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C_1-Symmetric Diphosphite Ligands Derived from Carbohydrates: Influence of Structural Modifications on the Rhodium-Catalyzed Asymmetric Hydroformylation of Styrene

Aitor Gual,[a] Cyril Godard,[a] Carmen Claver,*[a] and Sergio Castillón*[b]

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New 3,5-diphosphite-substituted xylofuranoside (**1b**, **25a**,**b**, and **26a**,**b**) and glucofuranoside (**3a**, **7a**, **8a**,**b**) ligands with C_1 symmetry have been prepared and used in the Rh-catalyzed asymmetric hydroformylation of styrene. The main structural features of these ligands are a) the presence of a 6-*O*-isopropyl group in ligands with a *gluco* configuration, b) the absence of 1,2-*O*-isopropylidene, a common group in many ligands with a furanoside skeleton, c) the presence of an alkyl chain bound to the 2-OH, and d) modification of the diol in the phosphite moiety. Modification of the carbohydrate backbone and diphosphite bridge affects the activity and selectivity of the reaction. Catalytic systems with ligands **1b** and **8b** were not active at 40 °C, although the formation of the expected hydride species [$RhH(CO)_2$(**1b**)] was demonstrated by NMR spectroscopy. The highest enantioselectivity (83 %) was obtained with the catalytic system Rh/**8a**. The complex [$RhH(CO)_2$(**8a**)] was characterized by NMR spectroscopy using high-pressure techniques and was shown to exist in solution as two isomers in equilibrium; the two isomers adopt an equatorial–equatorial (eq–eq) configuration.

Introduction

Owing to their structural properties, carbohydrates have been extensively used as starting materials for the synthesis of enantiomerically pure compounds. The presence of hydroxy groups facilitates the synthesis of oxygenated phosphorus functions and over the past decade, intensive work has been carried out by our group to develop ligands derived from carbohydrates and to analyze their behavior in asymmetric catalysis.[1] Most carbohydrates possess C_1 symmetry and as such the potential for the synthesis of ligand derivatives is very large. Furthermore, the successful use of C_1-symmetric diphosphite ligands has been reported in several asymmetric processes such as Pd-catalyzed allylic alkylation[2] and Rh-catalyzed hydrogenation.[3] Recently, the ability of these ligands to stabilize palladium nanoparticles was also demonstrated[4] and successfully applied in allylic alkylation.[4a,4b] Rhodium complexes containing C_1-symmetric diphosphites with a furanoside backbone **1**–**6** (Figure 1) behave as active catalysts in the asymmetric hydroformylation of vinylarenes.[5–7] In 1995, van Leeuwen and coworkers achieved excellent regioselectivity in the formation of branched aldehydes with enantioselectivities of up to 53% for the *S* product through the use of a catalytic system containing ligand **1**.[5a] Later, the ligand structure was modified to provide insights into the effect of different moieties in these ligands on the activity and/or selectivity of the catalytic system. The use of ligand **2** afforded 53% *ee* of the *R* product, which demonstrates that the configuration of the catalytic product is determined by the configuration at the C-3 stereocenter.[5b] The introduction of a new stereocenter at the C-5 position revealed that the value of the enantiomeric excess of the product is the result of a cooperative effect between the C-3 and C-5 stereocenters.[5c,5d] Within these ligand series, the highest selectivity in the asymmetric hydroformylation of vinylarenes was achieved by using the Rh/**3** system; the branched aldehydes were formed with regioselectivities of up to 98% and *ee*s of up to 93%.[5c,5d] In these studies the nature of the group contained within the phosphite moiety was also investigated and found to play an important role in the activity and enantioselectivity of the catalysts in this reaction.[5] Thus, the introduction of bulky substituents at the *ortho* position and electron-donating groups at the *para* position was found to be the most appropriate combination in terms of activity and selectivity.

Owing to the interesting results obtained by modifying ligands **1** and **2** at C-5, we decided to explore other modifications. We report herein the synthesis of new C_1-symmetric diphosphite ligands (**7** and **8**, Scheme 1) with a glucofuranoside backbone and their use in the rhodium-catalyzed hydroformylation of styrene. The main structural features

[a] Departament de Química Física i Química Inorgànica, Facultat de Química, Universitat Rovira i Virgili,
c/ Marcel.li Domingo s/n 43007 Tarragona, Spain
Fax: +34-977559563
E-mail: carmen.claver@urv.cat
[b] Departament de Química Analítica i Química Orgànica, Facultat de Química, Universitat Rovira i Virgili,
c/ Marcel.li Domingo s/n 43007 Tarragona, Spain
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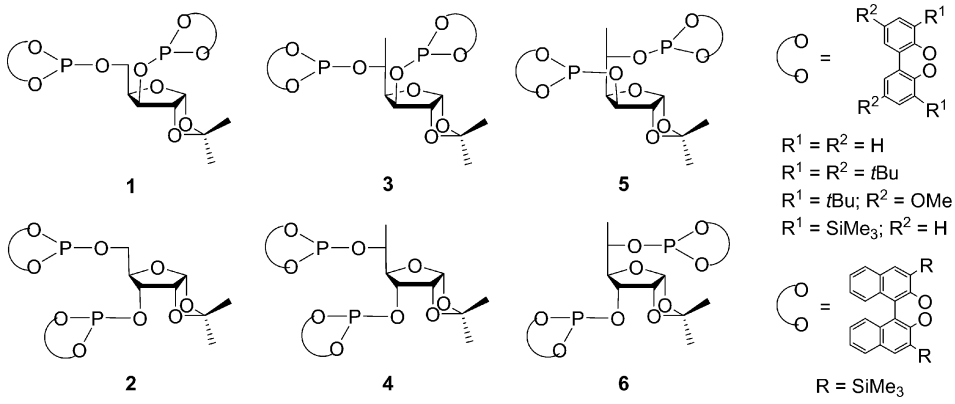
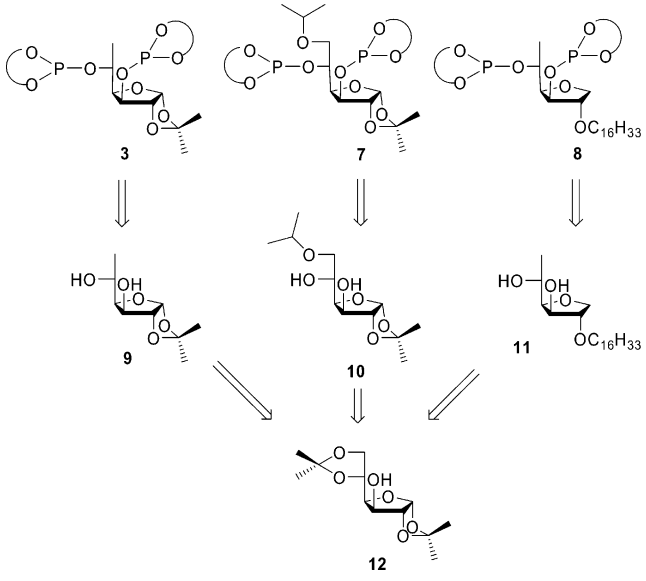


Figure 1. Reported diphosphites with a furanoside carbohydrate backbone.

of these new ligands with regard to compound **3** are the following: a) a higher substitution at the 6-position of the sugar to increase the steric hindrance in the proximity of the coordinating phosphorus atom, b) the absence of a 1,2-*O*-isopropylidene ring to increase the conformational freedom, and c) a new diol skeleton in the diphosphite moiety (see diol **b** in Scheme 5), which will provide a different environment around the rhodium center.



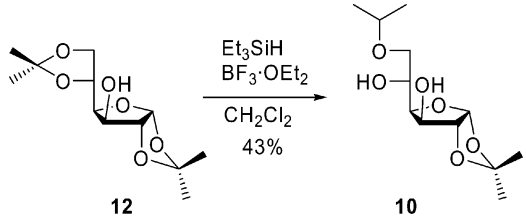
Scheme 1. Retrosynthetic strategies for the synthesis of **3**, **7**, and **8**.

Results and Discussion

Synthesis of Diphosphite Ligands with a Carbohydrate Backbone

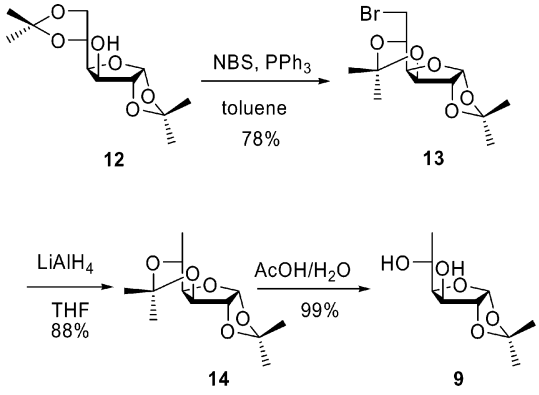
The general synthetic strategies used to obtain ligands **3**, **7**, and **8** from the commercially available compound **12** are shown in Scheme 1. Ligand **7** was prepared from diol **10**, which in turn can be easily prepared from **12**. The synthesis of ligand **8** from **12** requires the removal of the 5,6- and 1,2-*O*-isopropylidene groups, which can be carried out by controlled hydrolysis and reduction of the acetal function, respectively.

The diol **10** was synthesized in a straightforward manner by selective reductive opening of the 5,6-*O*-isopropylidene group of **12** by reaction with $BF_3{\cdot}Et_2O$ with triethylsilane as the hydride source (Scheme 2).[8]



Scheme 2. Synthesis of the diol backbone **10**.

