Asymmetric hydroformylation of styrene catalyzed by carbohydrate diphosphite-Rh(I) complexes

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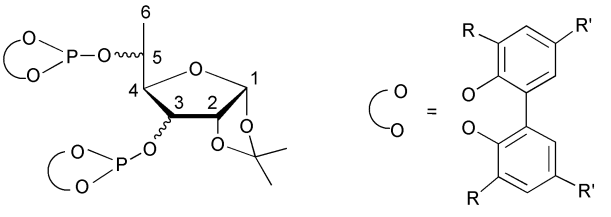
A series of new chelating diphosphite ligands with a furanoside backbone and axially chiral biphenyl or binaphthyl moieties have been synthesized. Their Rh(I) complexes have been tested as catalyst precursors for the asymmetric hydroformylation of styrene. Systematic variation in chirality at both chiral sugar backbone stereocenters (C-3 and C-5) and either the axial chiral biphenyl or binaphthyl substituents revealed a remarkable effect on the selectivity of the hydroformylation catalysts. In this way, by judicious choice of these elements, both regio- and enantioselectivities can be optimized. Thus, both high enantioselectivity (up to 93% *S*) and regioselectivity in 2-phenylpropanal (up to 98.8%) were found under mild reaction conditions (15–40 °C, 10 bar of syngas) for the ligand with a glucofuranoside backbone and bis(trimethylsilyl)-2,2′-biphenyl moiety. The solution structures of $HRh(L–L)(CO)_2$ complexes have been studied by high pressure NMR and IR. Varying the configuration of the binaphthyl moieties revealed a remarkable effect on the diphosphite coordination modes on the intermediate $HRh(L–L)(CO)_2$ species and, therefore, on enantioselectivity. Enantioselectivity was highest for ligands with a strong bis-equatorial coordination preference.

Asymmetric hydroformylation is an attractive way of synthesizing enantiomerically pure aldehydes, which are important precursors for synthesizing high value added compounds (*i.e.*, pharmaceuticals and agrochemicals).[1] Rhodium and platinum/tin catalytic systems modified with phosphine ligands have been widely used in asymmetric hydroformylation.[1] However, the enantioselectivity for rhodium systems[2] and the activity and regioselectivity for platinum/tin systems[3] have been highly disappointing. During the last decade, two new types of ligands, diphosphite[4] and phosphine-phosphite[5] ones, have emerged as suitable ligands for the Rh catalyzed asymmetric hydroformylation, providing better activities and selectivities than the phosphine-based catalytic systems. At the moment, the Rh/phosphine-phosphite (BINAPHOS) system is the only catalyst with a wide scope in asymmetric hydroformylation, although its difficult preparation, its high ligand-to-Rh ratio and the high pressures required limit its application.[5] Furthermore, its regioselectivity in 2-phenylpropanal is not completely satisfactory.[6] Therefore, much research still needs to be done to find readily available ligands that provide both good regio- and enantioselectivities in asymmetric hydroformylation.

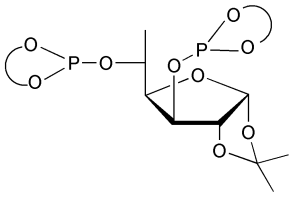
For this purpose, carbohydrates are particularly advantageous. They are readily available and highly functionalized compounds with several stereogenic centers. This allows a systematic regio- and stereoselective introduction of different functionalities in the synthesis of series of chiral ligands that can be screened in the search for high activities and enantioselectivities. In this context, we recently described the synthesis of new modular diphosphite ligands, **1**–**4**, that are readily available from carbohydrates and have different furanoside backbones. These were successfully used in the Rh asymmetric hydroformylation of styrene with an excellent combination of both regio- and enantioselectivities. The modular nature of these ligands enabled a systematic variation in the configuration at C-5 and C-3 of the sugar backbone. The results indicated that there is a cooperative effect between the two stereocenters that results in a matched combination for ligands with gluco- and talofuranoside backbones. Moreover, a relationship between the structure of the $[HRh(L–L)(CO)_2]$ species and their enantiodiscriminating performance was observed. Thus, enantioselectivities were highest with ligands (**1** and **4**) showing a strong bis-equatorial coordination preference, while an equilibrium of species with bis-equatorial and equatorial-axial coordination modes considerable reduced the ee's.[4d]



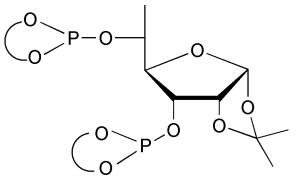
1	D gluco	(1*R*, 2*R*, 3*S*, 4*R*, 5*R*)
2	D allo	(1*R*, 2*R*, 3*R*, 4*R*, 5*R*)
3	L ido	(1*R*, 2*R*, 3*S*, 4*R*, 5*S*)
4	L talo	(1*R*, 2*R*, 3*R*, 4*R*, 5*S*)

On the other hand, a remarkable cooperative effect between the stereogenic centers of the ligand backbone and the stereogenic biaryl substituents has recently been described for other ligands.[1d,4b,7] In light of this, we decided to investigate the possibility of this type of cooperative effect in our furanoside diphosphite ligands **1**–**4**. This study will therefore provide more information about the parameters that control selectivity (regio- and enantioselectivity) and, at the same time, may help us to increase the efficiency of our catalytic system. For this, we prepared a series of new diphosphite ligands **5**–**12**, which contain different enantiomerically pure binapthyl

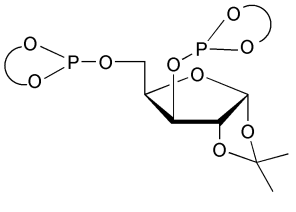
moieties. To further compare with ligands **7** and **8**, which contain ortho trimethylsilyl substituents in the enantiomerically pure binaphthyl moieties, we also synthesized the new ligands **13** and **14** with fluxional 3,3′-bis(trimethylsilyl)-2,2′-biphenyl moieties. We also report the spectroscopic study of the species formed under hydroformylation conditions.



