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Synthesis of achiral, but unsymmetric, seven-membered rhodium(I)-chelates for hydrogenation in the chiral environment of alkyl polyglucoside micelles

V. Fehring [a], R. Kadyrov [a], M. Ludwig [a], J. Holz [a], K. Haage [b], R. Selke [a,*]

[a] *Institut für Organische Katalyseforschung an der Universität Rostock, e.V., Buchbinderstr. 5-6, D18055 Rostock, Germany*
[b] *Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Abteilung Grenzflächen, Am Mühlenberg 2, Golm, D-14424 Potsdam, Germany*

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Dedicated to Professor H. Brunner on the occasion of his 65th birthday

Abstract

Chiral rhodium(I) chelates containing a seven-membered ring are well-known active catalysts for the asymmetric hydrogenation of amino acid precursors. A high conformational flexibility allows their enantioselectivity to be strongly influenced by modifiers. Now we show the nature of the counter-ions to have a large influence in apolar solvents. In addition, the presence of micelle forming alkyl polyglycosides as amphiphiles causes a remarkable increase in the enantiomeric excess (%ee). However, on achiral catalysts this enantioselectivity inducing effect scarcely exceeds the standard deviation for the gas chromatographic determination of the enantiomeric ratio. This is also true for the application of unsymmetric *P*,*P*′-ligands such as 3-phosphinopropyl-phosphinites or butane-1,4-diyl-bis(phosphines) carrying different *P*′-aryl groups, for which synthetic routes are given.

Keywords: Alkyl polyglycosides; Asymmetric hydrogenation; Counter-ions; Micelles; Rhodium(I) chelates; Unsymmetric bisphosphines

1. Introduction

Following the ideas of Oehme et al. [1] we found by the addition of amphiphiles an impressive increase in the enantioselectivity in water for a large number of chiral rhodium(I) chelates as asymmetric hydrogenation catalysts [2]. Recent investigations of Oehme et al. to try to realize asymmetric hydrogenations using achiral catalysts, relying only on the enantiodifferentiating action of chiral amphiphiles, led to very small effects [3]. The seven-membered rhodium(I) chelate of butane-1,4-diyl-bis(diphenylphosphines), [Rh(BDPP)(COD)]BF_4, gave reliable but unsatisfactory enantioselectivities of up to 8%ee when amphiphiles derived from enantiopure carbohydrates or amino acids were applied. In contrast the rhodium complex of propane-1,3-diyl-bis(diphenylphosphine), forming a six-membered chelate ring, proved to be unsuccessful in this respect.

The background for the preparation of unsymmetric ligands with two coordinatively distinguishable phosphorus atoms, which are here presented, was to attempt to enable its rhodium complexes to a higher stereodifferentiation in the chiral environment formed by micelles of alkyl polyglucosides. Considering the strong electronic effects of *P*-aryl substituents on the enantioselectivity of carbohydrate bisphosphinite catalysts found by RajanBabu et al. [4] we supposed that it might be important to differentiate the electronic state of both phosphorus atoms in the newly synthesized ligands to enable the chiral medium to take effect.

Seven-membered chelates were chosen because we had already shown that the enantioselectivity of such rhodium(I) chelates, caused by their high conformative flexibility, is strongly susceptible to the influences of solvents, substrates or additives [2,5]. In special cases this covers nearly the whole range of enantioselectivity from about 90%ee (*S*) to nearly 90%ee (*R*) for one and

* Corresponding author. Tel.: +49-381-4669335; fax: +49-381-4669324.
E-mail address: ruediger.selke@ifok.um-rostock.de (R. Selke).

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the same catalyst species [6]. Furthermore we state now an important unpublished influence of counter ions (see Fig. 1) on the enantioselectivity of the chiral [Rh(Ph-β-glup-OH)]$^+$ (**1**). This catalyst has already found industrial application [7] in L-DOPA production by ISIS Chemie Zwickau from 1986 to 1990.

However, the effect of chiral amphiphiles such as alkyl saccharides on the enantioselectivity of achiral catalysts was unsatisfactory, even using the new unsymmetric ligands for rhodium(I) and despite the large influence such amphiphiles have on the enantioselectivity of the chiral [Rh(HO-diop)]$^+$ (**2**) (see Table 1).

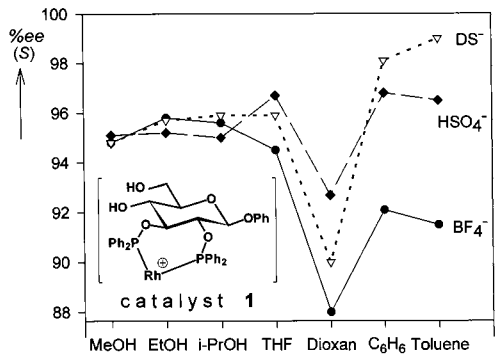


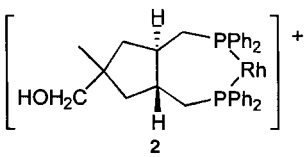
Fig. 1. Influence of anions on the enantioselectivity of [Rh(Ph-β-glup-OH)]$^+$ (**1**) in the hydrogenation of methyl (*Z*)-2-acetamidocinnamate: dependence of the applied solvents (DS^- equals the dodecylsulfate anion). Conditions: 1.0 mmol substrate, 0.01 mmol [**1**·(COD)]anion, 15 ml of solvent, 25°C, 0.1 MPa.

2. Results and discussion

2.1. Influence of counter-ions on the enantioselectivity of [Rh(Ph-β-glup-OH)]$^+$ (1)

The pre-catalysts for [Rh(Ph-β-glup-OH)]$^+$ (**1**), which contain *cis*,*cis*-cycloocta-1,5-diene (COD) for stabilisation were prepared as earlier reported [8]. The complex with the dodecylsulfate (DS^-) counter-ion was prepared according to an analogous method to that given in reference [2c]. In protic solvents, such as alcohols, the enantioselectivity is not controlled by the counter-ion because the catalysts act in the dissociated form, independently of the anion. However, in aprotic solvents we observed a considerable influence of the anion on the enantiomeric excess in the hydrogenation of methyl (*Z*)-2-acetamidocinnamate (see Fig. 1). A pronounced anion effect results in apolar solvents like aromatic hydrocarbons in which the catalyst is normally present as an ion pair [9]. Particularly high enantioselectivities of about 99%ee are found in toluene using the dodecyl sulfate anion. This prompts to be wary with the statement that micelle formation causes increased enantioselectivity under the action of amphiphiles [2a]. The insignificance of formation of reversed micelles for the increase of enantioselectivity was proven for apolar solvents [10]. In water, however, a relationship between the amphiphile aggregation and its effect on the enantioselectivity is plausible. We found for instance a remarkable parallel between the micelle

Table 1
Influence of alkyl polyglycosides on the enantioselectivity in asymmetric hydrogenations in water with catalyst **2** [Rh(Diop-OH)]$^+$ [a]



