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New carbohydrate bisphosphites as chiral ligands

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Abstract

The synthesis of the 2,3-bisphosphite derivatives of phenyl 4,6-*O*-benzylidene-β-D-glucopyranoside leads to new chelating ligands. Their rhodium(I) and platinum(II) complexes have been tested as catalysts for the asymmetric hydroformylation of vinyl acetate, allyl acetate and *p*-methoxystyrene. Good regioselectivity (>90% branched product), but an enantioselectivity of only ≤36% *ee* were found under mild reaction conditions (25–40°C, 40–70 bar syngas).

Investigations of carbohydrate vicinal bisphoshinites as chiral chelating ligands in asymmetric hydrogenations[1] and hydroformylation[2] of prochiral olefinic substrates with enantioselectivities reaching 99 or 72% *ee*, respectively, culminated in an industrial application for L-Dopa synthesis.[3] The fact that phosphites are suitable ligands for rhodium(I) catalyzed hydroformylation[4] tempted us to try the preparation of analogous hexopyranoside-2,3-*O*-bisphosphites. Previously high catalytic activities of diphosphite rhodium(I) chelates in hydroformylation reactions have been published[4a–c] but asymmetric induction was restricted to cases such as the hydroformylation of styrene with diphosphites based on chiral pentane-2,4-diol (90% *ee*).[4d] The highest enantioselectivity in an asymmetric hydroformylation was obtained with the phosphine–phosphite ligands introduced by Takaya and co-workers.[5]

Since aryl 4,6-*O*-benzylidene-β-D-glucopyranoside with only equatorial substituents led to the ligands with the highest enantioselectivity in asymmetric hydrogenation,[6] we started our synthetic work with that compound. We are aware that application of such phosphites, in particular in other reactions, might show distinct deviations to the case of the asymmetric hydrogenation with bisphosphinite chelates. However, we thought that the range of electronic properties and particularly steric requirements of the residue R in **2** may be large enough to generate interesting differences.

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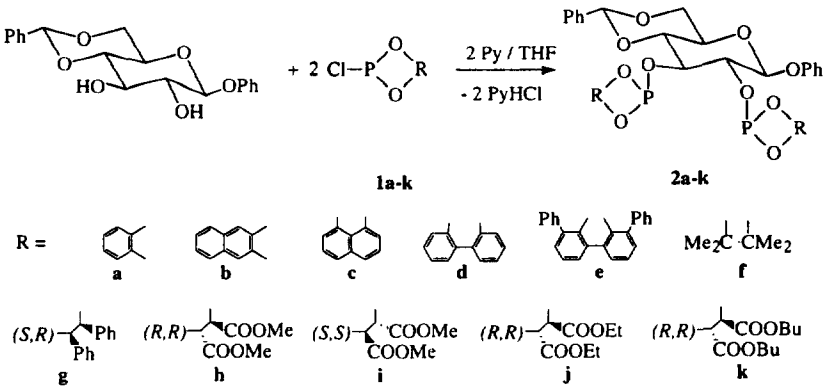
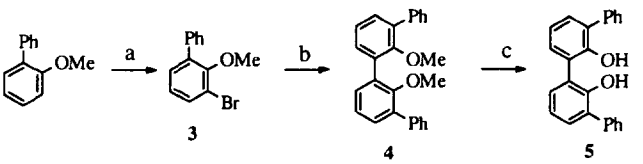


In order to examine the effect of the steric bulk of R on the selectivity of the hydroformylation reaction we synthesized *ortho* bisphenyl substituted ligand **2e**. The coupling of the 3,3′-dibromo-2,2′-dimethoxybiphenyl with PhMgBr in the presence of $Ni(dmpe)_2Cl_2$, according to the procedure reported for binaphthyl derivatives,[7] gives the product **4** only in very poor yield. In contrast, the simple route outlined in Scheme 1 allows the desired 3,3′-diphenyl-2,2′-biphenol **5** to be prepared in moderate yield.



