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Rhodium-catalyzed hydroformylation of allylbenzenes and propenylbenzenes: effect of phosphine and diphosphine ligands on chemo- and regioselectivity

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Abstract

Various allylbenzenes and propenylbenzenes have been hydroformylated with a 97–99% chemoselectivity using bis[(μ-acetate)(1,5-cyclooctadiene)rhodium(I)] as a catalyst precursor. Regioselectivity of the hydroformylation can be controlled by the nature of phosphorus auxiliary ligands. The Rh-NAPHOS (2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphthyl) system promotes the hydroformylation of allylbenzenes into linear aldehydes in near 95% selectivity and propenylbenzenes into branched aldehydes with a formyl group in α-position to phenyl ring in near 90% selectivity, while the Rh-dppp (1,3-bis(diphenylphosphino)propane) system gives branched aldehydes with a formyl group in β-position in near 70% selectivity starting from allylbenzenes. The regioselectivity of Rh-diphosphine systems correlates with a ligand bite angle. Both the rate and regioselectivity of the hydroformylation are largely influenced by the basicity of monophosphine auxiliary ligands, however, no correlation between their steric characteristics and the regioselectivity has been observed.

Keywords: Allylbenzenes; Regioselectivity; Hydroformylation; Ligands

1. Introduction

Selective functionalization of naturally occurring special olefins can provide oxygenated derivatives which are valuable materials in the fine chemicals industry. We have recently reported that allylic acetates, alcohols, aldehydes and carboxylic acid derivatives can be obtained in good yields by the metal complex catalyzed oxidation [1,2], hydroformylation [3,4] and alkoxycarbonylation [5] of some monoterpenes. Hydroformylation represents a versatile method for the production of commercially important aldehydes and alcohols, which are difficult to obtained by the conventional synthetic pathways. Aldehydes derived from substituted allylbenzenes and propenylbenzenes (Scheme 1), easily available from biomass, show biological and phytosanitary activities and are also useful in flavor, perfume and pharmaceutical industries [6,7]. However, the hydroformylation of these olefins has only little been studied hitherto [7–10]. High-pressure (600 MPa) hydroformylation of eugenol (**1a**) and isoeugenol (**2a**) results in a mixture of aldehydes **3a**, **4a** and **5a**, with regioselectivity being depending on temperature [7]. Aldehyde **3a** was obtained up to 95% selectivity from **2a**, while **1a** gave in all

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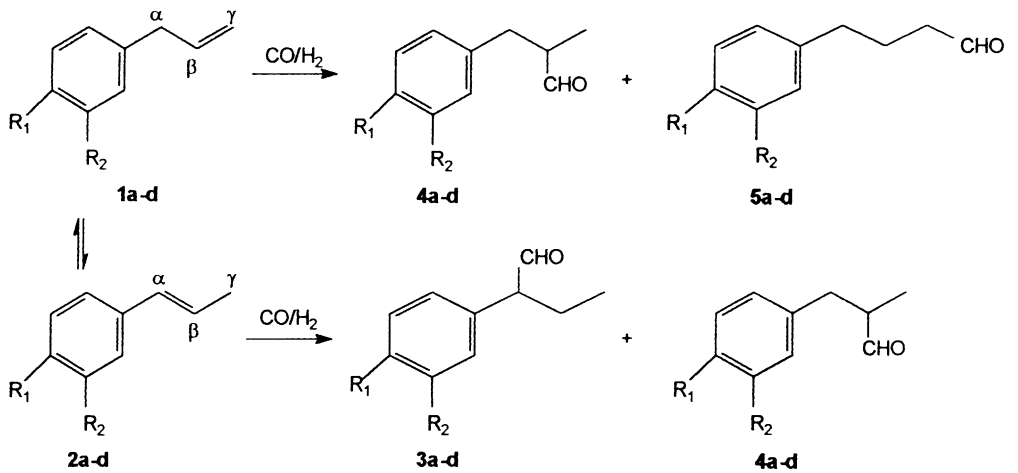

	Compound	R_1	R_2
1a	eugenol	OH	CH_3O
1b	eugenol methyl ether	CH_3O	CH_3O
1c	safrol	-O-CH_2-O-	
1d	estragol	CH_3O	H

Scheme 1.

cases the comparable amounts of two (**4a** and **5a**) or three (**3a**, **4a** and **5a**) aldehydes. Enantioselective platinum/tin- and rhodium-catalyzed hydroformylation of estragole (**1d**) and its isomer anethole (**2d**) has been reported recently [10], however, with low regioseletivity for aldehydes **4d** and **5d**. Kalck et al. [8,9] studied the hydroformylation of **1a**–**1d** using $[Rh_2(\mu\text{-}SR)_2(CO)_2L_2]$ as a catalyst precursor and achieved 96, 86, 88 and 80% selectivities for linear aldehydes **5a**–**5d**, respectively.

