Chiral Diphosphites Derived from D-Glucose: New Ligands for the Asymmetric Catalytic Hydroformylation of Vinyl Arenes

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Dedicated to Professor Rafael Usón on the occasion of his 75th birthday

Abstract: A series of novel diphosphite ligands derived from readily available D-(+)-glucose has been synthesized. These ligands have been applied to the Rh-catalyzed hydroformylation of vinyl arenes. Both excellent enantioselectivities (up to 91%) and regioselectivities (up to 98.8%) were achieved under mild conditions. The advantage of these ligands is that their modular natures allow facile, systematic variation in the configurations at the stereocenters [C(3), C(5)] at the ligand bridge and in the biphenyl substituents, enabling their effects on the stereoselectivity to be studied. Results show that the absolute configuration of the product is governed by the configuration at the stereogenic center C(3), while the level of the enantioselectivity is influenced by a cooperative effect between stereocenters C(3) and C(5). Replacement of the *tert*-butyl substituent by methoxy substituents at the *para* positions of the biphenyl moieties improved the enantioselectivities. We have characterized the rhodium complexes formed under CO/H_2 by NMR techniques and in situ IR spectroscopy and have observed that there is a relationship between the structure of the $[HRh(CO)_2(PP)]$ species and their enantiodiscriminating performance in hydroformylation. Enantioselectivities were highest with ligands with a strong bis-equatorial coordination preference, while an equilibrium of species with bis-equatorial and equatorial-axial coordination modes considerably reduced the *ee*'s.

Keywords: diphosphites · hydroformylation · P ligands · rhodium · sugar derivatives

Introduction

In the last few years, asymmetric hydroformylation has attracted much attention as a potential tool for preparing enantiomerically pure aldehydes, which are important precursors for the synthesis of fine chemicals.[1] From the early seventies, transition metal complexes based on rhodium and platinum have been used as catalysts in asymmetric hydroformylation.[1] High enantioselectivities have been obtained with Pt/diphosphine catalysts, but these suffer from low chemo- and regioselectivity.[2] In general, Rh/diphosphine catalysts have high catalytic activities and regioselectivities in branched aldehydes, but the ee's do not exceed 60%.[3] During the last decade, significant improvements have been made in rhodium-catal**yze**d asymmetric hydroformylation based on new diphosphite[4] and phosphine-phosphite[5] ligands. In situ spectroscopic studies of both types of ligands suggest that the presence of only one active diastereoisomeric hydridorhodiumcarbonyl species in solution is the key to controlling efficient chirality transfer.[4b, 5a] However, the mechanistic aspects of the asymmetric hydroformylation reaction are still not understood well enough for a priori prediction of the type of ligand needed for high enantioselectivities. Binaphos is so far the only ligand with a wide scope in asymmetric hydroformylation, although its difficult preparation and the high pressures (up to 100 bar) required limit its application.[5] In this context, much research still needs to be done to find ligands that are readily available and provide both good regio- and enantioselectivity in asymmetric hydroformylation.

One of the simplest methods for obtaining chiral ligands is the transformation or derivatization of natural chiral compounds, making tedious optical-resolution procedures unnecessary. Carbohydrates, which have been widely used in organic synthesis either as inexpensive starting materials or as chiral auxiliaries,[6] have only recently shown their huge potential as a source of highly effective chiral ligands in homogeneous catalysis.[7] Moreover, carbohydrates are highly

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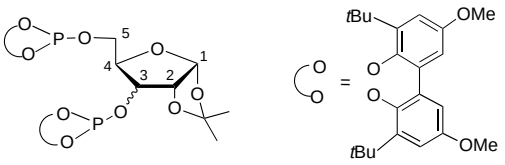
functionalized compounds with several stereogenic centers, which easily allow regio- and stereoselective introduction of different functionalities.[7] Their modular nature therefore permits the synthesis of systematic series of ligands that can be screened in the search for high regio- and enantioselectivities and, at the same time, can provide information about the origin of the stereoselectivity of the reaction.

In previous studies of diphosphite ligands with furanoside backbones (**1** and **2**), moderate success in asymmetric hydroformylation of styrene has been achieved.[7f, 8]



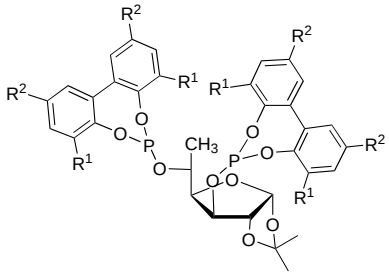
1 D-*xylo*

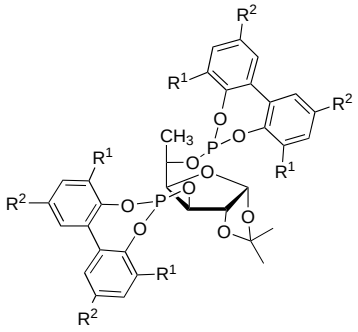
2 L-*ribo*

Since these ligands have a phosphorus moiety bound to the nonstereogenic center C(5), we decided to examine whether further modification of the ligands by introducing a new stereocenter at the carbon C(5) position would improve the enantioselectivity. With this aim in mind, we report here the synthesis of a series of new chiral diphosphite ligands **3**–**10**, related to **1** and **2** but with a new stereocenter at carbon C(5).[9] These ligands, which are easily prepared from readily available D-(+)-glucose, offer the prospect of systematic variation of the configurations at C(3) and C(5), and different substituents in the biphenyl moieties. We also report their use in the rhodium-catalyzed, asymmetric hydroformylation of vinyl arenes and investigate how the configuration of the stereogenic carbon atoms C(3) and C(5) affects the enantioselectivity, since their configurations are expected to be important for the course of the catalytic reaction, due to their close vicinity to the metal. The influence of the substituents on the biphenyl moieties is also studied. Furthermore, we have investigated the solution structures of the important intermediate species $[HRh(PP)(CO)_2]$, (PP = diphosphite).

Results and Discussion

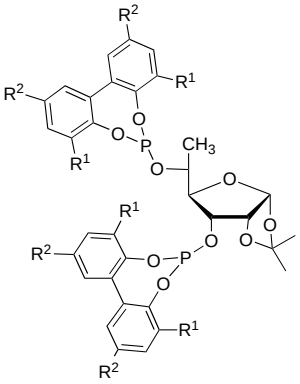
Synthesis of the chiral diphosphite ligands: Diphosphite ligands **3**–**10**, based on furanoside backbones, were synthesized from inexpensive D-(+)-glucose as shown in Scheme 1. These ligands constitute the four diastereomers that can be obtained by varying the configuration of the C(3) and C(5) atoms in the backbone in combination with two different substituted bulky 2,2′-biphenyl moieties. The absolute configuration of carbon atoms in the furanoside backbone of the synthesized diastereomers is given in a shorthand notation as, for example, (1*R*, 2*R*, 3*S*, 4*R*, 5*R*) for ligand **3**.

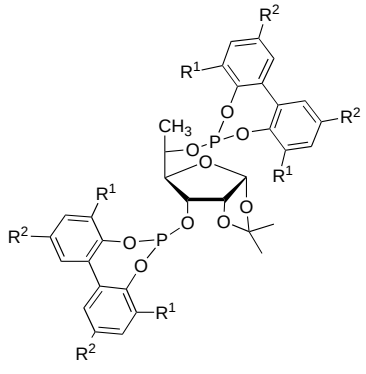




3 (1*R*, 2*R*, 3*S*, 4*R*, 5*R*) R^1 = *t*Bu; R^2 = OMe **5** (1*R*, 2*R*, 3*S*, 4*R*, 5*S*)

4 (1*R*, 2*R*, 3*S*, 4*R*, 5*R*) $R^1 = R^2$ = *t*Bu **6** (1*R*, 2*R*, 3*S*, 4*R*, 5*S*)



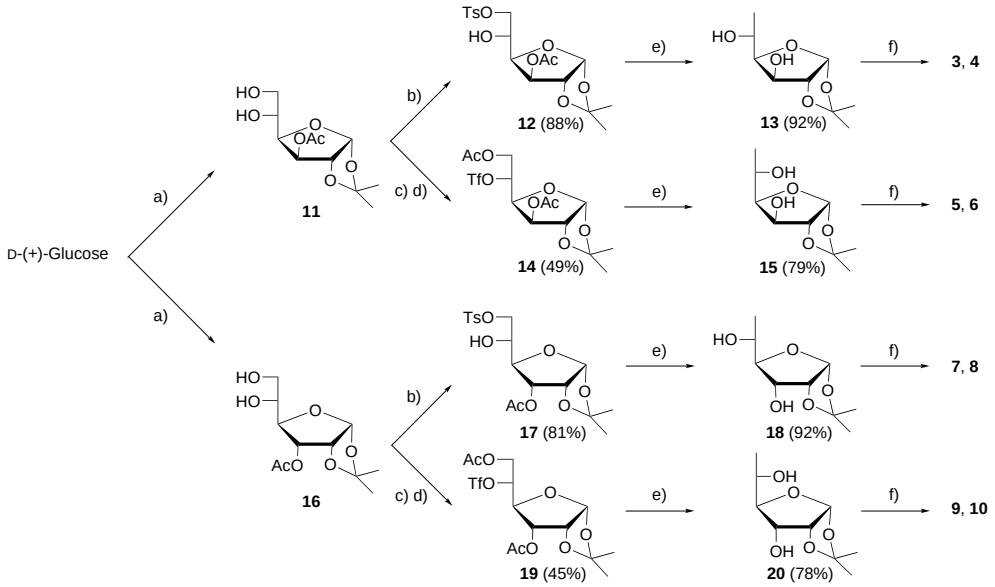


7 (1*R*, 2*R*, 3*R*, 4*R*, 5*R*) R^1 = *t*Bu; R^2 = OMe **9** (1*R*, 2*R*, 3*R*, 4*R*, 5*S*)

