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Asymmetric Hydrogenation - Influence of the Structure of Carbohydrate Derived Catalysts on the Relative Enantioselectivity $Q_{H/Me}$ Regarding Acid and Ester Substrates and its Inversion - Selectivity Increase in Water by Amphiphiles

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Abstract: 4,6-*O*-Benzylidene protected 2,3-bis(*O*-diphenylphosphino)-D-glycopyranoside rhodium(I) chelate precatalysts **1-4 e,f** showed for the hydrogenation of methyl (*Z*)-2-*N*-acylamidoacrylates **6-8** a stepwise decrease of the enantioselectivity with increasing number of axially oriented hexopyranoside substituents. The decrease is even stronger for the analogous *substrate acids* **6h-8h** resulting in an unusual low *relative enantioselectivity* $Q = q_H / q_{Me}$ of 0.3 for the precatalysts **4e** and **4f**. Deprotected, 4,6-OH-group bearing catalysts **1-4 g,h** generally show smaller differences of %*ee* in methanol or benzene, however, not in water. Under addition of amphiphiles **a** in comparison with blanks **b** the relative enantioselectivity $Q = q_a / q_b$ clearly increases for both groups of catalysts - in most cases to Q-values between 3 up to 8 - independent of a neutral or ionic nature of the amphiphile.

INTRODUCTION

D-Hexopyranoside-2,3-*O*-bis(diphenylphosphinites) have been used as chiral ligands to form seven-membered ring chelates very useful as catalysts for asymmetric reactions.[2] In particular, rhodium(I)-complexes are well investigated in asymmetric hydrogenation of 2-*N*-acyl-dehydroamino acid derivatives[2a,3] especially for the production of L-Dopa under application of phenyl 4,6-*O*-benzylidene-2,3-*O*-bis(diphenylphosphino)-β-D-glucopyranoside (Ph-β-glup, **1a**, Scheme 1).[4] Rajan-Babu et al. found an interesting electronic effect of ligand P-aryl groups: electon donating substituents in the *meta*- or *para*-position increase the enantioselectivity of the hydrogenation products.[3e]

We could state by *in situ* experiments that rhodium(I) chelates of 4,6-*O*-benzylidene-2,3-bis(*O*-diphenylphosphino) glycopyranosides with increasing number and bulkyness of *axially* oriented substituents on the hexopyranoside ring show a decrease of enantioselectivity in asymmetric hydrogenation of (*Z*)-2-*N*-acyl-dehydroamino acid esters.[2a]

Besides that we succeeded in preparation of two deprotected D-glucopyranoside-2,3-*O*-bis(diphenylphosphinite) rhodium(I) chelates carrying free hydroxy groups in 4,6-position of the hexoside: the phenyl-β-[5] as well as the methyl-α-[6a] derivative. These turned out to be very useful catalysts for measurements in water.[6] Addition of substoichiometric amounts of amphiphiles allowed an impressive enhancement of the hydrogenation rate as well as the enantioselectivity (even compared with blanks estimated in methanol as solvent).

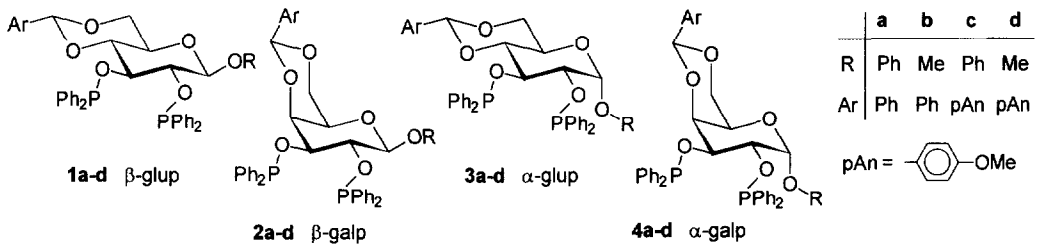
It was the target of this work:

- to prepare a series of benzylidene protected carbohydrate-bis(phosphinite) rhodium(I) chelates **1e,f - 4e,f** *in substance* (Scheme 2) as well as a series of analogous deprotected, hydroxy group carrying catalyst precursors **1g,h - 4g,h** (Scheme 3,) to prove them in asymmetric hydrogenation on a wide range of substrates and to compare them with single results obtained earlier by *in situ* measurements.
- to verify the rule of decreasing enantioselectivity found with an increasing number of *axially* oriented groups as hexopyranoside substituents deduced from *in situ* experiments also for the complexes prepared in substance, and to look for the validity of this rule in other solvents than in methanol and especially for the hydroxy group carrying catalysts thought to be conformationally more flexible than the protected analogous catalysts fixed by their anellated dioxane ring.
- to investigate all 16 precatalysts in water (11 of them are new species) and to extend the knowledge regarding the concept of Oehme *et al.*[7] about the influence of self-organizing amphiphiles on the enantioselectivity.

RESULTS AND DISCUSSION

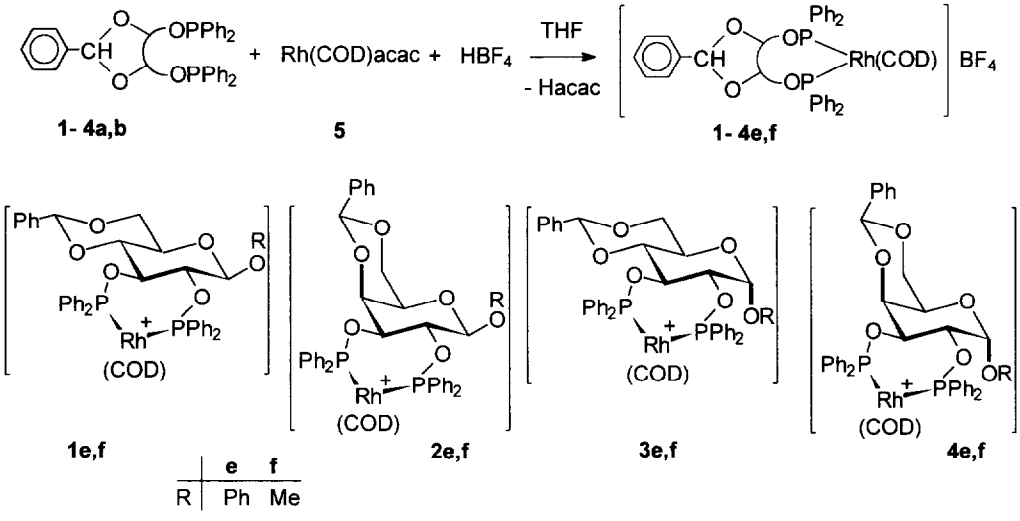
1. Preparative results

The synthesis of the 4,6-*O*-arylidene-2,3-bis(*O*-diphenylphosphino)-D-glycopyranosides**1-4a,b,c,d** (Scheme 1) followed in principle known methods[2a,3d,4a] and was improved by using tetrahydrofuran as solvent. Special attention has been devoted for the preparation of 4,6-*O*-*para*-anisylidene derivatives **1-4c,d** (Ar = *p*An = *para*-anisyl) which we have chosen for the synthesis of the deprotected, hydroxy group carrying precatalysts taking advantage of their higher susceptibility to solvolysis.[6a] The 4,6-*O*-*para*-anisylidene-glycopyranosides as precursors were synthesized analogously to the method of Patroni using *para*-methoxybenzylidene-dimethyl acetal;[8] the examples with phenyl as aglycon (R = Ph) are new compounds. In this way all 16 4,6-*O*-arylidene-2,3-bis(*O*-diphenylphosphino)-D-glycopyranosides **1a-d** to **4a-d** could be obtained in an analytically pure state by recrystallization from a mixture of triethylamine/toluene (30:70 v:v) and from toluene.



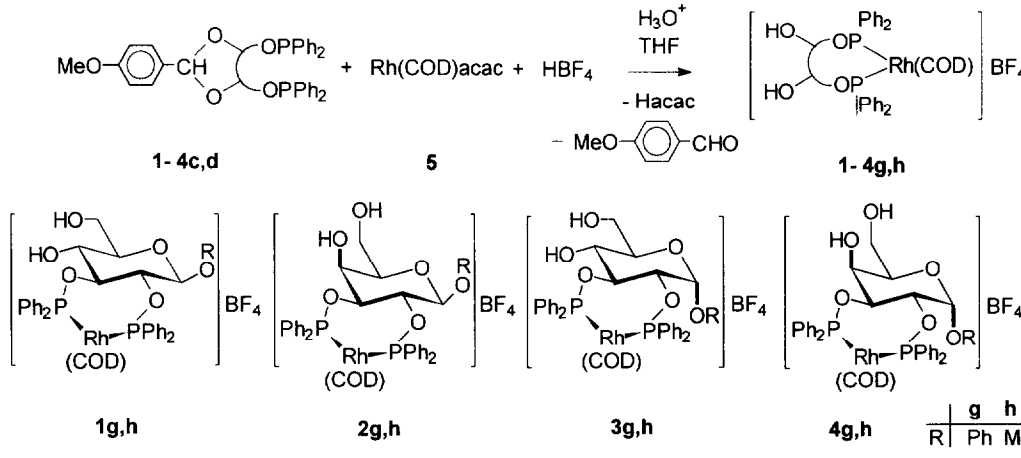
Scheme 1. 4,6-*O*-Arylidene-2,3-bis(*O*-diphenylphosphino)-D-glycopyranosides **1-4a,b,c,d**

The best way to prepare the benzylidene protected cationic chelates **1-4e,f** appeared to be the reaction of the bisphophinites with rhodium(I)-cyclooctadiene acetylacetonate **5** at ambient temperature using stoichiometric amounts of tetrafluoroboric acid (Scheme 2). After precipitation by diethyl ether the pure precatalysts have been obtained[5] in most cases of higher quality than those obtained by treatment with the sparingly soluble rhodium(I)-bis(cyclooctadiene) tetrafluoroborate.



Scheme 2. Preparation of the benzylidene protected cationic chelates **1-4e,f** : [Rhodium {4,6-*O*-benzylidene-2,3-bis(*O*-diphenylphosphino)-D-glycopyranoside}(cyclooctadiene)] tetrafluoroborates

All the deprotected hydroxy group carrying catalysts **1-4g,h** of Scheme 3 were synthesized in a similar way in acceptable yield by reaction at 65 °C with an excess of the tetrafluoroboric acid.

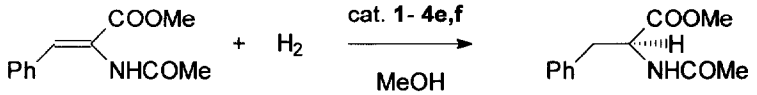


Scheme 3. [Rhodium {2,3-bis(*O*-diphenylphosphino)-D-glycopyranoside}(cyclooctadiene)] tetrafluoroborates

2. Hydrogenation using the 4,6-*O*-benzylidene protected precatalysts 1-4e,f

Comparison of the 4,6-*O*-benzylidene protected precatalysts **1-4e,f** for the hydrogenation of methyl (*Z*)-2-*N*-acetamido-cinnamate **6** in methanol showed the same tendency of decreasing enantioselectivity with increasing number of axially[9] oriented hexopyranoside substituents as found by measurements *in situ* (Table 1). This was not evidently without proof because we stated formerly in some cases an unexplained finding of higher enantioselectivities for experiments *in situ* which also now was found for both phenyl galactopyranoside derivatives **2e** and **4e**. The differences are not very high but beyond the experimental error, which we have proved to be distinctly less than ± 2 %*ee* in the region higher than 50 %*ee*.[10]

Table 1. Comparison of the benzylidene protected precatalysts **1-4e,f** in the hydrogenation of methyl (*Z*)-2-*N*-acetamido-cinnamate **6** with former *in situ* experiments[2a]



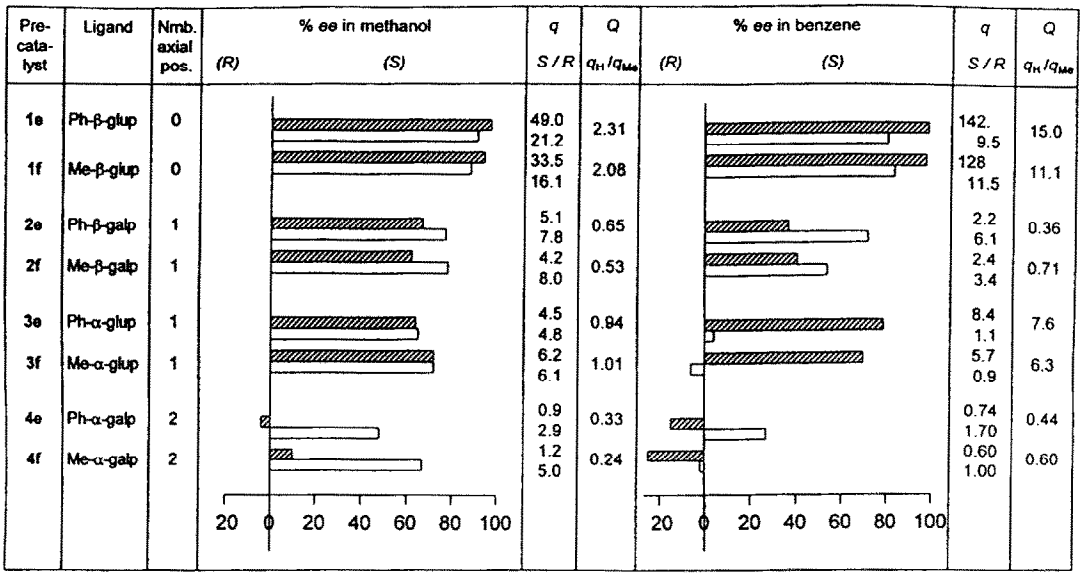
6 **9**

Precatalyst	Ligand	Number of axial substituents on hexopyranosides	%*ee* (*S*)-**9** precatalyst *in situ* generated	%*ee* (*S*)-**9** precatalyst added *in substance*
1e	Ph-β-glup	0	91	91
1f	Me-β-glup	0	89	88
2e	Ph-β-galp	1	**83**	**77**
2f	Me-β-galp	1	77	78
3e	Ph-α-glup	1	63	65
3f	Me-α-glup	1	73	72
4e	Ph-α-galp	2	**59**	**48**
4f	Me-α-galp	2	66	67

Conditions: Hydrogenation of 1 mmol substrate and 0.01 mmol precatalyst in 15 ml solvent under normal pressure at 25 °C.