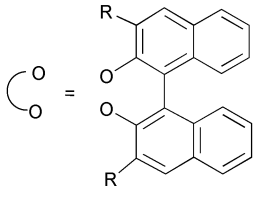
5-8, 13



9, 10, 14

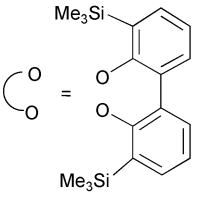


11, 12



5, 9, 11 (R^{ax}), R= H
6, 10, 12 (S^{ax}), R= H

7 (R^{ax}), R= $SiMe_3$
8 (S^{ax}), R= $SiMe_3$



13, 14

Results and discussion

Ligand design

To determine whether there is a cooperative effect between the enantiomerically pure binaphthyl phosphite moieties and the stereocenters of the ligand backbone, we designed a series of modular furanoside ligands **5**–**12**.

Initially, we investigated how the configuration of the binaphthyl phosphite moieties affects both regio- and enantioselectivity using ligands **5** and **6**, which have the same configuration at the ligand backbone (C-3 and C-5).

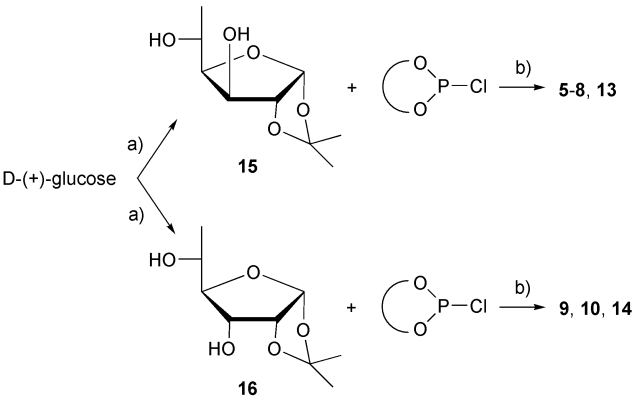
Next, we extended the study to ligands **9** and **10**, whose configuration at the stereogenic center C-3 is opposite to that of ligands **5** and **6**, and ligands **11** and **12**, which have the same configuration at C-3 as ligands **5** and **6** but do not have the stereogenic center at C-5.

To determine how the steric bulk affects the product outcome (conversion and selectivity), we compared ligands **7** and **8**, which contain bulky trimethylsilyl groups at the ortho binaphthyl positions, with unsubstituted ligands **5** and **6**.

Finally, we studied how introducing a fluxional biphenyl moiety affects the regio- and enantioselectivity using ligands **13** and **14**, which contain ortho trimethylsilyl substituents in the biphenyl moieties.

Synthesis of diphosphites

Ligands **5**–**14** incorporate a chiral 1,2-*O*-protected gluco-, allo- or xylofuranoside backbone, which determines their underlying structure and to which several phosphoric acid biaryl esters are attached.



Scheme 1 Synthesis of ligands **5**–**10**, **13** and **14**. (a) ref. 2*d*. (b) Py, toluene, 100 °C.

The new ligands **5**–**10**, **13** and **14** were synthesized very efficiently in one step from the corresponding diols **15** and **16**, which were easily prepared on a large scale from D-(+)-glucose using standard procedures (Scheme 1).[4d] Therefore, reacting the corresponding diol with 2 equiv of the desired *in situ* formed phosphorochloridite in the presence of base afforded the desired ligands as white air-stable solids in moderate to good overall yield.

The ^{1}H and ^{13}C NMR spectra were as expected for these C_1 ligands (see Experimental). The ^{31}P NMR spectra of allofuranoside ligands **9**, **10** and **14** displayed two singlets, one for each phosphorus moiety. For glucofuranoside ligands **5**, **6**, **8** and **13**, two doublets, one for each phosphorus, were observed. The large J_{PP} values for these ligands are similar to those of the related diphosphite ligands **1**.[4d] Unlike the ^{31}P NMR spectra of glucofuranoside ligands, no phosphorus–phosphorus coupling was observed for diphosphite **7**. Both the presence of bulky trimethylsilyl substituents in the ortho positions of the binaphthyl moieties and the inverse configuration of the axial chirality compared to ligand **8** probably gave rise to a solution structure without the correct conformation to give appreciable phosphorus–phosphorus coupling.[4b]

Asymmetric hydroformylation of styrene

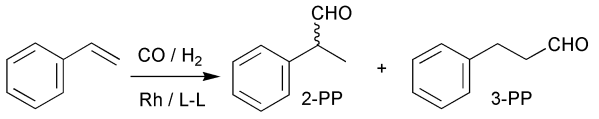
The catalytic performance of ligands **5**–**14** was thoroughly explored in the enantioselective rhodium-catalyzed hydroformylation of styrene over 16 h. The catalysts were prepared *in situ*.[4] The conversion and selectivity results are shown in Table 1. Hydrogenated or polymerized products of styrene were not observed in any case.

We investigated the effects of different reaction parameters for the catalytic precursor containing ligand **5**. After identical catalyst preparation, we performed hydroformylation experiments under several partial pressures of CO and H_2 (entries 1–3). Our results clearly show that higher partial pressures of H_2 led to higher initial turnover frequencies. Moreover, entries 1–3 show that regio- and enantioselectivity were not affected when the partial H_2 pressure was varied.

Varying the ligand-to-rhodium ratio showed that these catalyst systems are highly stable under hydroformylation conditions and that no excess of ligand is needed (entry 4). This is an important advantage over the most successful catalysts based on diphosphites[4a] and phosphine-phosphite[5], which need a larger excess of ligand.