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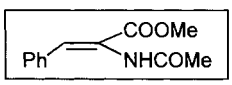
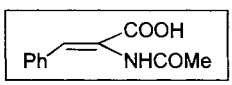
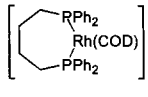
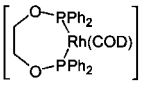
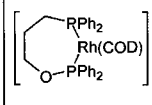
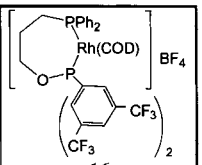
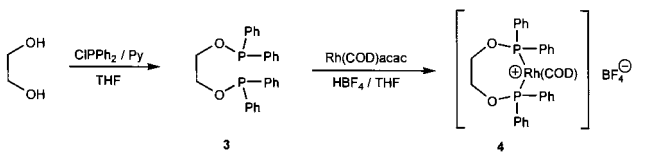
1 mmol substrate →	AMe 			AH 		
0.1 mmol amphiphile ↓	t/2	*%ee* (*R*)	$Q_{a/b}$	t/2	*%ee* (*R*)	$Q_{a/b}$
without amphiphile	7	2.2		8.8	34.4	
$C_{8/10}$-alkyl polyglycoside (GZ 1,5) APG 220 UP	≈ 700 ≈ 700	39.1 38.4	2.2 2.1	9.3	67.3	2.5
$C_{12/16}$-alkyl polyglycoside (GZ 1,4) APG 600 UP	236	58.7	3.7	4.9	**84.9**	**6.0**
Sodium dodecylsulfate (SDS)	5	76.6	7.3	3.0	72.8	3.1

[a] Conditions: 0.01 mmol [**2**·(COD)]BF_4, 15 ml of water, 25°C, 0.1 MPa; $Q_{a/b}$ represents the *relative enantioselectivity* [2b], the quotient of the ratio of product enantiomers er_a (in the presence of amphiphile a) and the enantiomeric ratio of the blank experiment er_b: $Q_{a/b} = er_a/er_b$.

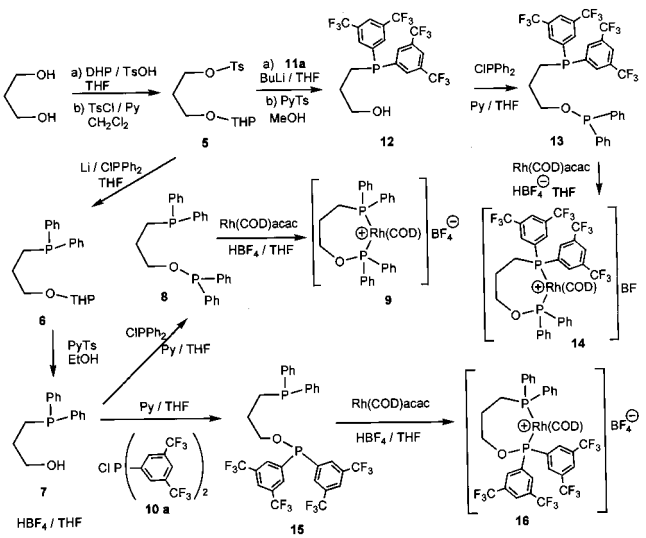
Table 2
Hydrogenation of 2-*N*-acetamidocinnamic acid (**AH**), its methyl ester (**AMe**) and methyl 2-*N*-acetamidoacrylate (**aMe**); influence of $C_{12/16}$-alkyl polyglycoside (+**a**) [a]

	pre-catalyst → amphiphile **a**				 **4**		 **9**		 **16**	
substr	↓	solvent	t/2 min	% ee	t/2 min	% ee	t/2 min	% ee	t/2 min	% ee
AMe	-	MeOH	1.1	0.5 *S*	3.3	0.7 *S*	19	0.4 *S*	15	0.3 *S*
aMe	-	10% MeOH in H_2O	4.0	1.4 *R*	100	2.4 *R*	375	0.1 *R*	858	1.5 *S*
AH	+**a**	H_2O	15	2.5 *R*	320	2.2 *R*			13 % conversion in 55 h	2.3 *S**
AH	+**a**	10% MeOH in H_2O 10 Mpa H_2					6 % onversion in 1 h	9 *S*	20 % conversion in 20 h	7 *S*

[a] Conditions: 1 mmol substrate, 0.01 mmol pre-catalyst, 15 ml of solvent, 0.1 mmol amphiphile **a**, $C_{12/16}$-alkyl polyglycoside (Henkel KGaA), 25°C, 0.1 MPa (if not otherwise noted). * In one preliminary experiment we received a much higher value of 23%ee (*S*); this could not be reproduced. **aMe** = methyl 2-acetamido-acrylate.



Scheme 1.



Scheme 2.

destroying action of added methanol and its decreasing influence on the selectivity enhancement by sodium dodecylsulfate [2b]. New investigations using PGSE-NMR experiments underline the importance of micelle formation in such cases [11].

2.2. Enhancement of the enantioselectivity of [Rh((*R*,*R*)-HO-diop)]$^+$ (**2**) by alkyl polyglucosides

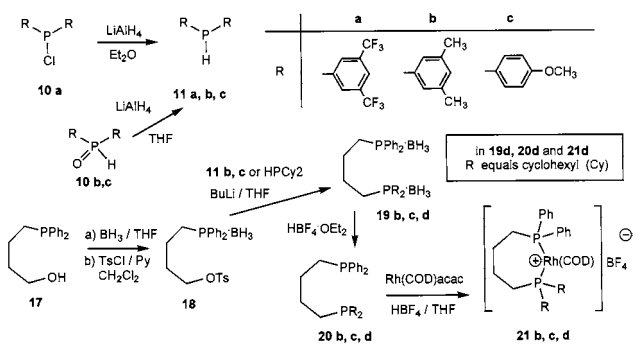
With regard to the former success in the application of alkyl glycosides [3a] and their easy accessibility as industrial products, we chose commercially available alkyl polyglucosides [12] as test examples for chiral amphiphiles. We applied [Rh((*R*,*R*)-HO-diop)]$^+$ (**2**) because of the particularly high susceptibility of its enantioselectivity to the presence of amphiphiles [2c]. We found a respectable increase in the enantioselectivity in the hydrogenation of methyl (*Z*)-2-acetamidocinnamate (**AMe**) and particularly its analogous acid (**AH**) in water (see Table 1). The distinct drop in the reaction rate in the presence of the alkyl glycosides for the hydrogenation of **AMe** is remarkable. This is in strong contrast to our experience with numerous amphiphiles, which without exception, and independent of the kind of substrate, led to a decrease of the reaction time in micellar dispersion. It seems possible, that the main quantity of the catalyst and the main amount of the substrate are located in different phases: the very polar catalyst predominantly in water, the poorly water soluble **AMe** mainly aggregated in the micelles formed by the polyglucosides. The less soluble **AH** should be even more concentrated in the micellar phase. This and the higher reactivity of **AH** compared with **AMe**, which is

well-known also by application of such catalysts in homogeneous solution, may compensate the assumed low concentration of the catalyst in the polyglucoside aggregates. Thus for **AH** the main part of the hydrogenation may occur within the supramolecular structures and explains at the same time the sixfold increase of the *relative enantioselectivity* (84.9%ee corresponds to $Q_{a/b} = 6.0$; see Table 1).