The trend to a decrease of the enantioselectivity with increase of axial hexopyranoside substituents has been proven to be more marked for analogous hydrogenations of (*Z*)-2-*N*-acetamido-cinnamic acid **6h** and especially for the galactopyranoside derived precatalysts **2e,f** and **4e,f** (Table 2). This tendency is pronounced in benzene as solvent where both α-D-galacto catalysts **4e** and **4f** even led to an excess of the enantiomeric (*R*)-product up to 25 %*ee*.

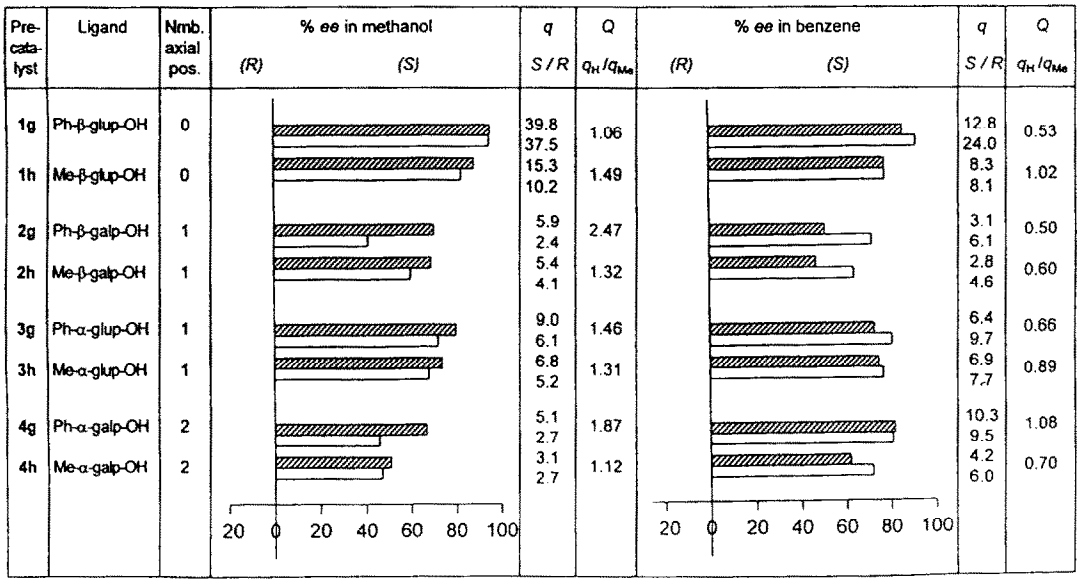
Table 2. Hydrogenation of *(Z)*-2-*N*-acetamido-cinnamic acid **6h** ▨ and its methyl ester **6** ▭ by the benzylidene protected catalyst type



Pre-catalyst	Ligand	Nmb. axial pos.	% *ee* in methanol (R)	% *ee* in methanol (S)	*q* S/R	*Q* q_H/q_{Me}	% *ee* in benzene (R)	% *ee* in benzene (S)	*q* S/R	*Q* q_H/q_{Me}
1e	Ph-β-glup	0			49.0	2.31			142.	15.0
					21.2				9.5	
1f	Me-β-glup	0			33.5	2.08			128	11.1
					16.1				11.5	
2e	Ph-β-galp	1			5.1	0.65			2.2	0.36
					7.8				6.1	
2f	Me-β-galp	1			4.2	0.53			2.4	0.71
					8.0				3.4	
3e	Ph-α-glup	1			4.5	0.94			8.4	7.6
					4.8				1.1	
3f	Me-α-glup	1			6.2	1.01			5.7	6.3
					6.1				0.9	
4e	Ph-α-galp	2			0.9	0.33			0.74	0.44
					2.9				1.70	
4f	Me-α-galp	2			1.2	0.24			0.60	0.60
					5.0				1.00	

Conditions see Table 1

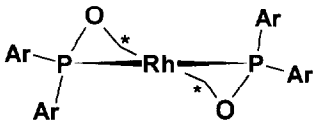
Table 3. Hydrogenation of *(Z)*-2-*N*-acetamido-cinnamic acid **6h** ▨ and its ester **6** ▭ by the deprotected catalyst type carrying OH groups



Pre-catalyst	Ligand	Nmb. axial pos.	% *ee* in methanol (R)	% *ee* in methanol (S)	*q* S/R	*Q* q_H/q_{Me}	% *ee* in benzene (R)	% *ee* in benzene (S)	*q* S/R	*Q* q_H/q_{Me}
1g	Ph-β-glup-OH	0			39.8	1.06			12.8	0.53
					37.5				24.0	
1h	Me-β-glup-OH	0			15.3	1.49			8.3	1.02
					10.2				8.1	
2g	Ph-β-galp-OH	1			5.9	2.47			3.1	0.50
					2.4				6.1	
2h	Me-β-galp-OH	1			5.4	1.32			2.8	0.60
					4.1				4.6	
3g	Ph-α-glup-OH	1			9.0	1.46			6.4	0.66
					6.1				9.7	
3h	Me-α-glup-OH	1			6.8	1.31			6.9	0.89
					5.2				7.7	
4g	Ph-α-galp-OH	2			5.1	1.87			10.3	1.08
					2.7				9.5	
4h	Me-α-galp-OH	2			3.1	1.12			4.2	0.70
					2.7				6.0	

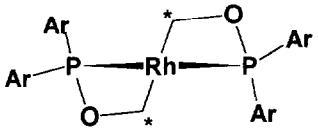
Conditions see Table 1

It is not easy to give a convincing explanation for the pronounced dependence of the enantioselectivity of the investigated catalysts on small changes in their structure and the applied solvent. Regarding the C_1-symmetry of the applied chiral ligands with two distinguishable phosphorus atoms, the optical induction will be determined by the concentration and interconversion rates of four (two *major* and two *minor* species) diastereomeric catalyst substrate complexes and their different reaction rates with hydrogen. However, we received by evaluation of NMR and CD spectra an important indication for a high solvent sensitivity of the seven-membered chelate ring conformation. It was possible to produce an enantiomorphic orientation of the phosphorus phenyl groups already for the cyclooctadiene containing precatalysts only by replacement of the solvent methanol by benzene.[11] This gives a hint for the validity of the model developed by Knowles,[12] Pavlov et al.,[13] and Seebach et al.[14] indicating the importance of the enantiomorphic arrangement of the alternating pseudoaxial-pseudoequatorial orientation of the P-aryl groups in the chelate rings for the ratio and/or the reactivity of the diastereomeric catalyst-substrate complexes. This orientation should be considerably changed by switching the seven-membered chelate ring conformation „twisted chair" to „twisted boat" as the two extrema



λ-twist chair
responsible for the formation of
(*S*)-amino acids

proved for precatalyst **1e**[9] and **3f**[11]
in $CDCl_3$ by NMR



δ-twist boat
responsible for the formation of
(*R*)-amino acids
a similar conformation was found for precatalyst
1g in $CDCl_3$ and **3f** in benzene-d_6 by NMR,[11]
for **1g** by X-ray structure[15]

Scheme 4. Extreme conformations of seven-membered ring chelates of the same configuration (at least in the shown part of the backbone carrying C*-O-P-Rh-P-O-C*) but with inverse (enantiomorph) arrangement of the P-aryl groups.

depicted in Scheme 4. The kind of precatalyst conformation, of course, does not indicate the extent of the enantioselectivity induction, which is determined in the step of the oxidative addition of hydrogen to the catalyst/substrate complex already having lost its diene. Nevertheless, it gives a clear idea of the ease of conformational rearrangement of such seven-membered ring chelates leading to enantiomorphic orientation of the P-aryl groups caused by small structural changes of the catalyst or the action of solvents.

The expression of enantioselectivities by the „enantiomeric ratio" $q = S / R$ is highly recommended,[16] (see also Seebach et al.[17] and Kagan[18]) particularly for comparison of two experiments with different catalysts, substrates, solvents or other modifiers. By formation of the quotient $Q = q_{varied} / q_{standard}$ which we called „relative enantioselectivity" we got an expression of the multiple of the enantiomeric ratio found by the

investigation of a variable. Recently we were able to show that such a Q-value concerning pairs of substrate acids and their related methyl esters ($Q_{H/Me} = q_H/q_{Me}$) may be constant for a catalyst independent of the rank of the substrate pairs in the scale of enantioselectivity. However, the structure of the catalysts ligand strongly influences the level of this constant $Q_{H/Me}$ for which values were given between 1 and 5.[19]

A look on the $Q_{H/Me}$-values of Table 2 indicates now a larger scope for Q from 0.2 to 15 and consolidates the observation on Diop derivatives[20] that a little change in the ligand structure of catalysts may lead to an inversion in the enantioselectivity rank of substrate acids versus esters leading to relative enantioselectivities smaller than one ($Q_{H/Me} < 1$). Surprising connections between Q and the ligand type deserve attention:

- Pairs of catalysts with equal carbohydrate configuration show similar Q-values that means the nature of the aglycon is of little influence - despite some obvious differences of single enantioselectivities as for instance between α-D-phenyl- and -methyl-galactopyranoside catalysts from **4e** and **4f**. It seems justifiable to form average values $\overline{Q}_{H/Me}$ for phenyl- and methyl-glycoside derived catalysts of the same configuration.
- An increasing number of axial pyranoside substituents leads to distinct decrease of such average $\overline{Q}_{H/Me}$-values for phenyl- and methyl-substituted catalysts:
  in MeOH: β-glup (2.2±0.2) > α-glup (1.0±0.1) > β-galp (0.59±0.08) > α-galp (0.29±0.06),
  in benzene: (13.1 ± 2.8) (7.0 ± 0.9) (0.54 ± 0.25) (0.52 ± 0.11).
  That indicates that the enantioselectivity of substrate acids is much more influenced by the ligand configuration than that of the methyl esters. We think that the special ability of the substrate acids to form hydrogen bonds may account for an enlargement in change of the ratios and reactivities of the catalyst-substrate complexes.
- The $Q_{H/Me}$-values for α-D-glucopyranoside generally exceed those for β-D-galactopyranoside derivatives despite the fact that both possess only one axially oriented substituent. This is especially valid in benzene as solvent in which, however, α-D-glycopyranoside derivatives generally give unusually low enantioselectivity for ester substrates.

In view of the surprising independence of the relative enantioselectivity $Q_{H/Me}$ from the nature of aglycon - phenyl or methyl - for all catalysts it seemed desirable to prove the constancy of the $Q_{H/Me}$-values also regarding other acid/ester substrate pairs as 2-*N*-acetamidoacrylic acid **7h** and its methyl ester **7** as well as the pair *(Z)*-2-*N*-benzamido-cinnamic acid **8h** and its methyl ester **8**. The result can be seen in Figure 1 and confirms the view of $Q_{H/Me}$ as being constant for a given catalyst structure. However, particularly both β-galactopyranoside derived species show a distinct increase from 0.41 ± 0.01 (**7h/7**) over 0.59 ± 0.08 (**6h/6**) to 1.05 ± 0.06 (**8h/8**) as can be taken in detail from Table 4. Nevertheless, the tendency of strong decrease of the relative enantioselectivity in the order β-glup > α-glup > β-galp > α-galp as deduced from Table 2 is valid

for all substrate pairs. Watching Figure 1 from the left- to the right-hand side indicates very impressively the change of ranking for the acid substrates regarding their enantioselectivity compared with that of the affiliated methyl esters which shows less susceptibility of the enantiomeric ratio to variation of the ligand structure.