Ligand **6**, which resulted from changing the configuration of the binaphthyl moieties from (*R*) in ligand **5** to (*S*), led to lower activity and enantioselectivity than the catalyst system Rh/**5**

Table 1 Asymmetric hydroformylation of styrene catalyzed by Rh(acac)$(CO)_2$/diphosphite **5**–**14**[a]



Entry	Ligand	TOF[b]	Conv[c]/%	2PP[d]/%	ee[e]/%
1	**5**	165	82	85	60 (*R*)
2[f]	**5**	123	63	85	60 (*R*)
3[g]	**5**	105	54	85	59 (*R*)
4[h]	**5**	166	80	85	60 (*R*)
5	**6**	153	78	85	25 (*S*)
6	**9**	178	83	86	20 (*R*)
7	**10**	158	77	84	5 (S)
8	**11**	126	66	80	44 (*R*)
9	**12**	85	46	83	37 (*S*)
10	**7**	99	52	86	30 (*S*)
11	**8**	149	73	84	68 (*S*)
12[i]	**8**	9	8[j]	89	86 (*S*)
13	**13**	151	72	96	76 (*S*)
14	**14**	147	73	95	30 (*R*)
15[i]	**13**	12	11[j]	98.8	93 (*S*)
16[i]	**14**	10	10[j]	98.1	62 (*R*)

[a] Reaction conditions: $T = 40\,^{\circ}C$, $P = 10$ bar, styrene (13 mmol), [Rh(acac)$(CO)_2$] (0.0135 mmol), ligand/Rh = 1.1, toluene (15 mL), $P_{CO}/P_{H2} = 0.5$. [b] TOF in mol styrene × mol $Rh^{-1} \times h^{-1}$ determined after 1 h reaction time by GC. [c] Conversion of styrene after 5 h. [d] Regioselectivity in 2-phenylpropanal. [e] Enantiomeric excess measured by GC. [f] $P_{CO}/P_{H2} = 1$. [g] $P_{CO}/P_{H2} = 2$. [h] Ligand/Rh = 2. [i] $T = 15\,^{\circ}C$. [j] Conversion after 10 h.

(entry 1 *vs.* 5). These results indicate a cooperative effect between the stereogenic centers of the ligand backbone and the stereogenic binaphthyl phosphite moieties on both activity and enantioselectivity. Moreover, the sense of the enantioselectivity was reversed; the (*S*) enantiomer was obtained with ligand **6** and the (*R*) enantiomer was obtained with ligand **5**.

Ligands **9** and **10**, whose configuration of carbon atom C-3 is opposite to that of ligands **5** and **6**, followed the same trend as catalyst precursors Rh/**5** and Rh/**6**. However, the enantiomeric excesses were smaller (entries 6 and 7).

In summary, the results with catalyst precursors containing glucofuranoside ligands **5** and **6** and allofuranoside ligands **9** and **10** can be summarized as follows. The value of the enantiomeric excess is controlled by two different cooperative effects: (1) the previously observed cooperative effect between the backbone stereocenters (namely C-3 and C-5)[4d] and (2) the cooperative effect between the sterogenic centers of the ligand backbone and the configuration of the binaphthyl moieties. The sense of the enantiomeric excess is controlled by the configuration of the binaphthyl phosphite moieties. The results of using ligands **11** and **12** provide further evidence. Thus, ligand **11** gives predominantly the (*R*) enantiomer whereas the (*S*) enantiomer is predominantly obtained with ligand **12** (entries 8 and 9).

As expected, ligand **8**, which results from introducing bulky trimethylsilyl substituents at the ortho positions of the (*S*)-binaphthyl moieties in ligand **6**, improved enantioselectivity (68% ee, entry 11). A remarkable increase in enantioselectivity (up to 86%, entry 12) was found by lowering the reaction temperature.

Surprisingly, ligand **7**, with bulky trimethylsilyl substituents at the ortho positions of the (*R*)-binaphthyl moieties, showed both lower activity and asymmetric induction than the less hindered ligand **5** (entry 1 *vs.* 10). This unexpectedly low enantioselectivity can be explained by considering that the bulky ligand probably reduces its steric congestion in the hydridorhodium complex by adopting an unfavorable conformation that reaches lower enantioselectivities.

Interestingly, ligand **13**, which resulted from changing the biaryl substituents from enantiopure binaphthyl in the diphosphite ligands **7** and **8** to fluxional biphenyl moieties, improved both regio- and enantioselectivity (entries 13 and 15). Entries 10, 11 and 13 suggest that the fast interchanging atropoisomers of ligand **13** predominantly adopt the same configuration as ligand **8**. The fact that the enantioselectivity for catalytic system Rh/**13** is higher than for Rh/**8** may be due to the different dihedral angles of the biphenyl and binaphthyl moieties, which affect the characteristics of the phosphorus and, therefore, the geometry of the hydridorhodium complex responsible for the catalytic activity.[4b]

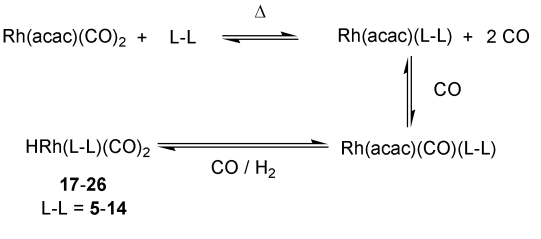
Characterization of $HRh(L–L)(CO)_2$ complexes

To obtain information about the species $HRh(L–L)(CO)_2$, which are known to be responsible for the catalytic activity,[1] we studied the solution structures of hydridorhodium diphosphite dicarbonyl species $HRh(L–L)(CO)_2$, where L–L = diphosphite ligand, by high pressure (HP)-NMR spectroscopy. These species were prepared *in situ* under hydroformylation conditions (see Experimental) by adding 1.1 equiv. of diphosphite ligand to the catalyst precursor Rh(acac)$(CO)_2$. Initially, the displacement by the ligand of two carbon monoxide molecules caused the formation of the Rh(acac)(L–L) complexes. After a short time under hydroformylation conditions, these evolved into the intermediate species Rh(acac)(L–L)(CO) with characteristic rhodium–phosphorus coupling constants of about 300 Hz.[8] Reaction times of 3–4 h were needed for the desired species $HRh(L–L)(CO)_2$ to completely form (Scheme 2). Table 2 shows selected data for the stable $HRh(L–L)(CO)_2$ complexes.