The extreme increase of the relative enantioselectivity in hydrogenation of **AH** in the presence of the $C_{12/16}$-alkyl polyglycoside has not yet been achieved for such substrate acids using other amphiphiles. Even with sodium dodecylsulfate (SDS), the prototype of an enantioselectivity increasing amphiphile, $Q_{a/b}$ did not generally reach 4.5 [2a], but remained in the case of catalyst **2** at 3.1. It seemed possible that the high increase in selectivity could be caused by a double stereo differentiation described by Masamune [13] corresponding to the chiral amphiphile forming a matching pair with the catalyst. In such a case one would expect a mismatching effect with lower selectivity if the enantiomer catalyst [Rh((*S*,*S*)-HO-diop)]$^+$ was applied. However, the effect has proved to be only very small (83.1%ee *S*-product, $Q_{a/b} = 5.3$).

2.3. Synthesis of achiral ligands and their chelates

Among the achiral rhodium(I) chelates, which were of interest for us, are some symmetric complexes for the comparison with the unsymmetric, but nevertheless achiral chelates (see Table 2). Particularly the synthesis of ethylene-bis(diphenylphosphinite) (Scheme 1) must be conducted carefully. This bisphosphinite **3** is known for its instability, caused by Michaelis Arbuzov like rearrangements leading to phosphinoxides [14]. Due to this reactivity the synthesis of ligand **3** is accomplished by adding chlorodiphenyl phosphine to glycol at -15°C. The reaction mixture had to be kept at this temperature even during work up to prevent any rearrangement. The resulting ligand **3** was therefore used without any further purification for the preparation of rhodium chelate **4**.



Scheme 3.

The synthesis of the asymmetric phosphino phosphinites **8**, **13**, and **15** was accomplished using the functionalised propane-1,3-diol **5** as the main building block according to Scheme 2. This was itself synthesised by the reaction of one hydroxy group of propane-1,3-diol with 3,4-dihydro-2*H*-pyran followed by protecting the second hydroxy group using tosyl chloride [15]. This unsymmetric protection permitted the regioselective synthesis of the phosphines **7** and **12** by the substitution of the tosyl groups by lithium phosphides and removal of the tetrahydro-2*H*-pyran protecting group. In the synthesis of phosphine **12** chloro - bis[3,5 - bis(trifluoromethyl)phenyl] - phosphine (**10a**) could not be directly converted to the corresponding lithium phosphide by the reaction with metallic lithium due to the electronic withdrawing effect of the trifluoromethyl groups. Therefore the chloro-phosphine **10a** was reduced to bis[3,5-bis(trifluoromethyl)phenyl]-phosphine (**11a**) by the reaction with lithium aluminium hydride (see Scheme 3) and subsequently converted to the corresponding lithium phosphide by butyl lithium. The final synthesis of the phosphinite substructures within the ligands **8**, **13** and **15** occurred by the reaction of the unprotected ligands **7** and **12** with pyridine and chlorodiphenylphosphine or compound **10a**, respectively. Due to the relative instability of the free ligands **8**, **13** and **15** no further purification steps were attempted. Attempts to recrystallize these ligands led to more contaminated products.

The ligands **3**, **8**, **13** and **15** were dissolved in tetrahydrofuran and treated with Rh(COD)acac followed by the dropwise addition of tetrafluoroboric acid [8]. The resulting rhodium complexes could then be precipitated by diethyl ether, giving brownish muddy solids. After removal of the solvent the residues were washed with diethyl ether several times. The rhodium chelates **9**, **14** and **16** started to crystallize during these wash procedures and this could be encouraged by scratching with a glass stick. Chelate **4** was not able to be obtained as a pure solid product just by washing with diethyl ether. After several wash steps the residue was dissolved in dichloromethane and filtered. THF was then carefully added to the clear solution and the chelate started to crystallize. All chelates were able to be recrystallized.

During hydrogenation experiments the catalysts containing ligands with one phosphinite group showed an unexpectedly rapid inactivation in solvents containing water (see Table 2). We have never observed this with the analogous chelates of carbohydrate-bisphosphinites. The assumption that hydrolysis of the less hindered *P-O* bond in the new complexes could be the reason for this inactivation prompted us to prepare the butane-1,4-diyl-bis(phosphine) ligands **20b**, **20c** and **20d** for similar unsymmetric seven-membered chelates **21b**, **21c** and **21d** without a *P-O* bond according to Scheme 3. For this purpose 4-hydroxybutyl-diphenylphosphine **17**

[16] in the borane protected form **18** was transferred to the diphosphines **20b**, **20c** and **20d**. The nucleophilic substitution was done by lithium phosphides obtained from the phosphines **11b**, **11c**, and the commercially available dicyclohexylphosphine. The purification was accomplished by a borane protection/deprotection process. Finally the rhodium chelates were prepared from the phosphines in the usual way [8].

2.4. Results of hydrogenation experiments

The results of the hydrogenation experiments with the rhodium(I) chelates of unsymmetric *P*,*P*′-ligands when compared to some symmetric catalysts were disappointing. The experimental error in the gas chromatographic estimation of the enantiomeric excess is particularly high in the racemate region and may reach ±2.5%ee as known from earlier error evaluation and can be deduced from the experiments with **AMe** and methyl 2-acetamidoacrylate (**aMe**) without any chiral additives (see Table 2). For the measurements modified with the chiral $C_{12/16}$-alkyl polyglycoside we chose the acid substrate **AH** because it displayed the highest relative enantioselectivity with catalyst **2** in the presence of this amphiphile (see Table 1). However, applying the achiral catalysts the enantioselectivity was lower than 2.5%ee and besides that the conversion time strongly increased. This may be caused by a hydrolysis of the *P*–*O* bond of the phosphinites even in the chelates by the action of water. We tried to improve the situation by applying 10% methanol to the solvent to increase the solubility of the substrate and the complexes, and chose 10 MPa hydrogen pressure to increase the reaction rate. The result was not much better, with the conversion not exceeding 20% in 20 h, which hindered a reliable %ee estimation. Since in these cases the amount of chiral amphiphile lay in the order of the hydrogenation product, substantial mistakes in the determination of the enantioselectivity are thinkable (selective association of one enantiomer). Indeed the reproducibility of the experiments was low with an error in the order of ±15%ee. This leds to doubts in any enantioselectivity enhancement.

To increase the complex stability we introduced the rhodium(I)-chelates **21b**, **21c** and **21d** containing unsymmetric butane-1,4-diyl-bis(phosphine) ligands. Indeed they showed no inactivation even in pure water and the hydrogenation could be completed in all cases within two hours. However, the enantioselectivity remained below 4%*ee* (*R*)-*N*-acetylphenylalanine (see Table 3).