8 (1*R*, 2*R*, 3*R*, 4*R*, 5*R*) $R^1 = R^2$ = *t*Bu **10** (1*R*, 2*R*, 3*R*, 4*R*, 5*S*)

Preparation of enantiomerically pure diols (13, 15, 18, 20): Diols **13** and **18** were synthesized stereospecifically in two steps from 1,2-protected-3-*O*-acetylated furanoses **11** and **16**, respectively (Scheme 1). Compounds **11** and **16** are easily prepared on a large scale by previously reported, highly effective methods from D-glucose.[10] Tosylation of diols **11** and **16** produced the expected 6-tosyl derivatives **12** and **17** in good yields.[11] Treatment of these tosylated compounds with sodium methoxide at room temperature, followed by reduction of the corresponding 5,6-anhydrosugars with lithium aluminium hydride, produced crystalline compounds **13** and **18**.[12]

An improved synthesis of diols **15** and **20** has been reported,[12] but attempts to reproduce this procedure were unsuccessful.[13] They were fi-

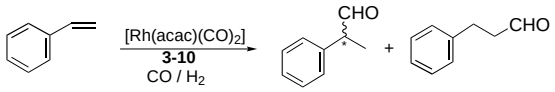


Scheme 1. Synthesis of ligands **3**–**10**. a) Ref. [10]. b) TsCl, Py, CH_2Cl_2, 16 h, −20 to 25 °C. c) Ac_2O, Py, CH_2Cl_2, 16 h, 0 to 25 °C. d) Tf_2O, Py, CH_2Cl_2, 20 min, 25 °C. e) NaOMe, CH_2Cl_2, 1 h, 25 °C; $LiAlH_4$, THF, 4 h, 60 °C. f) Phosphorochloridite, Py, toluene, 100 °C.

nally obtained, in three steps, from compounds **11** and **16** (Scheme 1) by acetylation of position 6 under standard conditions, followed by treatment with triflic anhydride to obtain triflates **14** and **19**. Treatment of a dichloromethane solution of compounds **14** and **19** with sodium methoxide afforded the corresponding 5,6-anhydrosugars with inversion of configuration at C(5).[12] Epoxide ring-opening by using $LiAlH_4$ afforded easy access to the desired diols **15** and **20**.[12]

Preparation of diastereomeric diphosphites 3–10: Optically pure diphosphite ligands **3**–**10** were easily prepared by treatment of the corresponding diol with two equivalents of the desired phosphorochloridite,[14] formed in situ (either 3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl phosphorochloridite or 3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl phosphorochloridite) in the presence of base (Scheme 1, step f). All the ligands were stable during purification on neutral silica gel under an atmosphere of argon and they were isolated in moderate to good yields (61–76%) as white solids. They were stable at room temperature and fairly robust toward hydrolysis. The ^1H and ^{13}C NMR spectra agree with those expected for these C_1 ligands (see Experimental Section). Rapid ring inversions (atropoisomerization) of the seven-membered dioxaphosphepin rings occurred on the NMR timescale, since the expected diastereoisomers were not detected by low temperature ^{31}P NMR.[15] Moreover, the ^{31}P NMR spectra of ligands **3**, **4**, **9**, and **10** showed phosphorus–phosphorus coupling constants, while ligands **5**–**8** gave rise to a structure in solution without the correct conformation to enhance phosphorus–phosphorus coupling. It is to be noted that the coupling constants for ligands **3** and **4** were much larger than other six-bond phosphorus–phosphorus coupling constants in similar diphosphites ($^6J(P,P) \leq 12$ Hz).[4b,15]

Asymmetric hydroformylation of vinyl arenes: Aldehydes derived from aryl-substituted olefins are of great interest, especially as intermediates for the synthesis of various pharmaceuticals such as anti-inflammatory agents.[16] In a first set of experiments, we used ligands **3**–**10** in the rhodium-catalyzed, asymmetric hydroformylation of styrene, which is widely used as a model substrate (Scheme 2).



Scheme 2. Hydroformylation of styrene with compounds **3**–**10**.

The catalysts were prepared in situ by adding one equivalent of the corresponding diphosphite ligand to [Rh(acac)-$(CO)_2$] (acac = acetylacetone) as a catalyst precursor, since other precursors were reported to be less enantioselective.[5a] The styrene hydroformylation results are summarized in Table 1. In no cases were hydrogenated or polymerized products of styrene observed.

The effects of different reaction parameters were investigated for the catalytic precursors containing ligands **3** and **9**; these ligands have opposite configurations at C(3) and C(5). Variation of the ligand-to-rhodium ratio showed that excess ligand was not needed to obtain good regio- and enantioselectivities (entries 1–3). This is an important advantage over the most successful catalysts based on diphosphites[4] and phosphine–phosphite,[5] for which larger excesses of ligand are required.

After identical catalyst preparation, hydroformylation experiments were carried out under different partial pressures of CO and H_2 (entries 1, 4, 5 and 6). The results clearly show that activities were best at low P_{CO}/P_{H_2}. There was therefore an inverse dependency on partial CO pressure and a positive dependency on partial H_2 pressure; this suggests that hydrogenolysis is the rate determining step. These results contrast with reported kinetic studies of rhodium-catalyzed hydro-

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Table 1. Asymmetric hydroformylation of styrene catalyzed by [Rh(acac)-$(CO)_2$]/diphosphite.[a]

Entry	Ligand	P_{CO}/P_{H2}	T [°C]	TOF[b]	% Conv [h][c]	% Regio[d]	% *ee*[e]
1	**9**	1	40	98	97 (10)	97.7	78 (*R*)
2[f]	**9**	1	40	97	96 (10)	97.6	78 (*R*)
3[g]	**9**	1	40	94	93 (10)	97.7	77 (*R*)
4	**9**	0.5	40	174	100 (6)	97.8	78 (*R*)
5	**9**	2	40	61	92 (15)	97.7	78 (*R*)
6	**9**	0.5[h]	40	198	100 (6)	97.8	77 (*R*)
7	**9**	0.5	20	17	80 (48)	98.3	89 (*R*)
8	**3**	0.5	40	174	100 (6)	97.9	78 (*S*)
9	**3**	0.5	20	18	83 (48)	98.6	90 (*S*)
10	**4**	0.5	20	19	85 (48)	98.4	74 (*S*)
11	**10**	0.5	20	16	79 (48)	98.7	76 (*R*)
12	**5**	0.5	20	12	59 (48)	97.6	64 (*S*)
13	**6**	0.5	20	15	71 (48)	97.4	52 (*S*)
14	**7**	0.5	20	13	60 (48)	97.2	58 (*R*)
15	**8**	0.5	20	14	61 (48)	97.1	46 (*R*)
16[i]	**1**	0.5	40	41	19 (5)	96	53 (*S*)
17[i]	**2**	0.5	40	50	20 (5)	95	51 (*R*)

[a] Reaction conditions: $P = 10$ bar, styrene (13 mmol), $[Rh(acac)(CO)_2]$ (0.013 mmol), toluene (15 mL), PP/Rh = 1.1. [b] Turn over frequency, i.e., mol styrene per mol Rh per h measured after 1 hour. [c] % Conversion of styrene. [d] % Regioselectivity in 2-phenylpropanal. [e] % Enantiomeric excess measured by GC. [f] PP/Rh = 2. [g] PP/Rh = 4. [h] $P_{CO} = 5$ bar, $P_{H_2} = 10$ bar. [i] Data from [7f].

formylation with bulky diphosphite, in which the rate determining step was the alkene coordination.[1d] Moreover, comparison of entries 1, 4 and 5 shows that regio- and enantioselectivity are not affected by varying the partial H_2 pressure. This contrasts with the results reported by Buisman et al. for the asymmetric hydroformylation of styrene by using diphosphite ligands, in which increasing the hydrogen partial pressure had a negative effect on regio- and enantioselectivity.[17]

Comparisons of entries 4 and 7, and also 8 and 9, show a remarkable increase in enantioselectivities (up to 90%) combined with excellent regioselectivities (up to 98.6%) on lowering the reaction temperature. Moreover, there were no changes in the enantioselectivities over time; this indicates that no decomposition of the catalysts took place. Furthermore, the catalytic systems with ligands **3** and **9** provided better activities and enantioselectivities than those with the related diphosphite ligands **1** and **2** with xylo- and ribofuranoside backbones[7f] (Table 1, entries 4 and 8 vs. 16 and 17).

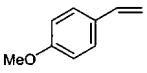
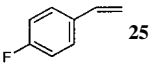
For comparative purposes, the rest of the ligands were tested under the conditions that gave the optimum compromise between enantioselectivities and reaction rates, that is a ligand to rhodium ratio of 1.1, a total pressure of 10 bar of synthesis gas, a temperature of 20 °C and a CO to H_2 ratio of 0.5. The use of ligands **4** and **10**, with *tert*-butyl groups instead of methoxy groups in the *para* positions of the biphenyl moieties, resulted in lower enantioselectivities but similar activities and regioselectivities (entries 10 and 11 vs 9 and 7). The use of ligands **5** and **7**, in which the configuration at carbon atom C(5) is the opposite of that in ligands **3** and **9**, produced lower reaction rates and enantioselectivities (entries 12 and 14 vs entries 9 and 7). This is also true for ligands **6** and **8**, which contain *tert*-butyl groups in the *para* positions of the biphenyl moieties (entries 13 and 15).