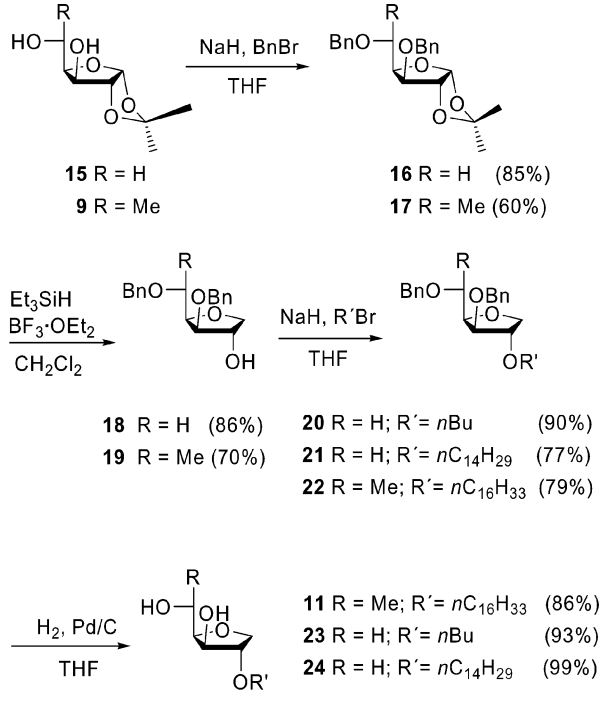
To explore new routes to the introduction of bulky substituents at the C-6 position, compound **12** was treated with *N*-bromosuccinimide (NBS)/PPh_3 to obtain the 6-bromo derivative **13**, which was isolated in 78% yield (Scheme 3).[9,10] This reaction involves the migration of the 5,6-*O*-isopropylidene group to the 3,5-position with entry of the bromine at the C-6 position.



Scheme 3. Synthesis of diol backbone **9**.

Various substitution reactions of the bromide in **13** were attempted, but all were unsuccessful because in all cases the major product was the elimination product. However, the reaction of **13** with $LiAlH_4$ afforded **14**; selective hydrolysis of the 3,5-*O*-isopropylidene acetal afforded **9**, thus completing a new and shorter synthetic route to the diol **9**, which is the precursor of the diphosphite **3**. The overall yield of the last three steps was 68% (Scheme 3).

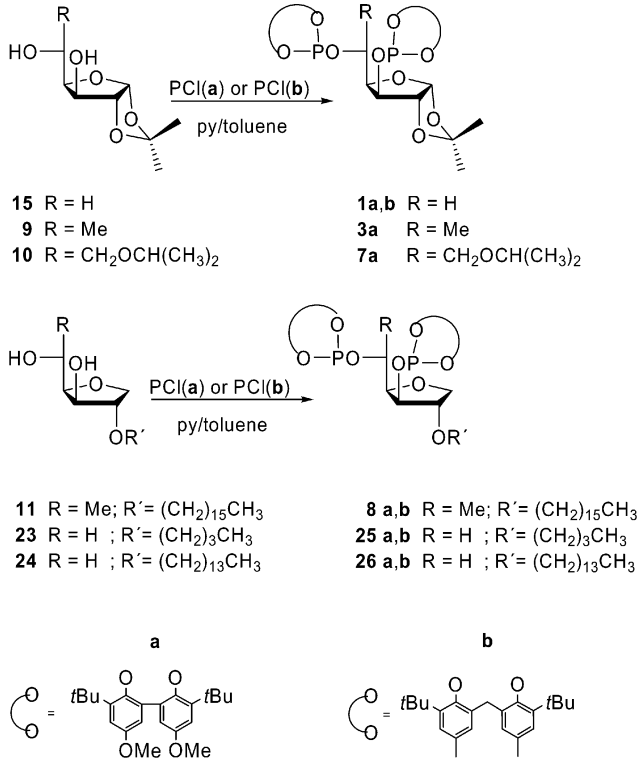
The diols **11**, **23**, and **24** (Scheme 4), were synthesized from compounds **9** and **15**, which were prepared for comparative purposes with the corresponding ligands.[5] Initially, the 3,5-hydroxy groups in compounds **15** and **9** were protected as benzyl ether groups by reaction with BnBr to give compounds **16** and **17** in 85 and 60% yields, respectively.[11] Treatment of **16** and **17** with $Et_3SiH/BF_3{\cdot}Et_2O$ afforded the alcohols **18** and **19** in high yields (86 and 70%, respectively).[12] However, the replacement of $BF_3{\cdot}Et_2O$ by trimethylsilyl triflate resulted in the formation of the 2-*O*-isopropyl derivatives (10–20%) as byproducts. The *p*-methoxybenzyl ether derivatives of **9** and **15** were also prepared in order to have alternative deprotection procedures.[11] However, when these compounds were treated with $Et_3SiH/BF_3{\cdot}Et_2O$ deprotection of the *p*MeO-benzyl ether groups occurred.



Scheme 4. Synthesis of the diol backbones **11**, **23**, and **24**.

Compounds **18** and **19** were treated with NaH and *n*BuBr, *n*-$C_{14}H_{29}Br$, or *n*-$C_{16}H_{33}Br$ to give compounds **20**–**22** in high yields (90, 77, and 70%, respectively). The benzyl groups were removed by hydrogenolysis using Pd/C as catalyst under 1 atm of H_2 to afford the diols **23**, **24**, and **11** in high yields (93, 99, and 86%, respectively; Scheme 4).

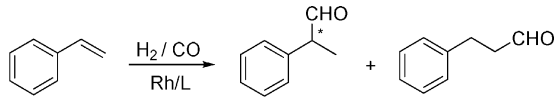
Finally, the diols **9**–**11**, **15**, **23**, and **24** were treated with phosphorochloridites derived from the bis-phenols **a** and **b** (Scheme 5), which had previously been synthesized in situ by standard procedures, to yield the corresponding diphosphite ligands **1a**,**b**, **3a**, **7a**, **8a**,**b**, **25a**,**b**, and **26a**,**b** in moderate-to-good yields (20–70%).[13] All these ligands were characterized by NMR spectroscopy and elemental analysis (see Exptl. Sect. for spectroscopic details). Ligands **8a**,**b**, **25a**,**b**, and **26a**,**b**, which contain an alkyl chain, were recently used to stabilize ruthenium nanoparticles and used as catalysts in arene hydrogenation.[14]



Scheme 5. Synthesis of diphosphite ligands.

Rh-Catalyzed Asymmetric Hydroformylation of Styrene

Catalytic systems containing the synthesized chiral diphosphites were used in the rhodium-catalyzed asymmetric hydroformylation of styrene (Scheme 6).



Scheme 6. Rhodium-catalyzed asymmetric hydroformylation of styrene.

The catalytic systems were formed in situ by the addition of 1.1 equiv. of the diphosphite ligand (L = **1a**,**b**, **3a**, **7a**, **8a**,**b**, **25a**,**b**, and **26a**,**b**) to a toluene solution of [Rh(acac)$(CO)_2$] (acac = acetylacetonate). The substrate was then added and the solution was introduced into an autoclave. Finally, the autoclave was pressurized with 25 bar of CO/H_2 (ratio 1:1) and heated at 40 °C for 15 h.

Total chemoselectivity to aldehydes was achieved in all cases. The results are summarized in Tables 1, 2, and 3.

Table 1 summarizes the results obtained for the rhodium-catalyzed hydroformylation of styrene using the xylofuranoside-derived ligands **1a**,**b**, **25a**,**b**, and **26a**,**b**. When the reaction was performed in the presence of ligand **1a**, the conversion was measured as 41% with a regioselectivity of 96% for the formation of the branched product and an *ee* of 50% (Entry 1, Table 1). This result is in agreement with that previously reported for this system.[5a]

Table 1. Rhodium-catalyzed hydroformylation of styrene using diphosphites **1a**,**b**, **25a**,**b**, and **26a**,**b**.[a,b]

Entry	Ligand	% Conversion	% Regioselectivity[c]	% *ee* (config.)
1	**1a**	41	96	50 (*S*)
2	**1b**	0	–	–
3[d]	**1b**	0	–	–
4[e]	**1b**	56	58	27 (*S*)
5	**25a**	11	97	61 (*S*)
6	**25b**	30	96	60 (*S*)
7	**26a**	23	96	60 (*S*)
8	**26b**	33	94	61 (*S*)

[a] Substrate/Rh ratio: 1000, styrene: 13 mmol, Rh/L = 1:1.1, [Rh(acac)(CO)$_2$]: 0.0135 mmol, P = 25 bar, $P_{CO/H2}$ = 1, toluene = 15 mL, t = 15 h, T = 40 °C. [b] The conversion of styrene and the regioselectivity and enantiomeric excess were determined by GC. [c] 2-Phenylpropanal. [d] Incubation: 16 h at 40 °C. [e] T = 80 °C.

Surprisingly, by using the catalytic system containing ligand **1b**, in which the bis-phenyl moiety was modified, no conversion was observed at 40 °C (Entry 2). An incubation period to promote the formation of the active species[5a,5b] did not promote activity (Entry 3). It was found that a temperature of 80 °C (Entry 4) is required to obtain significant conversion (56%), although the regio- and enantioselectivity decrease (58 and 27%, respectively), which suggests the formation of the [RhH(CO)$_4$] species. Further investigations into this system were performed in situ by using high-pressure NMR techniques and will be presented later in this article. When ligands **25a**,**b** and **26a**,**b** were used (Entries 5–8), the resulting catalytic systems were moderately active, achieving conversions of up to 33%. All these systems yielded the branched product with high regioselectivity (up to 97%) and moderate enantioselectivity (up to 61%). These results indicate that the use of ligands containing a monocyclic backbone provide higher *ee*s than the bicyclic ligand **1a**. However, slightly lower conversions were obtained and no effect was observed on the regioselectivity of the reaction.

Previously we have shown that the introduction of a stereogenic center at C-5 (glucofuranoside derivatives) improves the catalytic results.[5c,5d] Therefore, we considered it of interest to synthesize ligands **3a**, **7a**, and **8a**,**b** containing substituents at the C-5 position.