3. Experimental

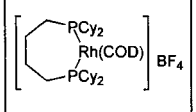
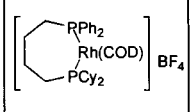
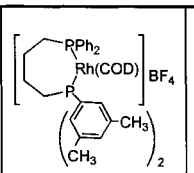
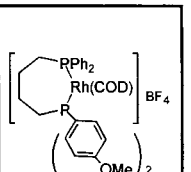
The alkyl polyglucosides [$C_{8/10}$-alkyl polyglycosid (GZ 1,5) APG 220 UP and $C_{12/16}$-alkyl polyglycosid (GZ 1,4) APG 600 UP] of the Henkel KGaA were freeze-dried at room temperature (r.t.) and extracted with *n*-hexane. The hydrogenations and gas chromatography of the products were conducted as described in Ref. [2a]. Acidic hydrogenation products were esterified before GC analysis. The gas chromatographic estimation of the enantioselectivity was controlled by HPLC. NMR spectra were recorded on a Bruker ARX 400; ^{1}H-NMR (400 MHz), ^{13}C-NMR (100 MHz), ^{31}P-NMR (162 MHz).

3.1. Preparation of compounds

3.1.1. *cis,cis*-Cycloocta-1,5-diene[phenyl 2,3-*O*-bis(diphenylphosphino)-β-D-glucopyranoside]rhodium(I) dodecylsulfate ([**1**(COD)]DS)

cis,cis-Cycloocta-1,5-diene[phenyl 2,3-*O*-bis(diphenylphosphino)-β-D-glucopyranoside]rhodium(I)tetrafluoroborate [8] ([**1**(COD)]BF_4, 920 mg, 1 mmol) and sodium

Table 3
No influence of the $C_{12/16}$-alkyl polyglycoside **a** (Henkel KGaA) on the selectivity in the hydrogenation with achiral rhodium(I)-chelates of unsymmetric 1,4-diphosphino-butane ligands [a]

	pre-catalyst →									
	amphiphile **a**				**21d**		**21b**		**21c**	
Substr.	↓	Lm:	t/2 min	% *ee*	t/2 min	% *ee*	t/2 min	% *ee*	t/2 min	% *ee*
AMe	-	MeOH	0.7	0.6 *S*						
aMe	-	10% MeOH in H_2O	4.6	0.6 *R*						
AH	+**a**	H_2O	15	1.3 *S*	21	0.9 *R*	15	2.0 *R*	9	3.6 *R*

[a] Standard conditions as in Table 2.

dodecylsulfate (287 mg, 1 mmol) were dissolved in 30 ml of methanol at 50°C while stirring. To the warm solution 150 ml of water were added slowly and the stirring continued over night. The yellow orange complex that separated from the nearly colourless solution on the flask walls, was washed twice with 10 ml water and dried under reduced pressure at 30°C. Yield: 0.781 g (71%); $C_{56}H_{71}O_{10}P_7RhS$ (1101.04) Calc.: C, 61.0; H, 6.5; P, 5.6; Rh, 9.4; S, 2.9; Anal. Found: C, 60.2; H, 6.1; P, 6.1; Rh, 9.8; S, 3.1%.

3.1.2. $[Rh(COD)(Ph_2POCH_2CH_2OPPh_2]BF_4$ (4)

A solution of abs. ethylene glycol (0.1 ml, 1.77 mmol), abs. pyridine (0.32 ml, 4.0 mmol) and abs. tetrahydrofuran (5 ml) was cooled under argon to −15°C and chlorodiphenyl phosphine (0.66 ml, 3.6 mmol) was added dropwise to the stirred solution. After stirring for 1 h at −15°C the precipitated pyridinium salt was removed by tube filtration and the filtrate was transferred to a precooled Schlenk vessel (−15°C) and the solvents were removed under reduced pressure. Simultaneously the temperature of the reaction mixture was kept as low as possible. The residue was dissolved in abs. tetrahydrofuran (3 ml) and treated with Rh(COD)acac (0.554 g, 1.77 mmol). This reaction mixture was allowed to warm up to r.t. and was then treated dropwise with tetrafluoroboric acid (0.195 ml, 50%). After stirring for 10 min diethyl ether (10 ml) was added and the product started to precipitate as a brownish muddy solid. The solvents were removed by tube filtration and the precipitate was washed several times with diethyl ether (2 × 5 ml). The solid product was dissolved in dichloromethane (5 ml, acid free) and the solution was filtered. THF was added to the surface of the clear solution and and by cooling of the mixture the product started to precipitate. Yield: 0.598 g (45.9%); ^{1}H-NMR (acetone-d_6): $\delta = 7.6–7.46$ (m, 10H, 2 Ph), 4.54–4.5 (m, 2H, HC=CH–CH_2), 2.96–2.82 (br, 2H, 2 CH_2), 2.52–2.35 (m, 4H, 4 HC=CH-CH_2); ^{13}C-NMR (acetone-d_6): $\delta = 132.3$, 132.0, 131.9, 129.2 (Ph), 105.1 (HC=CH–CH_2), 68.8 (O–CH_2), 30.2 (HC=CH–CH_2); ^{31}P-NMR (acetone-d_6): $\delta = 125.3$ (d, $J \approx 194.4$).

3.1.3. $TsO(CH_2)_3O–THP$ (5)

3,4-Dihydro-2*H*-pyran (4.5 g, 52 mmol) was added to a cooled solution of propane-1,3-diol (**4**) (10 g, 132 mmol) and toluene sulfonic acid (0.13 g) in abs. tetrahydrofuran (250 ml) in a dropwise manner. After stirring for 1 h at 0°C the reaction mixture was allowed to warm up to r.t. and was stirred for an additional hour before adding triethylamine (1.5 ml). The solvents were removed under reduced pressure and the residue was dissolved in a mixture of water (20 ml) and methanol (100 ml). After washing several times with hexane, the methanol was removed under reduced pressure. The remaining product was then extracted with diethyl ether (100 ml) from the aqueous phase, the organic phase was washed with brine several times, dried (sodium sulfate) and the solvent was removed under reduced pressure. The resulting residue was dissolved in abs. pyridine (5 ml) and dichloromethane (20 ml), the solution was treated with toluene sulfonyl chloride (3.0 g, in portions) and was stirred at r.t. for further 16 h. Then the reaction mixture was diluted with dichloromethane (40 ml), washed with hydrochloric acid (5%), aqueous bicarbonate solution and brine. After removing of the solvent under reduced pressure the final product **5** was purified by column chromatography giving a colourless oil; $R_f \approx 0.2$ (hexane/ethyl acetate 5:1, v/v).

3.1.4. $Ph_2P(CH_2)_3O–THP$ (6)

A stirred mixture of lithium (0.5 g) and tetrahydrofuran (25 ml) was treated dropwise with chlorodiphenyl phosphine (4.4 ml) at r.t. The first ten drops were added quite fast whereas the rest of the phosphine was not added before the solution started to get a red colour.