The aim of this work was to study the effect of various phosphine and diphosphine ligands on the hydroformylation of allylbenzenes **1a**–**1c** and propenylbenzenes **2a** and **2c** using bis[(μ-acetate)(1,5-cyclooctadiene)rhodium(I)] as a catalyst precursor. We found that chemo- and regioselectivity can be controlled by the ligand nature and developed the systems offering the preferential synthesis of either branched **3a** and **3c** (in near 90% regioselectivity), branched **4a**–**4c** (in near 70% regioselectivity) or linear **5a**–**5c** (in near 95% regioselectivity) aldehydes in very high chemoselectivities (>97%). The branched aldehydes derived from allylbenzenes and propenylbenzenes are precursors of various pharmacologically important compounds [10].

2. Experimental

All chemicals were purchased from Aldrich and used as received, unless otherwise indicated. Bis[(μ-acetate)(1,5-cyclooctadiene)rhodium(I)]—[Rh(COD)(OAc)]$_2$—was prepared by published procedure [11]. 2,2′-Bis[(diphenylphosphino)methyl]-1,1′-binaphthyl (NAPHOS) and 2,2′-bis[(diphenylphosphino)methyl]-1,1′-biphenyl (BISBI) were kindly donated by Prof. B. Hanson (Virginiatech, US). Benzene was purified under reflux with sodium wire/benzophenone for 6 h and then distilled under nitrogen.

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 $CDCl_3$. Mass spectra were

obtained on a Hewlett-Packard MSD 5890/Series II instrument operating at 70 eV.

In a typical run, a mixture of $[Rh(COD)(OAc)]_2$ (0.005 mmol), phosphine or diphosphine (0.10–0.20 mmol), substrate (10.0 mmol), and benzene (40 ml) was transferred from a Schlenck tube under nitrogen into a stainless steel magnetic stirred autoclave. The reactor was pressurized to 2 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. The assignment of ^{1}H and ^{13}C-NMR signals was made using HMQC, COSY and DEPT NMR experiments. Spectral simulations performed with the ADC/CNMR program were in agreement with the spectra observed.

*2-(4-Hydroxy-3-methoxyphenyl)-butanal (**3a**)*. MS (*m*/z/rel. int.): 194/17 (M^+); 165/197 (M^+-CHO); 137/100 ($M^+-C_2H_4CHO$). ^{1}H-NMR: δ, 0.90 (t, 3H, $^3J = 7.4$ Hz, C*H*$_3$); 1.66–1.75 (m, 1H, C*H*$_2$); 2.02–2.12 (m, 1H, C*H*$_2$); 3.33 (td, 1H, $^3J = 2.1$ Hz, $^3J = 7.4$ Hz, C*H*CHO); 3.87 (s, 3H, OC*H*$_3$); 6.64 (d, 1H, $^4J = 2.0$ Hz, aromatic (Ar): C*H*COCH$_3$); 6.71 (dd, 1H, $^4J = 2.0$ Hz, $^3J = 8.0$ Hz, Ar: C*H*CHCOH); 6.91 (d, 1H, $^3J = 8.0$ Hz, Ar: C*H*COH); 9.63 (d, 1H, $^3J = 2.1$ Hz, C*H*O). ^{13}C-NMR: δ, 11.63 (*C*H$_3$); 22.84 (*C*H$_2$); 55.94 (OCH$_3$); 60.45 (*C*HCHO); 111.06 (Ar: *C*HCOCH$_3$); 114.86 (Ar: *C*HCOH); 121.76 (Ar: *C*HCHCOH); 127.64 (Ar: *C*CHCHO); 145.20 (Ar: *C*OCH$_3$); 147.01 (Ar: *C*OH); 200.83 (*C*HO).

*2-(4-Hydroxy-3-methoxybenzyl)-propanal (**4a**)*. MS (*m*/z/rel. int.): 194/17 (M^+); 137/100 ($M^+-C_2H_4$CHO). ^{1}H-NMR: δ, 1.09 (d, 3H, $^3J = 6.9$ Hz, C*H*$_3$); 2.55 (dd, 1H, $^3J = 8.0$ Hz, $^2J = 13.6$ Hz, C*H*$_2$); 2.61–2.66 (m, 1H, C*H*CHO); 3.01 (dd, 1H, $^3J = 6.0$ Hz, $^2J = 13.6$ Hz, C*H*$_2$); 3.87 (s, 3H, OC*H*$_3$); 6.65–6.68 (m, 2H, Ar); 6.84 (d, 1H, $^3J = 8.6$ Hz, Ar: C*H*COH); 9.71 (d, 1H, $^3J = 1.6$ Hz, C*H*O). ^{13}C-NMR: δ, 13.32 (*C*H$_3$); 36.53 (*C*H$_2$); 48.27 (*C*HCHO); 55.99 (OCH$_3$); 111.62 (Ar); 114.49 (Ar: *C*HCOH); 121.81 (Ar); 130.69 (Ar: *C*CH$_2$); 145.50 (Ar: *C*OCH$_3$); 146.59 (Ar: *C*OH); 204.48 (*C*HO).

