3	17	75	5
2	$P(p\text{-}OCH_3Ph)_3$	10.50	145	100	43	95	5.8/1	5		81	14
3	$P(CH_2Ph)_3$	10.35	165	100	92	87	6.3/1	13		75	12
				60	20	70	22.3/1	8	22	67	3
4	$P(n\text{-Bu})_3$	5.25	132	100	61	96	8.6/1	4		86	10
5	PCy_3	1.40	170	100	42	94	22.5/1	6		90	4
6	$P(C_6F_5)_3$	34.80	184	100	98	46	1/10.5	51	3	4	42
				60	98	53	1/1.4	44	3	22	31
7	$P(o\text{-}CH_3Ph)_3$	10.65	194	100	97	42	1/7.4	57	1	5	37
8	$P(O\text{-}o\text{-}^t BuPh)_3$	30.50	175	100	99	62 [d]	1/1.2	38		26	32
				60	99	81	10.6/1	12	7	74	7
9	$P(OPh)_3$	30.20	128	100	95	78	1.6/1	22		48	30

Reaction conditions: β-pinene (3.7 mmol), $[Rh(COD)(OAc)]_2$ (0.014 mmol), phosphorus ligand (0.07 mmol), benzene (18 ml), 9.0 MPa ($CO–H_2$ = 1/1), reaction time: 4 h at 100 °C and 20 h at 60 °C. Conversion and selectivity were determined by GC.

[a] Cy, cyclohexyl; Bu, butyl.

[b] From ref. [23,24].

[c] Selectivity for hydroformylation products.

[d] Aldehyde **5** was formed (4%).

Table 4
Hydroformylation of β-pinene (**1**) and camphene (**2**): steric and electronic effects of auxiliary phosphorus ligand (L)

L [a]	Pcy_3	$P(n\text{-}Bu)_3$	$P(CH_2Ph)_3$	$P(p\text{-}OCH_3Ph)_3$	$P(o\text{-}CH_3Ph)_3$	PPh_3	$P(Oph)_3$	$P(O\text{-}o\text{-}^tBuPh)_3$	$P(C_6F_5)_3$	None
χ-value [b]	1.40	5.25	10.35	10.50	10.65	13.25	30.20	30.50	34.80	
Cone angle [b]	170	132	165	145	194	145	128	175	184	
1 (60 °C) [c]			20(70)			55(80)		99(81)	98(53)	90(41)
			22.3/1			*15.0/1*		*10.6/1*	*1/1.4*	*1/1.2*
1 (100 °C) [c]	42(94)	61(96)	92(87)	43(95)	97(42)	68(87)	95(78)	99(62)	98(46)	98(46)
	22.5/7	*8.6/1*	*6.3/1*	*5.8/1*	*1/7.4*	*3.8/1*	*1.6/1*	*1/1.2*	*1/10.5*	*1/8.2*
2 [d]	16		81	44		47		100	90	100
	1/1.5		*1/1.6*	*1/1.4*		*1/1.4*		*1/1.6*	*1/1.1*	*1/1.1*

[a] Cy, cyclohexyl; Bu, butyl.
[b] From ref. [23,24].
[c] Conversions, selectivities for hydroformylation products (in parentheses) and ratio of diastereomers **3a/3b** (in italic). Reaction conditions were the same as in Table 3, runs 1–9 and in Table 1, runs 1 (20 h) and 2 (4 h).
[d] Conversions and ratio of diastereomers **6a/6b** (in italic). Reaction conditions were the same as in Table 5, runs 1, 3, 9-1.

Table 4). In these systems, most of catalytically active rhodium complexes contain no phosphorous ligands. Both $P(o\text{-}CH_3Ph)_3$ and $P(C_6F_5)_3$ seem to be weak ligands under the reaction conditions (4.5 MPa of CO and sterically highly demanding substrate) because of their steric bulk, in spite of the former is a relatively strong electron donor (χ-value of 10.65). Thus, mono- and bisligand species, if formed, are virtually not involved in the β-pinene transformations due to steric reasons. On the other hand, a less bulky ligand, $P(O\text{-}o\text{-}^tBuPh)$ ($\theta = 175°$), although weakly electron-donating (χ-value of 30.50), is effectively coordinated on the rhodium complexes operating in hydroformylation: it shows a higher chemoselectivity and much higher preference for the *cis* aldehyde formation compared with the unmodified system (Table 1, runs 1 and 2 vs. Table 3, run 8; also Table 4). This effect is especially pronounced at 60 °C. For all modified systems, lower temperatures favor the formation of relatively larger amounts of *cis* isomer **3a** (Tables 3 and 4).