Scheme 1. (a) n-BuLi, TMEDA, Et_2O, 51%; (b) n-BuLi, $CuCl_2$, Et_2O, 40%; (c) BBr_3, CH_2Cl_2, H_2O, 99%

The chlorophosphites **1** are conveniently prepared from the proper diol and PCl_3 in the presence of base, except for **1a** and **1d**. These are synthesized by a modified procedure of Anschütz and co-workers.[8] Most of the chlorophosphites **1a–d**, **f** and **j** are known compounds.[4a,9] The reaction of phenyl 4,6-*O*-benzylidene-α-D-glucopyranoside with the corresponding chlorophosphites were carried out at 0°C, with aliphatic phosphites at −20°C, and produced the desired carbohydrate bisphosphites **2** in good yield. Phosphites **2a–e** are stable for some time in air and moisture, and can be washed with alcohol to spectroscopic purity. On the other hand, aliphatic derivatives **2f–l** are very sensitive to moisture and all procedures had to be performed under an inert atmosphere.

We are especially interested in these compounds as new chiral bidentate ligands which could be used in asymmetric synthesis catalyzed by rhodium(I). The representative carbohydrate bisphosphites **2c** and **2h** react readily with $[Rh(COD)_2]BF_4$ (COD=(*Z*,*Z*)-cycloocta-1,5-diene) to give high yields of the corresponding rhodium(I) complex salts.

$$[Rh(COD)_2]BF_4 + L \rightarrow \underset{\textbf{6c, 6h}}{[RhL(COD)]BF_4} + COD \qquad L = \textbf{2c, 2h}$$

The ^{31}P NMR spectra of the complexes show two signals split into clearly resolved double doublets (**6c**: $^2J_{P1P2}$=58.3, δ 109.9 $^1J_{RhP1}$=256.5, δ 110.4 $^1J_{RhP2}$=259.3 Hz; **6h**: $^2J_{P1P2}$=54.1, δ 140.8 $^1J_{RhP1}$=250.4, δ 144.53 $^1J_{RhP2}$=250.7 Hz). The assignment of the resonances in the ^1H NMR spectrum of complex **6c** was made by use of COSY-experiments and is given in the experimental section.

In order to investigate the platinum catalyzed hydroformylation with the obtained ligands, we have prepared two platinum(II) complexes. Treatment of the phosphites **2c** and **2d** with $[Pt(COD)Cl_2]$ yielded the corresponding Pt(II)-complexes **7c** and **7d**.

Table 1
Hydroformylation of vinyl acetate (X=OAc), allyl acetate (X=CH_2OAc) and *p*-methoxystyrene (X=C_6H_4OMe-*p*) using Rh- and Pt-catalysts[a]

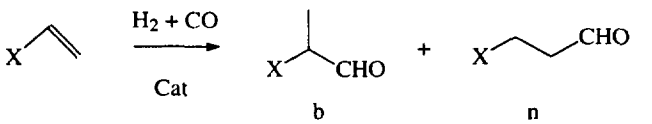
catalyst[a]	solv.	press., (bar)	T, (°C)	time, (h)	conv., (%)	b:n, (%)	*ee*, (%)
X = OAc							
6c	toluene	40	80	24	94	97:3	0
$[Rh(CO)_2acac]$ + **2c**	CH_2Cl_2	40	RT	1.5	7	-	-
$[Rh(CO)_2acac]$ + 4×**2c**	CH_2Cl_2	40	RT	18	12	-	-
X = CH_2OAc							
6c	THF	40	80	16	88	68:32	1
$[Rh(CO)_2acac]$ + **2c**	THF	40	80	3	63	59:41	1
$[Rh(CO)_2acac]$ + 4×**2c**	toluene	40	90	17	1	-	-
$[Rh(CO)_2acac]$ + **2h**	THF	40	RT	65	91	73:27	7(-)
$[Rh(CO)_2acac]$ + **2e**	THF	70	40	24	99	82:18	32(-)
$[Rh(CO)_2acac]$ + 10×**2e**	THF	70	40	3	73	60:40	22(-)
X = C_6H_4OMe-*p*							
$[Rh(CO)_2acac]$ + **2c**	THF	40	40	19	65	93:7	0
$[Rh(CO)_2acac]$ + **2e**	THF	40	40	19	65	93:7	4(-)
$[Rh(CO)_2acac]$ + 5×**2e**	THF	60	RT	72	92	96:4	20(-)
$[Rh(CO)_2acac]$ + **2k**	toluene	10	RT	96	11	99:1	-
7d	toluene	70	40	4	94[b]	99:1	14(-)
$[Pt(PhCN)_2Cl_2]$ + $SnCl_2$ + **2d**	toluene	70	40	22	89[c]	98:2	10(-)