*4-(4-Hydroxy-3-methoxyphenyl)-butanal (**5a**)*. MS (*m*/z/rel. int.): 194/24 (M^+); 150/90 (M^+-CH_3CHO); 137/100 ($M^+-C_2H_4CHO$). ^{1}H-NMR: δ, 1.91 (qi, 2H, $^3J = 7.4$ Hz, C*H*$_2$CH$_2$CHO); 2.44 (td, 2H, $^3J = 1.5$ Hz, $^3J = 7.3$ Hz, C*H*$_2$CHO); 2.57 (t, 2H, $^3J = 7.5$ Hz, CH$_2$C*H*$_2$CH$_2$); 3.85 (s, 3H, OC*H*$_3$); 6.65 (d, 1H, $^3J = 8.1$ Hz, Ar: C*H*CHCOH); 6.67 (s, 1H, Ar: C*H*COCH$_3$); 6.82 (d, 1H, $^3J = 8.1$ Hz, Ar: C*H*COH); 9.73 (t, 1H, $^3J = 1.6$ Hz, C*H*O). ^{13}C-NMR: δ, 23.77 (*C*H$_2$CH$_2$CHO); 34.54 (*C*H$_2$CH$_2$CH$_2$); 42.95 (*C*H$_2$CHO); 55.75 (OCH$_3$); 110.95 (Ar: *C*HCOCH$_3$); 114.21 (Ar: *C*HCOH); 120.87 (Ar: *C*HCHCOH); 133.01 (Ar: *C*CH$_2$); 143.79 (Ar: *C*OCH$_3$); 146.41 (Ar: *C*OH); 202.51 (*C*HO).

*2-(3,4-Dimethoxybenzyl)-propanal (**4b**)*. MS (*m*/z/rel. int.): 151/100 ($M^+-C_2H_4CHO$). ^{1}H-NMR: δ, 1.05 (d, 3H, $^3J = 6.8$ Hz, C*H*$_3$); 2.53–2.60 (m, 1H, C*H*$_2$); 2.60–2.64 (m, 1H, C*H*CHO); 2.98 (dd, 1H, $^3J = 5.2$ Hz, $^2J = 12.5$ Hz, C*H*$_2$); 3.81 (s, 3H, OC*H*$_3$); 3.84 (s, 3H, OC*H*$_3$); 6.66–6.80 (m, 3H, Ar); 9.65 (d, 1H, $^3J = 1.2$ Hz, C*H*O). ^{13}C-NMR: δ, 12.50 (*C*H$_3$); 35.60 (*C*H$_2$); 42.40 (*C*HCHO); 55.12 (OCH$_3$); 55.20 (OCH$_3$); 110.70 (Ar); 111.70 (Ar); 120.41 (Ar); 130.80 (Ar: *C*CH$_2$); 146.77 (Ar: *C*OCH$_3$); 148.32 (Ar: *C*OCH$_3$); 203.70 (*C*HO).

*4-(3,4-Dimethoxyphenyl)-butanal (**5b**)*. MS (*m*/z/rel. int.): 164/66 (M^+-CH_3CHO); 151/100 ($M^+-C_2H_4$CHO). ^{1}H-NMR: δ, 1.90 (qi, 2H, $^3J = 7.2$ Hz, $^3J = 7.5$ Hz, C*H*$_2$CH$_2$CHO); 2.40 (td, 2H, $^3J = 1.5$ Hz, $^3J = 7.2$ Hz, C*H*$_2$CHO); 2.57 (t, 2H, $^3J = 7.5$ Hz, CH$_2$C*H*$_2$CH$_2$); 3.81 (s, 3H, OC*H*$_3$); 3.84 (s, 3H, OC*H*$_3$); 6.66–6.80 (m, 3H, Ar); 9.69 (t, 1H, $^3J = 1.5$ Hz, C*H*O). ^{13}C-NMR: δ, 23.20 (*C*H$_2$CH$_2$CHO); 34.00 (CH$_2$C*H*$_2$CH$_2$); 42.40 (*C*H$_2$CHO); 55.12 (OCH$_3$); 55.20 (OCH$_3$); 110.70 (Ar); 111.20 (Ar); 119.72 (Ar); 133.32 (Ar: *C*CH$_2$); 146.99 (Ar: *C*OCH$_3$); 148.32 (Ar: *C*OCH$_3$); 201.60 (*C*HO).