The $^{31}P\{^1H\}$ NMR spectra of the complexes that contain the less bulky ligands **6**, **9**–**12** showed several signals that could not be reliably determined. In the ^1H NMR spectra, several signals in the hydride zone were detected between −9.0 and −11.0 ppm.

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of complex **17**, which contains ligand **5**, showed a sharp eight-line spectrum ($\Delta\omega_{1/2} = 10$ Hz) due to the two non-equivalent phosphorus atoms and a rhodium atom (ABX system). The ^1H NMR spectra in the hydride region revealed a double triplet due to the coupling with rhodium and the two phosphorus atoms. The double triplet rather than the expected double double doublet was caused by the accidental coincidence of the phosphorus–hydride coupling constants. The values of the phosphorus–hydride ($^2J_{P–H} = 56.1$ Hz) and phosphorus–phosphorus ($^2J_{P–P} = 208.2$ Hz) coupling constants indicate an equilibrium mixture of bis-equatorial (**ee**) and equatorial-axial (**ea**) species in fast exchange on the NMR time scale (Scheme 3).[8,9]

The $^{31}P\{^1H\}$ NMR spectrum at room temperature of complex **20**, which contains ligand **8**, showed a doublet at 172.4 ppm due to the ^{31}P, ^{103}Rh coupling. The doublet, not the expected eight-line spectrum, was caused by the accidental



Scheme 2 *In situ* preparation of $[HRh(L–L)(CO)_2]$ catalysts.

Table 2 Selected ^{1}H and ^{31}P NMR data for $HRh(L–L)(CO)_2$ complexes[a]

Complex	PP	δP_1	δP_2	$^{1}J_{Rh–P1}$	$^{1}J_{Rh–P2}$	$^{2}J_{P1–P2}$	δH	$^{2}J_{H–P}$	$^{2}J_{H–P}$	$^{1}J_{H–Rh}$
17	**5**	175.9	179.0	212.0	218.1	208.2	−8.47 (dt)	56.1	56.1	6.0
19	**7**	172.0	175.2	238.8	228.9	282.1	−10.40 (dt)	8.7	8.7	4.8
20[b]	**8**	171.8	174.9	231.4	235.2	275.3	−10.14 (q)	5.0	5.0	5.0
25[c]	**13**	159.0	166.3	229.2	240.7	272.8	−10.34 (q)	5.7	5.7	5.7
26	**14**	157.1	160.5	232.9	234.7	264.4	−10.11 (ddd)	9.0	6.9	4.8

[a] Prepared in toluene-d_8. NMR spectra recorded under atmospheric conditions at room temperature. δ in ppm. Coupling constants in Hz. [b] ^{31}P NMR data measured at −70 °C. [c] ^{31}P NMR data measured at −40 °C.

Scheme 3 Equilibrium between equatorial–equatorial (ee) and equatorial–axial (ea) species.

coincidence of the two phosphorus atoms in fluxional behavior.[4b] Fluxionality was frozen out at low temperature (−70 °C). As expected for the two non-equivalent phosphorus atoms, an eight-line spectrum was obtained. The ^{1}H NMR spectrum revealed a quadruplet in the hydride region at −10.14 ppm due to the coupling with rhodium and the two phosphorus atoms. The fact that there is a quadruplet instead of the expected double double doublet was caused by the accidental coincidence of the coupling constants. The values of the phosphorus–hydride coupling constants ($^{2}J_{P–H} = 5.0$ Hz) are typical of a trigonal bipyramidal (TBP) hydridorhodium dicarbonyl species with bis-equatorially (**ee**) coordinating diphosphites.[8,9]

At room temperature, the $^{31}P\{^{1}H\}$ NMR spectra of complex **25**, which contains ligand **13**, showed a broad signal at 161.4 ppm. These broad signals suggest a fluxional process on the NMR time scale.[4b] Fluxionality was frozen out at −40 °C. As expected for the two non-equivalent phosphorus atoms, an eight-line spectrum was obtained. The ^{1}H NMR spectrum revealed a quadruplet in the hydride region at −10.34 ppm due to the coupling with rhodium and the two phosphorus atoms. The values of the phosphorus–hydride coupling constants ($^{2}J_{P–H} = 5.7$ Hz) agree with an **ee** trigonal bipyramidal (TBP) hydridorhodium dicarbonyl species.[8,9]

In summary, the variable temperature NMR data for complexes **20** and **25** indicate the formation of a single bis-equatorial (**ee**) diastereomer of the $HRh(L–L)(CO)_2$ species.

The $^{31}P\{^{1}H\}$ NMR spectra at room temperature of complexes **19** and **26**, which contain ligands **7** and **14**, showed the expected sharp eight-line spectra (Table 2). The ^{1}H NMR spectra in the high-field region revealed a double triplet for complex **19** and a double double doublet for complex **26**. The values of the phosphorus–hydride coupling constants were slightly bigger than those of species **20** and **25**, and could suggest the presence of **ea** species in equilibrium with the **ee** species (Scheme 3).[8,9] This was confirmed by HP-IR. Thus, four carbonyl absorption bands at 2069 (**ee**), 2030 (**ea**), 2007 (**ee**) and 1988 (**ea**) cm^{-1} were observed for compound **26**.[4d,9d] The relative intensities of the absorption bands obtained from the HP-IR show that the proportion of **ea** species was rather low. This agrees with the results of NMR spectroscopy.

Comparing the solution structures of the $[HRh(L–L)(CO)_2]$ species with the hydroformylation results, we can conclude that they follow the general trend observed for ligands **1**–**4**, that is the enantiodiscriminating performance is highest for ligands with a strong bis-equatorial coordination preference (*vide supra*).[4d] However, this structure/selectivity relationship is not always straightforward. Thus, different considerations have to be taken into account.

(1) High bis-equatorial coordination preference does not always lead to high selectivity, as the enantiodiscrimination is very dependent on the exact ligand structure.[1d,e] Thus, ligand **7**, which shows a high bis-equatorial coordination preference (**ee** : **ea** ratio of 98 : 2)[10] shows a very low enantioselectivity (entry 10 in Table 1).