The Rh/**7a** catalytic system, in which the ligand is a bicyclic structure with an *O*-CH(CH$_3$)$_2$ substituent at the C-6 position, afforded 48% conversion, 97% regioselectivity, and 68% enantiomeric excess (Entry 1, Table 2). The catalytic system containing the monocyclic ligand **8a** provided a similar conversion and regioselectivity as ligand **7a**, but the *ee* increased to 75% (Entry 2, Table 2). The effect of the diphosphite bridge in **8a**,**b** (Entries 2–4) is similar to that described for ligands **1a**,**b** (Entries 1 and 2, Table 1). Again, a temperature of 80 °C was required to obtain significant conversions with **8b**, but the selectivity suggests the presence of the unmodified [RhH(CO)$_4$] active species under these conditions (Entry 4, Table 2).[15] As previously observed, the *ee* values obtained with the ligands with the glucofuranoside backbone (**7a** and **8a**; up to 75%) were higher than those obtained with ligands with a xylofuranoside backbone (**1a**, **25a**, and **26a**; up to 61%).[5c,5d]

Table 2. Rhodium-catalyzed hydroformylation of styrene using diphosphites **7a**, **8a**, and **8b**.[a,b]

Entry	Ligand	% Conversion	% Regioselectivity[c]	% *ee* (config.)
1	**7a**	48	97	68 (S)
2	**8a**	50	97	75 (S)
3	**8b**	0	–	–
4[d]	**8b**	97	54	–

[a] Substrate/Rh ratio: 1000, styrene: 13 mmol, Rh/L = 1:1.1, [Rh(acac)(CO)$_2$]: 0.0135 mmol, P = 25 bar, $P_{CO/H2}$ = 1, toluene: 15 mL, t = 15 h, T = 40 °C. [b] The conversion of styrene and the regioselectivity and enantiomeric excess were determined by GC. [c] 2-Phenylpropanal. [d] T = 80 °C.

The reaction conditions were optimized with catalytic systems containing ligands **7a** and **8a** and the results are presented in Table 3. Interestingly, when the total pressure was decreased from 25 to 10 bar, an increase in the activity of the catalytic system was observed without affecting the regio- or enantioselectivity of the reaction (Entries 1 and 2). Furthermore, lowering the CO/H$_2$ ratio also increased the conversion (83%), but the regio- and enantioselectivity remained unchanged (Entry 3). These results can be attributed to the presence of inactive carbonyl dinuclear or cluster species at high CO pressure.[16] When the temperature was decreased to 20 °C, the enantiomeric excess increased to 73% (Entry 4). However, no noticeable effect on the *ee* value was observed when the ligand/rhodium ratio was increased from 1.1 to 2 (Entry 5). The catalytic system containing ligand **8a** provided low conversions under these conditions and the enantioselectivity slightly increased to 79%.

Table 3. Rhodium-catalyzed hydroformylation of styrene using diphosphites **7a** and **8a**.[a,b]

Entry	L	P [bar]	$P_{CO/H2}$	T[a] [°C]	% Conv.	% Regioselectivity[c]	% *ee* (config.)
1	**7a**	25	1	40	48	97	68 (*S*)
2	**7a**	10	1	40	66	97	67 (*S*)
3	**7a**	10	0.5	40	83	97	67 (*S*)
4[d]	**7a**	10	0.5	20	78	99	73 (*S*)
5[d,e]	**7a**	10	0.5	20	38	96	76 (*S*)
6[d,e]	**8a**	10	0.5	20	10	97	79 (*S*)
7[d]	**8a**	10	0.5	20	29	98	83 (*S*)

[a] Substrate/Rh ratio: 1000, styrene: 13 mmol, Rh/L = 1:1.1, [Rh(acac)(CO)$_2$]: 0.0135 mmol, toluene: 15 mL. [b] The conversion of styrene and the regioselectivity and enantiomeric excess were determined by GC. [c] 2-Phenylpropanal. [d] t = 48 h, incubation: 16 h at 40 °C. [e] Rh/L = 1:2.0.

By using a lower ligand/metal ratio (Entry 7), the activity was found to increase (29%) without affecting the regio- (98%) and enantioselectivity (83%).

The enantiomeric excesses obtained with ligands **7a** and **8a** in the rhodium-catalyzed hydroformylation of styrene were both rather high (76 and 83%, respectively) although they do not exceed that previously reported for ligand **3a**.[5c,5d]

High-Pressure NMR Study

To gain information about the effect of modifications to the phosphite moieties as well as the sugar backbone, high-pressure NMR experiments of the systems containing **1b** and **8a** were performed.

The hydridorhodium diphosphite complexes [RhH-$(CO)_2$(L)] (L = bidentate ligand) are often observed as resting states in the hydroformylation reaction. Two isomeric tbpy structures can be formed with the coordinated bidentate ligand (Figure 2).[14] The complexes with an eq–eq (equatorial–equatorial) configuration are expected to exhibit $J_{P\text{-}H} < 10$ Hz and $J_{P\text{-}P} \approx 250$ Hz couplings, whereas for the eq–ax (equatorial–axial) configuration, $J_{P\text{-}H} \approx 180$–200 Hz and $J_{P\text{-}P} \approx 70$ Hz couplings are usually observed.[5,15,17–19]

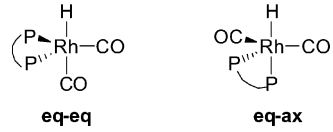
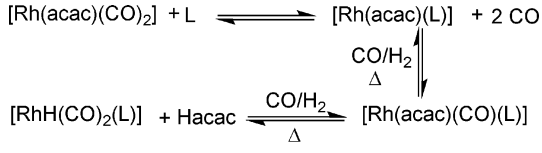


Figure 2. Equatorial–equatorial (eq–eq) and equatorial–axial (eq–ax) [RhH$(CO)_2$L] species.

One equivalent of the diphosphite ligand (**1b** or **8a**) was added to a 2 mM solution of [Rh(acac)$(CO)_2$] in [D_8]toluene in a 10 mm NMR tube at room temperature. In both cases, a rapid change of color was observed at this stage. The NMR tube was pressurized with syngas, shaken for 16 h at 40 °C, placed in the spectrometer, and the NMR spectra were recorded at various temperatures. Under these conditions, signals corresponding to the rhodium hydride species [RhH$(CO)_2$(L)] (L = **1b** and **8a**) were readily detected. The general mechanism for the formation of these species is shown in Scheme 7.



Scheme 7. Formation of [RhH$(CO)_2$(L)] from [Rh(acac)$(CO)_2$] and diphosphites (L = **1b**, **8a**).

The $^{31}P\{^1H\}$ NMR spectra of the solution containing [Rh(acac)$(CO)_2$]/**8a** under 10 bar of syngas at room temperature showed four doublets exhibiting a characteristic $^1J_{Rh\text{-}P} \approx 300$ Hz and $^2J_{P\text{-}P} \approx 100$ Hz, which were readily attributed to the [Rh(acac)(CO)(**8a**)] complex, together with a broad multiplet assigned to [RhH$(CO)_2$(**8a**)].[5c,5d] A broad hydride signal ($\Delta\omega_{1/2} \leq 90$ Hz) was detected in the corresponding ^{1}H NMR spectrum. Broadening of the signals was observed when the temperature was decreased to 233 K. Signals of the [RhH$(CO)_2$(**8a**)] complex were found to sharpen at 184 K with the detection of two second-order signals in the $^{31}P\{^1H\}$ NMR spectrum (Figure 3, d). In the corresponding ^{1}H NMR spectrum, two broad hydride peaks were detected.

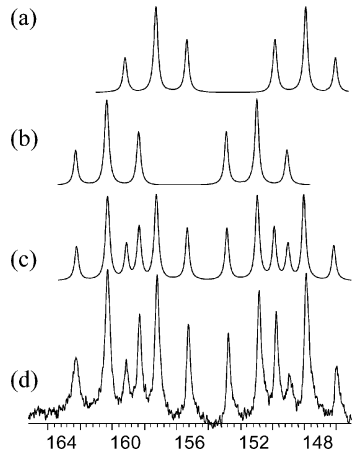


Figure 3. Simulated $^{31}P\{^1H\}$ NMR spectra corresponding to two isomers (traces a and b) of the complex [RhH$(CO)_2$(**8a**)] with **8a** in an eq–eq configuration; c) overlay of simulated spectra a + b; d) recorded $^{31}P\{^1H\}$ NMR spectra of the complex [RhH$(CO)_2$(**8a**)] formed from the precursor [Rh(acac)$(CO)_2$] in the presence of ligand **8a** under hydroformylation conditions (incubation: $t = 16$ h, $T = 40$ °C, $P = 10$ bar, $P_{CO/H2} = 0.5$) in [D_8]toluene. The spectrum was recorded at 184 K.

To determine the identity of these two species, the $^{31}P\{^1H\}$ NMR spectra were simulated by using the gNMR V4.0 software. The results of these simulations indicate that the spectrum obtained experimentally (Figure 3, trace d) corresponds to the sum of the signals (Figure 3, trace c) arising from two distinct species that exhibit coupling constants $J_{Rh\text{-}P}$ between 250 and 231 Hz and $J_{P\text{-}P}$ between 247 and 227 Hz, which is in agreement with eq–eq structures for both species. The simulated spectra corresponding to each species separately are shown in parts a and b of Figure 3. It was therefore concluded that two isomeric complexes of formula [(eq–eq)-RhH$(CO)_2$(**8a**)] coexist in solution.

Interestingly, in a previous report on the bicyclic diphosphite system Rh/**3a**, only one species containing the ligand coordinated in an eq–eq fashion was detected.[5c,5d] The flexibility induced by the monocyclic structure of ligand **8a** could explain the formation of two species that differ by spatial arrangement of the ring or by the relative position of the alkyl chain pointing towards/away from the phosphite moieties. The formation of two diastereoisomeric species can, however, not be discarded (Figure 4). The spectral features of the complex [RhH$(CO)_2$(**8a**)] at temperatures between 184 and 298 K are summarized in Table 4.

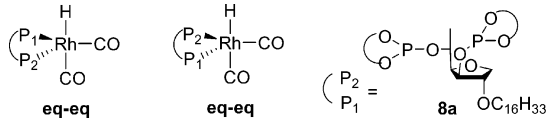


Figure 4. Schematic representation of two possible diastereoisomeric species of formula [RhH(CO)$_2$(**8a**)] detected by high-pressure NMR spectroscopy.

Table 4. Selected ^{1}H and ^{31}P{^{1}H} NMR spectroscopic data for the [RhH(CO)$_2$(**8a**)] complex.[a,b]

T [K]	δ(P1) [ppm]	δ(P1) [ppm]	J_{Rh-P1} [Hz]	J_{Rh-P2} [Hz]	J_{P1-P2} [Hz]	δ(H) [ppm]
298	153.3(m)	153.3(m)	–	–	–	–9.8
233	broad	broad	–	–	–	–9.8
193	160.3	151.0	241	229	235	–9.8
	157.1	148.0	231	225	228	–9.8
184	160.3	150.9	241	229	235	–9.7
	157.2	148.0	234	224	229	–9.9

[a] Rh/L ratio 1:1.1, solvent: [D$_8$]toluene, P = 10 bar, $P_{CO/H2}$ = 0.5, incubation: 16 h at 40 °C. [b] ^{31}P and ^{1}H NMR spectra recorded using a 10-mm high-pressure NMR tube.