*2-(3,4-Methylenedioxyphenyl)-butanal (**3c**)*. MS (*m*/z/rel. int.): 192/15 (M^+); 163/100 (M^+-CHO); 135/195 ($M^+-C_2H_4CHO$). ^{1}H-NMR: δ, 0.90 (t, 3H, $^3J = 7.4$ Hz, C*H*$_3$); 1.62–1.81 (m, 1H, C*H*$_2$); 1.95–2.13 (m, 1H, C*H*$_2$); 3.32 (td, 1H, $^3J = 2.0$ Hz, $^3J = 7.4$ Hz, C*H*CHO); 5.96 (s, 2H, O–C*H*$_2$–O); 6.59–6.83 (m, 3H, Ar); 9.63 (d, 1H, $^3J = 2.0$ Hz, C*H*O). ^{13}C-NMR: δ, 11.67 (*C*H$_3$); 22.93 (*C*H$_2$); 60.42 (*C*HCHO); 101.17 (O–*C*H$_2$–O); 108.73 (Ar); 108.86 (Ar); 122.21 (Ar); 132.52 (Ar: *C*HCH$_2$); 147.06 (Ar: *C*OCH$_2$); 148.27 (Ar: *C*OCH$_2$); 200.75 (*C*HO).

*2-(3,4-Methylenedioxybenzyl)-propanal (**4c**)*. MS (*m*/z/rel. int.): 192/20 (M^+); 135/100 ($M^+-C_2H_4CHO$); 77/19. ^{1}H-NMR: δ, 1.08 (d, 3H, $^3J = 6.8$ Hz, CH_3); 2.51–2.55 (m, 1H, CH_2CH); 2.59–2.63 (m, 1H, C*H*CHO); 2.99 (dd, 1H, $^3J = 5.5$ Hz, $^2J = 12.5$ Hz, CH_2CH); 5.92 (s, 2H, O–CH_2–O); 6.58–6.75 (m, 3H, Ar); 9.69 (d, 1H, $^3J = 1.5$ Hz, C*H*O). ^{13}C-NMR: δ, 13.09 (*C*H_3); 36.31 (*C*H_2CH); 48.14 (*C*HCHO); 100.83 (O–*C*H_2–O); 108.17 (Ar); 109.23 (Ar); 121.86 (Ar); 132.42 (Ar: *C*HCH_2); 145.74 (Ar: *C*OCH_2); 147.59 (Ar: *C*OCH_2); 204.35 (*C*HO).

*4-(3′-Methylenedioxyphenyl)-butanal (**5c**)*. MS (*m*/z/rel. int.): 192/25 (M^+); 148/100 (M^+-CH_3CHO); 135/100 ($M^+-C_2H_4CHO$); 77/44; 51/32. ^{1}H-NMR: δ, 1.91 (qi, 2H, $^3J = 7.2$ Hz, $^3J = 7.5$ Hz, CH_2CH_2CHO); 2.44 (td, 2H, $^3J = 1.5$ Hz, $^3J = 7.2$ Hz, CH_2CHO); 2.57 (t, 2H, $^3J = 7.5$ Hz, CH_2CH_2CH_2); 5.92 (s, 2H, O–CH_2–O); 6.58–6.75 (m, 3H, Ar); 9.75 (t, 1H, $^3J = 1.5$ Hz, C*H*O). ^{13}C-NMR: δ, 23.79 (*C*H_2CH_2CHO); 34.64 (*C*H_2CH_2CH_2); 42.93 (*C*H_2CHO); 100.83 (O–*C*H_2–O); 108.11 (Ar); 108.76 (Ar); 121.17 (Ar); 134.95 (Ar: *C*CH_2); 145.74 (Ar: *C*OCH_2); 147.59 (Ar: *C*OCH_2); 202.45 (*C*HO).

3. Results and discussion

Hydroformylation of eugenol **1a** (Table 1, run 1) occurs smoothly under mild conditions (60 °C, 2 MPa) with $[Rh(COD)(OAc)]_2$ used as a catalyst precursor, giving rise to a full conversion of the substrate within 3 h. Only trace amounts of the hydrogenated substrate are formed. However, in the absence of auxiliary phosphorus ligand, hydroformylation is strongly complicated by the excessive isomerization of a terminal C=C double bond. As a result, near 30% of isoeugenol **2a** is formed along with branched (**4a**) and linear (**5a**) aldehydes (***5***a/***4***a = 2.4). Hydroformylation of **2a** would give branched aldehydes **3a** and **4a** with the formyl group in α- and β-positions, respectively, however, the α-isomer has not been detected under the conditions used because of the lower reactivity of internal olefins in hydroformylation. The addition of triphenylphosphine (P/Rh = 10) dramatically improves the chemoselectivity of hydroformylation (up to nearly 100%) with the linearity being almost the same (***5***a/***4***a = 2.1) (Table 1, run 2). When triphenylphosphine is substituted by a less basic ligand, $OPPh_3$ (Table 1, run 3), the product distribution is rather similar to that observed in the absence of any auxiliary ligand (run 1). These results are completely consistent with the expected mechanism of eugenol hydroformylation and isomerization. The addition of rhodium(I) hydride to the coordinated olefin results in linear and branched rhodium alkyl intermediates (rhodium attached to γ- and β-carbons, respectively). The former then originates a linear aldehyde, while the latter could give either branched aldehyde **4a** via carbonylation or isomeric olefin **2a** via a rhodium hydride elimination, with hydrogen being abstracted from the α-carbon. Chemoselectivity is determined by relative reactivity of the branched alkyl intermediate towards carbonylation vs. β-hydride elimination. It is expected to be strongly affected by the ligand basicity. The presence of PPh_3, which is more basic ligand than CO, should disfavor the hydride transfer from the α-carbon to the rhodium atom bearing now a less positive partial charge. Moreover, it was found [12] 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 carbonylation of the alkyl intermediate is strongly favored.