[a] All reactions were carried out with 1 mmol substrate in 10 ml of solvent with a substrate/catalyst ratio of 100.
[b] 48 % as 4-ethylanisole. [c] 35 % as 4-ethylanisole.

$$[Pt(COD)Cl_2] + L \rightarrow [PtLCl_2] + COD \qquad L = \mathbf{2c}, \mathbf{2d}$$
$$\mathbf{7c}, \mathbf{7d}$$

Preliminary results of asymmetric hydrogenation of methyl (*Z*)-2-*N*-acetamidocinnamate in THF using rhodium(I) chelate **6c** showed a rather low enantioselectivity of 13% *ee* for (*S*)-methyl *N*-acetylphenylalanine. On account of lower phosphorus basicity their rhodium(I) chelates show the expected lower activity compared with the corresponding phosphinite complex.

The new diphosphites have been evaluated in the hydroformylation of vinyl acetate, allyl acetate and *p*-methoxystyrene. Table 1 lists some representative results obtained by use of complex **6c** or catalyst precursors prepared in situ by mixing $[Rh(CO)_2acac]$ and 1–10 equivalents of the ligands.



While complex **6c** has a good activity in the hydroformylation of vinyl acetate, catalysts prepared in situ show a low conversion. The highest enantiomeric excess (36% *ee* in the case of **2e**) was achieved by hydroformylating allyl acetate. A longer reaction time for **2e** resulted in a slight racemization of product from 36% after 2 h to 32% *ee* after 24 h. Unexpectedly, the higher L:Rh ratio of 10 improved

catalytic activity but the enantioselectivity was rather low. Usually, the catalyst activity decreases slightly on increasing the L:Rh ratio. For the hydroformylation of *p*-methoxystyrene, lower catalyst activity was found than for the allyl acetate. In this case, a higher L:Rh ratio leads to a better regio- and enantioselectivity. In comparison to the successful biphosphite–$PtCl_2(PhCN)_2$–$SnCl_2$ system of Bakos[10] (up to 91% *ee*) the phosphite chelate **7d** gave a mixture of the hydrogenation product 4-ethylanisole and the branched aldehyde with low enantiomeric excess (14% *ee*). However, with the catalysts prepared in situ by simple mixing $PtCl_2(PhCN)_2$, $SnCl_2$ and ligand the hydroformylation of *p*-methoxystyrene proceeds more slowly. In the experiments with vinyl acetate and allyl acetate under the typical conditions for platinum–tin catalyzed hydroformylation[11] no aldehyde formation was detected.