The red lithium diphenylphosphide solution was added dropwise to a stirred and ice cooled solution of tosylate **5** (3.0 g, 9.5 mmol) in abs. tetrahydrofuran (25 ml) until the red colour of the reaction mixture remained. The solution was then allowed to warm up to r.t. and more lithium diphenylphosphide solution was added until the red colour of the reaction mixture remained even at r.t. The solvent was then removed under reduced pressure and the residue was dissolved in dichloromethane (40 ml) and water (25 ml). After 16 h the organic phase was removed, dried (sodium sulfate) and the solvent was evaporated under reduced pressure. The final product was purified by column chromatography. Yield: 3.087 g (98%) **6**; $R_f \approx 0.5$ (hexane/ethyl acetate 8:1, v/v); ^{13}C-NMR ($CDCl_3$): $\delta = 137.8–127.4$ (2 Ph), 99.2 (O–CH–O), 68.4 (OCH_2), 62.8 (OCH_2), 31.2, 26.7, 25.9, 25.0, 20.1 (5 CH_2); ^{31}P-NMR ($CDCl_3$): $\delta = -15.6$ (s); $C_{20}H_{25}O_2P$ (328.39) Calc.: C, 73.2; H, 7.7; Anal. Found: C, 73.2; H, 7.6%.

3.1.5. $Ph_2P(CH_2)_3OH$ (7)

A solution of the diphenylphosphine **6** (1.91 g, 5.8 mmol) in abs. ethanol (20 ml) was treated with pyridinium *p*-toluene sulfonate (a few mg) and was slowly warmed up to 50°C. The reaction progress was followed by TLC. At the end of the reaction the solvent was removed under reduced pressure and the product was purified by column chromatography.

Yield: 1.11 g (78%) **7**; $R_f \approx$ (hexane/ethyl acetate 4:1, v/v); ^{1}H-NMR ($CDCl_3$): $\delta = 7.76–7.28$ (m, 10H, 2 Ph), 3.69 (2H, PCH_2), 2.14–2.1 (m, 2H, CH_2OH), 1.74–1.64 (m, 2H, CH_2); ^{13}C-NMR ($CDCl_3$): $\delta = 139.0–128.9$ (2 Ph), 63.8, 29.5, 24.7 (3 CH_2); ^{31}P-NMR ($CDCl_3$): $\delta = -15.7$ (s); $C_{15}H_{17}OP$ (244.27) Calc.: C, 73.8; H, 7.0; Anal. Found: C, 72.8; H, 6.9%.

*3.1.6. $Ph_2P(CH_2)_3OPPh_2$ (**8**)*

Chloro-diphenylphosphine (0.99 ml, 5.38 mmol) was added to a stirred and ice cooled solution of diphenylphosphine **7** (1.19 g, 4.89 mmol) and abs. pyridine (0.415 ml) in abs. tetrahydrofuran (15 ml). The reaction mixture was allowed to warm up to r.t. within 18 h and the precipitated pyridinium hydrochloride was removed by filtration. The salt was washed with abs. tetrahydrofuran (5 ml) and the combined filtrates were dried under reduced pressure.

Yield: 1.74 g (83%) **8**; ^{13}C-NMR ($CDCl_3$): $\delta = 142.6$–128.7 (4 Ph), 71.2, (OCH_2), 28.4 (CH_2), 24.8 (CH_2); ^{31}P-NMR ($CDCl_3$): $\delta = 113.2$ ($OP(Ph)_2$), -15.9 (H_2C–$P(Ph)_2$).

*3.1.7. $[Rh(COD)\{Ph_2P(CH_2)_3OPPh_2\}]BF_4$ (**9**)*

A stirred solution of propane **8** (0.8 g, 1.87 mmol) and Rh(COD)acac (0.579 g, 1.8 mmol) in abs. tetrahydrofuran (20 ml) was treated at r.t. with aqueous tetrafluoro-boric acid (0.233 ml, 50%). After stirring for 20 minutes the reaction mixture was diluted with abs. diethyl ether (20 ml) and the final product started to precipitate as a brownish muddy solid. The solvents were removed by tube filtration and the precipitate was washed several times with diethyl ether (3 × 10 ml). The solid product was dried under reduced pressure and was recrystallized from chloroform/hexane. Yield: 1.11 g (82%) **9**, red solid; ^{31}P-NMR ($CDCl_3$): $\delta = 134.5$ (dd, $J \approx 32.4$, $J \approx 162$, $OP(Ph)_2$), 9.45 (dd, $J \approx 40.5$, $J \approx 137.7$, H_2C–$P(Ph)_2$).

*3.1.8. $[3,5\text{-}(CF_3)_2C_6H_3]_2PCl$ (**10a**)*

Following a modified procedure of Casalnuovo et al. [17] a solution of $(NEt_2)PCl_2$ (13.3 g, 77 mmol) in ether (50 ml) was added slowly to a solution of 3,5-$(CF_3)_2C_6H_3MgBr$ [prepared from 49.8 g (0.17 mol) 3,5-bis(trifluoromethyl)-brombenzene and 4.5 g (0.18 mol) Mg] in ether (200 ml) at -50°C. The reaction mixture was warmed to r.t. and stirred 1 h, then cooled to 0°C and dry HCl was passed through the solution for 30 min. After removal of excess HCl in vacuo the resulting solids were filtered under argon atmosphere and the filtrate was concentrated to give an oil. High vacuum distillation gave **10a** as colourless oil. Yield: 20.9 g (55%); b.p. = 75–85/0.01 (Lit. 85–95/0.05 [18]); ^{31}P-NMR ($CDCl_3$): $\delta = 71.1$.

*3.1.9. $[3,5\text{-}Me_2C_6H_3]_2POH$ (**10b**)*

This compound was prepared from $(EtO)_2POH$ and 3,5-$Me_2C_6H_3MgBr$ (obtained from bromo-3,5-dimethylbenzene) by the method of Lorenz and Schrader [19]. The product crystallized upon storage. M.p. = 115–117°C; ^{1}H-NMR ($CDCl_3$): 2.33 (s, 6H), 7.17 (s, 2H), 7.30 (d, $J = 14.2$, 4H), 7.86 (d, $J = 540.1$, 1H); ^{13}C-NMR ($CDCl_3$): 21.2 (d, $J = 10$), 125.5, 128.6 (d, $J = 20$), 131.3 (d, $J = 100$), 134.7 (d, $J = 3$); ^{31}P-NMR ($CDCl_3$): 23.3.

*3.1.10. $(MeOC_6H_4)_2P(O)H$ (**10c**)*

This compound was prepared from $(EtO)_2POH$ and 4-$MeOC_6H_4MgBr$ (obtained from 4-bromoanisole) by the method of Lorenz and Schrader [19]. M.p. = 124–125°C; ^{1}H-NMR ($CDCl_3$): 3.71 (s, 6H), 6.92 (d, $J = 7$, 4H), 7.55 (dd, $J = 14.2$, $J = 7$, 4H), 7.94 (d, $J = 480$, 1H); ^{13}C-NMR ($CDCl_3$): 55.8, 114.7 (d, $J = 20$), 123.5 (d, $J = 110$), 133.0 (d, $J = 20$), 163.2 (d, $J = 10$); ^{31}P-NMR ($CDCl_3$): 20.9.