In an attempt to clarify the effect of phosphorus ligand nature and control the regioselectivity driving the reaction towards either the linear or branched aldehydes, we have studied the hydroformylation of eugenol **1a** in the presence of various phosphine (Table 2) and

Table 1
Hydroformylation of eugenol (**1a**) catalyzed by $[Rh(COD)(OAc)]_2$: effect of phosphorus ligand addition[a]

Run	Ligand	Time[b] (h)	Selectivity[c,d] (%)	Product distribution[d] (%)		
				2a	**4a**	**5a**
1	None	3	69	31	20	48
2	PPh_3	5	100	tr.[e]	28	72
3	$OPPh_3$	3	58	42	18	40

[a] Reaction conditions: substrate (10.0 mmol), $[Rh(COD)(OAc)]_2$ (0.005 mmol), phosphorus ligand (0.10 mmol), benzene (40 ml), 2 MPa ($CO/H_2 = 1/1$), 60 °C.

[b] Reaction time necessary for a 100% conversion.

[c] Selectivity for the hydroformylation products; hydrogenated substrate is detected in trace amounts.

[d] Determined by GC.

[e] Trace amounts.

Table 2
Hydroformylation of eugenol (**1a**) catalyzed by $[Rh(COD)(OAc)]_2$/L systems: steric and electronic effects of auxiliary phosphorus ligand (L)[a]

Run	Ligand[b]	Cone angle[c] (°)	ν[c,d] (cm^{-1})	Time[e] (h)	Product distribution[f] (%)		
					4a	**5a**	**5a/4a**
1	PPh_3	145	2068.9	1	31	68	2.1
2	$P(CH_2Ph)_3$	165	2066.4	2	32	68	2.1
3	$P(n\text{-}Bu)_3$	132	2056.1	7	48	52	1.1
4	$P(Cy)_3$	170	2056.4	5	45	55	1.2

[a] Reaction conditions: substrate (10.0 mmol), $[Rh(COD)(OAc)]_2$ (0.005 mmol), phosphorus ligand (0.10 mmol), benzene (40 ml), 2 MPa ($CO/H_2 = 1/1$), 80 °C.
[b] Bu: butyl, Cy: cyclohexyl.
[c] From Ref. [13].
[d] ν(CO) of $Ni(CO)_3L$ in CH_2Cl_2.
[e] Reaction time necessary for a 100% conversion.
[f] Determined by GC; hydrogenated substrate is detected in trace amounts.

diphosphine (Table 3) ligands. We chose a series of phosphines exerting different steric and electronic effects: triphenylphosphine, PPh_3; tribenzylphosphine, $P(CH_2Ph)_3$; tri(*n*-butyl)phosphine, $P(n\text{-}Bu)_3$; tricyclohexylphosphine, $P(Cy)_3$. The ligand cone angles, θ, and ν(CO) frequencies of a series of complexes of the type $Ni(CO)_3L$ were taken as the quantitative measures of steric and electronic effects, respectively, as proposed by Tolman [13]. The higher the cone angle, the greater steric crowding the phosphine ligand introduces to the metal center. The stronger donor phosphines increase the electron density on Ni, which transfers some of this increase along to the coordinated carbon monoxide by back donation. Thus, the ν(CO) frequency becomes lower with increase in the phosphine basicity.