1. Conclusion

Despite the acceptable activity and regioselectivity of the catalysts with the newly synthesized hexopyranoside-2,3-*O*-bisphosphites, the generally low enantioselectivity gives the impression that the butterfly-like arrangement of the bridged diaryls *O*-bounded on the phosphorus is no more favourable for reaching optimum space filling than that of *P*-diarylphosphines or analogous *C*-bonded bridged diaryls as in dibenzophosphole carrying diphosphines. Bis-*ortho*-aryl substitution of the cyclic diphenylphosphite as in **2e** leads only to a small improvement of the enantioselectivity up to 36% *ee* and also the rhodium(I) chelates of the bisphophites derived from tartaric acid esters as **2h** are disappointing. The results conform with the postulate of van Leeuwen that bisphophites of vicinal diols are less useful than analogous ligands derived from chiral 1,3-diols for asymmetric hydroformylation.[4h,i,l]

2. Experimental

Solvents were dried over appropriate drying agents and freshly distilled under argon before use. All reactions were carried out under an argon atmosphere by using standard Schlenk techniques. NMR data were recorded on a multi-nuclear FT-NMR spectrometer ARX300 and ARX400 (Bruker) with reference to TMS and H_3PO_4 (85%), respectively. Mass spectra (EI, 70 eV) were measured on a single focusing sector-field mass spectrometer AMD40 (Intectra).

The experimental procedures for the hydrogenation, the synthesis of the substrate, the derivatization and the determination of the hydrogenated products are described in the literature.[1a] The experimental procedure for the hydroformylation was first described in the preliminary communication.[12] Gas chromatographic analyses were carried out on a Hewlett–Packard 5890 Series II gas chromatograph with a flame ionization detector, using a 25 m fused silica (HP101, Chiraldex G-TA or Lipodex E) capillary column.

2.1. 3-Bromo-2-methoxybiphenyl 3

To a solution of 50 g (0.27 mol) 2-methoxybiphenyl and 81 ml (0.54 mol) TMEDA in 300 ml ether was added dropwise a 2.5 M solution of BuLi in hexane (217.1 ml). After 2 h the mixture was cooled to −78°C and a solution of 27.6 ml (0.54 mol) Br_2 in 60 ml hexane was added dropwise. The reaction mixture was allowed to warm, 100 ml 2 N HCl were added and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and the solvent evaporated. Distillation of the oily residue under vacuum gave 48.8 g (69% yield) of **3** as a colorless oil; b.p. 105°C/0.45 mbar.

^{1}H NMR ($CDCl_3$) δ=3.81 (s, 3H), 6.95–7.56 (m, 8H). ^{13}C NMR ($CDCl_3$) δ=60.4, 118.1, 125.3, 127.4, 128.1, 129.0, 130.3, 132.4, 136.8, 137.6, 154.4; MS m/z 263 (M^+). Anal. found C 60.49, H 4.30, Br 32.11; calcd for $C_{13}H_{11}BrO$ (263.12) C 59.34, H 4.21, Br 30.37.

2.2. 2′,2″-Dimethoxy-1,1′:3′,1″:3″,1‴-quaterphenyl **4**

A solution of 2.5 M BuLi in hexane (88.2 ml) was cooled to −78°C and a solution of 48.5 g (0.184 mol) **3** in 200 ml ether was slowly added. After the addition was complete, the reaction mixture was allowed to warm over 1 h, then again cooled to −78°C and with intensive stirring 49.5 g $CuCl_2$ was added portionwise. The resultant mixture was stirred at this temperature for 2 h and then allowed to warm. The reaction mixture was quenched with 30 ml H_2O and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to 100 ml. Crystals of **4** deposited on cooling. The precipitate was washed with hexane and dried under vacuum. Yield 5.4 g (39%), m.p. 139–140°C. ^{1}H NMR ($CDCl_3$) δ=3.26 (s, 6H), 7.2–7.7 (m, 16H). ^{13}C NMR ($CDCl_3$) δ=60.5, 123.6, 127.0, 128.2, 129.0, 129.5, 130.9, 132.9, 135.1, 138.8, 155.3. Anal. found C 85.05, H 5.99; calcd for $C_{26}H_{22}O_2$ (366.46) C 85.21, H 6.05.