(2) Having a mixture of bis-equatorial and equatorial-axial species does not always lead to low enantioselectivity, since product formation can be kinetically controlled. Thus, if one of the diastereoisomeric species inserts styrene into the Rh–H bond faster than the other species, a good selectivity can be obtained.[5a,11] The results using ligand **5** clearly illustrates this. Thus, despite having a 75 : 25 mixture of **ee** : **ea** species,[10] it provides good enantioselectivity at 40 °C (entry 1 in Table 1).

Conclusions

Variation in chirality at both chiral sugar backbone stereocenters (C-3 and C-5) and the axial chiral binaphthyl moieties in ligands **5**–**12** revealed a remarkable effect on the activity and enantioselectivity. The enantiomeric excess for these diastereoisomeric ligands was highest for glucofuranoside ligand **8**, with *S* and *R* configuration at C-3 and C-5, respectively, and ortho trimethylsilyl substituents in the enantiomerically pure (*S*)-binaphthyl moieties.

Changing the binaphthyl substituents in ligand **8** to fluxional 3,3′-bis(trimethylsilyl)-2,2′-biphenyl moieties (ligand **13**) improved both regioselectivity (up to 98.8%) and enantioselectivity (up to 93%).

We have characterized the rhodium complexes formed under CO/H_2 by NMR and *in situ* IR spectroscopy. The results indicate that varying the configuration of the binaphthyl moieties greatly influences the structure of the intermediate hydridodiphosphite dicarbonyl complexes. Therefore, the formation of only one bis-equatorial diastereomer of $HRh(L–L)(CO)_2$ was observed for ligands **8** and **13**. Also, a relationship between the structures of these intermediates and the enantioselectivity has been observed. In general, enantioselectivity is better with ligands that have a strong bis-equatorial coordination preference.

In summary, two cooperative effects are involved with this type of ligand: (1) one between the backbone stereocenters (C-3 and C-5) and (2) another between the stereogenic centers of the ligand backbone and the configuration of the binaphthyl phosphite moieties. Thus, the value of the enantiomeric excess is controlled by both cooperative effects whereas the sense of enantioselectivity is mainly controlled by the configuration of the binaphthyl phosphite moieties. Thus, the enantioselectivity found with ligand **13** suggests that the preferentially formed complex has the required conformation for

optimal chiral cooperativity that induces the highest enantioselectivity.

Experimental

Materials and methods

All experiments were carried out under argon atmosphere. All solvents were dried using standard methods and distilled prior to use. Compounds **15**[4d] and **16**[4d] and ligands **11**[12] and **12**[12] were prepared by previously described methods. Phosphorochloridites were prepared in analogy with literature procedures.[4b]

Elemental analyses were performed on a Carlo Erba EA-1108 instrument. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts were relative to $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. All assignments in NMR spectra were determined by COSY and HETCOR spectra. 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 home-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 comparing the retention times with optically pure (*S*)-(+)-2-phenylpropionic and (*R*)-(−)-2-phenylpropionic acids.

Syntheses

3,5-Bis{[(*R*)-1,1′-binaphthyl-2,2′-diyl]phosphite}-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (5). Following a standard procedure,[4d] *in situ* formed phosphorochloridite (2.2 mmol) was dissolved in toluene (5 mL) to which pyridine (0.36 mL, 4.6 mmol) was added. 6-Desoxy-1,2-*O*-isopropylidene-α-D-glucofuranose **15** (0.21 g, 1 mmol) was azeotropically dried with toluene (3 × 1 mL) and dissolved in toluene (10 mL), to which pyridine (0.18 mL, 2.3 mmol) had been added. The diol solution was slowly transferred over 30 min to the solution of phosphorochloridite at room temperature. 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 (eluent: toluene; R_f 0.45) to produce 0.45 g (55%) of a white powder. Anal. Calcd. for $C_{49}H_{38}O_9P_2$: C, 70.67; H, 4.60. Found: C, 70.74; H, 4.71. ^{31}P NMR, δ: 149.6 (d, 1P, $^{6}J_{P-P} = 34.2$ Hz), 153.1 (d, 1P, $^{6}J_{P-P} = 34.2$ Hz). ^{1}H NMR, δ: 1.28 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.47 (d, 3H, H-6, $^{3}J_{6-5} = 6.0$ Hz), 4.09 (dd, 1H, H-4, $^{3}J_{4-5} = 8.8$ Hz, $^{3}J_{4-3} = 2.4$ Hz), 4.70 (m, 1H, H-5), 4.74 (d, 1H, H-2, $^{3}J_{2-1} = 3.6$ Hz), 4.95 (dd, 1H, H-3, $^{3}J_{3-4} = 2.4$ Hz, $^{3}J_{3-P} = 8.8$ Hz), 5.86 (d, 1H, H-1, $^{3}J_{1-2} = 3.6$ Hz), 7.1–8.0 (m, 24H, CH=). ^{13}C NMR, δ: 20.9 (d, C-6, $J_{C-P} = 3.2$ Hz), 26.3 (CH_3), 26.7 (CH_3), 68.8 (d, C-5, $J_{C-P} = 21.2$ Hz), 77.1 (m, C-3), 82.8 (t, C-4, $J_{C-P} = 7.3$ Hz), 84.2 (d, C-2, $J_{C-P} = 3.4$ Hz), 104.9 (C-1), 112.3 (CMe_2), 121.1 (CH=), 121.7 (CH=), 124.8 (CH=), 124.9 (CH=), 125.0 (CH=), 125.2 (CH=), 126.1 (CH=), 126.2 (CH=), 126.3 (CH=), 127.0 (CH=), 127.1 (CH=), 128.2 (CH=), 128.3 (CH=), 129.0 (CH=), 129.8 (CH=), 130.1 (CH=), 130.3 (CH=), 130.5 (CH=), 131.4 (C), 131.7 (C), 131.8 (C), 132.9 (C), 133.0 (C), 146.9 (C), 147.1 (C), 147.4 (C).