Four couples of ligands exerting a similar steric effect but very different electronic effect have been tested (Tables 3 and 4): $P(n\text{-}Bu)_3$ (χ-value of 5.25) and $P(OPh_3)_3$ (χ-value of 30.20) with cone angles of ca. 130°; $P(CH_2Ph)_3$ (χ-value of 10.35) and $P(O\text{-}o\text{-}^tBuPh)_3$ (χ-value of 30.25) with cone angles of ca. 170°; PPh_3 (χ-value of 13.25) and $P(p\text{-}OCH_3Ph)_3$ (χ-value of 10.50) with cone angles of 145°; $P(Cy)_3$ (χ-value of 1.40) and $P(CH_2Ph)_3$ (χ-value of 10.35) with cone angles of ca. 167°. The comparison of the data obtained for each couple clearly reveals the following tendencies: the systems with more basic phosphorus ligands show lower activities, higher diastereoselectivities for *cis* aldehyde **3a** and, usually higher chemoselectivities. For example, $P(n\text{-}Bu)_3$ (χ-value of 5.25, $\theta = 132°$) promotes the formation of ca. 90% of *cis* isomer **3a**, whereas with $P(OPh_3)_3$ (χ-value of 30.20, $\theta = 128°$) the *cis*/*trans* ratio of only 1.6/1 has been observed (Table 3, cf. runs 4 and 9).

On the other hand, the ligands with similar basicity but different cone angles, i.e. $P(CH_2Ph)_3$ ($\theta = 165°$) and $P(p\text{-}OCH_3Ph)_3$ ($\theta = 145°$), both with χ-value of ca. 10, show very similar results in the hydroformylation of β-pinene in terms of chemo- and diastereoselectivity (Table 3, runs 2 vs. 7; also Table 4). Another couple of ligands, i.e. $P(OPh_3)_3$ ($\theta = 128°$) and $P(O\text{-}o\text{-}^tBuPh)_3$ ($\theta = 175°$), both with χ-value of ca. 30, also behave similarly (Table 3, runs 8 vs. 9; also Table 4). However, as mentioned above, in the system with bulky $P(O\text{-}o\text{-}^tBuPh)_3$, the rhodium species with no phosphorus ligand seem to contribute significantly, thus resulting in the increased amounts of α-pinene and *trans* aldehyde **3b**.

The formation of *cis* aldehyde **3a** occurs via the '*endo*' catalyst coordination to the less sterically hindered face of β-pinene. The diastereoselectivity of its hydroformylation is found to be largely influenced by the basicity of auxiliary phosphorus ligand, the most basic ligand (PCy_3) exhibiting the highest *cis*/*trans* ratio (ca. 23/1, Table 3, run 5). For all studied ligands, except the non-coordinating bulkiest $P(o\text{-}CH_3Ph)_3$ and $P(C_6F_5)_3$, the following general tendency has been observed at both 60 and 100 °C (Table 4): the stronger donor the ligand, the higher diastereoselectivity it shows towards the *cis* aldehyde independently on its steric bulk. These results can be reasonably understood taking into account that the presence of more basic ligands should favor a stronger π back-donation from the rhodium atom to β-pinene, which should result in shortening the rhodium–olefin bond length. Thus, the steric difference between the two diastereotopic faces of β-pinene becomes more pronounced and the catalyst makes a greater diastereofacial discrimination. This is highly unexpected if intermediate complexes with more than one phosphorus ligand, i.e. bisligand and trisligand species, are involved in the step which determines the reaction diastereoselectivity. In this case, more bulky ligands would strongly favor the formation of the less

sterically demanding '*endo*' coordination of β-pinene enhancing the *cis* aldehyde formation. Thus, we believe that active species containing one phosphorous ligand seem to operate in the step, which determines the diastereoselectivity. Phosphorus ligand can enter either in the apical or equatorial position in a trigonal-bipyramidal rhodium–olefin-hydride intermediate. The stereodiscrimination should be higher in the case of the apical ligand coordination. Since no correlation between the ligand steric characteristics and the diastereoselectivity of β-pinene hydroformylation has been observed, the equatorial coordination of the phosphorous ligand seems to be more expected. Noteworthy, in a recent related study of the rhodium catalyzed hydroformylation of various allylbenzenes [3], we have also found that both the rate and regioselectivity are largely influenced by the basicity of phosphine auxiliary ligands, but no correlation between their steric characteristics and the regioselectivity has been revealed.

As far as the activity is concerned, it can be seen from the data in Tables 3 and 4 that the systems with weaker donor ligands usually show higher activity in hydroformylation of β-pinene. The obtained results are in full agreement with the commonly observed effects of ligand basicity on the rate of hydroformylation: the more basic the phosphines, the less active they are. Due to their strong coordination ability, which also depends on their steric bulk, they 'block' the active center and increase a back-donation from rhodium to carbon monoxide, resulting in stronger binding the carbonyls and decreasing the rate of the formation or equilibrium concentrations of active species [21,25].

In the systems with the most basic ligands, i.e. $P(Cy)_3$ and $P(n\text{-}Bu)_3$, the induction periods of approximately 1 h have been observed, during which the increased amounts of α-pinene has been formed. We believe that in the case of stronger ligands, bisligand complexes rather inactive in β-pinene activation are readily formed in the reaction solutions. It takes more time to reach the stationary concentrations of the monoligand species active in hydroformylation, which causes the induction period.