The results of hydroformylation with catalyst precursors containing ligands **3**–**10** can be summarized as follows:

a) Both (*S*)- and (*R*)-2-phenylpropanal enantiomers can be obtained with excellent regio- and enantioselectivies by using diastereoisomeric ligands **3** and **9**, respectively (entries 7 and 9).
b) Methoxy substituents in the *para* positions of the biphenyl moieties always produced enantioselectivities better than those observed for the corresponding *tert*-butyl-substituted analogs (entries 7, 9 and 12, 14 vs 11, 10 and 13, 15). However, activity and regioselectivity were hardly affected.
c) The sense of the enantiodiscrimination is predominantly controlled by the configuration at C(3). Accordingly, ligands **3**–**6**, with *S* configuration at C(3), gave (*S*)-2-phenylpropanal, while ligands **7**–**10**, with *R* configuration at C(3), gave (*R*)-2-phenylpropanal.
d) The results also show a cooperative effect between stereocenters C(3) and C(5), that is, the value of enantioselectivity when C(3) has either an *R* or an *S* configuration depends on the configuration at C(5). Therefore, when the configuration of C(3) was *S*, changing C(5) from *R* (ligand **3**) to *S* (ligand **5**) resulted in a decrease in enantioselectivity from 90% *S* to 64% *S*. When the configuration of C(3) was *R*; however, the same change of C(5) from *R* (ligand **7**) to *S* (ligand **9**) resulted in an increase in enantioselectivity from 58% *R* to 89% *R*.
e) The presence of a methyl substituent at C(5) significantly increased the activity.

We next applied these new, highly efficient diphosphite ligands **3** and **9** in the Rh-catalyzed hydroformylation of other vinyl arenes (Table 2). As with styrene, excellent enantio- and regioselectivities were obtained in the branched aldehydes. Moreover, these results suggest that the presence of different substituents in the *para* position hardly affects conversion, regioselectivity or enantioselectivity.

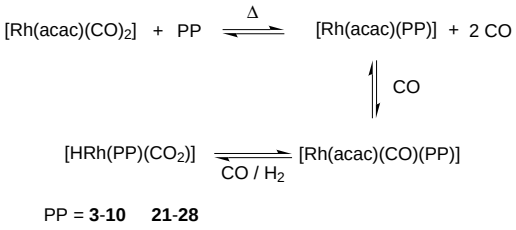
Table 2. Asymmetric hydroformylation of vinyl arenes with $[Rh(acac)(CO)_2]$/diphosphite.[a]

Entry	Substrates	Ligand	% Conv[b] [h]	% Regio[c]	% *ee*[d]
1	 **24**	**3**	81 (48)	98.6	91 (–)
2	**24**	**9**	80 (48)	98.7	89 (+)
3	 **25**	**3**	80 (48)	98.8	89 (+)
4	**25**	**9**	79 (48)	98.3	89 (–)

[a] Reaction conditions: $P = 10$ bar, $P_{CO}/P_{H_2} = 0.5$, $T = 20$ °C, substrate (13 mmol), $[Rh(acac)(CO)_2]$ (0.013 mmol), toluene (15 mL), PP/Rh = 1.1. [b] % Conversion measured by GC. [c] % Regioselectivity in branched aldehyde. [d] % Enantiomeric excess measured by GC.

Structures of $[HRh(PP)(CO)_2]$ complexes in solution: Hydridorhodium diphosphite dicarbonyl complexes denoted as $[HRh(PP)(CO)_2]$ (**21**–**28**), known to be responsible for the catalytic activity,[4, 5, 17, 18] were prepared in order to elucidate the solution structures of these catalysts. The complexes were prepared in situ under hydroformylation conditions (10 bar, 40 °C) by adding one equivalent of diphosphite ligand **3**–**10** to

the catalyst precursor [Rh(acac)(CO)$_2$] (Scheme 3). Initially, displacement of two carbon monoxide molecules by the ligands caused the formation of the [Rh(acac)(PP)] complexes, which after a short time under hydroformylation conditions evolved to the intermediate species [Rh(acac)-(CO)(PP)] with characteristic rhodium – phosphorus coupling constants around 300 Hz.[18] Reaction times of 3 – 4 hours were needed for the complete formation of the desired species [HRh(PP)(CO)$_2$] **21** – **28**.



Scheme 3. In situ preparation of catalysts.

Stable [HRh(PP)(CO)$_2$] complexes were obtained quantitatively for all the ligands, and no hydrolysis of the diphosphite ligands to H-diphosphonates was observed. NMR spectroscopy under atmospheric conditions showed no detectable decomposition of the complexes. Table 3 shows selected data obtained for complexes **21** – **28**.

At room temperature, the ^{31}P{^{1}H} NMR spectrum of complexes **21** and **22**, containing ligands **3** and **4**, showed a broad, eight-line spectrum ($\omega_{1/2} \approx 70$ Hz) due to the two nonequivalent phosphorus atoms and a rhodium atom (ABX system). These broad signals suggest a fluxional process on the NMR timescale.[4b] This was confirmed by measuring the ^{31}P NMR at variable temperature. At $-80\,^{\circ}$C, the ^{31}P resonances showed sharp signals ($\omega_{1/2} \approx 10$ Hz). ^{1}H NMR spectroscopy in the hydride region revealed a quadruplet, due to coupling with rhodium and the two phosphorus atoms. The fact that there is a quadruplet instead of the expected doublet of doublets is caused by the accidental coincidence of the coupling constants. The values of the phosphorus – hydride coupling constants (^2J(P,H) ≤ 4.2 Hz) are typical of a trigonal bipyramidal (TBP) hydridorhodium dicarbonyl species with bis-equatorially (**ee**) coordinating diphosphites. Small *cis* phosphorous – hydride coupling constants have been reported in [HRh(PP)(CO)$_2$] complexes with **ee** coordinating diphosphite ligands.[7f, 8, 17, 18]

At room temperature, ^{31}P {^{1}H} NMR spectra of complex **28**, which contains ligand **10**, showed a broad doublet at $\delta = 164.1$ ($\omega_{1/2} = 63$ Hz), due to ^{31}P – ^{103}Rh coupling. The fact that there is a broad doublet, not the expected eight-line spectrum, is caused by the accidental isocronicity of the two phosphorus atoms in fluxional behaviour. Fluxionality could be frozen out at low temperature ($-40\,^{\circ}$C). As expected for the two nonequivalent phosphorus atoms, an eight-line spectrum was obtained. The ^{1}H NMR spectrum revealed a pseudo-triplet of doublets in the hydride region at $\delta = -10.32$, due to coupling with two pseudo-equivalent phosphorus atoms (^2J(P,H) $= 5.9$ Hz) and with the rhodium atom.

In summary, NMR data for complexes **21**, **22**, **27**, and **28** indicate trigonal bipyramidal (TBP) hydridorhodium dicarbonyl species with **ee** coordinating diphosphites. Further evidence is provided by IR in situ measurements. Each of the spectra showed two carbonyl vibrations around 2070 and 2010 cm^{-1}; these are characteristic of **ee** isomers (Figure 1a).[19] Moreover, formation of only one diastereoisomer was detected by variable temperature NMR.

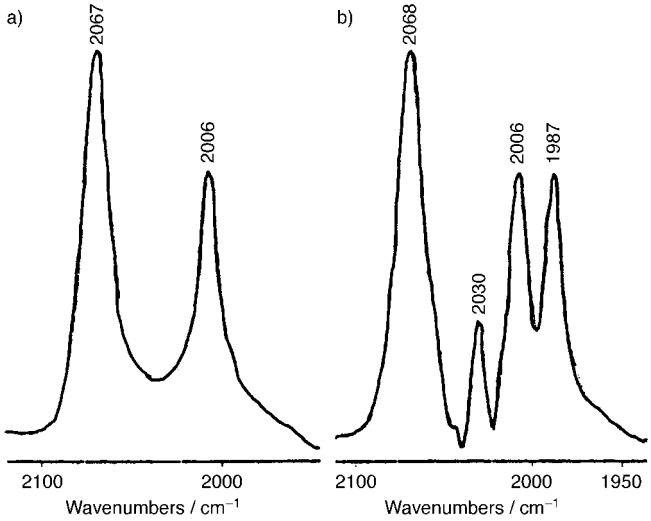


Figure 1. In situ IR spectrum of [HRh(PP)(CO)$_2$]. a) PP = **3**; b) PP = **8**.

The ^{31}P{^{1}H} NMR spectra at room temperature of complexes **23** – **26**, which contain ligands **5** – **8**, had eight sharp lines due to ^{31}P,^{31}P and ^{31}P,^{103}Rh couplings (ABX systems) (Table 3). The ^{1}H NMR spectra in the high-field region revealed a doublet of doublets for complexes **24** – **26**, due to the coupling constants of the hydride atom and the two

Table 3. Selected ^{1}H and ^{31}P NMR data for [HRh(PP)(CO)$_2$] complexes.[a]

Complex	δ P$_1$	δ P$_2$	^1J(Rh,P1)	^1J(Rh,P2)	^2J(P1,P2)	δH	^2J(H,P)	^2J(H,P)	^1J(H,Rh)
21	162.0	165.9	231.2	238.4	274.1	– 9.94(q)	4.2	4.2	4.2
22	159.4	163.2	229.1	231.3	269.3	– 9.89(q)	3.6	3.6	3.6
23	158.6	160.4	221.2	236.7	209.1	– 10.01(ddd)	30.0	4.2	1.2
24	153.4	155.1	218.1	229.4	201.7	– 9.72(dd)	28.1	5.0	–[c]
25	153.8	156.7	217.9	232.5	191.7	– 9.85(dd)	36.1	5.0	–[c]
26	152.6	156.2	224.4	231.9	204.8	– 9.68(dd)	27.0	4.8	–[c]
27	159.2	161.8	233.2	234.5	267.7	– 10.21(b)			
28[b]	161.1	166.0	232.7	237.8	286.5	– 10.32(dt)	5.9	5.9	3.3

[a] Prepared in [D$_8$]toluene. NMR spectra recorded under atmospheric conditions at room temperature. δ in ppm. Coupling constants in Hz. [b] ^{31}P NMR data measured at $-40\,^{\circ}$C. [c] Not observed.