Two groups of ligands with significantly different basicity are presented in Table 2: $PPh_3/P(CH_2Ph)_3$ and $P(n\text{-}Bu)_3/P(Cy)_3$, with the phosphines of the latter group being more basic than those of the former. In all the cases, no appreciable double bond isomerization was observed. The systems with weaker donor phosphines (runs 1 and 2) show much higher activity in hydroformylation of eugenol converting 100% of the substrate for 1–2 h, while the systems with $P(n\text{-}Bu)_3$ and $P(Cy)_3$ require 5–7 h to reach a 100% conversion (runs 3 and 4). The obtained results are in full agreement with the usually observed effects of ligand

Table 3
Hydroformylation of eugenol (**1a**) catalyzed by $[Rh(COD)(OAc)]_2$/diphosphine systems[a]

Run	Diphosphine[b]	Bite angle[c] (°)	Time (h)	Conversion[d] (%)	Product distribution[d] (%)		
					4a	**5a**	**5a/4a**
1	dppe	85	24	55	62	38	0.6
2	dppp	91	24	74	69	31	0.5
3	dppb	98	24	99	34	66	1.9
4[e]	BISBI	123	7	81	2	98	49.0
5[e]	NAPHOS	120	7	90	2	98	49.0

[a] Reaction conditions: substrate (10.0 mmol), $[Rh(COD)(OAc)]_2$ (0.005 mmol), diphosphine (0.20 mmol), benzene (40 ml), 2 MPa ($CO/H_2 = 1/1$), 80 °C.
[b] dppe: 1,2-bis(diphenylphosphino)ethane; dppp: 1,3-bis(diphenylphosphino)propane; dppb: 1,4-bis(diphenylphosphino)butane, NAPHOS: 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphthyl; BISBI: 2,2′-bis[(diphenylphosphino)methyl]-1,1′-biphenyl.
[c] From Ref. [15,16].
[d] Determined by GC; hydrogenated substrate is detected in trace amounts.
[e] Diphosphine: 0.10 mmol.

basicity on the hydroformylation rate: the more basic the phosphines, the less active they are [14]. Due to their strong coordination to the metal, they "block" the active center. PPh_3, as the poorest ligand in this series, promotes the fastest hydroformylation (run 1). As far as regioselectivity is concerned, it can be seen from the data in Table 2 that the stronger donor phosphines P(*n*-Bu)$_3$ and P(Cy)$_3$ favor the formation of branched aldehyde **4a** in larger amounts (**5a**/**4a** is ca. 1 in runs 3 and 4 vs. ca. 2 in runs 1 and 2). The branched aldehyde is formed via a hydride ligand transfer to the γ-olefinic carbon which bears a more positive fractional charge compared to the β-carbon (Scheme 1). The more basic phosphines increase the electron density on Rh, which transfers some of this increase along to the coordinated hydride facilitating its nucleophilic interaction with γ-carbon. In addition, the more nucleophilic the hydride is in a trigonal-bipyramidal intermediate, the more preferable the equatorial coordination of eugenol to Rh in the way which favors the hydride addition to the terminal γ-carbon (i.e., with the substituent at the olefinic bond oriented to the opposite to hydride ligand side of the equatorial plane) becomes. Thus, both the rate and regioselectivity of eugenol hydroformylation are largely influenced by basicity of phosphine auxiliary ligands.

An analysis of the data presented in Table 2 reveals that there is no correlation between the steric characteristics of the phosphines studied and regioselectivity of the catalytic system. Phosphines with the similar basicity but with very different cone angles (145° for PPh_3 vs. 165° for P(CH$_2$Ph)$_3$, and 132° for P(*n*-Bu)$_3$ vs. 170° for P(Cy)$_3$) showed rather similar results in eugenol hydroformylation. This is highly unexpected if intermediate complexes with more than one phosphine ligand, i.e., bisligand and trisligand species, are involved in the step which determines the reaction regioselectivity. In this case, more bulky phosphines would strongly favor the formation of a less sterically crowded straight chain σ-alkyl rhodium intermediate enhancing a terminal hydroformylation. Thus, we believe that active species containing one phosphine ligand seem to operate in the regioselectivity determining step under the conditions used.

Hydroformylation of eugenol **1a** in the presence of various diphosphine auxiliaries, which usually give an enhanced preference for bis(phosphine)rhodium complexes and offer more control over regioselectivity [15], is presented in Table 3. Indeed, we have found that the reaction regioselectivity depends on the diphosphine nature and clearly correlates with ligand bite angles. With BISBI and NAPHOS, bite angles near 120° [15,16], the linearity is as high as 98% (runs 4 and 5), while the use of 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp), bite angles near 90° [15], switches the selectivity from linear to branched aldehyde (up to ca. 70% of β-isomer **4a**) (runs 1 and 2).