In the ^{31}P{^{1}H} NMR spectrum of [RhH(CO)$_2$(**1b**)] under 25 bar of syngas at room temperature, two broad doublets arising from Rh–P coupling ($^1J_{Rh-P}$ = 232.08 Hz and $^1J_{Rh-P}$ = 233.90 Hz) were observed without discernible $^2J_{P-P}$ coupling. The hydride signal was observed in the ^{1}H NMR spectrum as a broad multiplet ($\Delta\omega$½ ≤ 36 Hz). Broad signals were again observed when ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at lower temperatures. In previous work on the system containing diphosphite ligand **1a**, only one ^{31}P doublet resonance was reported for the corresponding complex with a $^1J_{Rh-P}$ coupling constant close to 236 Hz and without a discernible $^2J_{P-P}$ coupling constant. An eq–eq configuration was then assigned to this complex.[5a] It was therefore concluded that, although no conversion was observed with this system (see Table 1, Entries 3 and 4), the hydride species was formed under these conditions. Thus, as modification of the phosphite moiety does not affect the formation of the hydride complex, the cause of the inactivity of this system must be arise at a later stage of the catalytic cycle. The steric bulk of this moiety could hinder the coordination of the substrate, thus hampering the reaction. At a higher temperature (80 °C) the results obtained support the formation of the unmodified rhodium hydride carbonyl system, which would explain why the reaction showed no enantioselectivity.

Conclusions

A new series of diphosphite ligands **1b**, **7a**, **8a**,**b**, **25a**,**b**, and **26a**,**b** with C_1 symmetry have been prepared by modifying the 1,2-*O*-isopropylidenefuranoside backbone, the substituent at C-6, and the diphosphite moiety. We have developed new synthetic routes to these ligands and also a shorter route to the reference ligand **3a**. These new diphosphite ligands were used in the Rh-catalyzed asymmetric hydroformylation of styrene. The introduction of a new phosphite bridge (ligands **1b**, **8b**, **25b**, and **26b**) led to a decrease or a lack of activity, depending on the substituents in the backbone. In spite of this lack of activity, the intermediate [RhH(CO)$_2$(L)] (L = **1b**) was observed by high-pressure NMR techniques, which demonstrates that the formation of this species is not a limiting step of the reaction. Enantioselectivities of up to 83% *ee* were obtained for ligand **8a**. The high-pressure NMR study provided a possible explanation for the lower *ee* value obtained with ligand **8a** when compared with that obtained with ligand **3a**. Two eq–eq [RhH(CO)$_2$L] isomers where detected for the ligand **8a**, whereas in the case of ligand **3a** only one species was formed.[5c,5d]

Experimental Section

General Methods: All syntheses were performed by using standard Schlenk techniques under N_2. Solvents were purified by standard procedures. All other reagents were used as received. Elemental analyses were performed with a Carlo–Erba EA-1108 instrument. Optical rotations were measured at room temperature in a 10-cm cell. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a Varian Gemini 400 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^{1}H and ^{13}C) as the internal standard or H_3PO_4 (^{31}P) as the external standard. All NMR spectral assignments were determined by COSY and HSQC spectra. Hydroformylation reactions were carried out in a 100 mL Berghof stainless steel autoclave. Gas chromatographic analyses were preformed with a Hewlett–Packard HP 5890A instrument (split/splitless injector, J&W Scientific, HP-5, 25 m column, internal diameter 0.25 mm, film thickness 0.33 mm, carrier gas 150 kPa He, FID detector) equipped with a Hewlett–Packard HP3396 series II integrator. The enantiomeric excesses of the hydroformylation reaction were measured after oxidation of the aldehydes to the corresponding carboxylic acids with a Hewlett–Packard HP 5890A gas chromatograph (split/splitless injector, J&W Scientific, FS-Cyclodex β-I/P 50 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas 100 kPa He, FID detector). Absolute configurations was determined by comparing retention times with optically pure (*S*)-(+)-2-phenylpropionic and (*R*)-(–)-2-phenylpropionic acids.

Synthesis of the Ligands

6-*O*-Isopropyl-1,2-*O*-isopropylidene-α-D-glucofuranoside (10): Et_3SiH (4.26 mL, 26.7 mmol) and $BF_3{\cdot}Et_2O$ (1.51 mL, 11.9 mmol) were added to a solution of **12** (1.76 g, 6.63 mmol) in CH_2Cl_2 (250 mL) cooled to –10 °C. The reaction mixture was stirred at –10 °C for 2 h and then quenched by careful addition to saturated $NaHCO_3/H_2O$ (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were washed with brine and dried with $MgSO_4$. Purification by flash chromatography (EtOAc, R_f = 0.42) gave compound **10** as a colorless oil (748 mg, 43%). $[\alpha]_D^{25}$ = –1.13 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 {d, J = 5.6 Hz, 6 H, [OCH(CH$_3$)$_2$]}, 1.32 [s, 3 H, O$_2$C(CH$_3$)$_2$], 1.49 [s, 3 H, O$_2$C(CH$_3$)$_2$], 3.54 (dd, J = 10, 5.6 Hz, 1 H, 6-H), 3.67 [m, 1 H, OCH(CH$_3$)$_2$], 3.74 (dd, J = 10, 3.2 Hz, 1 H, 6′-H), 4.08 (dd, J = 5.8, 2.7 Hz, 1 H, 4-H), 4.15 (m, 1 H, 5-H), 4.35 (br., 1 H, 3-H), 4.55 (d, J = 3.2 Hz, 1 H, 2-H), 5.97 (d, J = 3.6 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.1 [OCH(CH$_3$)$_2$], 26.3 [O$_2$C(CH$_3$)$_2$], 26.9 [O$_2$C(CH$_3$)$_2$], 68.9 (C-6), 69.7 (C-5), 72.7 [OCH(CH$_3$)$_2$], 76.0 (C-4), 80.2 (C-3), 85.2 (C-2), 105.0 (C-1), 111.7 [O$_2$C(CH$_3$)$_2$] ppm. $C_{12}H_{22}O_6$ (262.30): calcd. C 54.95, H 8.45; found C 54.59, H 8.70.

6-Bromo-6-deoxy-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranoside (13): Compounds **12** (5 g, 19.2 mmol), Ph_3P (8.31g, 31.7 mmol), and *N*-bromosuccinimide (5.13g, 28.8 mmol) were dissolved in toluene (50 mL). The resulting solution was heated at 90 °C for 2 h, then cooled, washed with 5% $NaHCO_3/H_2O$, and dried ($MgSO_4$). Purification by flash chromatography (EtOAc/hexane = 1:16, R_f = 0.25) gave **13** as a colorless oil (4.84 g, 78%). $[\alpha]_D^{25}$ = +31.82 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 {s, 3 H, $[O_2C(CH_3)_2]$}, 1.36 [s, 3 H, $O_2C(CH_3)_2$], 1.37 [s, 3 H, $O_2C(CH_3)_2$], 1.48 [s, 3 H, $O_2C(CH_3)_2$], 3.43 (dd, *J* = 11.2, 7.6 Hz, 1 H, 6-H), 3.60 (dd, *J* = 11.0, 3.4 Hz, 1 H, 6′-H), 3.73 (td, *J* = 7.2, 3.2 Hz, 1 H, 5-H), 4.22 (d, *J* = 4.4 Hz, 1 H, 3-H), 4.31 (dd, *J* = 7.2, 4.0 Hz, 1 H, 4-H), 4.58 (d, *J* = 3.6 Hz, 1 H, 2-H), 5.98 (d, *J* = 3.6 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.9 [$O_2C(CH_3)_2$], 24.0 [$O_2C(CH_3)_2$], 26.6 [$O_2C(CH_3)_2$], 27.3 [$O_2C(CH_3)_2$], 33.1 (C-6), 72.0 (C-5), 75.2 (C-3), 81.7 (C-4), 84.0 (C-2), 101.5 [$O_2C(CH_3)_2$], 106.5 (C-1), 112.5 [$O_2C(CH_3)_2$] ppm. $C_{12}H_{19}BrO_5$ (323.18): calcd. C 44.60, H 5.93; found C 44.28, H 6.12.

6-Deoxy-1,2:3,5-di-*O*-isopropylidene-α-D-glucofuranoside (14): $LiAlH_4$ (275mg, 7.0 mmol) was added to a solution of **13** (900 mg, 2.7 mmol) in THF (30 mL). The mixture was stirred overnight at room temperature. The reaction was quenched by careful addition of EtOAc and 2.5 M NaOH (5 mL). The precipitate formed was removed by filtration. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were washed with brine and dried with $MgSO_4$. Purification by flash chromatography (EtOAc/hexane = 1:14, R_f = 0.25) gave **14** as a colorless oil (581 mg, 88%). $[\alpha]_D^{25}$ = +34.43 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 [s, 3 H, $O_2C(CH_3)_2$], 1.30 [s, 6 H, $O_2C(CH_3)_2$], 1.31 (d, *J* = 4.0 Hz, 3 H, 6-H), 1.46 [s, 3 H, $O_2C(CH_3)_2$], 3.61 (m, 1 H, 5-H), 4.18 (dd, *J* = 7.2, 3.6 Hz, 1 H, 3-H), 4.17 (d, *J* = 3.6 Hz, 1 H, 4-H), 4.55 (d, *J* = 4.0 Hz, 1 H, 2-H), 5.96 (d, *J* = 3.6 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.7 (C-6), 24.2 [$O_2C(CH_3)_2$], 24.3 [$O_2C(CH_3)_2$], 26.7 [$O_2C(CH_3)_2$], 27.3 [$O_2C(CH_3)_2$], 68.0 (C-5), 74.9 (C-3), 84.3 (C-4), 85.0 (C-2), 100.7 [$O_2C(CH_3)_2$], 106.4 (C-1), 112.2 [$O_2C(CH_3)_2$] ppm. $C_{12}H_{20}O_5$ (244.28): calcd. C 59.00, H 8.25; found C 58.76, H 8.50.