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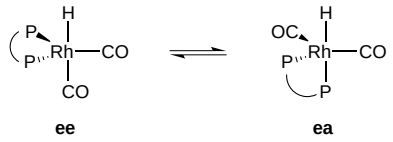
nonequivalent phosphorus atoms. The values of the phosphorus–phosphorus coupling constants are relatively small for a pure coordination in a TBP.[19] Two explanations can be put forward: firstly, the formation of a distorted TBP hydridorhodium dicarbonyl species with **ee** coordinating diphosphites,[8] or secondly, a fast equilibrium mixture of bis-equatorially and equatorial–axial (**ea**) species, giving averaged signals in the NMR spectra (Scheme 4).[20] Evidence for



ee **ea**

Scheme 4. Equilibrium between equatorial-equatorial (**ee**) and equatorial-axial (**ea**) species.

the latter should be supplied by the HP-IR spectra, thanks to the faster timescale of this technique. If an equilibrium between two isomers occurs, two sets of carbonyl frequencies originating from the two isomers should be observed.[20] In general, carbonyl bands of **ea** isomers are found at lower wavenumbers than those of **ee** isomers.[21] The infrared spectra of complexes **23**–**26** showed four carbonyl absorption bands in the 2100–1900 cm^{-1} region, which can be attributed to a mixture of **ee** and **ea** isomers (Table 4, Figure 1b).[19] The proportion of **ea** species was calculated from the NMR data, by using a *cis* phosphorus–proton coupling constant of -4 to $+4$ Hz and a *trans* phosphorus–proton coupling constant of 210 Hz, and is 15% on average.[19] The relative intensities of the absorption bands obtained from the HP-IR are in good agreement with the **ee**:**ea** ratios determined by NMR spectroscopy.

Table 4. Selected HP-IR data (cm^{-1}) for complexes **23**–**26**.

Complex	ν_1 (**ee**)	ν_2(**ea**)	ν_3 (**ee**)	ν_4 (**ea**)
23	2074 (s)	2032 (m)	2011 (s)	1985 (m)
24	2073 (s)	2031 (m)	2012 (s)	1989 (m)
25	2070 (s)	2029 (m)	2008 (s)	1988 (m)
26	2068 (s)	2030 (m)	2006 (s)	1987 (m)

Conclusion

A new family of C_1 diphosphite ligands containing different furanoside moieties as simple chiral backbones has been easily prepared in a few steps from readily available D-(+)-glucose. Their rhodium(I) complexes are highly efficient catalysts for the asymmetric hydroformylation of vinyl arenes. Both the *S* and the *R* enantiomers of 2-phenylpropanal can be obtained with excellent regio- and enantioselectivity under very mild reaction conditions. In addition, these catalyst systems are highly stable under hydroformylation conditions and no excess of ligand is needed. The type of substituents in the biphenyl moieties and the configuration of the stereocenters [C(3), C(5)] had remarkable effects on the enantioselectivity of the hydroformylation reactions. The absolute configuration of the product is therefore governed by the configuration of the stereogenic carbon atom C(3), while the level of enantioselectivity is a function of a cooperative effect between both stereocenters. Investigation of the hydridorhodium dicarbonyl complexes **21**–**28** under syngas pressure by NMR and in situ IR spectroscopy showed that the configurations of the stereogenic carbon atoms C(3) and C(5) greatly influence structure and, therefore, enantioselectivity. The best enantioselectivities were therefore obtained with ligands that have a strong **ee** coordination preference, while equilibria between **ee** and **ea** coordination modes in species **23**–**26** considerably lowered the ee's.

These results are among the best that have been reported for the asymmetric hydroformylation of vinyl arenes. Further research into more active catalysts is now in progress, exploiting the advantage that these sugar ligands can be so easily modified.

Experimental Section

General Comments: All syntheses were performed by using standard Schlenk techniques under an argon atmosphere. Solvents were purified by standard procedures. Compounds **11**,[10] **16**,[10] **12**,[11] **17**,[11] and phosphorochloridites[14] were prepared by methods described previously. All other reagents were used as commercially available. Elemental analyses were performed on a Carlo Erba EA-1108 instrument. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^1H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. All NMR spectral assignments were determined by COSY and HETCOR spectra. In situ high-pressure IR spectra were recorded on a Nicolet 510 FT-IR spectrometer. Gas chromatographic analyses were run on a Hewlett-Packard HP 5890A instrument (split/splitless injector, J&W Scientific, Ultra-2 25 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 150 kPa He, F.I.D. detector) equipped with a Hewlett-Packard HP 3396 series II integrator. Hydroformylation reactions were carried out in a custom-made 100 mL stainless steel autoclave. Enantiomeric excesses were measured after oxidation of the aldehydes to the corresponding carboxylic acids on 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, F.I.D. detector). Absolute configuration was determined by comparison of retention times with optically pure (S)-(+)-2-phenylpropionic and (R)-(−)-2-phenylpropionic acids.

3,5-Bis[(3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl)phosphite]-1,2-*O*-isopropylidene-6-deoxy-α-D-glucofuranose (3): Phosphorochloridite (2.2 mmol) produced in situ was dissolved in toluene (5 mL) and pyridine (0.36 mL, 4.6 mmol) was added. 1,2-*O*-Isopropylidene-6-deoxy-α-D-glucofuranose **13** (0.21 g, 1 mmol) was azeotropically dried with toluene ($3\times$ 1 mL) and then dissolved in toluene (10 mL), to which pyridine (0.18 mL, 2.3 mmol) had been added. The diol solution was transferred slowly over 30 min at room temperature to the solution of phosphorochloridite. The reaction mixture was stirred overnight at reflux, and the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash chromatography (toluene, $R_f = 0.13$) to produce a white powder. Yield: 0.70 g, 71%; ^1H NMR: $\delta = 1.12$ (s, 3H; CH_3), 1.28 (d, $^3J(6,5) = 6.3$ Hz, 3H; H-6), 1.38 (s, 3H; CH_3), 1.41 (s, 9H; CH_3, *t*Bu), 1.43 (s, 18H; CH_3, *t*Bu), 1.45 (s, 9H; CH_3, *t*Bu), 3.78 (s, 3H; OMe), 3.79 (s, 3H; OMe), 3.80 (s, 3H; OMe), 3.81 (s, 3H; OMe), 3.95 (d, $^3J(2,1) = 3.6$ Hz, 1H; H-2), 4.03 (dd, $^3J(4,3) = 2.7$ Hz, $^3J(4,5) = 8.1$ Hz, 1H; H-4), 4.70 (m, 1H; H-5), 4.79 (dd, $^3J(3,4) = 2.7$ Hz, $J(3,P) = 3.1$ Hz, 1H; H-3), 5.57 (d, $^3J(1,2) = 3.6$ Hz, 1H; H-1), 6.81 (m, 2H; CH=), 6.94 (m, 2H; CH=), 7.11 (m, 4H; CH=); ^{13}C NMR: $\delta = 19.8$ (C(6)), 25.7 (CH_3), 26.4 (CH_3), 31.1 (CH_3, *t*Bu), 31.2 (CH_3, *t*Bu), 35.1 (C, *t*Bu), 35.3 (C, *t*Bu), 55.4 (OMe), 55.5 (OMe), 68.6 (d, J(C,P) = 4.8 Hz, C(5)), 76.1 (C(3)), 82.9 (t, J(C,P) = 5.4 Hz, C(4)), 83.9 (C(2)), 104.6 (C(1)), 111.4 (CH=), 112.5 (CH=), 112.8 (CH=), 114.1 (CH=),

114.8 (CMe_2), 125.2 (CH=), 128.1 (CH=), 128.9 (CH=), 133.1 (C), 133.4 (C), 134.0 (C), 134.2 (C), 141.8 (C), 142.2 (C), 142.6 (C), 142.8 (C), 155.1 (C), 155.5 (C), 155.6 (C), 155.8 (C); ^{31}P NMR: $\delta = 144.9$ (s, 2P); ^{31}P NMR (CD_2Cl_2, 233 K): $\delta = 144.6$ (d, J(P,P) = 30.9 Hz, 1P), 145.1 (d, J(P,P) = 30.9 Hz, 1P); elemental analysis calcd (%) for $C_{57}H_{70}O_{13}P_2$: C 65.15, H 7.22; found: C 65.09, H 7.32.

1,2-*O*-Isopropylidene-3,5-bis[(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite]-6-deoxy-α-D-glucofuranose (4): Treatment of phosphorochloridite (2.2 mmol) produced in situ and **13** (0.21 g, 1 mmol), as described for compound **3**, afforded diphosphite **4**, which was purified by flash chromatography (toluene, $R_f = 0.18$) to produce a white powder. Yield: 0.80 g, 74%; ^{1}H NMR: $\delta = 1.02$ (s, 3H; CH_3), 1.09 (d, $^3J(6,5) = 4.2$ Hz, 3H; H-6), 1.24 (s, 9H; CH_3, *t*Bu), 1.26 (brs, 27H; CH_3, *t*Bu), 1.31 (s, 3H; CH_3), 1.35 (s, 9H; CH_3, *t*Bu), 1.39 (brs, 27H; CH_3, *t*Bu), 3.98 (m, 2H; H-2, H-4), 4.66 (m, 1H; H-5), 4.73 (dd, $^3J(3,4) = 2.4$ Hz, $J(3,P) = 6.3$ Hz, 1H; H-3), 5.38 (d, $^3J(1,2) = 3.6$ Hz, 1H; H-1), 7.12 (m, 4H; CH=), 7.36 (m, 4H; CH=); ^{13}C NMR: $\delta = 19.4$ (C(6)), 26.3 (CH_3), 26.7 (CH_3), 31.2 (CH_3, *t*Bu), 31.3 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 34.6 (C, *t*Bu), 34.7 (C, *t*Bu), 35.4 (C, *t*Bu), 68.9 (d, C(5), J(C,P) = 9.5 Hz), 76.2 (C(3)), 83.0 (t, C(2) or C(4), J(C,P) = 5.7 Hz), 84.2 (C(4) or C(2)), 104.7 (C-1), 111.6 (CMe_2), 124.0 (CH=), 124.2 (CH=), 126.55 (CH=), 126.6 (CH=), 132.4 (C), 132.6 (C), 133.1 (C), 133.2 (C), 139.7 (C), 140.2 (C), 140.3 (C), 145.9 (C), 146.4 (C), 146.5 (C), 146.8 (C); ^{31}P NMR: $\delta = 144.3$ (d, J(P,P) = 35.7 Hz, 1P), 145.3 (d, J(P,P) = 35.7 Hz, 1P); elemental analysis calcd (%) for $C_{65}H_{94}O_9P_2$: C 72.19, H 8.76; found: C 72.24, H 8.84.