2.3. 2′,2″-Dihydroxy-1,1′:3′,1″:3″,1‴-quaterphenyl **5**

BBr_3 (13 g, 52 mmol) was added at 0°C to a solution of 10 g (27.3 mmol) **3** in 100 ml CH_2Cl_2 and stirred overnight at room temperature. The excess of BBr_3 was decomposed by dropwise addition of 150 ml of H_2O and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to 15 ml. Crystals of **5** deposited on cooling. The precipitate was washed with hexane and dried under vacuum. Yield 7.72 g (84%), m.p. 129–130°C. ^{1}H NMR ($CDCl_3$) δ=5.7 (s, OH), 7.02 ('AB*X*', $0.5|J_{AX}+J_{BX}|$=7.59, H-5), 7.24 ('*A*BX', J_{AB}=1.76, J_{AX}=7.70, H-4 or H-6), 7.25 ('A*B*X', J_{BX}=7.52, H-6 or H-4), 7.28 (tt, *J*=1.4, *J*=7.42, H-*p*), 7.36 (m, 2H-*m*), 7.5 (m, 2H-*o*). ^{13}C NMR ($CDCl_3$) δ=121.8, 125.4, 128.1, 129.3, 129.8, 130.0, 131.1, 131.5, 137.9, 150.2. MS m/z 338 (M^+). Anal. found C 84.52, H 5.43; calcd for $C_{24}H_{18}O_2$ (338.38) C 85.18, H 5.36.

For the preparation of the chlorophosphite **1e** the product was additionally azeotropically dried with toluene.

2.4. 11-Chloro-2,9-diphenyl-(dibenzo[bd][1,3,2]dioxaphosphepin) **1e**

To a mixture of 2.5 ml (31 mmol) pyridine and 0.9 ml (10.3 mmol) PCl_3 was added dropwise a solution of 3.5 g (10.3 mmol) **5** in dry toluene (30 ml) at −20°C. The mixture was stirred overnight at room temperature and then filtered. Evaporation of the solvent gave a crude product which was used without further purification. Yield 3.5 g (85%). ^{31}P{^{1}H} NMR ($CDCl_3$) δ=178.3. ^{13}C NMR ($CDCl_3$) δ=126.0, 127.5, 128.1, 129.5, 129.7, 131.0, 132.0 (d, *J*=3.7), 135.3 (d, *J*=2.4), 137.8, 146.1 (d, *J*=5.3). MS m/z 402 (M^+), 367 (M^+-Cl). Anal. found C 71.71, H 4.00; calcd for $C_{24}H_{16}ClPO_2$ (402.83) C 71.56, H 4.00.

2.5. 2-Chloro-4,5-diphenyl-1,3,2-dioxaphospholane **1g**

A solution of 25 g (0.117 mol) of meso-hydrobenzoin and 19 ml (0.12 mol) of pyridine in 100 ml THF was added at −20°C to a stirred solution of 11 ml (0.12 mol) PCl_3 in 50 ml THF. The resulting slurry was filtered and the filtrate evaporated under vacuum. The solid residue was recrystallized from ether

and afforded at −78°C 25 g (77%) of **1g**, m.p. 61–63°C. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ=170.3. ^1H NMR ($CDCl_3$) δ=5.97 (d, *J*=2.1, H-4,5), 6.8–7.1 (m, 10H-aromatic). ^{13}C NMR ($CDCl_3$) δ=82.9 (d, *J*=6.8), 126.7, 127.9, 128.1, 134.3. Anal. found C 60.84, H 4.34; calcd for $C_{14}H_{12}ClO_2P$ (278.67) C 60.3, H 4.3.

*2.6. General procedure for the preparation of aliphatic chlorophosphites **1h–k***

A solution of 0.2 mol of the appropriate diol and 0.22 mol of the corresponding base (see below) in 100 ml ether was added at 0°C to a stirred solution of 19 ml (0.22 mol) PCl_3 in 100 ml ether. The reaction mixture was stirred for 4–6 h and the precipitate was filtered off. The resulting solution was concentrated under reduced pressure and the residue was subjected to fractional distillation.