*3.1.11. $[3,5\text{-}(CF_3)_2C_6H_3]_2PH$ (**11a**)*

Following a modified procedure of Casey et al. [20] a solution of **10a** (7.70 g, 16 mmol) in ether (50 ml) was added slowly to a suspension of $LiAlH_4$ (0.59 g, 16 mmol) in ether (150 ml). After refluxing for 2 h, 0.6 ml of H_2O was added and the resulting slurry filtered of. The filtrate was concentrated in vacuo to give **11a** as white solid. Yield: 6.78 g (95%); m.p. = 67–68 °C (Lit. 69–71°C [20]); ^{1}H-NMR ($CDCl_3$): 5.65 (d, $J = 230$, 1H), 7.85 (m, 6H); ^{13}C-NMR ($CDCl_3$): 123.1 (q, $J = 270$), 123.8 (dd, $J = 4$, $J = 3$), 133.0 (qd, $J = 34$, $J = 6$), 134.1 (d, $J = 18$), 136.6 (d, $J = 16$); ^{31}P-NMR ($CDCl_3$): -40.1.

*3.1.12. $(3,5\text{-}Me_2C_6H_3)_2PH$ (**11b**)*

Following the procedure similar to that used for dibutylphosphine [21] a solution of **10b** (40.5 g, 0.16 mol) in ether (50 ml) was added slowly to a suspension of $LiAlH_4$ (6 g, 0.16 mmol) in ether (500 ml). The reaction mixture was refluxed for 2 h and hydrolyzed with 10% H_2SO_4. The organic layer was separated and the aqeous layer was extracted with ether and toluene. The combined organic layers were washed with water, dried over Na_2SO_4 and evaporated to give a brownish oil. High vacuum fractional distillation gave **11b** as a colourless oil. Yield: 24.1 g (64%); b.p. = 105–106/0.02 (Lit. 120–145/0.01 [22]); ^{1}H-NMR ($CDCl_3$): 2.26 (s, 6H), 5.11 (d, $J = 230$, 1H), 6.92 (s, 2H), 7.11 (d, $J = 8.3$, 4H); ^{13}C-NMR ($CDCl_3$): 21.7, 130.2, 131.7 (d, $J = 18$), 134.5 (d, $J = 11$), 138.0 (d, $J = 7$); ^{31}P-NMR ($CDCl_3$): -39.1.

*3.1.13. $(MeOC_6H_4)_2PH$ (**11c**)*

A solution of **11b** (10 g, 38.1 mmol) in THF (50 ml) was added slowly to a suspension of $LiAlH_4$ (2 g, 52.7 mmol) at 0–5°C. The resulting suspension was stirred over night at r.t. and 2 h under reflux. Then NaOH (7%, 3 ml) was added, the formed white precipitate was filtered (G4) and the solvent removed in vacuo to give a yellow solid. Distillation in vacuo afforded the pure product. Yield: 1.3 g (14%); b.p. = 150/0.02 (Lit. 145–148/0.2 [23]); ^{1}H-NMR ($CDCl_3$): 3.72 (s, 6H), 6.76 (d, $J = 8$, 4H), 7.28 (d, $J = 8$, 4H); ^{13}C-NMR ($CDCl_3$): 55.6, 114.6 (d, $J = 7$), 126.2 (d, $J = 7$) 135.9 (d, $J = 18$), 160.5; ^{31}P-NMR ($CDCl_3$): -44.3.

*3.1.14. [3,5-$(CF_3)_2C_6H_3$]$_2$P$(CH_2)_3$OH (**12**)*

Butyl lithium (5.75 ml, 2.5 M solution in diethyl ether, 14.4 mmol) was carefully added to a stirred and cooled (-78°C) solution of phosphine **11a** (6.8 g, 14.84 mmol) in abs. tetrahydrofuran (40 ml). The reaction mixture was warmed up to r.t. and was stirred for 30 min. Then the red solution obtained was carefully added to a stirred solution of tosylate **5** (4.52 g, 14.4 mmol) in abs. tetrahydrofuran (30 ml). After 14 days the reaction mixture was evaporated nearly to dryness and the residue was dissolved in dichloromethane (50 ml) and water (40 ml). After complete phase separation the organic phase was removed, dried (sodium sulfate) and evaporated to dryness under reduced pressure. The remaining residue was purified by flash chromatography and the product obtained was dissolved in methanol (50 ml). After adding pyridinium tosylate (a few mg) to the stirred methanol solution the reaction progress was followed by TLC. At the end of the reaction the solvent was removed under reduced pressure and the product was purified by column chromatography. Yield: 1.99 g (26.8%) **12**; $R_f \approx 0.31$ (hexane/ethyl acetate 5:1, v/v); ^{31}P-NMR ($CDCl_3$): $\delta = -13.0$.

*3.1.15. [3,5-$(CF_3)_2C_6H_3$]$_2$P$(CH_2)_3$OPPh_2 (**13**)*

Chloro-diphenylphosphine (0.71 ml, 3.85 mmol) was added dropwise to a stirred and ice cooled solution of phosphine **12** (1.99 g, 3.85 mmol) and pyridine (0.405 ml) in tetrahydrofuran (15 ml). The reaction mixture was stirred for one hour at 0°C. After stirring for further 4 h at r.t. the precipitated pyridinium hydrochloride was removed by filtration. The salt was washed with abs. tetrahydrofuran (5 ml) and the combined filtrates were dried under reduced pressure. The residue was finally dissolved in diethyl ether (15 ml), filtered and evaporated to dryness under reduced pressure. Yield: 2.65 g (98%) **13**.

*3.1.16. [Rh(COD){{3,5-$(CF_3)_2C_6H_3$}$_2$P$(CH_2)_3$-OPPh_2}]BF_4 (**14**)*

A stirred solution of propane **13** (2.58 g, 3.68 mmol) and Rh(COD)acac (1.142 g) in tetrahydrofuran (10 ml) was treated at r.t. with aqueous tetrafluoroboric acid (0.459 ml, 50%). After stirring for 20 min the reaction mixture was diluted with abs. diethyl ether (30 ml) and stored at 0°C for 12 h. The solid product obtained was filtered and recrystallized from tetrahydrofuran.

*3.1.17. Ph_2P$(CH_2)_3$OP[3,5-$(CF_3)_2C_6H_3$]$_2$ (**15**)*

Chloro - bis[3,5 - bis(trifluoromethyl) - phenyl] - phosphine **10a** (4.32 g, 8.78 mmol) was added dropwise to a stirred and ice cooled solution of the diphenylphosphino substituted propanol **7** (1.95 g, 7.98 mmol) and abs. pyridine (0.66 ml) in abs. tetrahydrofuran (15 ml). The reaction mixture was allowed to warm up to r.t. within 18 h and the precipitated pyridinium hydrochloride was removed by filtration. The salt was washed with abs. tetrahydrofuran (5 ml) and the combined filtrates were dried under reduced pressure. Yield: 1.97 g (35%) **15**; ^{31}P-NMR ($CDCl_3$): $\delta = 104.7$ ($OP(Ph)_2$), -16.1 (H_2C–$P(Ph)_2$).