6-Deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoside (9): Compound **14** (1.0 g, 4.1 mmol) was dissolved in AcOH/H_2O (65%, 5 mL) and the mixture was stirred at 40 °C for 10 h. After cooling to room temperature, the solution was co-evaporated with EtOH and toluene at reduced pressure and the residue was purified by flash chromatography (EtOAc/hexane = 1:1, R_f = 0.1) to afford **9** as a colorless oil (829 mg, 99% yield). $[\alpha]_D^{25}$ = –10.43 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 [s, 3 H, $O_2C(CH_3)_2$], 1.37 (d, *J* = 6.0 Hz, 3 H, 6-H), 1.48 [s, 3 H, $O_2C(CH_3)_2$], 3.93 (m, 1 H, 5-H), 4.31 (m, 1 H, 3-H), 4.36 (d, *J* = 2.0 Hz, 1 H, 4-H), 4.52 (d, *J* = 3.6 Hz, 1 H, 2-H), 5.97 (d, *J* = 3.6 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.7 (C-6), 26.3 [$O_2C(CH_3)_2$], 26.9 [$O_2C(CH_3)_2$], 67.4 (C-5), 75.6 (C-3), 82.0 (C-4), 85.4 (C-2), 105.0 (C-1), 111.9 [$O_2C(CH_3)_2$] ppm. $C_9H_{16}O_5$ (204.22): calcd. C 52.90, H 7.90; found C 52.70, H 8.02.

General Procedure for the Benzylation of 9 and 15: NaH (653 mg, 16.0 mmol) was added to a solution of diol **9** or **15** (4.0 mmol) in THF (30 mL) at room temperature and the reaction was maintained for 1 h. Afterwards, benzyl bromide (1.94 mL, 16 mmol) was added and the reaction mixture was stirred overnight at room temperature. The reaction was quenched by careful addition of H_2O. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were washed with brine and dried with $MgSO_4$. Purification by flash chromatography gave the corresponding benzylated products **16** and **17**.

3,5-Di-*O*-benzyl-1,2-isopropylidene-α-D-xylofuranoside (16): Compound **16** was synthesized according to the general procedure described above. The product was isolated as a colorless oil in 85% yield (1.26g) after purification using the eluent system EtOAc/hexane = 1:8 (R_f = 0.34). $[\alpha]_D^{25}$ = –4.45 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 [s, 3 H, $O_2C(CH_3)_2$], 1.50 [s, 3 H, $O_2C(CH_3)_2$], 3.77 (m, 2 H, 5,5′-H), 3.99 (d, *J* = 3.2 Hz, 1 H, 3-H), 4.41 (dt, *J* = 6.8, 2.8 Hz, 1 H, 4-H), 4.52 (m, 2 H, OCH_2Ph), 4.62 (m, 3 H, 2-H, OCH_2Ph), 5.95 (d, *J* = 3.6 Hz, 1 H, 1-H), 7.32 (m, 10 H, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.5 [$O_2C(CH_3)_2$], 27.0 [$O_2C(CH_3)_2$], 67.7 (C-5), 72.2 (OCH_2Ph), 73.7 (OCH_2Ph), 79.4 (C-4), 81.9 (C-3), 82.6 (C-2), 105.3 (C-1), 111.9 [$O_2C(CH_3)_2$], 127.8–128.6 (aromatic), 137.7 (aromatic), 138.2 (aromatic) ppm. $C_{22}H_{26}O_5$ (370.44): calcd. C 71.33, H 7.07; found C 70.98, H 7.25.

3,5-Di-*O*-benzyl-6-deoxy-1,2-isopropylidene-α-D-glucofuranoside (17): Compound **17** was synthesized according to the general procedure described above. The product was isolated as a colorless oil in 60% yield (923 mg, 2.4 mmol) after purification using the eluent system EtOAc/hexane = 1:8 (R_f = 0.30). $[\alpha]_D^{25}$ = –26.83 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 [s, 3 H, $O_2C(CH_3)_2$], 1.41 (d, *J* = 6.0 Hz, 3 H, 6-H), 1.53 [s, 3 H, $O_2C(CH_3)_2$], 4.02 (m, 1 H, 5-H), 4.10 (dd, *J* = 9.0, 3.0 Hz, 1 H, 3-H), 4.15 (d, *J* = 2.8 Hz, 1 H, 4-H), 4.48 (m, 2 H, OCH_2Ph), 4.66 (br., 3 H, 2-H, OCH_2Ph), 5.95 (d, *J* = 3.6 Hz, 1 H, 1-H), 7.30 (m, 10 H, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.4 (C-6), 26.4 [$O_2C(CH_3)_2$], 26.9 [$O_2C(CH_3)_2$], 70.9 (C-5), 72.1 (OCH_2Ph), 72.2 (OCH_2Ph), 81.6 (C-4), 82.3 (C-2), 83.4 (C-3), 105.0 (C-1), 111.7 [$O_2C(CH_3)_2$], 127.6–128.5 (10 aromatic), 137.8 (aromatic), 138.7 (aromatic) ppm. $C_{23}H_{28}O_5$ (384.47): calcd. C 71.85, H 7.34; found C 71.58, H 7.47.

General Procedure for the Deprotection/Reduction of 1,2-*O*-Isopropylidenefuranosides: Et_3SiH (1.5 mL, 9.2 mmol) and $BF_3{\cdot}Et_2O$ (1.2 mL, 9.4 mmol) were added to a solution of the starting material **16** or **17** (2.0 mmol) in CH_2Cl_2 (15 mL) cooled to 0 °C. The reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by careful addition of saturated $NaHCO_3/H_2O$ (15 mL) and CH_2Cl_2 (40 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were washed with brine and dried with $MgSO_4$. Purification by flash chromatography gave the corresponding alcohols **18** and **19**.

1,4-Anhydro-3,5-di-*O*-benzyl-D-xylitol (18): Compound **18** was synthesized according to the general procedure described above. The product was isolated as a white solid in 86% yield (541 mg, 1.72 mmol) after purification using the eluent system EtOAc/hexane = 1:4 (R_f = 0.30). $[\alpha]_D^{25}$ = –11.09 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.74 (m, 3 H, 1′-H, 5,5′-H), 3.94 (d, *J* = 4.0 Hz, 1 H, 2-H), 4.19 (dd, *J* = 9.6, 4.4 Hz, 1 H, 1-H), 4.32 (m, 1 H, 4-H), 4.37 (m, 1 H, 3-H), 4.55 (m, 2 H, OCH_2Ph), 4.64 (m, 2 H, OCH_2Ph), 7.30 (m, 10 H, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 69.0 (C-5), 72.8 (C-1), 74.0 (OCH_2Ph), 74.1 (OCH_2Ph), 75.6 (C-3), 79.7 (C-4), 84.8 (C-2), 129.0–128.0 (aromatic), 138.1 (aromatic), 138.5 (aromatic) ppm. $C_{19}H_{22}O_4$ (314.38): calcd. C 72.59, H 7.05; found C 72.42, H 7.40.

1,4-Anhydro-3,5-di-*O*-benzyl-6-deoxy-D-glucitol (19): Compound **19** was synthesized according to the general procedure described above. The product was isolated as a white solid in 70% yield (460 mg, 1.40 mmol) after purification using the eluent system EtOAc/hexane = 1:3 (R_f = 0.20). $[\alpha]_D^{25}$ = –19.04 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.62 (d, *J* = 4.8 Hz, 3 H, 6-H), 3.95 (m, 1 H, 5-H), 4.19 (m, 2 H, 1,1′-H), 4.34 (dd, *J* = 6.6, 3.9 Hz, 1 H, 4-H), 4.48 (d, *J* = 3.6 Hz, 1 H, 3-H), 4.63 (m, 2 H, OCH_2Ph), 4.75 (m, 1 H, 2-H), 4.85 (m, 2 H, OCH_2Ph), 7.54 (m, 10 H,

Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.4 (C-6), 70.9 (C-5), 72.1 (OCH_2Ph), 72.9 (OCH_2Ph), 73.9 (C-1), 74.3 (C-3), 83.3 (C-4), 83.8 (C-2), 127.5–128.5 (aromatic), 138.2 (aromatic), 138.7 (aromatic) ppm. $C_{20}H_{28}O_4$ (332.43): calcd. C 73.15, H 7.37; found C 72.89, H 7.70.

General Procedure for the Etherification of 1,4-Anhydro-3,5-di-*O*-benzylalditols: NaH (320 mg, 8.0 mmol) was added to a solution of starting material **18** or **19** (2.0 mmol) in THF (15 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h and then the corresponding alkyl bromide (2.2 mmol) was added together with catalytic quantities of 18-crown-6 ether. The reaction mixture was stirred overnight at room temperature and then quenched by the careful addition of H_2O. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were washed with brine and dried with $MgSO_4$. Purification by flash chromatography gave the corresponding products **20**, **21**, and **22**.

1,4-Anhydro-2-*O*-butyl-3,5-di-*O*-benzyl-D-xylitol (20): Compound **20** was synthesized according to the general procedure described above. The product was isolated as a colorless syrup in 90% yield (667 mg, 1.80 mmol) after purification using the eluent system EtOAc/hexane = 1:8 (R_f = 0.30). $[\alpha]_D^{25}$ = –2.55 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 [t, J = 7.2 Hz, 3 H, $O(CH_2)_3CH_3$], 1.40 [m, 2 H, $O(CH_2)_3CH_3$], 1.58 [m, 2 H, $O(CH_2)_3CH_3$], 3.43 [t, J = 6.6 Hz, 2 H, $O(CH_2)_3CH_3$], 3.81 (m, 3 H, 1′-H, 5,5′-H), 4.01 (m, 2 H, 2-H, 3-H), 4.23 (m, 2 H, 1-H, 4-H), 4.57 (m, 2 H, OCH_2Ph), 4.67 (m, 1 H, OCH_2Ph), 7.35 (m, 10 H, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.1 [$O(CH_2)_3CH_3$], 19.4 [$O(CH_2)_3CH_3$], 32.0 [$O(CH_2)_3CH_3$], 68.7 (C-5), 69.6 [$O(CH_2)_3CH_3$], 71.9 (C-1), 74.0 (OCH_2Ph), 74.1 (OCH_2Ph), 75.6 (C-3), 79.7 (C-4), 82.9 (C-2), 128.7–127.8 (aromatic), 138.1 (aromatic), 138.5 (aromatic) ppm. $C_{23}H_{30}O_4$ (370.48): calcd. C 74.56, H 8.16; found C 74.31, H 8.35.