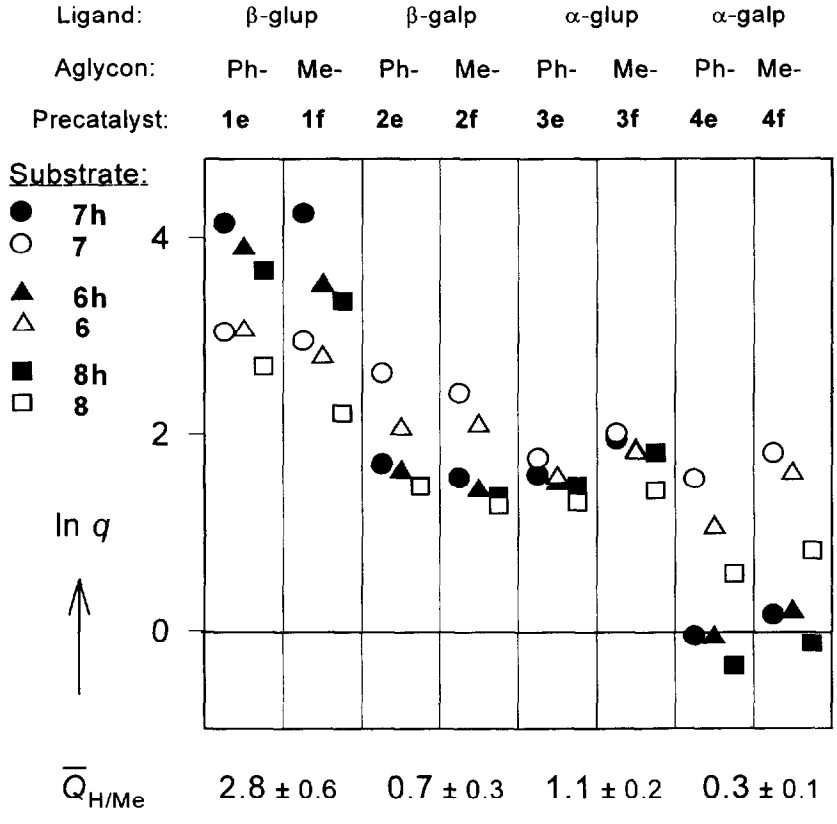


Figure 1. Hydrogenation in methanol, comparison of $\ln q$ obtained with the series of benzylidene protected precatalysts **1-4e,f** (enantiomeric ratio: $q = S/R$).

3. Hydrogenation using the deprotected precatalysts 1-4g,h carrying two hydroxy groups

This type without a stiffening anellated dioxane ring in the backbone shows much less movement of the enantioselectivity by structure changes of the catalysts (see Table 3). In methanol the decrease of enantiomeric excess with an increasing number of axially oriented substituents is still detectable but for the acid substrates the effect is distinctly less marked than with the protected catalysts. It becomes doubtful in benzene, in which β-galactopyranoside derived catalysts lead to lower induction than the α-anomers.

The relative enantioselectivities $Q_{H/Me}$ stay within closer limits (0.5 - 2.5) than for the protected catalysts (0.2 - 15). A remarkable small but distinct trend for all OH-group carrying catalysts is that the enantioselectivities in methanol for the acid substrate **6h** exceed those of the ester **6** ($Q_{H/Me} > 1$) but are inferior to them in benzene in nearly all cases ($Q_{H/Me} \leq 1$).

Table 4. Relative enantioselectivities $Q_{H/Me}$, single and average values

Precatalyst	Ligand	$Q_{7h/7}$	$Q_{6h/6}$	$Q_{8h/8}$	$\bar{Q}_{H/Me}$	$\bar{Q}_{H/Me}$
1e	Ph-β-glup	3.0	2.3	2.6	2.6 ± 0.4	2.8 ± 0.6
1f	Me-β-glup	3.7	2.1	3.1	3.0 ± 0.8	
2e	Ph-β-galp	0.40	0.65	1.0	0.7 ± 0.3	0.7 ± 0.3
2f	Me-β-galp	0.42	0.53	1.1	0.7 ± 0.4	
3e	Ph-α-glup	0.84	0.94	1.2	1.0 ± 0.2	1.1 ± 0.2
3f	Me-α-glup	0.94	1.01	1.5	1.1 ± 0.3	
4e	Ph-α-galp	0.20	0.33	0.39	0.3 ± 0.1	0.3 ± 0.1
4f	Me-α-galp	0.19	0.24	0.39	0.3 ± 0.1	
1g	Ph-β-glup-OH	1.4	1.1	1.4	1.3 ± 0.2	1.3 ± 0.2
1h	Me-β-glup-OH	1.1	1.5	1.3	1.3 ± 0.2	
2g	Ph-β-galp-OH	0.72	2.5	2.2	1.8 ± 0.9	1.5 ± 0.7
2h	Me-β-galp-OH	0.78	1.3	1.5	1.2 ± 0.4	
3g	Ph-α-glup-OH	0.71	1.5	1.3	1.2 ± 0.4	1.2 ± 0.4
3h	Me-α-glup-OH	0.74	1.3	1.5	1.2 ± 0.4	
4g	Ph-α-galp-OH	0.81	1.9	1.1	1.3 ± 0.6	1.1 ± 0.4
4h	Me-α-galp-OH	0.70	1.1	1.1	1.0 ± 0.2	

The interpretation of the average of the relative enantioselectivity $\bar{Q}_{H/Me}$ as being constant for a given catalyst structure calculated from the results for three substrate pairs seems to be somewhat doubtful for the deprotected catalysts because the standard deviation in most cases lies rather high and the couple of 2-*N*-acetamidoacrylic acid **7h** and its ester **7** shows particularly deviating low single values of $Q_{aH/aMe} < 1$ for all species with axial substituents (see Table 4, precatalysts **2-4g,h**). However, the eight types from **1** to **4g,h** exhibits very low differences of one under the other, and the average value obtained for 8 catalysts and 3 substrate couples is $\bar{Q}_{H/Me} = 1.3$ with the low standard deviation of $\sigma = \pm 0.2$. Thus all the deprotected type catalysts demonstrate in principle a very similar behaviour as an indication of a higher possibility to adapt by conformational flexibility in sharp contrast to the protected catalysts **1-4e,f** with their anellated dioxane rings.

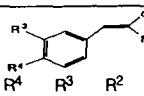
4. Hydrogenation in water in presence of amphiphiles

Preliminary investigations of the both earlier published hydroxy-group carrying species **1g** [Rh(Ph-β-glup-OH)(COD)]BF_4 and **3h** [Rh(Me-α-glup-OH)(COD)]BF_4 have shown that the hydrogenation rate and enantioselectivity in water increases to a considerable extent in the presence of amphiphiles.[6] With an enantiomeric excess of up to 98 %*ee* for substrate esters in water in presence of sodiumdodecyl sulfate (SDS) the best results received for this catalysts in methanol were distinctly exceeded.[6a] Even for **3h** carrying the axially oriented α-methyl aglycon an increase from 74 to 94 %*ee* corresponds to the fifefold relative enantioselectivity $Q_{a/b} = q_a / q_b = 5$ (**a** stands for the presence of amphiphile, **b** for the blank). We were interested to investigate both series of our new catalysts regarding their effects in water, to prove the influence of amphiphiles and to look for the effect of an increasing number of axial hexopyranoside substituents.

At first we directed our attention to the comparison of hydrogenation results for a representative row of substrate esters **6**,**7** and **10-14** of increasing solubility in 15 ml of water and some corresponding acids **6h**,**7h**,**10h** and **11h** with the precatalyst **3h**. Similar measurements were already done with the low soluble **1g** leading to very long reaction times for the blanks.[6a] The advantage of precatalyst **3h** was its much better solubility caused by the methyl group as aglycon. Thus we were able to finish all hydrogenation blanks in pure water, even those for the acid substrates (see Table 5). Independent of their very different solubility in 15 ml of water, all substrate *esters* show roughly the same increase of the relative enantioselectivity to about $\bar{Q}_{a/b} = 5.9 \pm 1.3$ under the influence of SDS. That indicates that the amphiphile effect on the enantioselectivity is realized mainly by action on the catalyst changing its selecting ability independent of the kind of the substrate structure. However, the increase seems to be clearly less for substrate *acids* with an average of $\bar{Q}_{a/b} = 3.8 \pm 0.5$.

Of experimental importance was the result that even for the completely soluble substrate **7** with its low half-life of 4 minutes as a blank arises such a high relative enantioselectivity of $Q_{a/b} = 6.5$ by addition of SDS. That predestines this substrate for the comparative study of all catalysts, even those with a very low solubility as the benzylidene protected species **1-4e**,**f**. From Table 6 we can see that the blanks of the protected catalysts **1e-4e** carrying a phenyl group as aglycon show extremely long reaction rates. However, the examples **1f-4f** with a methyl aglycon cause a marked decrease of the half-life to values between 14 and 90 minutes which diminishes to less than 10 minutes for the deprotected OH groups carrying methyl glycopyranoside catalysts **1h-4h**. Nevertheless, even for this latter catalyst type the increase of enantioselectivity induction by added amphiphiles is especially high with $\bar{Q}_{a/b} = 7.3 \pm 1.2$. It seems that the tendency for high relative enantioselectivity is more pronounced for the hydroxy group carrying catalysts with exception of the β-galactopyranoside species **2g**,**h**.

Table 5. Hydrogenation with the precatalyst **3h** [Rh(Me-α-glup-OH)(COD)]BF_4 in water as solvent in presence of sodiumdodecylsulfate (SDS)

	Substrate					Half-life $t_{1/2}$ (min)		Enantioselectivity %ee (*S*)	$Q=q_g/q_b$
					[a] solubility %	blank	+ 0.66 mmol SDS	□ blank ▨ + SDS	q_{SDS}/q_{blank}
	R^4	R^3	R^2	R^1				0 25 50 75 100	
10	MeO	MeO	Me	Me	1.6	750	235		4.8
11	AcO	MeO	Me	Me	2	230	26		5.2
12	HO	MeO	Ph	$(CH_2)_2OH$	4	225	36		5.5
6	H	H	Me	Me	21	35	2		8.6
13	HO	MeO	Me	Me	23	30	4		5.4
14	HO	MeO	Me	$(CH_2)_2OH$	31	97	7		5.0
7	H instead Ar		Me	Me	100	4	2		6.5
								$\bar{Q}_{ester}$ =	5.9±1.3
6h	H	H	Me	H	11	400	4		3.9
11h	AcO	MeO	Me	H	24	700	36		4.4
10h	MeO	MeO	Me	H	40	160	8		3.6
7h	H instead Ar		Me	H	40	6	2		3.3
								$\bar{Q}_{acid}$ =	3.8±0.5

[a] Solubility of the substrates as the percentage of 1 mmol wich dissolves in 15 ml water at 25 °C, conditions see Table 1.

Table 6. Hydrogenation of 1 mmol **6h** with 0.01 mmol [Rh(PP)COD]BF_4 in 15 ml H_2O at 25 °C

PP X ax gr.	Half-life t/2 min		Enantioselectivity % ee (*S*)		Rel. enantioselectivity
1 ß-glup 0 2 ß-galp 1 3 α-glup 1 4 α-galp 2	blank	+ SDS 0.1 mmol	blank	+ SDS 0.1 mmol	$Q = \frac{q_{SDS}}{q_{blank}}$
	0 20 40 60 80 100	0 20 40	0 20 40 60 80	0 20 40 60 80 100	0 5 10 15
Ph-X					
1e	415	35	13	85	9.6
2e	127	33	4	57	3.4
3e	360	30	1	62	4.2
4e	270	38	2	62	4.1
					$\bar{Q}$ = **5.3** ± 2.9
Me-X					
1f	61	4	67	87	2.8
2f	30	5	55	91	5.9
3f	90	8	22	53	2.1
4f	14	3	34	62	5.1
					$\bar{Q}$ = **4.0** ± 1.8
Ph-X-OH					
1g	32	3	77	95	5.2
2g	45	5	43	78	3.3
3g	110	5	36	89	8.4
4g	7	3	18	84	8.1
					$\bar{Q}$ = **6.3** ± 2.4
Me-X-OH					
1h	5	3	74	96	7.8
2h	4	3	43	87	5.5
3h	4	3	55	93	8.0
4h	7	3	21	84	7.9
					$\bar{Q}$ = **7.3** ±1.2

Another exception, but in the series of the protected catalysts, represents the Ph-β-glup derived catalyst **1e** leading to the 9.6-fold enantiomeric ratio by addition of the amphiphile - the highest enhancement found at all. However, this effect may be uncertain regarding the extremely long half-life of seven hours for the blank. This involves the risk of lowering the enantioselectivity by participation of unspecific hydrogenation caused by achiral impurities as metallic rhodium in the reaction mixture.