*3.1.18. [Rh(COD){Ph_2P$(CH_2)_3$OP{3,5-$(CF_3)_2$-C_6H_3}$_2$}]BF_4 (**16**)*

A stirred solution of ligand **15** (1.9 g, 2.71 mmol) and Rh(COD)acac (0.84 g, 2.71 mmol) in abs. tetrahydrofuran (20 ml) was treated at r.t. with aqueous tetrafluoro boric acid (0.338 ml, 50%). After stirring for 20 min the reaction mixture was diluted with abs. diethyl ether (20 ml) and the final product started to precipitate as a brownish muddy solid. The solvents were removed by tube filtration and the precipitate was washed several times with diethyl ether (3×10 ml). The solid product was dried under reduced pressure and was recrystallized from dichloromethane/tetrahydrofuran. Yield: 1.27 g (47%) red solid **16**; ^{31}P-NMR ($CDCl_3$): $\delta = 131.15$ (dd, $J \approx 32.4$, $J \approx 178.2$), 9.95 (dd, $J \approx 32.4$, $J \approx 137.7$).

*3.1.19. Ph_2P(BH_3)-$(CH_2)_4$-OTs (**18**)*

To a solution of $Ph_2P(CH_2)_4OH$ (8.5 g, 32.9 mmol) (**17**) [16] in THF (30 ml) was added a solution of BH_3 (35 ml, 1 M) in THF at 0°C. The solvent was evaporated and the resulting solid was dissolved in CH_2Cl_2 (30 ml) and pyridin (9 ml). After addition of TsCl (5.7 g, 30 mmol) at 0°C in portions the resulting solution was stirred for 1 h at 0°C and stood at 5°C over night. After stirring for 30 min at r.t. the solution was neutralized (H_2SO_4, 5%) and washed with a solution of $NaHCO_3$ and with water. The aqueous solutions were extracted with CH_2Cl_2 and the combined organic fractions were dried and evaporated to give the crude product as a clear oil. Yield: 13 g (93%). Recrystallization from ethanol (200 ml) afforded **18** as a white solid (5.8 g, 41%); ^{1}H-NMR ($CDCl_3$): 1.54 (2H, m), 1.73 (2H, m), 2.15 (2H, m), 2.42 (3H, s), 3.99 (2H, t, $J = 6.3$ Hz), 7.30 (2H, d, $J = 7.9$ Hz), 7.46 (6H, m), 7.64 (4H, m), 7.73 (2H, d, $J = 8.4$ Hz); ^{13}C-NMR ($CDCl_3$): 19.3, 21.6, 25.0 (d, $J = 37.2$ Hz), 29.9 (d, $J = 13.4$), 69.5, 127.8, 128.9 (d, $J = 9.5$), 129.1 (d, $J = 53.4$ Hz), 129.9, 131.3 (d, $J = 2.9$ Hz), 132.1 (d, $J = 9.5$), 132.8, 144.9; ^{31}P-NMR ($CDCl_3$): 16.2 (d, $J = 63.2$ Hz).

*3.1.20. Ph_2P(BH_3)–$(CH_2)_4$–P$(BH_3)R_2$ (**19b**, **19c** and **19d**)*

A solution of BuLi (8.8 ml, 1.9 M, 16.8 mmol) in THF was added at 0°C to HPR_2 (16.8 mmol) in THF (40 ml). The resulting deep red solution was stirred for 1 h at 0°C and 20 min without cooling. The resulting solution of $LiPR_2$ was added at 0°C to $Ph_2P(BH_3)$–$(CH_2)_4$–OTs (**18**) (6.5 g, 15.25 mmol) in THF (40 ml) and stirring was continued for 1 h at 0°C and the solution allowed to stand at 5°C over night. After addition of BH_3 or

$BH_3{\cdot}SMe_2$ (1 M or 10 M, 36.6 mmol) the main part of the solvent was evaporated and the residue hydrolyzed with a solution of NH_4Cl and diluted with CH_2Cl_2. The organic phase was washed with brine and water, dried and evaporated to give the crude product.

*3.1.20.1. $Ph_2P(BH_3)$–$(CH_2)_4$–$P(BH_3)(3,5\text{-}Me_2C_6H_3)_2$ (**19b**).* Yield (crude): 6.7 g. The crude product was boiled with ethanol (200 ml) for extraction. The filtrate was cooled to r.t. affording the pure product **19b**. Yield: 1.4 g (12%); ^{1}H-NMR ($CDCl_3$): 0.5–1.4 (6H, br), 1.58 (4H, m), 2.15 (4H, m), 2.31 (12H), 7.08 (2H), 7.21 (4H, m), 7.43 (6H, m), 7.63 (4H, m); ^{13}C-NMR ($CDCl_3$): 21.3, 24.7 (d, $J = 15.3$), 25.4 (dd, $J = 37.2$, 10.5), 128.8 (d, $J = 9.5$), 129.1 (d, $J = 33.4$), 129.6 (d, $J = 9.5$), 131.2 (d, $J = 2.9$), 132.1 (d, $J = 8.6$), 133.0 (d, $J = 2.0$), 138.4 (d, $J = 10.5$); ^{31}P-NMR ($CDCl_3$): 14.9 (br), 15.8 (br).

*3.1.20.2. $Ph_2P(BH_3)$–$(CH_2)_4$–$P(BH_3)(4\text{-}C_6H_4OCH_3)_2$ (**19c**).* Yield (crude): 6.6 g (84%). The crude product **19c** was used without purification. ^{31}P-NMR ($CDCl_3$): 12.9 (br), 16.1 (br).

*3.1.20.3. $Ph_2P(BH_3)$-$(CH_2)_4$-$P(BH_3)Cy_2$ (**19d**).* The crude product was extracted with hot ethanol (500 ml). The filtrate was cooled to 5°C giving **19d** as a white solid. Yield: 1.5 g (21%); ^{1}H-NMR ($CDCl_3$): 1.22 (10H, m), 1.48–1.82 (18H, m), 2.23 (2H, m), 7.41–7.51 (6H, m), 7.63–7.70 (4H, m); ^{13}C-NMR ($CDCl_3$): 19.5 (d, $J = 31.5$), 25.6 (d, $J = 13.4$), 25.7 (d, $J = 18.1$), 26.0 (d, 4.8), 26.4, 27.1 (d, $J = 1.9$), 27.2 (d, $J = 1.9$), 27.3, 32.1 (d, $J = 32.4$), 129.3 (d, $J = 9.5$), 129.8 (d, $J = 55.3$), 131.7 (d, $J = 2.9$), 132.5 (d, $J = 8.6$); ^{31}P-NMR ($CDCl_3$): 16.0 (d, $J = 55.5$), 25.0 (d, $J = 66.6$).

*3.1.21. Ph_2P–$(CH_2)_4$–PR_2 (**20b**, **20c** and **20d**)*

To a cool solution (−10°C) of the phosphinoborane $Ph_2P(BH_3)$-$(CH_2)_4$-$P(BH_3)R_2$ (**19**) (2.15 mmol) in CH_2Cl_2 (25 ml) was added $HBF_4{\cdot}OEt_2$ (3 ml, 7.2 M, 21.5 mmol). The resulting solution was stirred over night at r.t. Then ether was added until the solution became turbid. The mixture was washed twice with a solution of $NaHCO_3$. The aqueous solutions were extracted with ether and the combined organic fractions were washed with water and brine. The etheric solution was dried and evaporated to give a slightly yellow oil, which crystallized after a long time.