3,5-Bis[(3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl)phosphite]-1,2-*O*-isopropylidene-6-deoxy-β-L-idofuranose (5): Treatment of phosphorochloridite (1.1 mmol) produced in situ and 1,2-*O*-isopropylidene-6-deoxy-β-L-idofuranose **15** (0.11 g, 0.5 mmol), as described for compound **3**, afforded diphosphite **5**, which was purified by flash chromatography (toluene, $R_f = 0.12$) to give a white powder. Yield: 0.29 g, 60%; ^{1}H NMR: $\delta = 1.04$ (s, 3H; CH_3), 1.13 (d, $^3J(6,5) = 6.3$ Hz, 3H; H-6), 1.37 (s, 3H; CH_3), 1.42 (s, 9H; CH_3, *t*Bu), 1.44 (s, 9H; CH_3, *t*Bu), 1.49 (s, 18H; CH_3, *t*Bu), 3.74 (s, 3H; OMe), 3.76 (brs, 9H; OMe), 3.99 (d, $^3J(2,1) = 3.6$ Hz, 1H; H-2), 4.12 (m, $^3J(4,5) = 6.8$ Hz, $^3J(4,3) = 3.0$ Hz, 1H; H-4), 4.78 (m, 2H; H-3, H-5), 5.62 (d, $^3J(1,2) = 3.6$ Hz, 1H; H-1), 6.84 (m, 4H; CH=), 7.04 (m, 4H; CH=); ^{13}C NMR: $\delta = 18.5$ (C(6)), 26.1 (CH_3), 26.7 (CH_3), 30.8 (CH_3, *t*Bu), 31.2 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 35.3 (C, *t*Bu), 35.4 (C, *t*Bu), 55.6 (OMe), 69.3 (d, J(C,P) = 6.3 Hz, C(3)), 75.2 (C(3)), 82.7 (t, J(C,P) = 4.2 Hz, C-4), 84.2 (C(2)), 103.9 (C(1)), 112.8 (CH=), 113.2 (CH=), 113.5 (CH=), 114.0 (CMe_2), 123.8 (CH=), 123.9 (CH=), 124.2 (CH=), 124.5 (CH=), 133.6 (C), 133.7 (C), 142.2 (C), 142.8 (C), 142.9 (C), 155.0 (C), 155.2 (C), 155.3 (C), 155.4 (C); ^{31}P NMR: $\delta = 145.5$ (s, 1P), 146.7 (s, 1P); elemental analysis calcd (%) for $C_{57}H_{70}O_{13}P_2$: C 65.15, H 7.22; found: C 65.34, H 7.25.

1,2-*O*-Isopropylidene-3,5-bis[(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite]-6-deoxy-β-L-idofuranose (6): Treatment of phosphorochloridite (2.2 mmol) produced in situ and **15** (0.21 g, 1 mmol), as described for compound **3**, afforded diphosphite **6**, which was purified by flash chromatography (toluene, $R_f = 0.19$) to afford a white powder. Yield: 0.69 g, 65%; ^{1}H NMR: $\delta = 0.99$ (d, $^3J(6,5) = 6.3$ Hz, 3H; H-6), 1.12 (s, 3H; CH_3), 1.24 (s, 18H; CH_3, *t*Bu), 1.26 (s, 18H; CH_3, *t*Bu), 1.32 (s, 9H; CH_3, *t*Bu), 1.34 (brs, 27H; CH_3, *t*Bu), 1.41 (s, 3H; CH_3), 4.01 (d, 1H; H-2, $^3J(2,1) = 3.6$ Hz), 4.09 (m, 1H; H-4), 4.10 (m, 1H; H-2), 4.68 (m, 1H; H-5), 4.72 (m, 1H; H-3), 5.42 (d, 1H; H-1, $^3J(1,2) = 3.6$ Hz), 7.06 (m, 4H; CH=), 7.31 (m, 4H; CH=); ^{13}C NMR: $\delta = 18.9$ (brs, C(6)), 25.9 (CH_3), 26.5 (CH_3), 31.3 (CH_3, *t*Bu), 31.4 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 34.9 (C, *t*Bu), 34.6 (C, *t*Bu), 35.1 (C, *t*Bu), 68.1 (t, C(5), J(C,P) = 10.1 Hz), 75.8 (C(3)), 82.4 (t, C(4), J(C,P) = 4.2 Hz), 84.1 (C(2)), 103.9 (C(1)), 113.4 (CMe_2), 123.8 (CH=), 123.9 (CH=), 124.2 (CH=), 124.4 (CH=), 131.9 (C), 132.2 (C), 132.4 (C), 132.5 (C), 139.9 (C), 140.2 (C), 140.4 (C), 145.2 (C), 145.8 (C), 146.0 (C), 146.2; ^{31}P NMR: $\delta = 144.6$ (s, 1P), 145.3 (s, 1P); elemental analysis calcd (%) for $C_{65}H_{94}O_9P_2$: C 72.19, H 8.76; found: C 72.41, H 8.82.

3,5-Bis[(3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl)phosphite]-1,2-*O*-isopropylidene-6-deoxy-α-D-allofuranose (7): Treatment of phosphorochloridite (2.2 mmol) produced in situ and 1,2-*O*-isopropylidene-6-deoxy-α-D-allofuranose **18** (0.21 g, 1 mmol), as described for compound **3**, afforded diphosphite **7**, which was purified by flash chromatography (toluene, $R_f = 0.12$) to give a white powder. Yield: 0.49 g, 50%; ^{1}H NMR: $\delta = 0.87$ (d, $^3J(6,5) = 6.9$ Hz, 3H; H-6), 1.14 (s, 3H; CH_3), 1.24 (s, 18H; CH_3, *t*Bu), 1.28 (s, 9H; CH_3, *t*Bu), 1.30 (s, 9H; CH_3, *t*Bu), 1.37 (s, 3H; CH_3), 3.62 (s, 9H; OMe), 3.64 (s, 3H; OMe), 3.92 (m, 1H; H-4), 4.09 (m, 1H; H-2), 4.11 (m, 1H; H-3), 4.52 (m, 1H; H-5), 5.53 (d, 1H; H-1, $^3J(1,2) = 3.6$ Hz), 6.58 (m, 4H; CH=), 6.81 (m, 4H; CH=); ^{13}C NMR: $\delta = 17.1$ (m, C(6)), 26.7 (CH_3), 26.8 (CH_3), 30.9 (CH_3, *t*Bu), 31.0 (CH_3, *t*Bu), 35.2 (C, *t*Bu), 55.5 (OMe), 55.6 (OMe), 70.5 (t, C(3), J(C,P) = 6.8 Hz), 72.5 (m, C(5)), 78.6 (C(2)), 81.8 (t, C(4), J(C,P) = 3.1 Hz), 104.0 (C(1)), 112.6 (CH=), 112.9 (CH=), 113.1 (CH=), 113.5 (CMe_2), 114.0 (CH=), 126.8 (C), 128.1 (C), 129.3 (C), 130.2 (C), 141.8 (C), 141.9 (C), 142.1 (C), 143.2 (C), 155.3 (C), 155.6 (C), 155.8 (C); ^{31}P NMR: $\delta = 144.2$ (s, 1P), 147.0 (s, 1P); elemental analysis calcd (%) for $C_{57}H_{70}O_{13}P_2$: C 65.15 H, 7.22; found: C 65.07, H, 7.42.

1,2-*O*-Isopropylidene-3,5-bis[(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite]-6-deoxy-α-D-allofuranose (8): Treatment of phosphorochloridite (2.2 mmol) produced in situ and **18** (0.21 g, 1 mmol), as described for compound **3**, afforded diphosphite **8**, which was purified by flash chromatography (toluene, $R_f = 0.15$) to produce a white powder. Yield: 0.65 g, 60%; ^{1}H NMR: $\delta = 0.85$ (m, 3H; H-6), 1.15 (s, 3H; CH_3), 1.20 (s, 27H; CH_3, *t*Bu), 1.22 (s, 18H; CH_3, *t*Bu), 1.24 (s, 9H; CH_3, *t*Bu), 1.26 (s, 9H; CH_3, *t*Bu), 1.28 (s, 9H; CH_3, *t*Bu), 1.38 (s, 3H; CH_3), 3.80 (m, 1H; H-2), 4.00 (m, 1H; H-4), 4.39 (m, 1H; H-5), 4.55 (m, 1H; H-3), 5.41 (d, $^3J(1,2) = 3.3$ Hz, 1H; H-1), 6.98 (m, 2H; CH=), 7.03 (m, 2H; CH=), 7.11 (m, 1H; CH=), 7.17 (m, 1H; CH=), 7.23 (m, 1H; CH=), 7.26 (m, 1H; CH=); ^{13}C NMR: $\delta = 16.9$ (C(6)), 26.9 (CH_3), 31.0 (CH_3, *t*Bu), 31.1 (CH_3, *t*Bu), 31.4 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu) 34.5 (C, *t*Bu), 34.6 (C, *t*Bu), 34.7 (C, *t*Bu), 35.2 (C, *t*Bu), 35.3 (C, *t*Bu), 35.4 (C, *t*Bu), 70.4 (d, C(3), J(C,P) = 16.6 Hz), 72.0 (C(5)), 78.7 (C(2)), 81.9 (t, C(4), J(C,P) = 5.2 Hz), 104.0 (C(1)), 113.0 (CMe_2), 123.8 (CH=), 123.9 (CH=), 124.0 (CH=), 1126.3 (CH=), 126.5 (CH=), 126.7 (CH=), 132.7 (C), 132.9 (C), 139.7(C), 139.9 (C), 140.2 (C), 140.4 (C), 145.8 (C), 146.0 (C), 146.2 (C), 146.3 (C); ^{31}P NMR: $\delta = 143.6$ (s, 1P), 146.5 (s, 1P); elemental analysis calcd (%) for $C_{65}H_{94}O_9P_2$: C 72.19, H 8.76; found: C 72.34, H 8.81.