3,5-Bis{[(*S*)-1,1′-binaphthyl-2,2′-diyl]phosphite}-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (6). Treatment of *in situ* formed phosphorochloridite (2.2 mmol) and **15** (0.21 g, 1 mmol) as described for compound **5** afforded diphosphite **6**, which was purified by flash chromatography (eluent: toluene; R_f 0.45) to produce 0.42 g (51%) of a white powder. Anal. Calcd. for $C_{49}H_{38}O_9P_2$: C, 70.67; H, 4.60. Found: C, 70.88; H, 4.98. ^{31}P NMR, δ: 146.8 (d, 1P, $^{6}J_{P-P} = 12.1$ Hz), 151.0 (d, 1P, $^{6}J_{P-P} = 12.1$ Hz). ^{1}H NMR, δ: 1.11 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.45 (d, 3H, H-6, $^{3}J_{6-5} = 6.0$ Hz), 4.02 (dd, 1H, H-4, $^{3}J_{4-5} = 8.8$ Hz, $^{3}J_{4-3} = 2.4$ Hz), 4.31 (d, 1H, H-2, $^{3}J_{2-1} = 3.2$ Hz), 4.77 (m, 1H, H-5), 4.92 (dd, 1H, H-3, $^{3}J_{3-4} = 2.4$ Hz, $^{3}J_{3-P} = 7.6$ Hz), 5.73 (d, 1H, H-1, $^{3}J_{1-2} = 3.2$ Hz), 7.1–8.0 (m, 24H, CH=). ^{13}C NMR, δ: 21.2 (d, C-6, $J_{C-P} = 3.8$ Hz), 26.2 (CH_3), 26.8 (CH_3), 69.3 (d, C-5, $J_{C-P} = 16.6$ Hz), 77.8 (m, C-3), 82.8 (t, C-4, $J_{C-P} = 7.6$ Hz), 84.3 (C-2), 105.0 (C-1), 112.3 (CMe_2), 121.8 (CH=), 121.9 (CH=), 122.0 (CH=), 122.1 (CH=), 125.0 (CH=), 125.2 (CH=), 125.3 (CH=), 125.4 (CH=), 126.3 (CH=), 126.4 (CH=), 126.6 (CH=), 127.1 (CH=), 127.2 (CH=), 127.3 (CH=), 128.4 (CH=), 128.5 (CH=), 128.6 (CH=), 129.2 (CH=), 130.0 (CH=), 130.2 (CH=), 130.4 (CH=), 130.5 (CH=), 130.8 (CH=), 132.8 (C), 132.9 (C), 133.1 (C), 147.6 (C), 148.2 (C), 148.3 (C), 148.4 (C).

3,5-Bis{[(*R*)-3,3′-bistrimethylsilyl-1,1′-binaphthyl-2,2′-diyl]-phosphite}-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (7). Treatment of *in situ* formed phosphorochloridite (2.2 mmol) and **15** (0.21 g, 1 mmol) as described for compound **5** afforded diphosphite **7**, which was purified by flash chromatography (eluent: toluene; R_f 0.50). Yield: 0.41 g (36%) of a white powder. Anal. Calcd. for $C_{61}H_{70}O_9P_2Si_4$: C, 65.33; H, 6.29. Found: C, 65.51; H, 6.43. ^{31}P NMR, δ: 145.3 (s), 148.7 (s). ^{1}H NMR, δ: 0.32 (s, 9H, CH_3–Si), 0.34 (s, 9H, CH_3–Si), 0.35 (s, 9H, CH_3–Si), 0.40 (s, 9H, CH_3–Si), 0.84 (s, 3H, CH_3), 1.11 (d, 3H, H-6, $^{3}J_{6-5} = 8.0$ Hz), 1.25 (s, 3H, CH_3), 4.07 (dd, 1H, H-4, $^{3}J_{4-5} = 3.2$ Hz, $^{3}J_{4-3} = 2.8$ Hz), 4.15 (d, 1H, H-2, $^{3}J_{2-1} = 3.2$ Hz), 4.24 (dd, 1H, H-3, $^{3}J_{3-P} = 8.8$ Hz, $^{3}J_{4-3} = 2.8$ Hz), 4.36 (m, 1H, H-5), 5.70 (d, 1H, H-1, $^{3}J_{1-2} = 3.2$ Hz), 7.0–7.4 (m, 12H, CH=), 7.8–8.1 (m, 8H, CH=). ^{13}C NMR, δ: −0.9 (CH_3–Si), −0.1 (CH_3–Si), 0.1 (CH_3–Si), 0.2 (CH_3–Si), 18.5 (C-6), 25.4 (CH_3), 29.7 (CH_3), 71.0 (d, C-5, $J_{C-P} = 6.4$ Hz), 78.5 (C-3), 82.5 (b, C-4), 83.3 (m, C-2), 104.4 (C-1), 111.4 (CMe_2), 123.6 (CH=), 123.9 (CH=), 124.5 (CH=), 124.8 (CH=), 126.1 (CH=), 126.5 (CH=), 126.6 (CH=), 126.8 (CH=), 127.5 (CH=), 128.1 (CH=), 128.3 (CH=), 128.4 (CH=), 129.2 (CH=), 130.5 (C), 130.6 (C), 130.8 (C), 130.9 (C), 132.3 (C), 132.4 (C), 133.5 (C), 133.6 (C), 133.8 (C), 134.2 (C), 136.3 (CH=), 136.7 (CH=), 137.0 (CH=), 151.1 (C), 151.3 (C).