The enlargement of the hydrogenation rate can only roughly be estimated by measuring the half-life of the substrate conversion. Its decrease is thought to result from the dispersing power of the amphiphile on the catalyst as well as on the substrate by inclusion in micelles formed by SDS.[21] However, the effect is still to be recognized for hydrogenation of the completely soluble substrate **7** by the catalyst precursors **1-4h** which also show considerable solubility and indicates a second effect. We believe that the concentration of substrate and catalyst in the Stern layer[22] of the micelles explains in the best manner the enlargement of successful events of molecular collision. On the other hand, we know that the reaction rate in water is lower than in methanol for all catalysts examined. This means the solvatation by water may be stronger than by alcohols.[23] One role of the amphiphile may be the desolvatation of the catalyst and/or the substrate leading to an increase of the reaction rate.

It is not easy to explain the notable increase of enantioselectivity of all the sixteen investigated catalysts under the action of amphiphiles. We thought that the change in orientation of the phosphorus phenyl groups as found for the precatalysts under the alteration of the solvent methanol by benzene[11] could be important also in this case of changing the environment of the chelate in the Stern layer of the amphiphiles. However, up to now we could not find data to substantiate this hypothesis: CD-spectra in water in presence or absence of amphiphiles looked nearly identically. An enantioselectivity decreasing influence of a solvatation on the catalyst/substrate complexes might be counteracted by the amphiphiles and may explain the special position of the acid substrates with their pronounced ability to form hydrogen bridges.

The unexpected similar $Q_{a/b}$-values (5.9 ± 1.3) for all ester substrates hydrogenated by **3h** (Table 5) indicate that predominantly the influence on the conformation of the catalyst determines the increase of the enantioselectivity and that the structure of the substrates is of less importance. However, the remarkable deviation in the case of all substrate acids ($\bar{Q}_{a/b}$= 3.8 ± 0.5) corresponding to a similar drop of $\bar{Q}_{a/b}$ for (*Z*)-2-*N*-acetamido-cinnamic acid **6h** obtained with the catalyst **1g** [Rh(Ph-β-glup-OH)(COD)]BF_4[6a] shows us that we have to consider the influence on the whole substrate-catalyst complex in the transition state of hydrogenation. Again the special position of the substrate acids by their ability to form hydrogen bonds has to be taken into account.

Another point of discussion is the necessity of micelle formation by the applied amphiphiles to observe the maximum effect for the enantioselectivity. We believe to have good arguments for the importance of the micelle formation by the observation that polymerized micelles act in a distinctly lower concentration than analogous monomolecular amphiphiles.[6a] Grassert et al. showed the significance of achieving the critical micelle concentration (cmc) for amphiphilic zwitterionic sulfobetains to get the optimum of enantioselectivity in similar systems with Achiwa's rhodium-BPPM catalyst.[21] However, own, unpublished results with new catalysts carrying ligands of the hydroxy-DIOP type[20] show that the increase in enantioselectivity starts with a concentration of sodium dodecyl sulfate already two orders of magnitude below its cmc in pure water. This special result for anionic amphiphiles indicates the exchange of the counterions in the catalyst and forces us to be careful in the interpretation of the results. Recently impressive experiments by Buriak and Osborn[24] gives evidence that a similar effect on the hydrogenation of prochiral imines caused by sodium bis(2-ethyl-hexyl) sulfosuccinate (AOT) in benzene is not connected with the formation of reversed micelles, but may be simulated also by nonsurfactant sulfonates, for which bidentate coordination to the rhodium is stated. Nevertheless, our experiments applying alkyl sulfates with increasing length of the alkyl chain indicate that growing ability to a self-organisation in micelles corresponds with an increase of enantioselectivity and reaches a final value for dodecyl which cannot be exceeded by hexadecyl sulfate (Table 7).

Table 7. Influence of the length of the alkyl chain of alkylsulfates on the enantioselectivity of **3h** in water

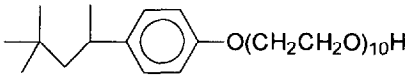
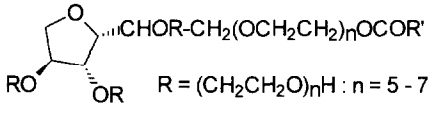
$C_nH_{2n+1}OSO_3Na$ (0.02 mmol **a** *)	Critical micelle concentration (cmc) [25]	t/2 (min)	*%ee (S)*	$Q_{a/b} = q_a / q_b$
blank		35	61	1.0
n = 4		19	65	1.1
8	1.3×10^{-1}	50	73	1.6
12	8.1×10^{-3}	2	95	9.5
16	4.5×10^{-4}	4	95	9.5

* Concentration of amphiphile: 1.3×10^{-2}. Standard conditions for the hydrogenation of **6** see Table 1.

Again it can be seen that the comparison of $Q_{a/b}$-values, making an impressive jump moving from octyl to dodecyl sulfate, is much more informative than the stepwise increase of the enantiomeric excesses *%ee*. This corresponds with a sudden dip of the half-life which shows an irregularity for the presence of octyl sulfate (t/2 = 50 min) caused by loss of parts of active chelate by agglomeration to insoluble particles, which can be dispersed again by additional octyl sulfate.

Nonionic surfactants as Triton X100® as well as some representatives of Tween® or Brij®, respectively, show a distinctly lower effect on the hydrogenation of **6** with **3h** [Rh(Me-α-glup-OH)(COD)]BF_4 as precatalyst and lead to astonishingly similar relative enantioselectivities in the region of $Q_{a/b}$ = 3.0 ± 0.4 (Table 8). This excludes an explanation of the amphiphile action only by formation of ionic pairs with the cationic rhodium(I) catalyst. However, in comparison with the much higher value for the relative enantioselectivity up to more than eight ($Q_{a/b} \geq 8$) applying anionic surfactants especially for hydrogenation of this substrate **6** it seems plausible that the ionic interconversion leads to particularly advantageous conditions for a high increase of enantioselectivity in our case.

Table 8. Hydrogenation of **6** using precatalyst **3h** in water in the presence of nonionic or cationic surfactants

Surfactant (0.02 mmol)			t/2 min	%*ee* (*S*)	$Q = q_a/q_b$
		blank	35	61	
Nonionic surfactants:					
		Triton X100®	4	87	**3.5**
	R'				
	$C_{11}H_{23}$	Tween 20®	7	86	3.2
	$C_{15}H_{31}$	Tween 40®	6	86	3.2
	$C_{17}H_{35}$	Tween 60®	7	85	3.0
	$C_{17}H_{33}$	Tween 80®	8	87	3.5
					3.2 ± 0.2
$HO(CH_2CH_2O)n(CH_2)mCH_3$	n m				
	10 15	Brij 56	6	83	2.6
	20 15	Brij 58	5	85	3.0
	10 17	Brij 76	7	83	2.5
	20 17	Brij 78	6	82	2.6
					2.7 ± 0.2
Cationic surfactant:					
$C_{16}H_{33}NMe_3^+HSO_4^-$			8	81	**2.3**

* Concentration of amphiphile: 1.3×10^{-2}. Standard conditions for the hydrogenation of **6** see Table 1.

The investigation of hexadecyltrimethylammonium hydrogensulfate as a representative cationic amphiphile shows still a somewhat lower relative enantioselectivity of $Q_{a/b}$ = 2.3. Compared with earlier results using the rhodium-BPPM catalyst[21] for which all proved anionic, neutral and cationic surfactants led to very similar optimum relative enantioselectivities of $Q_{a/b}$= 4 ± <1 at least our standard catalyst **3h** [Rh(Me-α-glup-OH)(COD)]BF_4 shows the distinctly deviating result of a differentiated action of anionic amphiphiles with an effect of more than the double value for the relative enantioselectivity in comparison with all proved neutral or cationic surfactants.

CONCLUSIONS

1. The investigation of two types of rhodium(I)-bis(phosphinite) catalysts derived from 2,3-bis(*O*-diphenylphosphino)-D-glycopyranosides showed that the 4,6-*O*-benzylidene protected representatives give much more differentiation in %*ee* in dependence on the structure and the applied solvent than the series of deprotected, hydroxy groups carrying catalysts.
2. In nearly all cases the increase of the number of axially oriented pyranoside substituents causes a decrease of enantioselectivity.
3. Regarding the ranking of acid substrates and their esters with respect of obtaining high enantioselectivity induction we find a clear, structure dependent inversion of the potency of the protected type of catalysts expressed by the relative enantioselectivity $Q_{H/Me}$ which covers the range from 0.2 to 15. Further evidence for the Q-value to be characteristic and constant for each catalyst and changing with its structure is given. Axial pyranoside substituents result in a particularly large decrease in induction to the acid (*S*)-products. For ester substrates the trend is much less.
4. In water as solvent the addition of surfactants such as sodium dodecyl sulfate generally leads to a remarkable increase of the (*S*)-selectivity.
5. For methyl 2-*N*-acetamidoacrylate the relative enantioselectivity in comparison to the blank is in most cases higher for the deprotected type of catalyst: $\bar{Q}_{a/b}$ = 7 ± 2 instead of 5 ± 2 for the series of protected catalysts. That deviates from the lower differentiation of the hydroxy groups carrying catalysts in other solvents (see point 1).
6. The formation of micelles seems to be of importance to reach the optimum relative enantioselectivity ($Q_{a/b}$ = 9.5) at least in the case of added alkyl sulfates. Nonionic or cationic surfactants show lower effects ($\bar{Q}_{a/b} \cong 3$).

EXPERIMENTAL

General Methods

NMR spectra were recorded on Bruker ARX-300 and ARX-400 spectrometers (δ ^{31}P in ppm rel. H_3PO_4, δ ^{1}H and ^{13}C in ppm rel. TMS). Gas chromatography was performed with a Hewlett Packard (5890 series II) gas chromatograph. Mass spectra were obtained using a AMD 402 spectrometer (FAB^+, sulfolan-matrix). Elemental analyses were carried out on a LECO CHNS-932. THF, diethyl ether, benzene, toluene and triethylamine were dried with sodium and distilled under argon. Pyridine and $CHCl_3$ were distilled under argon from P_2O_5. DMF was dried after following reported procedure.[26]

Reactions to phosphinites and rhodium complexes were carried out in argon atmosphere using standard Schlenk techniques.

The experimental procedures for the hydrogenation, the synthesis of the substrates, the derivatization of the hydrogenated products and the determination of the enantioselectivity are described or referred to in ref. [6,16].

Preparation of 4,6-*O*-arylidene-D-glycopyranosides

General Procedure A:[8] D-Glycopyranoside (52 mmol) and pyridinium p-toluenesulfonate (100 mg, 0.4 mmol) were dissolved in dry dimethylformamide (100 ml, 80 °C). A solution of benzaldehyde dimethylacetal (9.4 g, 62 mmol) respectively p-methoxybenzaldehyde dimethylacetal (11.3 g, 62 mmol) in dry dimethylformamide (100 ml) was then added dropwise while stirring under a stream of argon (2.5 h, 80 °C). Evaporation after addition of some $NaHCO_3$ and recrystallisation from ethanol containing KOH gave 4,6-*O*-arylidene-D-glycopyranosides as colorless needles.