3,5-Bis[(3,3′-bis-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl)phosphite]-1,2-*O*-isopropylidene-6-deoxy-β-L-talofuranose (9): Treatment of phosphorochloridite (1.1 mmol) produced in situ and 1,2-*O*-isopropylidene-6-deoxy-β-L-talofuranose **20** (0.11 g, 0.5 mmol), as described for compound **3**, afforded diphosphite **9**, which was purified by flash chromatography (toluene, $R_f = 0.10$) to afford a white powder. Yield: 0.24 g, 50%; ^{1}H NMR: $\delta = 0.98$ (brs, 3H; H-6), 1.21 (s, 3H; CH_3), 1.25 (s, 9H; CH_3, *t*Bu), 1.38 (s, 9H; CH_3, *t*Bu), 1.41 (s, 18H; CH_3, *t*Bu), 1.44 (s, 3H; CH_3), 3.81 (s, 12H; OMe), 4.01 (m, 1H; H-4), 4.40 (m, 2H; H-2, H-3), 4.44 (m, 1H; H-5), 5.71 (d, 1H; H-1, $^3J(1,2) = 3.9$ Hz), 6.82 (m, 4H; CH=), 6.99 (m, 4H; CH=); ^{13}C NMR: $\delta = 18.9$ (d, C(6), J(C,P) = 7.2 Hz), 26.7 (CH_3), 26.8 (CH_3), 30.8 (CH_3, *t*Bu), 31.0 (CH_3, *t*Bu), 35.2 (C, *t*Bu), 35.3 (C, *t*Bu), 55.4 (OMe), 55.6 (OMe), 71.4 (d, C(3), J(C,P) = 10.9 Hz), 73.6 (d, C(5), J(C,P) = 6.7 Hz), 78.7 (d, C(2), J(C,P) = 2.4 Hz), 81.7 (t, C(4), J(C,P) = 2.6 Hz), 103.8 (C(1)), 112.5 (CH=), 112.7 (CH=), 112.8 (CH=), 113.2 (CMe_2), 114.8 (CH=), 125.2 (C), 128.2 (C), 129.0 (C), 142.4 (C), 142.5 (C), 155.3 (C), 155.4 (C), 155.6 (C); ^{31}P NMR: $\delta = 145.4$ (d, J(P,P) = 4.5 Hz, 1P), 146.3 (d, J(P,P) = 4.5 Hz, 1P); elemental analysis calcd (%) for $C_{57}H_{70}O_{13}P_2$: C 65.15, H 7.22; found: C 65.23, H 7.17

1,2-*O*-Isopropylidene-3,5-bis[(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite]-6-deoxy-β-L-talofuranose (10): Treatment of phosphorochloridite (2.2 mmol) produced in situ and **20** (0.21 g, 1 mmol), as described for compound **3**, afforded diphosphite **10**, which was purified by flash chromatography (toluene, $R_f = 0.19$) to give a white powder. Yield: 0.72 g, 67%; ^{1}H NMR: $\delta = 1.02$ (d, $^3J(6,5) = 6$ Hz, 3H; H-6), 1.18 (brs, 27H; CH_3, *t*Bu), 1.24 (s, 3H; CH_3), 1.27 (s, 18H; CH_3, *t*Bu), 1.29 (s, 9H; CH_3, *t*Bu), 1.30 (s, 9H; CH_3, *t*Bu), 1.32 (s, 9H; CH_3, *t*Bu), 1.36 (s, 3H; CH_3), 3.66 (m, 1H; H-3), 3.90 (dd, 1H; H-4, $^3J(4,5) = 5.7$ Hz, $^3J(4,3) = 3.2$ Hz), 4.10 (m, 1H; H-2), 4.28 (m, 1H; H-5), 5.49 (d, 1H; H-1, $^3J(1,2) = 3.0$ Hz), 7.02 (m, 4H; CH=), 7.25 (m, 4H; CH=); ^{13}C NMR: $\delta = 18.6$ (d, J(C,P) = 5.3 Hz, C(6)), 26.8 (CH_3), 26.9 (CH_3), 31.0 (CH_3, *t*Bu), 31.1 (CH_3, *t*Bu), 31.3 (CH_3, *t*Bu), 31.4 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 34.5 (C, *t*Bu), 34.6 (C, *t*Bu), 35.3 (C, *t*Bu), 55.6 (d, J(C,P) = 4.3 Hz, C(3)), 72.0 (dd, J(C,P) = 11.5 Hz, J(C,P) = 3.2 Hz, C(5)), 78.8 (d, J(C,P) = 2.7 Hz, C(2)), 81.8 (t, J(C,P) = 3.9 Hz, C(4)), 103.8 (C(1)), 113.2 (CMe_2), 123.9 (CH=), 124.1 (CH=), 126.5 (CH=), 126.6 (CH=), 132.5 (C), 132.7 (C), 140.0 (C), 140.2 (C), 145.6 (C), 146.2 (C), 146.3 (C), 146.6 (C); ^{31}P NMR: $\delta = 145.9$ (d, J(P,P) = 5.2 Hz, 1P), 146.8 (d, 1P, J(P,P) = 5.2 Hz).Elemental analysis calcd (%) for $C_{65}H_{94}O_9P_2$: C 72.19, H, 8.76; found: C 72.01, H 8.91.

3,6-Di-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-(trifluoromethane)sulfonyl-α-D-glucofuranose (14): Anhydrous pyridine (2 mL, 20 mmol) was added to a solution of **11** (5.2 g, 20 mmol) in dichloromethane (40 mL). After 10 min,

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acetic anhydride (1.9 mL, 20 mmol) was added dropwise over 30 min at 0 °C and the mixture was allowed to react at room temperature. After 16 h, water (50 mL) was added, and the mixture was extracted with dichloromethane (3 × 50 mL). The organic layer was washed with dilute sulphuric acid and water, dried over $MgSO_4$, and evaporated. The residue was purified by flash chromatography (ethyl acetate/hexane 1:2) to obtain the diacetylated compound as a colorless liquid. Yield: 3.8 g, 62%; ^{1}H NMR: $\delta = 1.26$ (s, 3H; CH_3), 1.51 (s, 3H; CH_3), 2.03 (s, 3H; OAc), 2.08 (s, 3H; OAc), 3.51 (br s, 1H; OH), 3.98 (dd, $^2J(6',6) = 9.6$ Hz, $^3J(6',5) = 5.1$ Hz, 1H; H-6′), 4.10 (m, 1H; H-5), 4.15 (m, 1H; H-3), 4.21 (dd, $^2J(6',6) = 9.6$ Hz, $^3J(6,5) = 2.9$ Hz, 1H; H-6), 4.80 (d, $^3J(2,1) = 3.6$ Hz, 1H; H-2), 4.89 (dd, $^3J(4,3) = 6.9$ Hz, $^3J(4,5) = 3.9$ Hz, 1H; H-4), 5.79 (d, $^3J(1,2) = 3.6$ Hz, 1H; H-1); ^{13}C NMR: $\delta = 20.6$ (OAc), 20.8 (OAc), 26.6 (CH_3), 64.5 (C(3)), 69.9 (C(6)), 71.5 (C(5)), 77.6 (C(4)), 77.7 (C(2)), 104.0 (C(1)), 113.2 (CMe_2), 170.2 (CO), 171.0 (CO).

Anhydrous pyridine (0.5 mL, 5 mmol) was added to a solution of 3,6-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1.52 g, 5 mmol) in dichloromethane (20 mL). After 10 min, trifluoromethanesulfonic anhydride (0.85 mL, 5 mmol) was added dropwise at −20 °C, and the mixture was allowed to react at room temperature for 20 min, after which the solvent was evaporated. The residue was purified by flash chromatography on a small column of neutral silica (hexane/ethyl acetate 1:1) to produce the triflate as a colorless liquid. Yield: 1.4 g, 72%; ^{1}H NMR: $\delta = 1.33$ (s, 3H; CH_3), 1.51 (s, 3H; CH_3), 2.11 (s, 3H; OAc), 2.14 (s, 3H; OAc), 4.16 (dd, $^2J(6',6) = 10.6$ Hz, $^3J(6',5) = 5.9$ Hz, 1H; H-6′), 4.38 (m, 2H; H-3, H-6), 4.82 (dd, $^3J(4,3) = 4.8$ Hz, $^3J(4,5) = 2.7$ Hz, 1H; H-4), 4.89 (d, $^3J(2,1) = 3.6$ Hz, 1H; H-2), 5.28 (m, 1H; H-5), 5.81 (d, 1H; H-1, $^3J(1,2) = 3.6$ Hz).