*3.1.21.1. Ph_2P–$(CH_2)_4$–$P(3,5\text{-}Me_2C_6H_3)_2$ (**20b**).* Yield: 1.0 g (96%); ^{1}H-NMR ($CDCl_3$): 1.47 (4H, m), 1.93 (4H, m), 2.20 (12H), 6.86 (2H, m), 6.92 (2H, m), 6.94 (2H, m), 7.23 (6H, m), 7.30 (4H, m); ^{13}C-NMR ($CDCl_3$): 20.4, 26.6 (m), 127.3 (d, $J = 13.4$), 127.4, 129.2, 129.4 (d, $J = 13.4$), 131.7 (d, $J = 18.1$), 136.7 (d, $J = 6.7$), 137.8 (d, $J = 13.4$); ^{31}P-NMR ($CDCl_3$): −16.0, −15.8.

*3.1.21.2. Ph_2P-$(CH_2)_4$-$P(4\text{-}C_6H_4OCH_3)_2$ (**20c**).* Yield: 0.55 g (53%); ^{1}H-NMR ($CDCl_3$): 1.53 (br), 1.95 (br), 2.01 (br), 3.77, 6.85 (m), 7.28–7.34, 7.37–7.40; ^{13}C-NMR ($CDCl_3$): 28.8 (d, $J = 37.2$), 28.1 (d, $J = 12.4$), 28.7 (d, $J = 9.5$), 55.6, 114.5 (d, $J = 6.7$), 128.7 (d, $J = 13.4$), 128.8, 133.1 (d, $J = 18.1$), 134.4 (d, $J = 20.0$), 139.2 (d, $J = 13.4$), 160.5; ^{31}P-NMR ($CDCl_3$): −19.2, −15.7.

*3.1.21.3. Ph_2P–$(CH_2)_4$–PCy_2 (**20d**).* Yield: 1.1 g (99%); ^{1}H-NMR ($CDCl_3$): 1.0–1.2, 1.27 (br), 1.36–1.50, 1.60–1.70, 1.98 (m), 7.22–7.26, 7.31–7.36; ^{13}C-NMR ($CDCl_3$): 20.0 (d, $J = 16.2$), 25.5, 26.3, 26.3 (d, $J = 17.2$), 26.8 (d, $J = 11.4$), 27.0 (dd, $J = 16.2$, 12.4), 28.0 (d, $J = 7.6$), 29.1 (dd, $J = 18.6$, 11.9), 29.3 (d, $J = 14.3$), 32.3 (d, $J = 12.4$), 127.4 (d, $J = 11.4$), 127.4, 131.7 (d, $J = 18.1$), 137.9 (d, $J = 13.4$); ^{31}P-NMR ($CDCl_3$): −15.9, −3.5.

*3.1.22. $[Rh(P–P')(COD)]BF_4$ (**21b**, **21c**, **21d** and $[Rh(Cy_2P–(CH_2)_4–PCy_2)(COD)]BF_4$)*

The complexes were prepared analogously to compound **9** from Rh(COD)acac, the diphosphines P–P' and HBF_4 as previously reported.

*3.1.22.1. $[Rh(Ph_2P–(CH_2)_4–P(3,5\text{-}Me_2C_6H_3)_2(COD)]BF_4$ (**21b**).* Yield: 73%; ^{1}H-NMR ($CDCl_3$): 1.63 (m), 2.14 (m), 2.30, 4.40 (d, $J = 32.7$), 7.10 (br), 7.13 (br), 7.45–7.55; ^{13}C-NMR ($CDCl_3$): 21.9, 25.1 (d, $J = 16.2$), 30.9 (d, $J = 16.2$), 100.3 (dt, $J = 59.4$, 8.3), 129.7 (d, $J = 9.5$), 131.2 (d, $J = 9.5$), 131.8, 132.7 (d, $J = 15.3$), 133.1 (d, $J = 16.2$), 133.4, 133.5, 139.3 (d, $J = 9.5$); ^{31}P-NMR ($CDCl_3$): 23.5 (dd, $J = 143.4$, 38.9), 24.4 (dd, 144.6, 38.9).

*3.1.22.2. $[Rh(Ph_2P–(CH_2)_4–P(4\text{-}C_6H_4OCH_3)_2)(COD)]BF_4$ (**21c**).* Yield: 63%; ^{1}H-NMR ($CDCl_3$): 1.89 (d, $J = 21.6$), 2.10 (m), 2.45 (br), 2.62 (br), 2.73, 3.99 (m), 4.16, 4.70 (d, $J = 21.2$), 7.31–7.36, 7.75–7.91; ^{13}C-NMR ($CDCl_3$): 25.1, 26.0, 30.8, 31.8 (d, $J = 25.2$), 32.4 (d, $J = 24.8$), 56.0, 68.4, 100.6 (dt, $J = 46.7$, 7.6), 115.4 (d, $J = 10.5$), 123.4 (d, $J = 46.7$), 129.7 (d, $J = 9.5$), 131.8, 133.1 (d, $J = 42.0$), 133.6 (d, $J = 10.5$), 135.1 (d, $J = 11.4$), 162.3; ^{31}P-NMR ($CDCl_3$): 22.1 (dd, $J = 142.9$, 40.2), 25.1 (dd, $J = 145.0$, 39.5).

*3.1.22.3. $[Rh(Ph_2P–(CH_2)_4–PCy_2)(COD)]BF_4$ (**21d**).* Yield: 56%; ^{1}H-NMR ($CDCl_3$): 1.33 (br), 1.48 (br), 1.78 (m), 1.70–1.90, 2.01 (br), 2.27 (br), 2.24 (br), 2.50 (br), 3.67 (m), 3.95 (br), 5.03 (br), 7.5 (m), 7.6 (m); ^{13}C-NMR ($CDCl_3$): 13.9 (d, $J = 25.7$), 14.3, 21.5 (dd, $J = 7.6$, 2.9), 23.6, 24.6, 25.2, 25.9 (d, $J = 8.6$), 26.4 (d, $J = 12.4$), 26.6 (d, $J = 24.8$), 27.9 (d, $J = 2.9$), 29.1, 30.2 (d, $J = 21.0$), 36.3 (d, $J = 21.0$), 64.8, 67.0, 96.0 (dt, $J = 137.3$, 8.1), 128.2 (d, $J = 9.5$), 130.3 (d, $J = 1.9$), 130.6 (d, $J = 42.0$), 131.9 (d, $J = 10.5$); ^{31}P-NMR

($CDCl_3$): 12.5 (dd, $J = 145.8$, 34.8), 39.9 (dd, $J = 139.3$, 34.0).

3.1.23. [Rh(Cy_2P–$(CH_2)_4$–PCy_2)(COD)]BF_4

Yield: 73%; ^{1}H-NMR ($CDCl_3$): 1.2–1.4, 1.68–1.88, 2.11 (br), 2.29 (br), 3.67 (m), 4.81; ^{13}C-NMR ($CDCl_3$): 17.8 (t, $J = 11.0$), 24.3, 26.0, 26.6, 27.5 (t, $J = 4.3$), 28.1 (t, $J = 5.7$), 29.5, 31.3, 32.0, 38.3 (t, $J = 10.0$), 68.4, 93.2 (m); ^{31}P-NMR ($CDCl_3$): 24.5 (d, $J = 140.1$).

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