General Procedure B only for 4,6-*O*-benzylidene-β-D-galactopyranoside: Following the reported method.[27]

Table 9. Data for 4,6-*O*-arylidene-D-glycopyranosides[28]

arylidene	aglycon	pyranoside	procedure	yield [g, %]	m.p. [°C]	elemental analyses Calcd.	Found
benzylidene	Me	α-gal	A	9.8, 67	168-170	C, 59.15; H, 6.04.	C, 59.86; H, 6.20.
„	Me	β-gal	B	9.2, 63	192-194	C, 59.15; H, 6.04.	C, 59.52; H, 6.01.
„	Ph	α-gal	A	13.0, 73	191-193	C, 66.47; H, 5.54.	C, 66.12; H, 5.23.
„	Ph	β-gal	A	10.7, 60	243-244	C, 66.47; H, 5.54.	C, 66.91; H, 5.60.
„	Me	α-glc	A	9.2, 63	166-167	C, 59.15; H, 6.04.	C, 59.72; H, 6.03.
„	Me	β-glc	A	11.8, 81	196-199	C, 59.15; H, 6.04.	C, 59.51; H, 5.98.
„	Ph	α-glc	A	10.2, 57	214-216	C, 66.47; H, 5.54.	C, 66.23; H, 5.44.
anisylidene	Me	α-gal	A	15.8, 98	93-107	C, 57.88; H, 6.11.	C, 57.77; H, 6.06.
„	Me	β-gal	A	9.1, 56	204-207	C, 57.88; H, 6.11.	C, 57.91; H, 6.20.
„	Ph	α-gal	A	15.9, 82	154-156	C, 64.34; H, 5.63.	C, 64.30; H, 5.61.
„	Ph	β-gal	A	11.1, 57	195-197	C, 64.34; H, 5.63.	C, 64.42; H, 5.62.
„	Me	α-glc	A	10.7, 66	183-186	C, 57.88; H, 6.11.	C, 57.78; H, 6.09.
„	Me	β-glc	A	7.8, 48	172-174	C, 57.88; H, 6.11.	C, 57.89; H, 5.12.
„	Ph	α-glc	A	10.1, 52	147-152	C, 64.34; H, 5.63.	C, 64.23; H, 5.54.
„	Ph	β-glc	A	12.0, 62	175-180	C, 64.34; H, 5.63.	C, 64.31; H, 5.59.

General Procedure: Preparation of 4,6-*O*-arylidene-2,3-bis(*O*-diphenylphosphino)-D-glycopyranosides (1 - 4a-d).

To a stirred solution of freshly distilled chlorodiphenylphosphine (12.9 ml, 70.4 mmol) in tetrahydrofuran (100 ml) a solution of 4,6-*O*-arylidene-D-glycopyranoside (32 mmol) in dry pyridine (5.4 ml, 67.2 mmol at least) was added dropwise. After stirring the reaction mixture for 4 h at room temperature the suspension was filtered and the residue was extracted with dry tetrahydrofuran several times. The filtrate was evaporated to 50 ml and after crystallization at 5 °C and filtration, the solid residue was recrystallized from triethylamine/toluene (30:70, v:v) (2 ml per 1g product) and then from toluene (2 ml per 1g product). The colorless crystalls were dried over P_2O_5 in *vacuo* (3 d, 100 °C).

Phenyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-β-D-glucopyranoside (**1a**) was prepared following literature.[29]

Methyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-β-D-glucopyranoside (**1b**) (81 %) was prepared following the General Procedure, mp: 131-134 °C. MS *m/z* 650 (M^+), 573 (M^+-77), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 183 ($P(C_6H_4\text{-}C_6H_4)^+$), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 94 ($C_6H_5OH^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 116.2 (d, J=1.5 Hz), 114.5 (d, J=1.5 Hz). ^{13}C NMR (pyridine-D_5) δ 101.4 (C-1), 84.2 (dd, J=5.1 and 18.9 Hz), 83.2 (dd, J=4.8 and 17.4 Hz), 80.8 (m), 66.1 (s, C-2,3,4,5), 68.8 (C-6), 104.4 (C-7), 56.4 ($O\underline{C}H_3$), 126.8-139.0 (C_{aryl}). Anal. calcd. for $C_{38}H_{36}O_6P_2$: C, 70.15; H, 5.53; P, 9.54. Found: C, 70.38; H, 5.61; P, 10.31.

Phenyl 4,6-O-anisylidene-2,3-bis(O-diphenylphosphino)-β-D-glucopyranoside (**1c**) (67 %) was prepared following the General Procedure, mp: 108-113 °C. MS *m/z* 742 (M^+), 711 (M^+-OCH_3), 665 (M^+-77), 649 (M^+-93), 557 (M^+-185), 386 (Ph_2P-P (Ph_2)O^+), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 118.3 (d, J=2.6 Hz), 114.1 (d, J=2.6 Hz). ^{13}C NMR (pyridine-D_5) δ 100.3 (C-1), 83.8 (m), 83.0 (m), 80.5 (m), 66.4 (s, C-2,3,4,5), 68.7 (C-6), 101.5 (C-7), 157.0 (C-1'), 116.6 (C-2'), 129.5 (C-3'), 123.0 (C-4'), 55.2 (an-$O\underline{C}H_3$), 135.8 (*ipso*-C_{an}), 113.7 (*meta*-C_{an}), 126.9-139.0 ($C_{aryl.}$), 160.2 (*para*-C_{an}). Anal. calcd. for $C_{44}H_{40}O_7P_2$: C, 71.16; H, 5.39; P, 8.35. Found: C, 71.10; H, 5.31; P, 8.62.

Methyl 4,6-O-anisylidene-2,3-bis(O-diphenylphosphino)-β-D-glucopyranoside (**1d**) (69 %) was prepared following the General Procedure, mp: 148-151 °C. MS *m/z* 680 (M^+), 649 (M^+-OCH_3), 603 (M^+-77), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 183 ($P(C_6H_4\text{-}C_6H_4)^+$), 149 ($PhCHO_2$ $(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 94 ($C_6H_5OH^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 116.5 (s), 114.5 (s). ^{13}C NMR (pyridine-D_5) δ 101.5 (C-1), 84.2 (d, J=12.3 Hz), 83.1 (d, J=13.4 Hz), 80.8 (m), 66.2 (s) (C-2,3,4,5), 68.8 (C-6), 104.5 (C-7), 55.4 and 54.3 ($O\underline{C}H_3$, an-$O\underline{C}H_3$), 135.5 (*ipso*-C_{an}), 128.2-128.6 (C_{aryl}), 113.7 (*meta*-C_{an}), 160.4 (*para*-C_{an}). Anal. calcd. for $C_{39}H_{38}O_7P_2$: C, 68.82; H, 5.59; P, 9.12. Found: C, 68.64; H, 5.55; P, 9.99.

Phenyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-β-D-galactopyranoside (**2a**) (58 %) was prepared following the General Procedure, mp: 170-172 °C. MS *m/z* 712 (M^+), 635 (M^+-77), 511 (M^+-185), 386 (Ph_2P-P (Ph_2)O^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 183 ($P(C_6H_4\text{-}C_6H_4)^+$), 149 ($PhCHO_2(CH_2)_2^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 118.8, 110.5. ^{13}C NMR (pyridine-D_5) δ 100.2 (C-1), 80.6 (dd, J=3.8 and 17.9 Hz), 80.3 (dd, J=6.5 and 19.9 Hz), 75.1 (d, J=6.7 Hz), 67.0 (s, C-2,3,4,5), 69.0 (C-6), 101.2 (C-7), 157.0 (C-1'), 116.6 (C-2'), 129.5 (C-3'), 122.4 (C-4'), 126.9-138.9 ($C_{aryl.}$). Anal. calcd. for $C_{43}H_{38}O_6P_2$: C, 72.47; H, 5.85; P, 8.71. Found: C, 72.12; H, 5.38; P, 9.98.

Methyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-β-D-galactopyranoside (**2b**) (63 %) was prepared following the General Procedure, mp: 166-174 °C. MS *m/z* 650 (M^+), 619 (M^+-OCH_3), 573 (M^+-77)$^+$, 465 (M^+-185), 449 (M^+-201), 419 (M^+-377), 386 (Ph_2P-P(Ph_2)O^+), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P)$^+$, 149 ($PhCH(O_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 91 ($C_7H_7^+$), 77

($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 117.0 (d, J=1.9 Hz), 110.7 (d, J=1.9 Hz). ^{13}C NMR (pyridine-D_5) δ 101.2 (s, C-1), 80.8 (d, J=6.0 Hz), 80.6 (d, J=6.0 Hz), 75.4 (d, J=5.8 Hz), 66.7 (s, C-2,3,4,5), 69.2 (C-6), 104.2 (C-7), 56.3 ($O\underline{C}H_3$), 126.9-138.9 ($C_{aryl.}$). Anal. calcd. for $C_{38}H_{36}O_6P_2$: C, 70.15; H, 5.53; P, 9.54. Found: C, 69.91; H, 5.51; P, 10.36.

Phenyl 4,6-O-anisylidene-2,3-bis(O-diphenylphosphino)-β-D-galactopyranoside (**2c**) (73 %) was prepared following the General Procedure, mp: 154-160 °C. MS *m/z* 742 (M^+), 675 (M^+-77), 541 (M^+-185), 386 (Ph_2P-$P(Ph_2)O^+$), 262 (Ph_3POH^+-OH), 201 (Ph_2PO^+), 185 (Ph_2P^+), 183 ($P(C_6H_4$-$C_6H_4)^+$), 149 ($PhCHO_2(CH_2)_2^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). Not enough soluble for NMR measurements. Anal. calcd. for $C_{44}H_{40}O_7P_2$: C, 71.16; H, 5.39; P, 8.35. Found: C, 70.88; H, 5.34; P, 9.02.

Methyl 4,6-O-anisylidene-2,3-bis(O-diphenylphosphino)-β-D-galactopyranoside (**2d**) (65 %) was prepared following the General Procedure, mp: 177-180 °C. MS *m/z* 680 (M^+), 649 (M^+-OCH_3), 603 (M^+-77), 495 (M^+-185), 479 (M^+-201), 449 (M^+-377), 386 (Ph_2P-$P(Ph_2)O^+$), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 117.0 (s), 110.0 (s). ^{13}C NMR (pyridine-D_5) δ 101.2 (C-1), 80.8 (m), 80.6 (m), 75.3 (d, J=5.7 Hz), 66.7 (s, C-2,3,4,5), 69.1 (C-6), 104.2 (C-7), 56.3 and 55.2 ($O\underline{C}H_3$, an-$O\underline{C}H_3$), 135.8 (*ipso*-C_{an}), 128.4-128.7 (C_{aryl}), 113.8 (*meta*-C_{an}), 160.5 (*para*-C_{an}). Anal. calcd. for $C_{39}H_{38}O_7P_2$: C, 68.82; H, 5.59; P, 9.12. Found: C, 68.75; H, 5.57; P, 10.01.

Phenyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-α-D-glucopyranoside (**3a**) (57 %) was prepared following the General Procedure, mp: 187-189 °C. MS *m/z* 712 (M^+), 635 (M^+-77), 619 (M^+-93), 511 (M^+-185), 386 (Ph_2P-$P(Ph_2)O^+$), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 117.2 (s), 115.4 (s). ^{13}C NMR (pyridine-D_5) δ 97.9 (d, J=6.0 Hz, C-1), 80.9 (dd, J=5.8 and 14.3 Hz), 80.7 (dd, J=4.6 and 16.9 Hz), 82.2 (m), 66.1 (s, C-2,3,4,5), 68.8 (C-6), 102.4 (C-7), 156.9 (C-1'), 117.1 (C-2'), 129.9 (C-3'), 122.9 (C-4'), 126.8-139.0 ($C_{aryl.}$). Anal. calcd. for $C_{43}H_{38}O_6P_2$: C, 72.47; H, 5.85; P, 8.71. Found: C, 72.41; H, 5.32; P, 8.83.

Methyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-α-D-glucopyranoside (**3b**) (60 %) was prepared following the General Procedure, mp: 154-156 °C. MS *m/z* 650 (M^+), 573 (M^+-77), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 183 ($P(C_6H_4$-$C_6H_4)^+$), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 94 ($C_6H_5OH^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 116.7 (d, J=2.4 Hz), 113.7 (d, J=2.4 Hz). ^{13}C NMR (pyridine-D_5) δ 99.9 (d, J=6.3 Hz, C-1), 80.0 (dd, J=6.0 and 17.2 Hz), 80.0 (dd, J=8.1 and 13.9 Hz), 81.7 (m), 63.1 (s, C-2,3,4,5), 69.1 (C-6), 101.7 (C-7), 54.9 ($O\underline{C}H_3$), 126.9-138.2 ($C_{aryl.}$). Anal. calcd. for $C_{38}H_{36}O_6P_2$: C, 70.15; H, 5.53; P, 9.54. Found: C, 69.78; H, 5.51; P, 10.23.

Phenyl 4,6-O-anisylidene-2,3-bis(O-diphenylphosphino)-α-D-glucopyranoside (**3c**) (35 %) was prepared following the General Procedure, mp: 207-210 °C. MS *m/z* 742 (M^+), 711 (M^+-OCH_3), 665 (M^+-77), 649 (M^+-93), 557 (M^+-185), 386 (Ph_2P-$P(Ph_2)O^+$), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). Not enough soluble for NMR measurements. Anal. calcd. for $C_{44}H_{40}O_7P_2$: C, 71.16; H, 5.39; P, 8.35. Found: C, 70.87; H, 5.40; P, 8.54.