3,5-Bis{[(*S*)-3,3′-bistrimethylsilyl-1,1′-binaphthyl-2,2′-diyl]-phosphite}-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (8). Treatment of *in situ* formed phosphorochloridite (2.2 mmol) and **15** (0.21 g, 1 mmol) as described for compound **5** afforded diphosphite **8**, which was purified by flash chromatography (eluent: toluene; R_f 0.50). Yield: 0.37 g (34%) of a white powder. Anal. Calcd. for $C_{61}H_{70}O_9P_2Si_4$: C, 65.33; H, 6.29. Found: C, 65.61; H, 6.33. ^{31}P NMR, δ: 147.2 (d, 1P, $^{6}J_{P-P} = 31.6$ Hz), 147.5 (d, 1P, $^{6}J_{P-P} = 31.6$ Hz). ^{1}H NMR, δ: 0.25 (s, 9H, CH_3–Si), 0.26 (s, 9H, CH_3–Si), 0.28 (s, 9H, CH_3–Si), 0.33 (s, 9H, CH_3–Si), 0.73 (d, 3H, H-6, $^{3}J_{6-5} = 6.4$ Hz), 1.03 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.54 (d, 1H, H-2, $^{3}J_{2-1} = 3.6$), 3.69 (dd, 1H, H-4, $^{3}J_{4-5} = 9.0$ Hz, $^{3}J_{4-3} = 2.7$ Hz), 4.46 (m, 1H, H-5), 4.57 (m, 1H, H-3), 4.99 (d, 1H, H-1, $^{3}J_{1-2} = 3.6$ Hz), 6.9–7.3 (m, 12H, CH=), 7.7–7.9 (m, 8H, CH=). ^{13}C NMR, δ: 0.3 (CH_3–Si), 20.0 (C-6), 26.2 (CH_3), 29.7 (CH_3), 68.0 (C-5), 77.4 (m, C-3), 82.5 (m, C-4), 83.5 (C-2), 104.6 (C-1), 111.0 (CMe_2), 124.4 (CH=), 124.6 (CH=), 124.8 (CH=), 125.0 (CH=), 126.1 (CH=), 126.3 (CH=), 126.5 (CH=), 126.7 (CH=), 128.2 (CH=), 128.4 (CH=), 129.0 (CH=), 130.4 (C), 130.5 (C),

130.8 (C), 130.9 (C), 132.7 (C), 132.8 (C), 132.9 (C), 133.0 (C), 133.7 (C), 133.8 (C), 133.9 (C), 136.2 (CH=), 136.4 (CH=), 136.8 (CH=), 137.1 (CH=), 150.1 (C), 150.3 (C).

3,5-Bis{[(*R*)-1,1′-binaphthyl-2,2′-diyl]phosphite}-6-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose (9). Treatment of *in situ* formed phosphorochloridite (2.2 mmol) and 6-desoxy-1,2-*O*-isopropylidene-α-D-allofuranose **16** (0.21 g, 1 mmol) as described for compound **5** afforded diphosphite **9**, which was purified by flash chromatography (eluent: toluene; R_f 0.45) to produce 0.39 g (48%) of a white powder. Anal. Calcd. for $C_{49}H_{38}O_9P_2$: C, 70.67; H, 4.60. Found: C, 70.39, H, 4.68. ^{31}P NMR, δ: 140.3 (s), 146.3 (s). ^{1}H NMR, δ: 1.05 (d, 3H, H-6, $^3J_{6-5} = 6.4$ Hz), 1.31 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 4.12 (m, 1H, H-4), 4.28 (m, 2H, H-2, H-3), 4.59 (m, 1H, H-5), 5.62 (d, 1H, H-1, $^3J_{1-2} = 3.2$ Hz), 6.8–7.8 (m, 24H, CH=). ^{13}C NMR, δ: 17.1 (d, C-6, $J_{C-P} = 3$ Hz), 26.7 (CH_3), 26.9 (CH_3), 71.0 (m, C-5), 72.0 (C-3), 79.0 (d, C-2, $J_{C-P} = 1.9$ Hz), 81.2 (m, C-4), 103.7 (C-1), 113.5 (CMe_2), 121.5 (CH=), 121.7 (CH=), 121.9 (CH=), 124.8 (CH=), 124.9 (CH=), 125.0 (CH=), 126.1 (CH=), 126.3 (CH=), 126.8 (CH=), 126.9 (CH=), 127.0 (CH=), 128.1 (CH=), 128.3 (CH=), 128.4 (CH=), 128.5 (CH=), 129.6 (CH=), 130.3 (CH=), 132.5 (C), 132.5 (C), 132.6 (C), 132.7 (C), 146.8 (C), 147.4 (C), 147.7 (C), 148.5 (C).

3,5-Bis{[(*S*)-1,1′-binaphthyl-2,2′-diyl]phosphite}-6-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose (10). Treatment of *in situ* formed phosphorochloridite (2.2 mmol) and **16** (0.21 g, 1 mmol) as described for compound **5** afforded diphosphite **9**, which was purified by flash chromatography (eluent: toluene; R_f 0.45) to produce 0.42 g (51%) of a white powder. Anal. Calcd. for $C_{49}H_{38}O_9P_2$: C, 70.67; H, 4.60. Found: C, 70.84; H, 4.78. ^{31}P NMR, δ: 144.4 (s), 147.9 (s). ^{1}H NMR, δ: 1.22 (d, 3H, H-6, $^3J_{6-5} = 7.2$ Hz), 1.32 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 4.08 (d, 1H, H-4, $^3J_{4-5} = 7.2$ Hz), 4.50 (m, 2H, H-2, H-3), 4.62 (m, 1H, H-5), 5.63 (d, 1H, H-1, $^3J_{1-2} = 3.2$ Hz), 7.0–8.0 (m, 24H, CH=). ^{13}C NMR, δ: 18.3 (C-6), 26.8 (CH_3), 26.9 (CH_3), 70.6 (d, C-5, $J_{C-P} = 12.9$ Hz), 73.2 (d, C-3, $J_{C-P} = 9.1$ Hz), 79.3 (C-2), 80.7 (m, C-4), 103.6 (C-1), 113.3 (CMe_2), 121.8 (CH=), 121.9 (CH=), 121.9 (CH=), 122.2 (CH=), 124.7 (CH=), 124.8 (CH=), 125.0 (CH=), 125.1 (CH=), 125.3 (CH=), 126.8 (CH=), 127.0 (CH=), 128.1 (CH=), 128.3 (CH=), 128.9 (CH=), 129.4 (CH=), 129.7 (CH=), 130.3 (CH=), 131.0 (CH=), 131.5 (CH=), 132.2 (C), 132.6 (C), 132.7 (C), 132.8 (C), 146.9 (C), 147.4 (C), 147.9 (C), 148.4 (C).