3,6-Di-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-trifluoromethanesulfonyl-α-D-allofuranose (19): Treatment of 3,6-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-allofuranose[22] (1.52 g, 5 mmol), obtained by treating **16** with acetic anhydride as described before, with trifluoromethanesulfonic anhydride (0.85 mL, 5 mmol), as described for **14**, afforded triflate **19**. This was purified by column chromatography on neutral silica (hexane/ethyl acetate 1:1) to produce a colorless liquid. Yield: 1.38 g, 71%; ^{1}H NMR: $\delta = 1.31$ (s, 3H; CH_3), 1.52 (s, 3H; CH_3), 2.06 (s, 3H; OAc), 2.12 (s, 3H; OAc), 4.12 (dd, $^2J(6',6) = 10.2$ Hz, $^3J(6',5) = 6.2$ Hz, 1H; H-6′), 4.31 (dd, $^3J(3,4) = 5.2$ Hz, $^3J(3,2) = 2.4$ Hz, 1H; H-3), 4.42 (dd, $^2J(6,6') = 9.6$ Hz, $^3J(6,5) = 2.9$ Hz, 1H; H-6), 4.72 (dd, $^3J(4,3) = 5.2$ Hz, $^3J(4,5) = 3.9$ Hz, 1H; H-4), 4.84 (dd, $^3J(2,1) = 3.6$ Hz, $^3J(2,3) = 2.4$ Hz, 1H; H-2), 5.21 (m, 1H; H-5), 5.79 (d, $^3J(1,2) = 3.6$ Hz, 1H; H-1); ^{13}C NMR: $\delta = 20.4$ (OAc), 20.5 (OAc), 26.5 (CH_3), 26.7 (CH_3), 61.1 (C(3)), 72.5 (C(6)), 75.4 (C(4)), 77.1 (C(2)), 84.2 (C(5)), 104.1 (C(1)), 113.7 (CMe_2), 119.4 (q, CF_3, $^1J(C,F) = 309$ Hz), 170.1 (CO), 170.6 (CO).

In situ HP-NMR hydroformylation experiments: In a typical experiment, a sapphire tube ($\phi = 10$ mm) was filled under argon with a solution of [Rh(acac)(CO)$_2$] (0.030 mmol) and ligand (molar ratio PP/Rh = 1.1) in [D$_8$]toluene (1.5 mL). The HP-NMR tube was purged twice with CO and pressurized to the appropriate pressure of CO/H_2. After a reaction time of 16 hours' shaking at the desired temperature, the solution was analyzed.

[HRh(CO)$_2$(3)] (21): ^{1}H NMR: $\delta = -9.94$ (q, $^2J(P,H) = 4.7$ Hz, $^1J(Rh,H) = 4.7$ Hz, 1H), 0.95 (m, 3H; H-6), 1.12 (s, 3H; CH_3), 1.31 (s, 3H; CH_3), 1.45 (s, 9H; CH_3, *t*Bu), 1.48 (s, 9H; CH_3, *t*Bu), 1.49 (s, 9H; CH_3, *t*Bu), 1.51 (s, 9H; CH_3, *t*Bu), 3.28 (br s, 12H; OMe), 3.74 (d, $^3J(2,1) = 3.6$ Hz, 1H; H-2), 4.12 (m, 1H; H-4), 4.22 (m, 1H; H-3), 5.49 (m, 1H; H-5), 5.71 (d, $^3J(1,2) = 3.6$ Hz, 1H; H-1), 6.82 (m, 2H; CH=), 7.10 (m, 6H; CH=); ^{13}C NMR: $\delta = 19.6$ (m, C(6)), 26.2 (CH_3), 26.9 (CH_3), 31.4 (CH_3, *t*Bu), 31.9 (CH_3, *t*Bu), 32.3 (CH_3, *t*Bu), 32.4 (CH_3, *t*Bu), 35.2 (C, *t*Bu), 35.5 (C, *t*Bu), 54.8 (OMe), 54.9 (OMe), 55.0 (OMe), 69.1 (m, C(3)), 76.2 (m, C(5)), 78.7 (m, C(2)), 83.5 (m, C(4)), 102.4 (C(1)), 113.0 (CMe_2), 114.0 (CH=), 114.8 (CH=), 115.3 (CH=), 115.5 (CH=), 131.1 (C), 131.4 (C), 132.0 (C), 132.5 (C), 145.1 (C), 145.3 (C), 145.7 (C), 155.3 (C), 155.4 (C), 156.0 (C).

[HRh(CO)$_2$(4)] (22): ^{1}H NMR: $\delta = -9.89$ (q, 1H; $^2J(P,H) = 3.6$ Hz, $^1J(Rh,H) = 3.6$ Hz), 0.92 (m, 3H; H-6), 1.25 (s, 9H; CH_3, *t*Bu), 1.28 (s, 9H; CH_3, *t*Bu), 1.31 (s, 18H; CH_3, *t*Bu), 1.36 (s, 3H; CH_3), 1.57 (s, 3H; CH_3), 1.62 (s, 18H; CH_3, *t*Bu), 1.64 (s, 9H; CH_3, *t*Bu), 1.66 (s, 9H; CH_3, *t*Bu), 3.79 (d, $^3J(2,1) = 3.6$ Hz, 1H; H-2), 4.25 (dd, $^3J(4,5) = 7.2$ Hz, $^3J(4,3) = 2.8$ Hz, 1H; H-4), 4.82 (m, 1H; H-5), 5.21 (m, 1H; H-5), 5.72 (d, 1H; H-1, $^3J(1,2) = 3.6$ Hz), 7.11 (m, 3H; CH=), 7.14 (m, 1H; CH=), 7.21 (m, 2H; CH=); ^{13}C NMR: $\delta = 19.7$ (m, C(6)), 26.2 (CH_3), 27.0 (CH_3), 31.5 (CH_3, *t*Bu), 32.0 (CH_3, *t*Bu), 35.7 (C, *t*Bu), 36.3 (C, *t*Bu), 70.9 (m, C(5)), 78.2 (m, C(3)), 83.1 (m, C(4)), 84.5 (m, C(2)), 104.9 (C(1)), 112.6 (CMe_2), 124.4 (CH=), 124.8 (CH=), 126.5 (CH=), 126.9 (CH=), 132.0 (C), 132.3 (C), 132.4 (C), 140.0 (C), 140.2 (C), 146.5 (C), 146.6 (C), 146.9 (C).

[HRh(CO)$_2$(5)] (23): ^{1}H NMR: $\delta = -10.01$ (dd, $^2J(P,H) = 30.6$ Hz, $^2J(P,H) = 4.2$ Hz, 1H), 1.02 (m, 3H; H-6), 1.12 (s, 3H; CH_3), 1.35 (s, 3H; CH_3), 1.45 (s, 9H; CH_3, *t*Bu), 1.48 (s, 18H; CH_3, *t*Bu), 1.51 (s, 9H; CH_3, *t*Bu), 3.29 (s, 12H; OMe), 4.02(d, $^3J(2,1) = 3.9$ Hz, 1H; H-2), 4.43 (m, 1H; H-4), 4.72 (m, 1H; H-3), 4.99 (m, 1H; H-5), 5.69 (d, $^3J(1,2) = 3.9$ Hz, 1H; H-1), 6.82 (m, 4H; CH=), 6.92 (m, 2H; CH=), 6.95 (m, 2H; CH=); ^{13}C NMR: $\delta = 19.9$ (m, C(6)), 27.1 (CH_3), 27.8 (CH_3), 31.5 (CH_3, *t*Bu), 31.7 (CH_3, *t*Bu), 34.8 (C, *t*Bu), 35.0 (C, *t*Bu), 54.9 (OMe), 55.0 (OMe), 77.1 (m, C(5)), 78.5 (m, C(3)), 81.2 (m, C(4)), 83.2 (m, C-2), 104.2 (C(1)), 112.6 (CMe_2), 113.5 (CH=), 114.1 (CH=), 114.3 (CH=), 114.5 (CH=), 133.4 (C), 133.5 (C), 134.2 (C), 134.3 (C), 145.9 (C), 146.3 (C), 146.5 (C), 155.8 (C), 155.9 (C), 156.3 (C).

[HRh(CO)$_2$(6)] (24): ^{1}H NMR: $\delta = -9.72$ (dd, $^2J(P,H) = 28.1$ Hz, $^1J(P,H) = 5.0$ Hz, 1H), 1.03 (m, 3H; H-6), 1.20 (s, 3H; CH_3), 1.23 (s, 9H; CH_3, *t*Bu), 1.27 (s, 18H; CH_3, *t*Bu), 1.29 (s, 9H; CH_3, *t*Bu), 1.35 (s, 3H; CH_3), 1.52 (s, 9H; CH_3, *t*Bu), 1.53 (s, 9H; CH_3, *t*Bu), 1.56 (s, 18H; CH_3, *t*Bu), 4.11 (d, $^3J(2,1) = 3.0$ Hz, 1H; H-2), 4.15 (m, 1H; H-4), 4.97 (m, 1H; H-3), 5.08 (m, 1H; H-5), 5.71 (d, $^3J(1,2) = 3.0$ Hz, 1H; H-1), 7.30 (m, 4H; CH=), 7.41 (m, 4H; CH=); ^{13}C NMR: $\delta = 19.1$ (m, C(6)), 26.5 (CH_3), 27.2 (CH_3), 31.3 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 32.1 (CH_3, *t*Bu), 35.1 (C, *t*Bu), 35.3 (C, *t*Bu), 35.8 (C, *t*Bu), 68.3 (m, C(5)), 71.3 (m, C(3)), 80.1 (m, C(4)), 81.9 (m, C-2), 103.4 (C(1)), 112.9 (CMe_2), 124.7 (CH=), 124.8 (CH=), 125.0 (CH=), 125.2 (CH=), 132.3 (C), 132.5 (C), 133.0 (C), 133.2 (C), 145.9 (C), 146.3 (C), 146.5 (C), 146.8 (C), 147 (C).