Methyl 4,6-O-anisylidene-2,3-bis(O-diphenylphosphino)-α-D-glucopyranoside (**3d**) (62 %) was prepared following the General Procedure, mp: 175-178 °C. MS *m/z* 680 (M^+), 649 (M^+-OCH_3), 603 (M^+-77), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 183 ($P(C_6H_4$-$C_6H_4)^+$), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 94 ($C_6H_5OH^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 116.5 (d, J=2.5 Hz), 113.6 (d, J=2.5 Hz). ^{13}C NMR (pyridine-D_5) δ 99.5 (d, J=6.0 Hz, C-1), 79.9 (m), 79.6 (m), 81.2 (m), 62.6 (s, C-2,3,4,5), 68.7 (C-6), 101.3 (C-7), 54.8 and 54.5 ($O\underline{C}H_3$, an-$O\underline{C}H_3$), 135.4 (*ipso*-C_{an}), 128.0-128.3 (C_{aryl}), 113.3 (*meta*-C_{an}), 160.0 (*para*-C_{an}). Anal. calcd. for $C_{39}H_{38}O_7P_2$: C, 68.82; H, 5.59; P, 9.12. Found: C, 68.54; H, 5.58; P, 9.87.

Phenyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-α-D-galactopyranoside (**4a**) (73 %) was prepared following the General Procedure, mp: 155-158 °C. MS *m/z* 712 (M^+), 635 (M^+-77), 511 (M^+-185), 386 (Ph_2P-$P(Ph_2)O^+$), 262 (Ph_3POH^+-OH), 201 (Ph_2PO^+), 185 (Ph_2P^+), 183($P(C_6H_4$-$C_6H_4)^+$), 149 ($PhCHO_2(CH_2)_2^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 114.8 (d, *J*=1.6 Hz), 110.2 (d, *J*=1.6 Hz). ^{13}C NMR (pyridine-D_5) δ 97.6 (d, *J*=4.8 Hz, C-1), 77.4 (dd, *J*=6.7 and 19.0 Hz), 76.8 (dd, *J*=6.2 and 20.5 Hz), 75.9 (d, *J*=5.6 Hz), 64.2 (s, C-2,3,4,5), 69.2 (C-6), 101.0 (C-7), 157.4 (C-1'), 117.0 (C-2'), 129.7 (C-3'), 122.7 (C-4'), 126.9-139.0 ($C_{aryl.}$). Anal. calcd. for $C_{43}H_{38}O_6P_2$: C, 72.47; H, 5.85; P, 8.71. Found: C, 72.56; H, 5.41; P, 9.03.

Methyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-α-D-galactopyranoside (**4b**) (57 %) was prepared following the General Procedure, mp: 129-136 °C. MS *m/z*: 650 (M^+), 619 (M^+-31), 573 (M^+-77), 465 (M^+-185), 449 (M^+-201), 419 (M^+-377), 386 (Ph_2-$P(Ph_2)O^+$), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 112.6 (d, *J*=2.3 Hz), 110.4 (d, *J*=2.3 Hz). ^{13}C NMR (pyridine-D_5) δ 100.2 (d, *J*=5.7 Hz, C-1), 77.3 (dd, *J*=6.5 and 13.8 Hz), 77.1 (dd, *J*=6.9 and 16.2 Hz), 76.1 (d, *J*=5.2 Hz), 63.2 (s, C-2,3,4,5), 69.3 (C-6), 101.0 (C-7), 55.0 ($O\underline{C}H_3$), 126.9-139.0 ($C_{aryl.}$). Anal. calcd. for $C_{38}H_{36}O_6P_2$: C, 70.15; H, 5.53; P, 9.54. Found: C, 69.81; H, 5.54; P, 99.

Phenyl 4,6-O-anisylidene-2,3-bis(O-diphenylphosphino)-α-D-galactopyranoside (**4c**) (60 %) was prepared following the General Procedure, mp: 164-167 °C. MS *m/z* 742 (M^+), 675 (M^+-77), 541 (M^+-185), 386 (Ph_2P-$P(Ph_2)O^+$), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 183 ($P(C_6H_4$-$C_6H_4)^+$), 149 ($PhCHO_2(CH_2)_2^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). Not enough soluble for NMR measurements. Anal. calcd. for $C_{44}H_{40}O_7P_2$: C, 71.16; H, 5.39; P, 8.35. Found: C, 71.00; H, 5.41; P, 8.54.

Methyl 4,6-O-anisylidene-2,3-bis(O-diphenylphosphino)-α-D-galactopyranoside (**4b**) (83 %) was prepared following the General Procedure, mp: 175-178 °C. MS *m/z* 680 (M^+), 649 (M^+-OCH_3), 603 (M^+-77), 495 (M^+-185), 479 (M^+-201), 449 (M^+-377), 386 (Ph_2P-$P(Ph_2)O^+$), 279 (Ph_3POH^+), 262 (279-OH^+), 201 (Ph_2PO^+), 185 (Ph_2P^+), 149 ($PhCHO_2(CH_2)_2^+$), 106 ($C_6H_5COH^+$), 105 ($C_6H_5CO^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$). ^{31}P NMR (pyridine-D_5) δ 113.2 (s), 110.4 (s). ^{13}C NMR (pyridine-D_5) δ 100.3 (d, *J*=5.6 Hz, C-1), 84.2 (m), 83.2 (m), 76.0 (d, *J*=5.0 Hz), 63.2 (s, C-2,3,4,5), 69.3 (C-6), 101.1 (C-7), 55.2 and 55.1 ($O\underline{C}H_3$, an-$O\underline{C}H_3$), 135.8 (*ipso*-C_{an}), 128.2-128.7 (C_{aryl}), 113.9 (*meta*-C_{an}), 160.5 (*para*-C_{an}). Anal. calcd. for $C_{39}H_{38}O_7P_2$: C, 68.82; H, 5.59; P, 9.12. Found: C, 68.80; H, 5.58; P, 9.81.

General Procedure: Preparation of [Rhodium{4,6-*O*-benzylidene-2,3-bis(*O*-diphenylphosphino)-D-glycopyranoside}(cyclooctadiene)]tetrafluoroborate (1e,f - 4e,f).

To a stirred yellow solution of rhodium(cyclooctadiene)acetylacetonate **5** (1.55 g, 5 mmol) and 4,6-*O*-benzylidene-2,3-bis(*O*-diphenylphosphino)-D-glycopyranoside (5 mmol) in dry THF (5 ml) HBF_4 (40 %, 0.68 ml, 5 mmol) was added. After stirring of the red solution for 5 to 10 min at room temperature diethyl ether (40 ml) was added to the mixture. The ether layer was decanted and to the red sirup diethyl ether was added once more. After crystallization the solid residue was filtered off and washed with diethyl ether three times and dried *in vacuo* at 60 °C. The orange product can be recrystallized from *iso*-propanol.

[Rhodium{phenyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-β-D-glucopyranoside}(cyclooctadiene)]-tetrafluoroborate (**1e**) (4.2 g, 83 %) was prepared following the General Procedure from **1a** (3.6 g, 5 mmol) in 5 min at room temperature. FAB$^+$-MS 923 (M^+-BF_4), 815 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 136.9 (dd, *J*=178.7 and 27.5 Hz), 138.0 (dd, *J* =177.8 and 27.5 Hz). ^{13}C NMR ($CDCl_3$) δ 100.2 (C-1), 66.0 (s), 78.6 (d, *J*=3.3 Hz), 78.6 (dd, *J*=6.0 and 1.6 Hz), 79.4 (d, *J*=8.4 Hz, C-2,3,4,5), 68.2 (C-6), 101.5 (C-7), 156.6 (C_{ipso}/OPh), 28.4-31.6 (m, COD-$\underline{C}H_2$), 101.5-107.1 (m, COD-$\underline{C}H$), 117.4 (C-2'), 129.6 (C-3'), 123.7 (C-4'), 128.0-134.5 (arom. C). ^1H NMR ($CDCl_3$) δ 4.75 (1, d, *J*=7.7 Hz, H-1), 4.10 (1, d, *J*=12.1, H-2), 4.43

(1, ddd, *J*= 9.2, 9.3 and 11.6 Hz, H-3), 3.45 (1, m, H-4), 3.29 (1, dd, *J*=9.3, 10.0 and 4.9 Hz, H-5), 3.60, 4.24 (2, dd, *J*=10.6, H-6), 5.29 (1, s, H-7), 2.21-2.57 (8, m, COD-C$\underline{H}_2$), 4.38-4.88 (4, br., COD-C$\underline{H}$), 6.68-7.33 (30, m, arom. H). Anal. calcd. for $C_{51}H_{50}BF_4O_6P_2Rh$: C, 60.61; H, 4.99; P, 6.13; Rh, 10.18. Found: C, 59.23; H, 4.86; P, 6.21; Rh, 10.10.

[Rhodium{methyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-β-D-glucopyranoside}(cyclooctadiene)]-tetrafluoroborate (**1f**) (3.8 g, 80 %) was prepared following the General Procedure from **1b** (3.3 g, 5 mmol) in 5 min at room temperature. FAB$^+$-MS 861 (M^+-BF_4), 753 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 135.9 (dd, *J*=177.7 and 27.9 Hz), 136.4 (dd, *J*=176.9 and 27.9 Hz). ^{13}C NMR ($CDCl_3$) δ 102.7 (d, *J*=5.7 Hz, C-1), 66.1 (s), 79.1 (d, *J*=2.5 Hz), 79.6 (d, *J*=5.7 Hz), 80.2 (d, *J*=7.9 Hz, C-2,3,4,5), 68.6 (C-6), 101.8 (C-7), 58.1 (O$\underline{C}H_3$), 28.8-32.1 (COD-$\underline{C}H_2$), 103.5-106.8 (m, COD-$\underline{C}H$), 128.4-135.3 (arom. C). ^{1}H NMR ($CDCl_3$) δ 3.01 (3, m, O$\underline{CH}_3$), 3.35 (1, d, *J*=3.8 Hz, H-1), 3.97 (1, m, H-2), 4.90 (1, m, H-3), 3.62 (1, m, H-4), 3.23 (1, m, H-5), 3.70 (2, m, H-6), 5.13 (1, s, H-7), 2.10-2.80 (8, m, COD-C$\underline{H}_2$), 4.30-5.14 (4, br., COD-C$\underline{H}$), 7.10-7.90 (25, m, arom. H). Anal. calcd. for $C_{46}H_{48}BF_4O_6P_2Rh$: C, 58.25; H, 5.10; P, 6.53; Rh, 10.85. Found: C, 57.14; H, 4.91; P, 6.14; Rh, 10.50.

[Rhodium{phenyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-β-D-galactopyranoside}(cyclooctadiene)]-tetrafluoroborate (**2e**) (4.1 g, 81 %) was prepared following the General Procedure from **2a** (3.6 g, 5 mmol) in 10 min at room temperature. FAB$^+$-MS 923 (M^+-BF_4), 815 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 125.9 (dd, *J*=173.9 and 31.7 Hz), 132.7 (dd, *J*=173.9 and 31.7 Hz). ^{13}C NMR ($CDCl_3$) δ 98.1 (C-1), 66.6 (s), 75.9 (d, *J*=6.7 Hz), 77.9 (dd, *J*=8.9 and 4.2 Hz), 78.4 (d, *J*=7.8 Hz, C-2,3,4,5), 68.9 (C-6), 100.7 (C-7), 157.6 (C_{ipso}/OPh), 28.0-32.6 (m, COD-$\underline{C}H_2$), 102,5 (dd, *J*=11.2 and 6.2 Hz), 105.1 (dd, *J*=10.9 and 5.6 Hz), 106.0 (dd, *J*=14.9 and 7.5 Hz), 108.4 (dd, *J*=13.5 and 6.7 Hz) (COD-$\underline{C}H$), 117.0 (C-2'), 129.5 (C-3'), 122.9 (C-4'), 128.4-135.0 (arom. C). ^{1}H NMR ($CDCl_3$) δ 4.00 (1, d, *J*=3.5 Hz, H-1), 4.51 (1, m, H-2), 5.36 (1, m, H-3), 4.82 (1, m, H-4), 5.78 (1, m, H-5), 4.16, 4.23 (2, m, H-6), 5.65 (1, s, H-7), 2.15-2.52 (8, m, COD-C$\underline{H}_2$), 4.22-5.53 (4, br., COD-C$\underline{H}$), 7.10-7.90 (30, m, arom. H). Anal. calcd. for $C_{51}H_{50}BF_4O_6P_2Rh$: C, 60.61; H, 4.99; P, 6.13; Rh, 10.18. Found: C, 59.14; H, 4.98; P, 6.19; Rh, 9.73.