3,5-Bis[(3,3′-bistrimethylsilyl-1,1′-biphenyl-2,2′-diyl)phosphite]-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (13). Treatment of *in situ* formed phosphorochloridite (2.2 mmol) and **15** (0.21 g, 1 mmol) as described for compound **5** afforded diphosphite **11**, which was purified by flash chromatography (eluent: toluene; R_f 0.85) to produce 0.80 g (86%) of a white powder. Anal. Calcd. for $C_{45}H_{62}O_9P_2Si_4$: C, 58.67; H, 6.78. Found: C, 58.87; H, 6.86. ^{31}P NMR, δ: 146.2 (d, 1P, $^6J_{P-P} = 23$ Hz), 147.3 (d, 1P, $^6J_{P-P} = 23$ Hz). ^{1}H NMR, δ: 0.35 (s, 18H, CH_3–Si), 0.36 (s, 9H, CH_3–Si), 0.41 (s, 9H, CH_3–Si), 1.02 (s, 3H, CH_3), 1.08 (d, 3H, H-6, $^3J_{6-5} = 6$ Hz), 1.38 (s, 3H, CH_3), 3.38 (d, 1H, H-2, $^3J_{2-1} = 3.6$ Hz), 4.03 (dd, 1H, H-4, $^3J_{4-5} = 7.6$ Hz, $^3J_{4-3} = 2.4$ Hz), 4.68 (m, 1H, H-5), 4.70 (dd, 1H, H-3, $^3J_{3-4} = 2.4$ Hz, $J_{3-P} = 5.2$ Hz), 5.41 (d, 1H, H-1, $^3J_{1-2} = 3.6$ Hz), 7.0–7.6 (m, 12H, CH=). ^{13}C NMR, δ: −0.2 (CH_3–Si), 0.1 (CH_3–Si), 0.2 (CH_3–Si), 19.7 (C-6), 25.7 (CH_3), 26.4 (CH_3), 68.6 (C-5), 76.4 (d, C-3, $J_{C-P} = 9.2$ Hz), 82.7 (t, C-4, $J_{C-P} = 4.8$ Hz), 83.8 (C-2), 104.6 (C-1), 111.4 (CMe_2), 124.4 (CH=), 124.6 (CH=), 124.9 (CH=), 130.9 (C), 131.1 (C), 131.2 (C), 132.0 (CH=), 132.2 (CH=), 132.5 (CH=), 134.9 (CH=), 135.1 (CH=), 153.4 (C), 153.5 (C), 153.6 (C).

3,5-Bis[(3,3′-bistrimethylsilyl-1,1′-biphenyl-2,2′-diyl)phosphite]-6-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose (14). Treatment of *in situ* formed phosphorochloridite (2.2 mmol) and **16** (0.21 g, 1 mmol) as described for compound **5** afforded diphosphite **14**, which was purified by flash chromatography (eluent: toluene; R_f 0.85) to produce 0.79 g (86%) of a white powder. Anal. Calcd. for $C_{45}H_{62}O_9P_2Si_4$: C, 58.67; H, 6.78. Found: C, 58.76; H, 6.89. ^{31}P NMR, δ: 145.0 (s), 145.5 (s). ^{1}H NMR, δ: 0.24 (s, 9H, CH_3–Si), 0.26 (s, 9H, CH_3–Si), 0.27 (s, 9H, CH_3–Si), 0.35 (s, 9H, CH_3–Si), 0.63 (d, 3H, H-6, $^3J_{6-5} = 7.2$ Hz), 1.25 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 3.88 (t, 1H, H-2, $^3J_{2-1} = 3.6$ Hz, $^3J_{2-3} = 3.6$ Hz), 4.05 (d, 1H, H-4, $^3J_{4-5} = 6.8$ Hz), 4.36 (m, 1H, H-3), 4.48 (m, 1H, H-5), 5.56 (d, 1H, H-1, $^3J_{1-2} = 3.6$ Hz), 7.1–7.5 (m, 12H, CH=). ^{13}C NMR, δ: 0.1 (CH_3–Si), 0.2 (CH_3–Si), 0.2 (CH_3–Si), 16.9 (C-6), 27.1 (CH_3), 27.3 (CH_3), 71.2 (C-5), 72.9 (d, C-3, $J_{C-P} = 6.4$ Hz), 78.9 (C-2), 83.1 (m, C-4), 104.8 (C-1), 113.8 (CMe_2), 124.7 (CH=), 124.8 (CH=), 124.9 (CH=), 130.8 (C), 130.9 (C), 131.1 (C), 132.3 (CH=), 132.5 (CH=), 132.6 (CH=), 134.8 (CH=), 135.1 (CH=), 135.3 (CH=), 150.9 (C), 151.1 (C), 151.2 (C).

Hydroformylation of styrene

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 h to form the active catalyst. The autoclave was depressurized and a solution of styrene (13 mmol) in toluene (5 mL) was added to the autoclave, which was pressurized again. During the course of 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.

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 L–L/Rh = 1.1) in toluene-d_8 (1.5 mL). The HP-NMR tube was purged twice with CO and after pressurization with the appropriate pressure of CO/H_2 the tube was placed in the NMR spectrometer and the spectra were recorded and analyzed.

In situ HP-IR hydroformylation experiments

These experiments were performed in a homemade SS 316 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.[13] Infrared spectra were recorded in a Brucker Equinox 55 FT-IR spectrophotometer. In a typical experiment a degassed solution of $Rh(acac)(CO)_2$ (0.013 mmol) and diphosphite (0.015 mmol) in 2-methyltetrahydrofuran (15 mL) was introduced into the high-pressure IR autoclave. The autoclave was purged twice with CO, after which it was pressurized and the mixture was heated. The autoclave was placed in the infrared spectrometer and, while the sample was stirred, the infrared spectra were recorded. The reaction was completed in 3–4 h.

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