1,4-Anhydro-3,5-di-*O*-benzyl-2-*O*-tetradecyl-D-xylitol (21): Compound **21** was synthesized according to the general procedure described above. The product was isolated as a colorless syrup in 77% yield (812 mg, 1.54 mmol) after purification using the eluent system EtOAc/hexane = 1:8 (R_f = 0.37). $[\alpha]_D^{25}$ = –0.94 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 [t, J = 9.2 Hz, 3 H, $O(CH_2)_{13}CH_3$], 1.29 [s, 22 H, $O(CH_2)_{13}CH_3$], 1.54 [m, 2 H, $O(CH_2)_{13}CH_3$], 3.43 [t, J = 6.6 Hz, 2 H, $O(CH_2)_{13}CH_3$], 3.80 (m, 3 H, 1′-H, 5,5′-H), 4.01 (m, 2 H, 2-H, 3-H), 4.23 (m, 2 H, 1-H, 4-H), 4.59 (m, 2 H, OCH_2Ph), 4.69 (m, 2 H, OCH_2Ph), 7.37 (m, 10 H, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.3 [$O(CH_2)_{13}CH_3$], 22.9 [$O(CH_2)_{13}CH_3$], 26.3 [$O(CH_2)_{13}CH_3$], 30.0–29.6 [9 × CH_2, $O(CH_2)_{13}CH_3$], 32.1 [$O(CH_2)_{13}CH_3$], 68.7 (C-5), 69.9 [$O(CH_2)_{13}CH_3$], 71.9 (C-1), 74.0 (OCH_2Ph), 74.1 (OCH_2Ph), 79.7 (C-3), 82.2 (C-4), 82.9 (C-2), 128.6–127.8 (aromatic), 138.2 (aromatic), 138.5 (aromatic) ppm. $C_{33}H_{50}O_4$ (510.75): calcd. C 77.60, H 9.81; found C 77.2, H 10.9.

1,4-Anhydro-3,5-di-*O*-benzyl-2-*O*-hexadecyl-D-glucitol (22): Compound **22** was synthesized according to the general procedure described above. The product was isolated as a colorless syrup in 79% yield (797 mg, 1.40 mmol) after purification using the eluent system EtOAc/hexane = 1:14 (R_f = 0.40). $[\alpha]_D^{25}$ = –12.79 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 [t, J = 6.8 Hz, 3 H, $O(CH_2)_{15}CH_3$], 1.27 [s, 26 H, $O(CH_2)_{15}CH_3$], 1.36 (d, J = 6.0 Hz, 3 H, 6-H), 1.52 [m, 2 H, $O(CH_2)_{15}CH_3$], 3.36 [m, 2 H, $O(CH_2)_{15}CH_3$], 3.75 (dd, J = 10, 1.6 Hz, 1 H, 5-H), 3.82 (dd, J = 8.6, 3.4 Hz, 1 H, 1′-H), 3.93 (m, 2 H, 2-H, 1-H), 4.07 (d, J = 3.6 Hz, 1 H, 3-H), 4.13 (dd, J = 9.8, 4.6 Hz, 1 H, 4-H), 4.42 (m, 2 H, OCH_2Ph), 4.60 (m, 2 H, OCH_2Ph), 7.30 (m, 10 H, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.7 [$O(CH_2)_{15}CH_3$], 17.8 (C-6), 23.2 [$O(CH_2)_{15}CH_3$], 26.6 [$O(CH_2)_{15}CH_3$], 30.2–29.9 [11 × CH_2, $O(CH_2)_{15}CH_3$], 32.4 [$O(CH_2)_{15}CH_3$], 70.1 (C-5), 71.1 {[$O(CH_2)_{15}CH_3$]}, 72.4 (C-1), 72.5 (OCH_2Ph), 73.0 (OCH_2Ph), 81.7 (C-3), 82.9 (C-4), 84.3 (C-2), 128.8–127.8 (aromatic), 138.6 (aromatic), 139.3 (aromatic) ppm. $C_{37}H_{60}O_4$ (568.87): calcd. C 78.12, H 10.63; found C 77.88, H 10.50.

General Procedure for Removing Benzyl Groups from the 1,4-Anhydro-3,5-di-*O*-benzyl-2-alkylalditols: A catalytic amount of Pd/C (0.5 mmol) was added to a solution of **20**, **21**, or **22** (5 mmol) in THF (15 mL). The reaction mixture was stirred for 12 h over 1 bar H_2 pressure. The H_2 pressure was then purged. The mixture was filtered though Celite to obtain the corresponding diols **23**, **24**, and **11**.

1,4-Anhydro-2-*O*-butyl-D-xylitol (23): Compound **23** was synthesized according to the general procedure described above. The product was isolated as a white solid in 93% yield (885 mg, 4.65 mmol). $[\alpha]_D^{25}$ = –8.74 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 [t, J = 6.0 Hz, 3 H, $O(CH_2)_3CH_3$], 1.40 [m, 2 H, $O(CH_2)_3CH_3$], 1.55 [m, 2 H, $O(CH_2)_3CH_3$], 3.48 [m, 2 H, $O(CH_2)_3CH_3$], 3.79 (dd, J = 10.0, 2.4 Hz, 1 H, 1′-H), 3.88 (dd, J = 4.4, 2.0 Hz, 1 H, 2-H), 3.95 (d, J = 2.8 Hz, 1 H, 4-H), 4.00 (m, 1 H, 5′-H), 4.05 (m, 1 H, 5-H), 4.19 (dd, J = 10, 2.4 Hz, 1 H, 1-H), 4.29 (m, 1 H, 3-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.1 [$O(CH_2)_3CH_3$], 19.4 [$O(CH_2)_3CH_3$], 32.0 [$O(CH_2)_3CH_3$], 60.5 (C-5), 70.5 [$O(CH_2)_3CH_3$], 72.3 (C-1), 77.7 (C-3), 79.4 (C-4), 86.3 (C-2) ppm. $C_9H_{18}O_4$ (190.24): calcd. C 56.82, H 9.54; found C 56.57, H 9.80.

1,4-Anhydro-2-*O*-tetradecyl-D-xylitol (24): Compound **24** was synthesized according to the general procedure described above. The product was isolated as a white solid in 99% yield (1.64 g, 4.95 mmol). $[\alpha]_D^{25}$ = –2.07 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 [t, J = 6.0 Hz, 3 H, $O(CH_2)_{13}CH_3$], 1.25 [s, 22 H, $O(CH_2)_{13}CH_3$], 1.58 [m, 2 H, $O(CH_2)_{13}CH_3$], 3.48 [m, 2 H, $O(CH_2)_{13}CH_3$], 3.79 (dd, J = 9.2, 2.0 Hz, 1 H, 1′-H), 3.90 (m, 1 H, 2-H), 3.98 (m, 1 H, 4-H), 4.02 (m, 1 H, 5-H), 4.10 (m, 1 H, 5′-H), 4.20 (dd, J = 10.0, 4.8 Hz, 1 H, 1-H), 4.31 (m, 1 H, 3-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.7 [$O(CH_2)_{13}CH_3$], 23.2 [$O(CH_2)_{13}CH_3$], 26.6 [$O(CH_2)_{13}CH_3$], 30.3–29.9 [9 × CH_2, $O(CH_2)_{13}CH_3$], 32.5 [$O(CH_2)_{13}CH_3$], 62.3 (C-5), 70.5 [$O(CH_2)_{13}CH_3$], 72.3 (C-1), 77.7 (C-3), 79.4 (C-4), 86.2 (C-2) ppm. $C_{19}H_{38}O_4$ (330.50): calcd. C 69.05, H 11.59; found C 68.78, H 11.78.

1,4-Anhydro-2-*O*-hexadecyl-D-glucitol (11): Compound **11** was synthesized according to the general procedure described above. The product was isolated as a white powder in 86% yield (1.60 g, 4.30 mmol). $[\alpha]_D^{25}$ = –16.59 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 [t, J = 6.8 Hz, 3 H, $O(CH_2)_{15}CH_3$], 1.26 [s, 26 H, $O(CH_2)_{15}CH_3$] 1.39 (d, J = 6.4 Hz, 3 H, 6-H), 1.55 [m, 2 H, $O(CH_2)_{15}CH_3$], 3.48 [m, 2 H, $O(CH_2)_{15}CH_3$], 3.75 (dd, J = 3.8 Hz, 1 H, 4-H), 3.82 (dd, J = 9.4, 1.4 Hz, 1 H, 1′-H), 3.89 (d, J = 4.4 Hz, 1 H, 2-H), 4.23 (dd, J = 9.6, 4 Hz, 1 H, 1-H), 4.28 (dd, J = 7.0, 4.2 Hz, 1 H, 5-H), 4.33 (d, J = 2.4 Hz, 1 H, 3-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.7 [$O(CH_2)_{15}CH_3$], 18.3 (C-6), 22.3 [$O(CH_2)_{15}CH_3$], 26.0 [$O(CH_2)_{15}CH_3$], 30.2–29.7 [11 × CH_2, $O(CH_2)_{15}CH_3$], 31.8, 67.8 (C-5), 69.7 [$O(CH_2)_{15}CH_3$], 71.9 (C-1), 75.1 (C-3), 82.3 (C-4), 85.1 (C-2) ppm. $C_{22}H_{44}O_4$ (372.58): calcd. C 70.92, H 11.90; found C 70.65, H 12.03.

General Procedure for the Synthesis of the Diphosphite Ligands: A solution of the diol **9**, **10**, **11**, **15**, **23**, or **24** (1.0 mmol), previously azeotropically dried with toluene (3 × 1 mL), in dry and degassed toluene (10 mL) and cooled to 0 °C, was slowly added to a solution of phosphorochloridites **a** or **b** (2.1 mmol), synthesized in situ by

standard procedures, in dry and degassed pyridine (1.5 mL). The mixture was allowed to warm to room temperature and stirred overnight. The mixture was then filtered to eliminate the pyridine salts and the filtrate was concentrated to dryness. The white foam obtained was purified by flash chromatographic techniques over nitrogen.