Ligand natural bite angles near 90° would induce an apical-equatorial coordination of bidentate dppe and dppp ligands in a trigonal-bipyramidal rhodium-olefin-hydride intermediate; while BISBI and NAPHOS with bite angles near 120° enforce a diequatorial chelation [15,17]. Thus, in the five-coordinated Rh-dppe and Rh-dppp intermediates, the apical hydride is *trans* to the phosphine ligand and is expected to be less acidic than the hydride of the BISBI and NAPHOS complexes, which is *trans* to a less basic CO ligand. This increase in the electron density on hydride facilitates its nucleophilic interaction with γ-carbon of the coordinated olefin resulting in branched aldehyde **4a**, as discussed above. On the other hand, the system with 1,4-bis(diphenylphosphino)butane (dppb), bite angle 98°, which is expected to bind as an apical-equatorial chelate, does not promote the preferential formation of branched aldehydes and show a 66% linearity, which is almost the same as that of monodentate triphenylphosphine (cf. run 3 in Table 3, and run 1 in Table 2). It could be explained by increasing flexibility of a ligand backbone in dppb vs. dppp which raises the chance of an arm-off η^1-coordination [15]. Different efficiency of dppb compared to dppp was earlier observed in various reactions. Excellent linearities of up to 98% are achieved with BISBI and NAPHOS (runs 4 and 5). High selectivity towards linear aldehydes of a BISBI-based rhodium catalytic system, patented by Eastman Kodak in 1987 [18], was also observed in the hydroformylation of 1-hexene [19] and 1-octene [20]. Although the reasons for the increased regioselectivity of hydroformylation seen for diphosphines with large natural bite angles are not yet fully understood, both the preference of these chelates to occupy diequatorial sites in the trigonal-bipyramidal intermediate and their increased steric bulk more likely contribute to this effect [15,17].

Table 4
Hydroformylation of allylbenzenes **1a**–**1c** catalyzed by $[Rh(COD)(OAc)]_2$/diphosphine systems[a]

Run	Allylbenzene	Diphosphine[b]	Conversion[c] (%)	Product distribution[c] (%)			
				2a–**2c**	**4a**–**4c**	**5a**–**5c**	Hydrogenated substrate
1	**1a**	dppp	74	tr.[d]	69	31	tr.
2	**1b**	dppp	50	tr.	66	33	1
3	**1c**	dppp	62	tr.	65	33	2
4	**1a**	NAPHOS	100	tr.	2	98	tr.
5	**1b**	NAPHOS	100	3	6	90	1
6	**1c**	NAPHOS	100	1	5	93	2

[a] Reaction conditions: substrate (10.0 mmol), $[Rh(COD)(OAc)]_2$ (0.005 mmol), dppp (0.20 mmol), NAPHOS (0.10 mmol), benzene (40 ml), 2 MPa ($CO/H_2 = 1/1$), 80 °C, reaction time = 24 h.
[b] dppp: 1,3-bis(diphenylphosphino)propane; NAPHOS: 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphthyl.
[c] Determined by GC.
[d] Trace amounts.

The rhodium-diphosphine systems were found to be also very efficient in controlling the regioselectivity of the hydroformylation of other allylbenzenes, i.e., eugenol methyl ether **1b** and safrol **1c**. The results are presented in Table 4. The Rh-NAPHOS catalyst converts **1a**–**1c** into corresponding linear aldehydes **5a**–**5c** in a 90–98% regioselectivity (runs 4–6), while the Rh-dppp catalyst allows the preferential formation of the branched aldehydes (β-isomers) (runs 1–3). Excellent chemoselectivity is achieved in all cases with only small amounts (2%) of the hydrogenated substrate being detected.

Starting from naturally occurring isomers of eugenol and safrol, i.e. propenylbenzenes **2a** and **2c**, it is possible to obtain selectively the other branched aldehydes—α-isomers **3a** and **3c** (Table 5). Hydroformylation of **2a** and **2c** expectedly proceeds at much slower rates, than that of allylbenzenes. The double bonds in these substrates are internal and, in addition, conjugated with the phenyl ring, with a positive partial charge being expected on α-carbon atoms due to the M^+ effect of the phenyl ring. Only 14% conversion of **2a** occurs for 24 h under the conditions similar to those used for allylbenzenes (run 1). Aldehyde

Table 5
Hydroformylation of propenylbenzenes **2a** and **2c** catalyzed by $[Rh(COD)(OAc)]_2$[a]

Run	Substrate	Auxiliary ligand[b]	Pressure (MPa)	Temperature (°C)	Time (h)	Conversion[c] (%)	Product distribution[c] (%)			
							3	**4**	**5**	Hydrogenated substrate
1	**2a**	None	2	80	24	14	76	24	–	–
2	**2a**	None	6	80	6	82	41	56	–	3
3[d]	**2a**	None	6	80	6	73	45	52	–	3
4[d]	**2a**	None	6	100	6	80	32	53	12	3
5	**2a**	None	9	130	4	100	28	44	19	9
6	**2a**	dppp	9	130	24	53	63	26	–	11
7	**2a**	NAPHOS	9	130	24	52	92	5	–	3
8	**2c**	dppp	9	130	24	54	74	21	–	5
9	**2c**	NAPHOS	9	130	24	54	93	4	2	1

[a] Reaction conditions: substrate (10.0 mmol), $[Rh(COD)(OAc)]_2$ (0.005 mmol), auxiliary ligand (if any) (0.20 mmol), benzene (40 ml), $CO/H_2 = 1/1$.
[b] dppp: 1,3-bis(diphenylphosphino)propane; NAPHOS: 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphthyl.
[c] Determined by GC.
[d] $CO/H_2 = 2/1$.