*2.6.1. 2-Chloro-(4R,5R)-dicarbomethoxy-1,3,2-dioxaphospholane **1h***

Colorless oil; b.p. 93–95°C/10^{-3} mbar; base: $PhNEt_2$; yield 39.4 g (81%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ=175.6. ^1H NMR ($CDCl_3$) δ=3.84 (s, 3H), 3.85 (s, 3H), 5.01 (dd, *J*=6.3, J_{PH}=9.5, 1H), 5.45 (d, *J*=6.3, 1H); ^{13}C NMR (C_6D_6) δ=53.5, 78.3 (br.), 168.4 (br.).

*2.6.2. 2-Chloro-(4S,5S)-dicarbomethoxy-1,3,2-dioxaphospholane **1i***

Colorless oil; b.p. 93–95°C/10^{-3} mbar; base: $PhNEt_2$; yield 45.1 g (93%); $^{31}P\{^1H\}$ NMR (C_6D_6) δ=175.7. ^1H NMR (C_6D_6) δ=3.33 (s, 3H), 3.41 (br, 3H), 4.86 (dd, *J*=6.1, J_{PH}=8.7, 1H), 5.61 (d, *J*=6.1, 1H).

*2.6.3. 2-Chloro-(4R,5R)-dicarboethoxy-1,3,2-dioxaphospholane **1j***

Colorless oil; b.p. 119–121°C/0.1 mbar (lit. b.p. 113°C/0.28 mm Hg)[13]; base: $PhNEt_2$; yield 30.4 g (56%). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ=175.4 (lit. 175.4)[13]; ^1H NMR (C_6D_6) δ=1.20 (t, *J*=7.1, 3H), 1.24 (t, *J*=7.2, 3H), 4.19 (q, *J*=7.1, 2H), 4.24 (q, *J*=7.3, 2H), 5.20 (dd, *J*=6.2, J_{PH}=9.5, 1H), 5.85 (d, *J*=6.2, 1H); ^{13}C NMR (C_6D_6) δ=14.5, 63.2, 78.1 (d, *J*=9.4), 79.1 (d, *J*=8.8), 167.0 (d, *J*=3.6), 168.2.

2.6.4. 2-Chloro-(4S,5S)-dicarboethoxy-1,3,2-dioxaphospholane

Colorless oil; b.p. 103°C/10^{-3} mbar; base: Py; yield 31.7 g (58%). $^{31}P\{^1H\}$ NMR (C_6D_6) δ=175.8; ^1H NMR (C_6D_6) δ=1.28 (t, *J*=7.1, 6H), 4.27 (q, *J*=7.1, 4H), 4.95 (dd, *J*=5.9, J_{PH}=9.3, 1H), 5.38 (d, *J*=5.9, 1H); ^{13}C NMR (C_6D_6) δ=14.5, 63.2, 78.1 (d, *J*=9.1), 79.1 (d, *J*=8.6), 167.7 (d, *J*=4.1), 168.3.

2.6.5. 2-Chloro-(4R,5R)-dicarboisopropoxy-1,3,2-dioxaphospholane

Colorless oil; b.p. 104–105°C/10^{-3} mbar (lit.[4a] b.p. 108–110°C/10^{-3} mm Hg); base: $PhNEt_2$; yield 46.5 g (78%). $^{31}P\{^1H\}$ NMR (C_6D_6) δ=175.9; ^1H NMR (C_6D_6) δ=1.25 (d, *J*=5.8, 12H), 4.87 (dd, *J*=6.6, J_{PH}=9.2, 1H), 5.09 (sept, *J*=6.0, 1H), 5.11 (sept, *J*=6.1, 1H), 5.31 (d, *J*=6.6, 1H); ^{13}C NMR (C_6D_6) δ=21.4, 21.6, 70.87, 70.92, 77.0 (d, *J*=9.3), 78.1 (d, *J*=8.7), 166.6 (d, *J*=4.7), 167.0.