3,5-Bis-*O*-(4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]-dioxaphosphocin-2-yl)-1,2-*O*-isopropylidene-α-D-xylofuranoside (1b): Compound **1b** was synthesized according to the general procedure described above. The product was isolated as a white solid in 65% yield (603 mg, 0.65 mmol) after purification by flash column chromatography (toluene, R_f = 0.60). $[a]_D^{25}$ = –2.08 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50 [s, 3 H, $O_2C(CH_3)_2$], 1.58 [4×s, 36 H, *o*C$(CH_3)_3$], 1.73 [s, 3 H, $O_2C(CH_3)_2$], 2.45 (2×s, 12 H, *p*CH_3), 3.53 (dd, *J* = 12.8, 5.6 Hz, 2 H, $PhCH_2Ph$), 4.53 (m, 2 H, $PhCH_2Ph$), 5.04 (m, 3 H, 4-H, 5,5′-H), 5.63 (d, *J* = 2.4 Hz, 1 H, 2-H), 5.79 (d, *J* = 6.0 Hz, 1 H, 3-H), 6.31 (d, *J* = 3.6 Hz, 1 H, 1-H), 7.41–7.16 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.4 (*p*CH_3), 26.6 [$O_2C(CH_3)_2$], 27.0 [$O_2C(CH_3)_2$], 31.1 [*o*C$(CH_3)_3$], 34.9 ($PhCH_2Ph$), 61.6 (C-5), 77.3 (C-3), 80.4 (C-4), 84.3 (C-2), 105.3 (C-1), 112.3 [$O_2C(CH_3)_2$], 146.0–125.4 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 129.2 (s), 132.1 (s) ppm. $C_{54}H_{72}O_9P_2$ (927.09): calcd. C 69.96, H 7.83; found C 69.67, H 8.01.

3,5-Bis-*O*-[(3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl-dioxy)phosphanyl]-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranoside (3a): Compound **3a** was synthesized according to the general procedure described above. The product was isolated as a white solid in 50% yield (489 mg, 0.5 mmol) after purification by flash column chromatography (toluene/THF = 99:1, R_f = 0.25). $[a]_D^{25}$ = +110.12 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 [s, 3 H, $O_2C(CH_3)_2$], 1.30 (d, *J* = 6.4 Hz, 3 H, 6-H), 1.47–1.42 [s, 39 H, *o*C$(CH_3)_3$, $O_2C(CH_3)_2$], 3.83–3.80 (s, 12 H, *p*OCH_3), 3.97 (d, *J* = 3.6 Hz, 1 H, 2-H), 4.05 (dd, *J* = 8.2, 2.6 Hz, 1 H, 4-H), 4.73 (m, 1 H, 5-H), 4.82 (d, *J* = 2.8 Hz, 1 H, 3-H), 5.59 (d, *J* = 3.2 Hz, 1 H, 1-H), 6.99–6.70 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.1 (C-6), 26.0 [$O_2C(CH_3)_2$], 26.7 [$O_2C(CH_3)_2$], 31.3–29.7 [*o*C$(CH_3)_3$], 35.6–35.4 [*o*C$(CH_3)_3$], 55.8 (*p*OCH_3), 68.9 (C-5), 76.3 (C-3), 83.2 (C-4), 84.2 (C-2), 104.9 (C-1), 111.7 [$O_2C(CH_3)_2$], 156.3–113.2 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 144.8 (s, *J* = 43.9 Hz, 2 P) ppm. ^{31}P NMR (161.97 MHz, [D_8]toluene): δ = 144.8 (d, *J* = 35.3 Hz), 145.3 (d, *J* = 35.3 Hz) ppm. $C_{53}H_{70}O_{13}P_2$ (977.06): calcd. C 65.15, H 7.22; found C 64.95, H 7.45.

3,5-Bis-*O*-[(3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl-dioxy)phosphanyl]-6-*O*-isopropyl-1,2-*O*-isopropylidene-α-D-glucofuranoside (7a): Compound **7a** was synthesized according to the general procedure described above. The product was isolated as a white solid in 54% yield (559 mg, 0.54 mmol) after purification by flash column chromatography (toluene/THF = 95:5, R_f = 0.35). $[a]_D^{25}$ = +129.49 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 [dd, *J* = 6.4 Hz, 6 H, $OCH(CH_3)_2$], 1.20 [s, 3 H, $O_2C(CH_3)_2$], 1.50 [4×s, 39 H, $O_2C(CH_3)_2$, *o*C$(CH_3)_3$], 3.54 [m, 1 H, $OCH(CH_3)_2$], 3.80 (dd, *J* = 11.0, 5.4 Hz, 1 H, 6-H), 3.85–3.89 (s, 14 H, 2-H, 6-H, *p*OCH_3), 4.41 (d, *J* = 6.4 Hz, 1 H, 4-H), 4.71 (m, 1 H, 5-H), 4.89 (d, *J* = 4.4 Hz, 1 H, 3-H), 5.67 (d, *J* = 3.6 Hz, 1 H, 1-H), 7.30–6.70 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.1 [2×C, $OCH(CH_3)_2$], 26.1 [$O_2C(CH_3)_2$], 26.8 [$O_2C(CH_3)_2$], 31.2 [*o*C$(CH_3)_3$], 35.6 [*o*C$(CH_3)_3$], 55.8 (*p*OCH_3), 68.0 (C-6), 72.2 [$OCH(CH_3)_2$], 72.4 (C-5), 76.7 (C-3), 79.2 (C-4), 83.8 (C-2), 105.0 (C-1), 111.8 [$O_2C(CH_3)_2$], 156.0–112.7 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 144.5 (d, *J* = 30.9 Hz), 145.8 (d, *J* = 30.9 Hz) ppm. $C_{56}H_{76}O_{14}P_2$ (1035.14): calcd. C 64.98, H 7.40; found C 64.76, H 7.59.

1,4-Anhydro-3,5-bis-*O*-[(3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyldioxy)phosphanyl]-2-*O*-butyl-D-xylitol (25a): Compound **25a** was synthesized according to the general procedure described above. The product was isolated as a white solid in 71% yield (684 mg, 0.71 mmol) after purification by flash column chromatography (toluene/THF = 98:2, R_f = 0.35). $[a]_D^{25}$ = –3.30 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 [t, *J* = 6.4 Hz, 3 H, $O(CH_2)_3CH_3$], 1.40 [m, 40 H, *o*C$(CH_3)_3$, $O(CH_2)_3$-CH_3], 3.14 [m, 2 H, $O(CH_2)_3CH_3$], 3.60 (m, 2 H, 1′-H, 4-H), 3.80 (2×s, 12 H, *p*OCH_3), 3.90 (dd, *J* = 9.6, 4.4 Hz, 1 H, 1-H), 4.00 (m, 2 H, 5,5′-H), 4.08 (m, 1 H, 2-H), 4.70 (dd, *J* = 8.0, 2.0 Hz, 1 H, 3-H), 6.97–6.67 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.3 [$O(CH_2)_3CH_3$], 19.3 [$O(CH_2)_3CH_3$], 31.2 [*o*C$(CH_3)_3$], 31.9 [$O(CH_2)_3CH_3$], 35.6 [*o*C$(CH_3)_3$], 55.8 (*p*OCH_3), 62.8 (C-5), 69.6 [$O(CH_2)_3CH_3$], 71.9 (C-1), 76.5 (C-3), 79.4 (C-4), 84.2 (C-2), 156.0–113.0 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 136.3 (s), 143.2 (s) ppm. $C_{53}H_{72}O_{12}P_2$ (963.08): calcd. C 66.10, H 7.54; found C 65.90, H 7.67.

1,4-Anhydro-3,5-bis-*O*-(4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo-[*d*,*g*][1,3,2]dioxaphosphocin-2-yl)-2-*O*-butyl-D-xylitol (25b): Compound **25b** was synthesized according to the general procedure described above. The product was isolated as a white solid in 55% yield (510 mg, 0.55 mmol) after purification by flash column chromatography (toluene, R_f = 0.60). $[a]_D^{25}$ = –2.15 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 [t, *J* = 10.0 Hz, 3 H, $O(CH_2)_3CH_3$], 1.41 [m, 2 H, $O(CH_2)_3CH_3$], 1.55 [s, 36 H, *o*C$(CH_3)_3$], 1.71 [m, 2 H, $O(CH_2)_3CH_3$], 2.45 (2×s, 12 H, *p*CH_3), 3.54 (dd, *J* = 11.2, 5.6 Hz, 2 H, $PhCH_2Ph$), 3.77 [m, 1 H, $O(CH_2)_3$-CH_3], 3.87 [m, 1 H, $O(CH_2)_3CH_3$], 4.12 (d, *J* = 13.2 Hz, 1 H, 1′-H), 4.50 (m, 2 H, $PhCH_2Ph$), 4.57 (dd, *J* = 13.2, 5.6 Hz, 1 H, 1-H), 4.77 (m, 1-H, 4-H), 4.90 (m, 1 H, 5′-H), 5.00 (d, *J* = 5.2 Hz, 1 H, 2-H), 5.08 (m, 1 H, 5-H), 5.75 (dd, *J* = 8.4, 4.4 Hz, 1 H, 3-H), 7.21–7.17 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.2 [$O(CH_2)_3CH_3$], 19.5 [$O(CH_2)_3CH_3$], 21.3 (*p*CH_3), 31.3 [*o*C$(CH_3)_3$], 32.1 [$O(CH_2)_3CH_3$], 34.9 ($PhCH_2Ph$), 62.5 (C-5), 69.9 [$O(CH_2)_3CH_3$], 72.3 (C-1), 77.4 (C-3), 80.3 (C-4), 84.3 (C-2), 142.3–125.5 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 129.3 (s), 131.6 (s) ppm. $C_{55}H_{76}O_8P_2$ (927.13): calcd. C 71.25, H 8.26; found C 70.95, H 8.40.