[HRh(CO)$_2$(7)] (25): ^{1}H NMR: $\delta = -9.85$ (dd; $^2J(P,H) = 36.1$ Hz, $^2J(P,H) = 5.0$ Hz, 1H), 0.93 (s, 3H; CH_3), 1.14 (d, $^3J(6,5) = 5.7$ Hz, 3H; H-6), 1.35 (s, 3H; CH_3), 1.65 (s, 9H; CH_3, *t*Bu), 1.68 (s, 9H; CH_3, *t*Bu), 1.69 (s, 9H; CH_3, *t*Bu), 1.72 (s, 9H; CH_3, *t*Bu), 3.33 (s, 12H; OMe), 4.07 (m, 1H; H-4), 4.50 (dd, $^3J(2,1) = 3.9$ Hz, $^3J(2,3) = 2.4$ Hz, 1H; H-2), 4.72 (m, 1H; H-3), 4.80 (m, 1H; H-5), 5.40 (d, 1H; H-1, $^3J(1,2) = 3.9$ Hz), 6.51 (m, 2H; CH=), 6.60 (m, 2H; CH=), 6.65 (m, 2H; CH=), 6.68 (m, 2H; CH=); ^{13}C NMR: $\delta = 20.5$ (m, C-6), 26.5 (CH_3), 26.7 (CH_3), 31.7 (CH_3, *t*Bu), 32.9 (CH_3, *t*Bu), 33.0 (CH_3, *t*Bu), 35.7 (C, *t*Bu), 36.2 (C, *t*Bu), 54.6 (OMe), 54.7 (OMe), 54.8 (OMe), 76.0 (d, $J = 9.1$ Hz, C(5)), 76.9 (C(3)), 79.9 (C(2)), 80.8 (t, $J = 8.9$ Hz, C(4)), 103.9 (C(1)), 112.8 (CMe_2), 113.7 (CH=), 113.8 (CH=), 114.5 (CH=), 114.7 (CH=), 115.7 (CH=), 115.9 (CH=), 133.2 (C), 133.8 (C), 133.9 (C), 134.2 (C), 141.2 (C), 142.0 (C), 142.5 (C), 143.0 (C), 156.1 (C), 156.4 (C), 156.5 (C), 156.6 (C).

[HRh(CO)$_2$(8)] (26): ^{1}H NMR: $\delta = -9.68$ (dd, $^2J(P,H) = 27.0$ Hz, $^2J(P,H) = 4.8$ Hz, 1H), 0.92 (m, 3H; H-6), 1.22 (s, 9H; CH_3, *t*Bu), 1.24 (s, 9H; CH_3, *t*Bu), 1.29 (s, 18H; CH_3, *t*Bu), 1.32 (s, 3H; CH_3), 1.59 (s, 3H; CH_3), 1.70 (s, 9H; CH_3, *t*Bu), 1.74 (s, 9H; CH_3, *t*Bu), 1.76 (s, 9H; CH_3, *t*Bu), 1.79 (s, 9H; CH_3, *t*Bu), 4.10 (m, 1H; H-4), 4.52 (t, $^3J(2,1) = 3.6$ Hz, 1H; H-2), 4.72 (m, 1H; H-5), 4.75 (m, 1H; H-3), 5.49 (d, $^3J(1,2) = 3.6$ Hz, 1H; H-1), 7.19 (m, 4H; CH=), 7.56 (m, 2H; CH=), 7.62 (m, 2H; CH=); ^{13}C NMR: $\delta = 19.6$ (C-6), 26.8 (CH_3), 31.4 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 31.9 (CH_3, *t*Bu), 32.0 (CH_3, *t*Bu), 32.9 (CH_3, *t*Bu), 33.2 (CH_3, *t*Bu), 35.7 (C, *t*Bu), 35.8 (C, *t*Bu), 36.2 (C, *t*Bu), 36.3 (C, *t*Bu), 76.1 (d, C(5), $J = 9.8$ Hz), 76.9 (C(3)), 79.9 (C-2), 81.2 (t, $J = 7.9$ Hz, C(4)), 104.1 (C(1)), 112.9 (CMe_2), 124.3 (CH=), 124.6 (CH=), 124.7 (CH=), 125.0 (CH=), 125.4 (CH=), 125.6 (CH=), 125.9 (CH=), 132.5 (C), 132.6 (C), 133.1 (C), 133.6 (C), 139.9 (C), 140.3 (C), 140.9 (C), 146.2 (C), 146.8 (C), 146.9 (C), 147.1 (C).

[HRh(CO)$_2$(9)] (27): ^{1}H NMR: $\delta = -10.21$ (br s, 1H), 1.11 (m, 3H; H-6), 1.34 (s, 3H; CH_3), 1.41 (s, 9H; CH_3, *t*Bu), 1.45 (s, 3H; CH_3), 1.52 (s, 9H; CH_3, *t*Bu), 1.54 (s, 9H; CH_3, *t*Bu), 1.58 (s, 9H; CH_3, *t*Bu), 3.21 (s, 3H; OMe), 3.23 (s, 3H; OMe), 3.24 (s, 3H; OMe), 3.26 (s, 3H; OMe), 4.14 (m, 1H; H-4), 4.60 (dd, $^3J(2,1) = 3.0$ Hz, $^3J(2,3) = 4.2$ Hz, 1H; H-2), 5.03 (m, 1H; H-3), 5.08 (m, 1H; H-5), 5.77 (d, 1H; H-1, $^3J(1,2) = 3.0$ Hz), 6.62 (m, 4H; CH=), 6.81 (m, 4H; CH=); ^{13}C NMR: $\delta = 18.3$ (m, C(6)), 26.3 (CH_3), 26.8 (CH_3), 30.7 (CH_3, *t*Bu), 31.3 (CH_3, *t*Bu), 31.7 (CH_3, *t*Bu), 32.3 (CH_3, *t*Bu), 35.3 (C, *t*Bu), 35.5 (C, *t*Bu), 35.8 (C, *t*Bu), 36.0 (C, *t*Bu), 55.1 (OMe), 68.8 (m, C(3)), 73.8 (t, C(5), $J = 6.5$ Hz), 79.2 (m, C(2)), 81.0 (m, C(4), 104.1 (C(1)), 113.0 (CH=), 113.5 (CMe_2), 113.9 (CH=), 114.7 (CH=), 115.5 (CH=), 132.6 (C), 132.7 (C), 132.9 (C), 133.4 (C), 141.3 (C), 141.7 (C), 142.0 (C), 142.4 (C), 156.2 (C), 156.5 (C), 146.7 (C), 157.0 (C).

[HRh(CO)$_2$(10)] (28): ^{1}H NMR: $\delta = -10.32$ (dt, $^1J(Rh,H) = 3.3$ Hz, $^2J(P,H) = 5.9$ Hz, 1H), 1.08 (m, 3H; H-6), 1.19 (s, 3H; CH_3), 1.21 (s, 9H;

CH_3, *t*Bu), 1.22 (s, 9H; CH_3, *t*Bu), 1.23 (s, 9H; CH_3, *t*Bu), 1.24 (s, 9H; CH_3, *t*Bu), 1.33 (s, 3H; CH_3), 1.52 (s, 9H; CH_3, *t*Bu), 1.56 (s, 9H; CH_3, *t*Bu), 1.61 (s, 9H; CH_3, *t*Bu), 1.64 (s, 9H; CH_3, *t*Bu), 4.18 (m, 1H; H-4), 4.62 (dd, $^3J(2,1) = 3.3$ Hz, $^3J(2,3) = 4.2$ Hz, 1H; H-2), 5.01 (m, 1H; H-3), 5.09 (m, 1H; H-5), 5.79 (d, $^3J(1,2) = 3.3$ Hz, 1H; H-1), 7.31 (m, 4H; CH=), 7.52 (m, 4H; CH=); ^{13}C NMR: $\delta = 18.3$ (m, C(6)), 26.4 (CH_3), 26.8 (CH_3), 31.3 (CH_3, *t*Bu), 31.4 (CH_3, *t*Bu), 31.8 (CH_3, *t*Bu), 32.0 (CH_3, *t*Bu), 32.2 (CH_3, *t*Bu), 35.5 (C, *t*Bu), 35.6 (C, *t*Bu), 35.7 (C, *t*Bu), 35.8 (C, *t*Bu), 69.2 (m, C(3)), 74.4 (m, C(5)), 79.2 (t, C(2), $J = 3.9$ Hz), 81.2 (t, C(4), $J = 4.3$ Hz), 104.2 (C(1)), 113.2 (CMe_2), 124.7 (CH=), 125.0 (CH=), 127.6 (CH=), 127.9 (CH=), 128.2 (CH=), 129.2 (CH=), 131.3 (C), 131.7 (C), 132.4 (C), 133.0 (C), 146.0 (C), 146.2 (C), 146.6 (C), 146.9 (C); ^{31}P NMR: $\delta = 164.0$ (bd, ^1J(Rh,P) = 234.2 Hz, 2P).

High-pressure IR experiments: These experiments were performed in an SS316 50 mL autoclave equipped with IRTRAN windows (ZnS, transparent up to 70 cm^{-1}, 10 mm i.d., optical path length 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure device. In a typical experiment, a degassed solution of [Rh(acac)$(CO)_2$] (0.013 mmol) and diphosphite (0.015 mmol) in methyltetrahydrofuran (15 mL) was introduced into the high pressure IR autoclave. The autoclave was purged twice with CO, pressurized to 10 bar of CO/H_2 and heated to 40 °C. The reaction was usually completed in 3–4 hours.

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) and diphosphite (0.015 mmol) in toluene (10 mL). After pressurizing to the desired pressure with syngas and heating the autoclave to the reaction temperature, the reaction mixture was stirred for 16 hours to form the active catalyst. In situ IR measurements indicate shorter reaction times (3–4 hours) for the complete formation of the active catalysts. The autoclave was depressurized and a solution of styrene (13 mmol) in toluene (5 mL) was introduced into the autoclave, which was pressurized again. During the reaction several samples were taken from the autoclave. After the desired reaction time, the autoclave was cooled to room temperature and depressurized. The reaction mixture was analyzed by gas chromatography.

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