3a is formed as a main product in a 76% regioselectivity and virtually 100% chemoselectivity. Varying the reaction conditions, such as temperature, pressure and CO/H_2 ratio (runs 1–5), hydroformylation has been accelerated significantly (100% conversion for 4 h, run 5), however, at the expense of regioselectivity—a mixture of all three isomeric aldehydes **3a**, **4a** and **5a** in comparable amounts is formed along with 9% of hydrogenated substrate. Thus, the partial isomerization of **2a** into **1a** and fast hydroformylation of the latter occurs in the reaction solutions. The introduction of auxiliary diphosphines, dppp or NAPHOS, lowers the hydroformylation rate and strongly orients the selectivity towards α-isomer **3a** (runs 6–9 vs. run 5). As expected, the natural bite angle of the chelating diphosphine dramatically influences the regioselectivity. Interestingly, it has been observed that the higher the bite angle, the larger amounts of the branched aldehyde with the formyl group in a sterically more demanding α-position are formed. NAPHOS with bite angle of 120° gives 92–93% of α-isomer **3** (runs 7 and 9), while in the systems with dppp, bite angle 91°, the selectivity for **3** is much lower (63–76%, runs 6 and 8). As-mentioned above, in the hydroformylation of terminal olefins, the opposite effect was observed. Diphosphines with larger bite angles (near 120°), which chelate almost exclusively to diequatorial sites in five coordinate rhodium complexes, have showed much higher linearity in hydroformylation of terminal olefins than diphosphines with bite angles near 90° and enhanced preference to form apical-equatorial complexes. The reasons for the correlation between the ligand bite angle and regioselectivity in hydroformylation have been widely discussed, however remain so far unraveled [15,19–22]. Purely steric explanations based on increasing steric bulk of phosphine ligand were considered and ruled out [21]. On the other hand, purely electronic arguments also failed to explain satisfactorily the data obtained [22], thus the consideration of both electronic and steric properties is required to understand the effect.

The results on the hydroformylation of propenylbenzenes obtained in our work show that in this specific case the electronic effects should be more important than steric difference between dppp and NAPHOS, because despite the increase of the effective steric bulk compared to dppp, NAPHOS promotes the formation of more sterically hindered α-aldehydes **3a** and **3c** in higher than 90% selectivity. In the five coordinated Rh-dppp complex, the apical hydride is *trans* to the strong donor phosphine, while the hydride of the Rh-NAPHOS complexes is *trans* to a less basic CO ligand and would be expected to be more acidic. Decreasing the electron density on hydride facilitates its interaction with a β-carbon atom of the coordinated olefin bearing a negative partial charge. This results in the formation of branched aldehydes **3a** and **3b** with the formyl group incorporated in α-position. Such a consideration gives a reasonable explanation for the increase in selectivity for α-aldehydes in going from the Rh-dppp to Rh-NAPHOS catalyst. However, it fails to explain the higher regioselectivity of the Rh-NAPHOS catalyst (Table 5, run 7) compared to the unprompted rhodium system (Table 5, run 5), in which the apical hydride of the intermediate in the regioselectivity determining step is also *trans* to a CO ligand. Undoubtedly, in this case, not only the nature of the ligand *trans* to the apical hydride, but also the major steric and electronic differences between CO and NAPHOS ligands, e.g. the presence of two strong donor phosphines in the equatorial plane in Rh-NAPHOS complexes which increases a back donation from rhodium to the equatorial olefin ligand and could change the relative charges on carbon atoms, should be taken into account to interpret the results of the hydroformylation of propenylbenzenes.

4. Conclusions

This study shows that chemo- and regioselectivity of the hydroformylation of allylbenzenes **1a**–**1c** and propenylbenzenes **2a** and **2c** using bis[(μ-acetate)(1,5-cyclooctadiene)rhodium(I)] as a catalyst precursor can be controlled by the nature of phosphorous auxiliary ligands. The Rh-NAPHOS system promotes the formation of linear aldehydes **5a**–**5c** (formyl group in γ-position) in near 95% regioselectivity starting from allylbenzenes and branched aldehydes **3a** and **3c** (formyl group in α-position) in near 90% regioselectivity starting from propenylbenzenes; while the Rh-dppp system gives branched aldehydes **4a**–**4c** (formyl group in β-position) in near 70% regioselectivity starting from allylbenzenes. All these reactions proceed with very high chemoselectivities (97–99%). The regioselectivity of the Rh-diphospine

systems correlates with the bite angles of the chelating ligands. Both the rate and regioselectivity of the hydroformylation of **1a** are largely influenced by the basicity of monophosphine auxiliary ligands, however, no correlation between their steric characteristics and the regioselectivity of the catalytic system has been revealed.

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