1,4-Anhydro-3,5-bis-*O*-[(3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyldioxy)phosphanyl]-2-*O*-tetradecylxylitol (26a): Compound **26a** was synthesized according to the general procedure described above. The product was isolated as a white solid in 27% yield (298 mg, 0.27 mmol) after purification by flash column chromatography (toluene/THF = 98:2, R_f = 0.35). $[a]_D^{25}$ = –0.60 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 [t, *J* = 6.4 Hz, 3 H, $O(CH_2)_{13}CH_3$], 1.40 [m, 60 H, *o*C$(CH_3)_3$, $O(CH_2)$-$_{13}CH_3$], 3.14 [m, 2 H, $O(CH_2)_{13}CH_3$], 3.60 (m, 2 H, 1′-H, 4-H), 3.82–3.80 (s, 12 H, *p*OCH_3), 3.92 (dd, *J* = 10.0, 4.4 Hz, 1 H, 1-H), 4.01 (m, 2 H, 5,5′-H), 4.09 (m, 1 H, 2-H), 4.71 (dd, *J* = 8.8, 3.2 Hz, 1 H, 3-H), 6.97–6.67 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.3 [$O(CH_2)_{13}CH_3$], 26.2 [$O(CH_2)_{13}$-CH_3], 29.2 [$O(CH_2)_{13}CH_3$], 29.8 [$O(CH_2)_{13}CH_3$], 31.2 [*o*C$(CH_3)_3$], 32.1 [$O(CH_2)_{13}CH_3$], 35.6 [*o*C$(CH_3)_3$], 55.8 (*p*OCH_3), 62.8 (C-5), 70.0 [$O(CH_2)_{13}CH_3$], 71.9 (C-1), 76.5 (C-3), 79.3 (C-4), 84.2 (C-2), 156.0–113.0 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 136.3 (s), 143.2 (s) ppm. $C_{63}H_{92}O_{12}P_2$ (1103.34): calcd. C 68.58, H 8.40; found C 68.27, H 8.57.

1,4-Anhydro-3,5-bis-*O*-(4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin-2-yl)-2-*O*-tetradecyl-D-xylitol

(26b): Compound **26b** was synthesized according to the general procedure described above. The product was isolated as a white solid in 50% yield (534 mg, 0.50 mmol) after purification by flash column chromatography (toluene, R_f = 0.60). $[a]_D^{25}$ = –0.82 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 [t, J = 10.0 Hz, 3 H, $O(CH_2)_{13}CH_3$], 1.28 [m, 22 H, $O(CH_2)_{13}CH_3$], 1.43 [s, 36 H, $oC(CH_3)_3$], 1.61 [m, 2 H, $O(CH_2)_{13}CH_3$], 2.31 (2 × s, 12 H, pCH_3), 3.40 (dd, J = 12.8, 8.4 Hz, 2 H, $PhCH_2Ph$), 3.64 [m, 1 H, $O(CH_2)_{13}CH_3$], 3.70 [m, 1 H, $O(CH_2)_{13}CH_3$], 3.99 (d, J = 10.0 Hz, 1 H, 1′-H), 4.36 (m, 2 H, $PhCH_2Ph$), 4.42 (dd, J = 9.6, 4.4 Hz, 1 H, 1-H), 4.63 (m, 1 H, 4-H), 4.78 (m, 1 H, 5′-H), 4.86 (d, J = 4.0 Hz, 1 H, 2-H), 4.94 (m, 1 H, 5-H), 5.60 (dd, J = 6.0, 3.2 Hz, 1 H, 3-H), 7.14–7.01 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.6 [$O(CH_2)_{13}CH_3$], 21.5 (pCH_3), 23.1 [$O(CH_2)_{13}CH_3$], 26.6 [$O(CH_2)_{13}CH_3$], 29.9 [$O(CH_2)_{13}CH_3$], 30.1 [$oC(CH_3)_3$], 31.4 [$O(CH_2)_{13}CH_3$], 35.2 ($PhCH_2Ph$), 62.7 (C-5), 70.5 [$O(CH_2)_{13}CH_3$], 72.5 (C-1), 77.4 (C-3), 80.5 (C-4), 84.5 (C-2), 136.6–127.2 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 129.7 (s), 132.1 (s) ppm. $C_{65}H_{96}O_8P_2$ (1067.40): calcd. C 73.14, H 9.07; found C 73.00, H 9.24.

1,4-Anhydro-3,5-bis-*O*-[(3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyldioxy)phosphanyl]-6-deoxy-2-*O*-hexadecyl-D-glucitol (8a): Compound **8a** was synthesized according to the general procedure described above. The product was isolated as a white solid in 50% yield (573 mg, 0.5 mmol) after purification by flash column chromatography (toluene/THF = 99:1, R_f = 0.25). $[a]_D^{25}$ = –0.34 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 [t, J = 6.4 Hz, 3 H, $O(CH_2)_{15}CH_3$], 1.27 [s, 26 H, $O(CH_2)_{15}CH_3$], 1.33 (d, J = 6.4 Hz, 3 H, 6-H), 1.46 [m, 36 H, $oC(CH_3)_3$], 1.40 [m, 2 H, $O(CH_2)_{15}CH_3$], 3.23 [m, 1 H, $O(CH_2)_{15}CH_3$], 3.35 [m, 1 H, $O(CH_2)_{15}CH_3$], 3.60 (m, 1 H, 1′-H), 3.65 (m, 1 H, 4-H), 3.82–3.80 (s, 13 H, 1-H, $pOCH_3$), 3.87 (dd, J = 8.0, 2.8 Hz, 1 H, 2-H), 4.72 (m, 1 H, 5-H), 4.82 (dd, J = 7.0, 2.6 Hz, 1 H, 3-H), 6.97–6.70 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.3 [$O(CH_2)_{15}CH_3$], 20.3 (C-6), 23.3 [$O(CH_2)_{15}CH_3$], 26.7 [$O(CH_2)_{15}CH_3$], 29.9 [$O(CH_2)_{15}CH_3$], 30.4 [$O(CH_2)_{15}CH_3$], 31.7 [$oC(CH_3)_3$], 32.5 [$O(CH_2)_{15}CH_3$], 35.9 [$oC(CH_3)_3$], 56.1 ($pOCH_3$), 69.7 (C-5), 70.5 [$O(CH_2)_{15}CH_3$], 72.6 (C-1), 76.0 (C-3), 84.0 (C-4), 84.5 (C-2), 156.3–113.2 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 144.0 (d, J = 43.9 Hz), 146.5 (d, J = 43.7 Hz) ppm. $C_{66}H_{98}O_{12}P_2$ (1105.42): calcd. C 69.21, H 8.62; found C 69.02, H 8.79.

1,4-Anhydro-3,5-bis-*O*-(4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo-[*d*,*g*][1,3,2]dioxaphosphocin-2-yl)-6-deoxy-2-*O*-hexadecyl-D-glucitol (8b): Compound **8b** was synthesized according to the general procedure described above. The product was isolated as a white solid in 51% yield (566 mg, 0.51 mmol) after purification by flash column chromatography (toluene, R_f = 0.64). $[a]_D^{25}$ = –20.04 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 [t, J = 6.8 Hz, 3 H, $O(CH_2)_{15}CH_3$], 1.27 [s, 26 H, $O(CH_2)_{15}CH_3$], 1.44 [s, 36 H, $oC(CH_3)_3$], 1.60 [m, 2 H, $O(CH_2)_{15}CH_3$], 1.88 (d, J = 6.4 Hz, 3 H, 6-H), 2.30 (s, 12 H, pCH_3), 3.50 (dd, J_1 = J_2 = 12 Hz, 2 H, $PhCH_2Ph$), 3.65 [m, 1 H, $O(CH_2)_{15}CH_3$], 3.75 [m, 1 H, $O(CH_2)_{15}CH_3$], 3.99 (d, J = 9.6 Hz, 1 H, 1′-H), 4.36 (ddd, J = 17.9, 12.7, 2.7 Hz, 2 H, $PhCH_2Ph$), 4.45 (dd, J = 9.8, 4.6 Hz, 1 H, 1-H), 4.62 (dd, J_1 = J_2 = 3.6 Hz, 1 H, 4-H), 4.92 (d, J = 3.6 Hz, 1 H, 2-H), 5.55 (m, 1 H, 3-H), 5.58 (m, 1 H, 5-H), 7.00–7.30 (m, 8 H, aromatic) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.0 [$O(CH_2)_{15}CH_3$], 19.3 (C-6), 20.9 (pCH_3), 21.4 [$O(CH_2)_{15}CH_3$], 22.6 [$O(CH_2)_{15}CH_3$], 26.2 [$O(CH_2)_{15}CH_3$], 29.3 [$O(CH_2)_{15}CH_3$], 29.5 [$O(CH_2)_{15}CH_3$], 30.7 [$oC(CH_3)_3$], 31.8 [$O(CH_2)_{15}CH_3$], 34.6 ($PhCH_2Ph$), 70.0 [$O(CH_2)_{15}CH_3$], 71.9 (C-5), 72.2 (C-1), 78.0 (C-3), 83.8 (C-2, C-4), 142.1–125.1 (aromatic) ppm. ^{31}P NMR (161.97 MHz, $CDCl_3$): δ = 131.9 (s), 133.5 (s) ppm. $C_{68}H_{102}O_8P_2$ (1109.48): calcd. C 73.61, H 9.27; found C 73.31, H 9.42.

In Situ High-Pressure NMR Experiments: In a typical experiment, a sapphire tube ($ø$ = 10 mm) was filled under argon with a solution of [Rh(acac)(CO)$_2$] (2.10–2 mM) and the ligand (molar ratio L/Rh = 1.1) in [D$_8$]toluene (2 mL). The solution was analyzed and then the high-pressure NMR tube was purged three times with CO and pressurized to the appropriate pressure of CO/H_2. After the reaction, during which the solution was shaken at 40 °C, the solution was analyzed.

Hydroformylation Experiments: In a typical experiment, the autoclave was purged three times with CO. The solution was formed from [Rh(acac)(CO)$_2$] (0.013 mmol), diphosphite (0.015 mmol), and styrene (13 mmol) in toluene (15 mL). The autoclave was pressurized to the desired pressure of CO/H_2. After the desired reaction time, the autoclave was cooled to room temperature and depressurized. The reaction mixture was analyzed by gas chromatography. The aldehydes obtained from the hydroformylation were oxidized to carboxylic acids to determine the enantiomeric excesses.

Supporting Information (see also the footnote on the first page of this article): ^{1}H, ^{13}C, and ^{31}P NMR spectra of the new ligands, and ^{1}H and ^{31}P NMR spectra of complexes Rh/**1b** and Rh/**8a** recorded under reaction conditions.

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