[Rhodium{methyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-β-D-galactopyranoside}(cyclooctadiene)]-tetrafluoroborate (**2f**) (4.0 g, 84 %) was prepared following the General Procedure from **2b** (3.3 g, 5 mmol) in 2 min at room temperature. FAB$^+$-MS 861 (M^+-BF_4), 753 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 124.7 (dd, *J*=173.8 Hz and 32.5 Hz), 132.0 (dd, *J*=175.3 and 32.5 Hz). ^{13}C NMR ($CDCl_3$) δ 100.5 (C-1), 66.4 (s), 76.2 (d, *J*=6.9 Hz), 78.1 (dd, *J*=5.8 and 3.7 Hz), 79.3 (d, *J*=7.8 Hz, C-2,3,4,5), 69.0 (C-6), 100.7 (C-7), 56.6 (O$\underline{C}H_3$), 28.1-32.4 (m, COD-$\underline{C}H_2$), 102.2 (dd, *J*=11.1 and 6.5 Hz), 105.7 (dd, *J*=10.2 and 5.1 Hz), 105.9 (dd, *J*=14.6 and 7.4 Hz), 108.2 (dd, *J*=14.1 and 7.0 Hz) (COD-$\underline{C}H$), 128.4-135.0 (arom. C). ^{1}H NMR ($CDCl_3$) δ 3.01 (3, m, O$\underline{CH}_3$), 3.36 (1, d, *J*=3.5 Hz, H-1), 4.29 (1, m, H-2), 4.23 (1, m, H-3), 4.20 (1, m, H-4), 3.54 (1, m, H-5), 4.16 (2, m, H-6), 5.60 (1, s, H-7), 7.14-7.95 (25, m, arom. H), 2.28-2.51 (8, m, COD-C$\underline{H}_2$), 4.23-5.44 (4, br., COD-C$\underline{H}$). Anal. calcd. for $C_{46}H_{48}BF_4O_6P_2Rh$: C, 58.25; H, 5.10; P, 6.53; Rh, 10.85. Found: C, 56.46; H, 5.05; P, 6.77; Rh, 9.67.

[Rhodium{phenyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-α-D-glucopyranoside}(cyclooctadiene)]-tetrafluoroborate (**3e**) (4.3 g, 86 %) was prepared following the General Procedure from **3a** (3.6 g, 5 mmol) in 5 min at room temperature.FAB$^+$-MS 923 (M^+-BF_4), 815 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 134.5 (dd, *J*=176.3 and 28.6 Hz), 136.9 (dd, *J*=179.3 and 28.6 Hz). ^{13}C NMR ($CDCl_3$) δ 97.6 (d, *J*=5.7 Hz, C-1), 63.3 (s), 76.9 (dd, *J*=7.1 and 2.8 Hz), 77.9 (d, *J*=8.3 Hz), 78.6 (d, *J*=2.5 Hz, C-2,3,4,5), 68.8 (C-6), 101.4 (C-7), 157.8 (C_{ipso}/OPh), 28.8-31.8 (m, COD-$\underline{C}H_2$), 104.3-107.3 (m, COD-$\underline{C}H$), 117.6 (C-2'), 129.6 (C-3'), 123.5 (C-4'), 128.0-134.6 (arom. C). ^{1}H NMR ($CDCl_3$) δ 5.08 (1, d, *J*= 3.5 Hz, H-1), 4.02 (1, m, H-2), 4.25 (1, m, H-3), 3.61 (1, m, H-4), 3.40 (1, m, H-5), 3.81, 3.50 (2, m, H-6), 5.16 (1, s, H-7), 2.10-2.60 (8, m, COD-C$\underline{H}_2$), 4.51-4.89 (4, br., COD-C$\underline{H}$), 7.25-8.00 (30, m, arom. H). Anal. calcd. for $C_{51}H_{50}BF_4O_6P_2Rh$: C, 60.61; H, 4.99; P, 6.13; Rh, 10.18. Found: C, 58.47; H, 5.00; P, 5.98; Rh, 10.03.

[Rhodium{methyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-α-D-glucopyranoside}(cyclooctadiene)]-tetrafluoroborate (**3f**) (4.0 g, 85 %) was prepared following the General Procedure from **3b** (3.3 g, 5 mmol) in 5 min at room temperature.FAB$^+$-MS 861 (M^+-BF_4), 753 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 136.1 (dd, J=178.9 and 29.0 Hz), 137.7 (dd, J=176.2 and 29.0 Hz). ^{13}C NMR ($CDCl_3$) δ 99.0 (d, J=7.3 Hz, C-1), 61.9 (s), 77.0 (dd, J=7.7 and 3.0 Hz), 77.5 (d, J=8.0 Hz),78.5 (d, J=2.0 Hz, C-2,3,4,5), 68.5 (C-6), 101.0 (C-7), 55.6 (O$\underline{C}H_3$), 28.4-31.1 (COD-$\underline{C}H_2$), 103.5 (dd, J=9.6 and 6.6 Hz), 104.8 (dd, J=9.6 and 6.6 Hz), 105.5 (dd, J=10.1 and 6.4 Hz), 106.8 (dd, J=10.1 and 6.4 Hz) (COD-$\underline{C}H$), 128.0-135.1 (arom. C). ^{1}H NMR ($CDCl_3$) δ 3.23 (3, m, O$\underline{CH}_3$), 4.65 (1, d, J=3.8 Hz, H-1), 4.25 (1, ddd, J=20.0, H-2), 4.19 (1, ddd, J=9.3, 9.3 and 13.2 Hz, H-3), 2.86 (1, m, H-4), 3.41 (1, ddd, J=9.3, 10.3 and 4.3 Hz, H-5), 3.32, 4.01 (2, m, H-6), 4.97 (1, s, H-7), 2.10-2.58 (8, m, COD-C$\underline{H}_2$), 4.23-4.98 (4, br., COD-C$\underline{H}$), 7.10-7.90 (25, m, arom. H). Anal. calcd. for $C_{46}H_{48}BF_4O_6P_2Rh$: C, 58.25; H, 5.10; P, 6.53; Rh, 10.85. Found: C, 57.81; H, 4.99; P, 6.91; Rh, 10.32.

[Rhodium{phenyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-α-D-galactopyranoside}(cyclooctadiene)]-tetrafluoroborate (**4e**) (3.6 g, 72 %) was prepared following the General Procedure from **4a** (3.6 g, 5 mmol) in 10 min at room temperature. FAB$^+$-MS 923 (M^+-BF_4), 815 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 138.7 (dd, J=180.7 and 23.3 Hz), 139.6 (dd, J=182.7 and 23.3 Hz). ^{13}C NMR ($CDCl_3$) δ 97.8 (d, J=3.9 Hz, C-1), 63.9, 74.2 (d, J=9.6 Hz), 75.4 (d, J=10.2 Hz), 75.8 (C-2,3,4,5), 69.1 (C-6), 100.7 (C-7), 157.0 (C_{ipso}/OPh), 29.0-31.9 (m, COD-$\underline{C}H_2$), 101.6 (dd, J=9.8 and 6.0 Hz), 102.1 (dd, J=15.4 and 8.6 Hz), 108.8 (dd, J=16.2 and 8.5 Hz), 108.4 (dd, J=15.0 and 6.5 Hz) (COD-$\underline{C}H$), 116.8 (C-2'), 129.4 (C-3'), 123.3 (C-4'), 128.4-135.0 (arom. C). ^{1}H NMR ($CDCl_3$) δ 5.40 (1, d, J=3.5 Hz, H-1), 4.34 (1, m, H-2), 4.45 (1, m, H-3), 4.27 (1, m, H-4), 3.66 (1, m, H-5), 4.04 (2, m, H-6), 5.50 (1, s, H-7), 2.28-2.51 (8, m, COD-C$\underline{H}_2$), 4.40, 4.81 (4, br., COD-C$\underline{H}$), 7.10-7.90 (30, m, arom. H). Anal. calcd. for $C_{51}H_{50}BF_4O_6P_2Rh$: C, 60.61; H, 4.99; P, 6.13; Rh, 10.18. Found: C, 59.37; H, 4.89; P, 5.98; Rh, 9.51.

[Rhodium{methyl 4,6-O-benzylidene-2,3-bis(O-diphenylphosphino)-α-D-galactopyranoside}(cyclooctadiene)]-tetrafluoroborate (**4f**) (4.3 g, 90 %) was prepared following the General Procedure from **4b** (3.3 g, 5 mmol) in 10 min at room temperature. FAB$^+$-MS 861 (M^+-BF_4), 753 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 136.3 (dd, J=179.5 and 25.2 Hz), 136.8 (dd, J=181.2 and 25.2 Hz). ^{13}C NMR ($CDCl_3$) δ 99.1 (d, J=3.8 Hz, C-1), 62.3 (s), 74.7 (d, J=8.5 Hz), 74.9 (d, J=8.7 Hz), 75.6 (d, J=3.4 Hz, C-2,3,4,5), 68.5 (C-6), 99.7 (C-7), 55.6 (O$\underline{C}H_3$), 25.3- 30.8 (COD-$\underline{C}H_2$), 101.7-107.8 (COD-$\underline{C}H$), 128.3-134.9 (arom. C). ^{1}H NMR ($CDCl_3$) δ 3.23 (3, m, O$\underline{CH}_3$), 4.19 (1, d, J=3.5 Hz, H-1), 4.32 (1, m, H-2), 4.35 (1, m, H-3), 4.20 (1, m, H-4), 3.54 (1, m, H-5), 4.08 (2, m, H-6), 5.48 (H-7), 7.10-7.90 (25, m, arom. H), 2.28-2.48 (8, m, COD-C$\underline{H}_2$), 4.38, 4.77 (4, br., COD-C$\underline{H}$). Anal. calcd. for $C_{46}H_{48}BF_4O_6P_2Rh$: C, 58.25; H, 5.10; P, 6.53; Rh, 10.85. Found: C, 58.10; H, 4.77; P, 6.87; Rh, 10.51.

General Procedure: Preparation of [Rhodium{2,3-bis(*O*-diphenylphosphino)-D-glycopyranoside}(cyclooctadiene)]tetrafluoroborate (1g,h - 4g,h).

To a stirred yellow solution of rhodium(cyclooctadiene)acetylacetonate **5** (1.55 g, 5 mmol) and 4,6-*O*-anisylidene-2,3-bis(*O*-diphenylphosphino)-D-glycopyranosides (5 mmol) in tetrahydrofuran (5 ml) HBF_4 (40 %, 1.36 ml , 10 mmol) was added. After stirring of the red solution for 5 min to 3 h at 65 °C or 48 h at 25 °C diethylether (40 ml) was added to the mixture. The ether layer was decanted and diethylether was added to the red sirup once more. After the crystallisation the solid residue was filtered and washed with diethylether three times and dried *in vacuo* at 60 °C. The orange product was recrystallized from *iso*-propanol.

[Rhodium{phenyl 2,3-bis(O-diphenylphosphino)-β-D-glucopyranoside}(cyclooctadiene)]tetrafluoroborate (**1g**) (3.7 g, 81 %) was prepared following the General Procedure from **1c** (3.7 g, 5 mmol) in 0.1 h at 65 °C. FAB$^+$-MS 836 (M^+-BF_4), 728 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 125.8 (dd, J=173.2 and 31.6 Hz), 131.7 (dd,

J=174.0 and 31.6 Hz). ^{13}C NMR ($CDCl_3$) δ 97.4 (C-1), 70.6 (d, *J*=5.5 Hz), 75.4 (m), 79.8 (d, *J*=7.2 Hz), 82.8 (dd, *J*=7.0 and 11.0 Hz, C-2,3,4,5), 61.7 (C-6), 156.4 (C_{ipso}/OPh), 27.7-31.8 (m, COD-$\underline{C}H_2$), 102.4-107.9 (m, COD-$\underline{C}H$), 128.5-134.6 (arom. C), 116.3 (C-2'), 128.8 (C-3'), 122.7 (C-4'). ^{1}H NMR ($CDCl_3$) δ 3.85 (1, d, *J*=8.4 Hz, H-1), 4.03 (1, m, H-2), 5.14 (1, m, H-3), 3.76 (1, m, H-4), 3.42 (1, ddd, *J*=4.4 and 3.5 and 9.8 Hz, H-5), 3.85 (2, m, H-6), 2.20-2.98 (8, m, COD-C$\underline{H}_2$), 4.30-5.32 (4, br., COD-C$\underline{H}$), 6.45, 6.92, 7.09 (5, m, arom. H_{OPh}), 7.25-8.00 (20, m, arom. H). Anal. calcd. for $C_{44}H_{46}BF_4O_6P_2Rh$: C, 57.29; H, 5.03; P, 6.72; Rh, 11.16. Found: C, 56.92; H, 5.04; P, 6.75; Rh, 10.38.