3.2. Hydroformylation of camphene

The hydroformylation of camphene (**2**) under the conditions similar to those used for β-pinene also proceeds smoothly to give linear aldehyde **6** with virtually 100% regioselectivity (linear/branched aldehydes) and chemoselectivity in both modified and unmodified systems (Table 5, Scheme 2). The extent of diastereoselectivity is low in the unmodified system: the diastereoisomers **6a** and **6b** are formed in approximately equal amounts (run 1). The addition of triphenylphosphine slightly improves the diastereoselectivity for *endo* isomer **6b** (**6a/6b** = 1/1.4) (run 2). Varying the P–Rh ratio (runs 2–4), temperature (runs 4–7) and $CO–H_2$ pressure (runs 5 and 8) have caused the expected changes in catalyst activity, while no appreciable effect on diastereoselectivity has been observed.

We have also studied the hydroformylation of camphene in the presence of various phosphines and phosphites (Tables 4 and 5): $P(p\text{-}OCH_3Ph)_3$, $P(CH_2Ph)_3$, $P(Cy)_3$, $P(O\text{-}o\text{-}^tBuPh)_3$ and $P(C_6F_5)_3$. The

Table 5
Hydroformylation of camphene (**2**) catalyzed by $[Rh(COD)(OAc)]_2$–L systems

Run	Ligand [a]	χ-value [b]	Cone angle (°) [b]	P–Rh [a]	Temperature (°C)	Time (h)	Conversion (%)	Product distribution (%)	
								6a	**6b**
1	None				100	4	100	48	52
2	PPh_3	13.25	145	2	100	4	100	41	59
3	PPh_3			5	100	4	47	41	59
4	PPh_3			10	100	4	26	38	62
						20	71	38	62
5	PPh_3			10	60	20	25	41	59
6	PPh_3			10	80	20	36	41	59
7	PPh_3			10	110	20	77	42	58
8 [c]	PPh_3			10	60	20	15	41	59
9	$P(p\text{-}OCH_3Ph)_3$	10.50	145	5	100	4	44	41	59
10	$P(CH_2Ph)_3$	10.35	165	5	100	4	81	39	61
11	PCy_3	1.40	170	5	100	4	16	40	60
12	$P(O\text{-}o\text{-}^tBuPh)_3$	30.50	175	5	100	4	100	38	62
13	$P(C_6F_5)_3$	34.80	184	5	100	4	90	47	53

Reaction conditions; camphene (3.7 mmol), $[Rh(COD)(OAc)]_2$ (0.014 mmol), benzene (18 ml), 9.0 MPa ($CO–H_2$ = 1/1). Conversion and selectivity were determined by GC.

[a] Cy, cyclohexyl; Bu, butyl.

[b] From ref. [23,24].

[c] 4.4 MPa.

2 6a 6b

Scheme 2.

systems with more basic ligands usually show lower activity. The Rh–$P(CH_2Ph)_3$ system promotes an unexpectedly fast reaction, probably due to the increased contribution of the rhodium complexes containing no phosphine. Differently from β-pinene, neither steric nor electronic parameters of the ligands influence the diastereoselectivity: the **6a/6b** ratio of ca. 1/1.5 has been obtained for all modified systems except the one with $P(C_6F_5)_3$ (run 13). As mentioned above, this weakly basic and bulk phosphine seems to be a poor ligand under the reaction conditions and the diastereoselectivity is similar to that observed in the absence of any auxiliary (**6a/6b** = 1/1.1). The same result has been obtained for β-pinene. Thus, as the steric difference between the diastereotopic faces of camphene is much less pronounced than that of β-pinene, rhodium catalysts with achiral ligands make no effective diastereofacial discrimination, similarly to what has been reported for platinum–tin systems [14,15]. It is remarkable that platinum catalysts promote the preferential formation of the thermodynamically more stable *exo* isomer, while in rhodium systems, *endo* aldehyde **3b** originating from the catalyst coordination to the less sterically hindered face of olefin, *syn* to the methylidene bridge, is formed in larger amounts.

4. Conclusions

Both the rate and diastereoselectivity of the rhodium catalyzed hydroformylation of β-pinene are largely influenced by the basicity of auxiliary ligands, but no correlation between their steric characteristics and the diastereoselectivity of the catalytic system has been revealed for the ligands with cone angles of 128–165°. The systems with more basic ligands show lower activities, higher diastereoselectivities and usually higher chemoselectivities in the β-pinene hydroformylation. The addition of phosphorus auxiliary favors the formation of *endo* aldehyde from camphene, however, neither steric nor electronic parameters of the ligands have been found to influence the diastereoselectivity. All studied catalysts make a much lesser effective diastereofacial discrimination for camphene than for β-pinene, when the diastereoselectivity reaches ca. 95% either for *trans* (unmodified systems) or *cis* (modified systems) aldehyde.

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