[Rhodium{methyl 2,3-bis(O-diphenylphosphino)-β-D-glucopyranosides} (cyclooctadiene)]tetrafluoroborate (**1h**) (3.1 g, 73 %) was prepared following the General Procedure from **1d** (3.4 g, 5 mmol) in 1 h at 65 °C. FAB$^+$-MS 773 (M^+-BF_4), 665 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 132.7 (dd, *J*=178 and 27 Hz), 137.3 (dd, *J*=181 and 27 Hz). ^{13}C NMR ($CDCl_3$) δ 101.1 (C-1), 70.5 (d, *J*=5.1 Hz), 74.9 (m), 80.3 (d, *J*=7.3 Hz), 82.9 (dd, *J*=6.8 and 5.0 Hz, C-2,3,4,5), 61.6 (C-6), 56.3 (O$\underline{C}H_3$), 27.8-31.8 (m, COD-$\underline{C}H_2$), 102.3-107.4 (m, COD-$\underline{C}H$), 128.5-134.6 (arom. C). ^{1}H NMR ($CDCl_3$) δ 3.01 (3, m, 3H, OC$\underline{H}_3$), 3.34 (1, d, *J*=8.1 Hz, H-1), 3.75 (1, m, H-2), 4.91 (1, dd, *J*=10.0 and 8.7 Hz, H-3), 3.65 (1, m, H-4), 3.21 (1, ddd, *J*=3.8, 3.8 and 10.0 Hz, H-5), 3.77 (2, m, 2H, H-6), 2.10-2.81 (8, m, COD-C$\underline{H}_2$), 4.32-5.20 (4, br., COD-C$\underline{H}$), 7.10-7.90 (20, m, arom. H). Anal. calcd. for $C_{39}H_{44}BF_4O_6P_2Rh$: C, 54.44; H, 5.15; P, 7.21; Rh, 11.96. Found: C, 53.38; H, 5.14; P, 7.11; Rh, 11.86.

[Rhodium{phenyl 2,3-bis(O-diphenylphosphino)-β-D-galactopyranosides} (cyclooctadiene)]tetrafluoroborate (**2g**) (2.6 g, 57 %) was prepared following the General Procedure from **2c** (3.7 g, 5 mmol) in 1 h at 65 °C. FAB$^+$-MS 836 (M^+-BF_4), 728 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 136.9 (dd, *J*=177.7 and 29.7 Hz), 132.4 (dd, *J*=177.7 and 29.9 Hz). ^{13}C NMR ($CDCl_3$) δ 98.1 (C-1), 69.1 (d, *J*=6.2 Hz), 73.6 (m), 78.1 (d, *J*=8.1 Hz), 89.5 (dd, *J*=4.7 and 4.7 Hz, C-2,3,4,5), 61.3 (C-6), 156.7 (C_{ipso}/OPh), 27.7-31.8 (m, COD-$\underline{C}H_2$), 102.8-107.6 (m, COD-$\underline{C}H$), 128.5-134.6 (arom. C), 116.6 (C-2'), 129.1 (C-3'), 122.6 (C-4'). ^{1}H NMR ($CDCl_3$) δ 3.96 (1, d, *J*=8.1 Hz, H-1), 4.37 (1, m, H-2), 4.97 (1, br., *J*=10.0 and 3.0 Hz, H-3), 4.50 (1, d, H-4), 3.58 (1, t, *J*=5.8, 5.8 and 0.0 Hz, H-5), 3.78 (2, m, H-6), 2.05-2.50 (8, m, COD-C$\underline{H}_2$), 4.21-5.33 (4, br., COD-C$\underline{H}$), 6.50, 6.89, 7.06 (5, m, arom. H_{OPh}), 7.00-8.00 (20, m, arom. H). Anal. calcd. for $C_{44}H_{46}BF_4O_6P_2Rh$: C, 57.29; H, 5.03; P, 6.72; Rh, 11.16. Found: C, 56.02; H, 5.09; P, 6.52; Rh, 10.12.

[Rhodium{methyl 2,3-bis(O-diphenylphosphino)-β-D-galactopyranosides} (cyclooctadiene)]tetrafluoroborate (**2h**) (3.8 g, 66 %) was prepared following the General Procedure from **2d** (3.4 g, 5 mmol) in 1 h at 65 °C. FAB$^+$-MS 773 (M^+-BF_4), 665 (M^+-108). ^{1}P NMR ($CDCl_3$) δ 134.9 (dd, *J*=176.8 and 30.5 Hz), 127.8 (dd, *J*=174.7 and 30.5 Hz). ^{13}C NMR ($CDCl_3$) δ 100.1 (C-1), 66.1 (s), 75.0 (d, *J*=7.1 Hz), 77.9 (dd, *J*=5.4 and 4.0 Hz), 80.1 (d, *J*=7.5 Hz, C-2,3,4,5), 69.0 (C-6), 56.5 (O$\underline{C}H_3$), 28.0-32.5 (m, COD-$\underline{C}H_2$), 102.2-108.2 (m, COD-$\underline{C}H$), 128.0-135.3 (arom. C). ^{1}H NMR ($CDCl_3$) δ 3.00 (3, m, OC$\underline{H}_3$), 3.41 (1, d, *J*=3.5 Hz, H-1), 4.25 (1, m, H-2), 4.20 (1, m, H-3), 4.12 (1, m, H-4), 3.51 (1, m, H-5), 4.23 (2, m, H-6), 7.10-7.98 (20, m, arom. H), 2.28-2.52 (8, m, COD-C$\underline{H}_2$), 4.31-5.40 (4, br., COD-C$\underline{H}$). Anal. calcd. for $C_{39}H_{44}BF_4O_6P_2Rh$: C, 54.44; H, 5.15; P, 7.21; Rh, 11.96. Found: C, 53.06; H, 5.30; P, 7.12; Rh, 11.01.

[Rhodium{phenyl 2,3-bis(O-diphenylphosphino)-α-D-glucopyranosides}(cyclooctadiene)]tetrafluoroborate (**3g**) (2.9 g, 62 %) was prepared following the General Procedure from **3c** (3.7 g, 5 mmol) in 3 h at 65 °C. FAB$^+$-MS 836 (M^+-BF_4), 728 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 139.0 (dd, *J*=182.6 and 25.5 Hz), 134.0 (dd, *J*=178.3 and 25.5 Hz). ^{13}C NMR ($CDCl_3$) δ 96.7 (d, *J*=5.1 Hz, C-1), 70.5 (d, *J*=5.1 Hz), 67.6 (s), 72.0 (m), 76.2 (d, *J*=8.0 Hz), 80.5 (d, *J*=10.2 Hz, C-2,3,4,5), 60.2 (C-6), 156.5 (C_{ipso}/OPh), 28.8-31.1 (m, COD-$\underline{C}H_2$), 101.6-107.0 (m, COD-$\underline{C}H$), 128.5-134.6 (arom. C) 116.8 (C-2'), 129.4 (C-3'), 122.7 (C-4'). ^{1}H NMR ($CDCl_3$) δ 5.14 (1, d, *J*=3.5 Hz, H-1), 4.03 (1, m, H-2), 4.30 (1, ddd, *J*=10.4 and 9.2 Hz, H-3), 3.67 (1, m, H-4), 3.43 (1, ddd, *J*=2.8, 3.8 and 10.0 Hz, H-5), 3.75, 3.48 (2, d, *J*=3.8 Hz), 4.36-4.87 (4, br.,

COD-CH), 2.10-2.60 (8, m, COD-CH_2), 6.82, 6.94, 7.18 (5, m, arom. H_{OPh}), 7.25-8.00 (20, m, arom. H). Anal. calcd. for $C_{44}H_{46}BF_4O_6P_2Rh$: C, 57.29; H, 5.03; P, 6.72; Rh, 11.16. Found: C, 55.57; H, 5.24; P, 6.82; Rh, 10.15.

[Rhodium{methyl 2,3-bis(O-diphenylphosphino)-α-D-glucopyranosides} (cyclooctadiene)]tetrafluoroborate (**3h**) (3.9 g, 90 %) was prepared following the General Procedure from **3d** (3.4 g, 5 mmol) in 48 h at 25 °C. FAB^+-MS 773 (M^+-BF_4), 665 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 132.7 (dd, J=178 and 27 Hz), 137.3 (dd, J=181 and 27 Hz). ^{13}C NMR ($CDCl_3$) δ 98.3 (d, J=4 Hz, C-1), 68.7 (s), 70.7 (m), 76.2 (d, J=8 Hz), 80.8 (d, J=9 Hz) (C-2,3,4,5), 60.9 (C-6), 55.1 (OCH_3), 27.9-30.9 (m, COD-CH_2), 101.5-102.2 (m, COD-CH), 128.5-134.6 (arom. C). ^1H NMR ($CDCl_3$) δ 4.73 (1, d, J=3.5 Hz, H-1), 3.86 (1, m, H-2), 4.14 (1, ddd, H-3), 3.15 (1, m, H-4), 3.27 (1, ddd, J=3.1, 2.8 and 9.9 Hz, H-5), 3.56 (2, m, H-6), 2.18-2.45 (8, m, COD-CH_2), 4.37-4.83 (4, br., COD-CH), 7.10-7.90 (20, m, arom. H). Anal. calcd. for $C_{39}H_{44}BF_4O_6P_2Rh$: C, 54.44; H, 5.15; P, 7.21; Rh, 11.96. Found: C, 52.11; H, 5.10; P, 7.22; Rh, 11.04.

[Rhodium{phenyl 2,3-bis(O-diphenylphosphino)-α-D-galactopyranosides} (cyclooctadiene)]tetrafluoroborate (**4g**) (3.6 g, 79 %) was prepared following the General Procedure from **4c** (3.7 g, 5 mmol) in 3 h at 65 °C. FAB^+-MS 836 (M^+-BF_4), 728 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 138.2 (dd, J=185.8 and 24.5 Hz), 136.4 (dd, J=181.3 and= 24.5 Hz). ^{13}C NMR ($CDCl_3$) δ 97.6 (d, J=4.1 Hz, C-1), 65.1 (s), 74.0 (d, J=9.1 Hz), 74.8 (d, J=10.2 Hz), 75.5 (C-2,3,4,5), 69.0 (C-6), 157.0 (C_{ipso}/OPh), 29.1-31.9 (m, COD-CH_2), 101.6-108.4 (m, COD-CH), 116.5 (C-2'), 129.4 (C-3'), 123.2 (C-4'), 128.4-135.0 (arom. C). ^1H NMR ($CDCl_3$) δ 5.38 (1, d, J=3.5 Hz, H-1), 4.30 (1, m, H-2), 4.42 (1, m, H-3), 4.30 (1, m, H-4), 3.71 (1, m, H-5), 4.07 (2, m, H-6), 2.31-2.55 (8, m, COD-CH_2), 4.34-4.80 (4, br., COD-CH), 7.10-7.90 (25, m, arom. H). Anal. calcd. for $C_{44}H_{46}BF_4O_6P_2Rh$: C, 57.29; H, 5.03; P, 6.72; Rh, 11.16. Found: C, 55.87; H, 5.10; P, 6.68; Rh, 10.46.

[Rhodium{methyl 2,3-bis(O-diphenylphosphino)-α-D-galactopyranosides} (cyclooctadiene)]tetrafluoroborate (**4h**) (4.0 g, 92 %) was prepared following the General Procedure from **4d** (3.4 g, 5 mmol) in 1 h at 65 °C. FAB^+-MS 773 (M^+-BF_4), 665 (M^+-108). ^{31}P NMR ($CDCl_3$) δ 135.9 (dd, J=179.8 and 26.2 Hz), 135.4 (dd, J=180.0 and 26.2 Hz). ^{13}C NMR ($CDCl_3$) δ 99.3 (d, J=3.7 Hz, C-1), 62.2 (s), 75.0 (d, J=8.1 Hz), 74.6 (d, J=8.8 Hz), 75.8 (d, J=3.4 Hz, C-2,3,4,5), 68.7 (C-6), 55.4 (OCH_3), 25.9-31.8 (COD-CH_2), 101.7-107.8 (COD-CH), 128.2-135.0 (arom. C). ^1H NMR ($CDCl_3$) δ 3.20 (3, m, OCH_3), 4.17 (1, d, J=3.5 Hz, H-1), 4.35 (1, m, H-2), 4.37 (1, m, H-3), 4.26 (1, m, H-4), 3.41 (1, m, H-5), 4.28 (2, m, H-6), 7.10-7.90 (20, m, arom. H), 2.30-2.50 (8, m, COD-CH_2), 4.35-4.78 (4, br., COD-CH). Anal. calcd. for $C_{39}H_{44}BF_4O_6P_2Rh$: C, 54.44; H, 5.15; P, 7.21; Rh, 11.96. Found: C, 53.41; H, 5.11; P, 7.16; Rh, 11.10.

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