*2.6.6. 2-Chloro-(4R,5R)-dicarbo-n-butoxy-1,3,2-dioxaphospholane **1k***

Colorless oil; b.p. 102°C/10^{-3} mbar; base: Py; yield 35.3 g (54%). $^{31}P\{^1H\}$ NMR (C_6D_6) δ=175.7; ^1H NMR (C_6D_6) δ=0.85 (m, 6H), 1.22 (m, 4H), 1.38 (m, 4H), 4.1 (m, 4H), 5.00 (dd, *J*=6.6, J_{PH}=9.3, 1H) 5.70 (dd, *J*=6.6, J_{PH}=4.5, 1H).

2.7. General procedure for carbohydrate bisphosphite synthesis

A solution of phenyl 4,6-*O*-benzylidene-β-D-glucopyranoside (10 mmol) and anhydrous pyridine (1.7 ml, 21 mmol) in 40 mL of THF was added dropwise over 30 min to a stirred solution of chlorophosphite **1** (20 mmol) in 20 mL THF under an argon atmosphere at 0°C or −20°C. The mixture was stirred overnight at room temperature and then filtered. The solvent was evaporated under vacuum and necessarily ether or pentane was added to induce crystallization. The product was purified by extraction and recrystallization from a proper solvent (see below).

2.7.1. Phenyl 2,3-O-bis(benzo[1,3,2]dioxaphospholyl-2)-4,6-O-benzylidene-β-D-glucopyranoside ***2a***

Colorless solid; recrystallized from toluene; m.p. 169–172°C; $[\alpha]_D^{24}=-42.1$ (c 1.0, THF); yield 3.6 g (57%). ^{31}P NMR ($CDCl_3$) δ=135.8 (J_{PH}=7.3), 137.3 (J_{PH}=8.1). ^{1}H NMR ($CDCl_3$) δ=3.28 (ddd, $J_{56'}$=5.0, J_{56}=9.7, J_{54}=9.6, H-5), 3.45 (dd, 0.5|J_{43}+J_{45}|=9.3, H-4), 3.68 (dd, 0.5|J_{65}+$J_{66'}$|=10.3, H-6), 3.99–4.03 (m, H-2 and H-3), 4.28 (dd, $J_{56'}$=5.0, $J_{66'}$=10.6, H-6′), 4.99 (d, J_{12}=7.0, H-1), 5.46 (s, H-b), 6.89–7.57 (m, 18H-aromatic). ^{13}C NMR ($CDCl_3$) δ=66.7, 68.7, 75.7 (dd, J_{PC}=10.0, J_{PC}=1.5), 76.3 (dd, J_{PC}=10.4, J_{PC}=2.3), 78.8, 101.0, 101.6, 111.7 (d, J_{PC}=9.3), 112.9, 117.9, 123.1 (d, J_{PC}=8.3), 123.3 (d, J_{PC}=6.5), 126.6, 128.1, 128.3, 128.6, 128.7, 130.0, 145.5 (dd, J_{PC}=15.6, J_{PC}=7.3), 145.7 (dd, J_{PC}=7.0, J_{PC}=9.8), 157.5. MS m/z 620 (M^+). Anal. found C 59.96, H 4.31, P 9.61; calcd for $C_{31}H_{26}O_{10}P_2$ (620.47) C 60.00, H 4.22, P 9.98.

2.7.2. Phenyl 4,6-O-benzylidene-2,3-O-bis(naphtho[2,3-d][1,3,2]dioxaphospholyl-2)-β-D-glucopyranoside ***2b***

Colorless solid; recrystallized from THF; m.p. 149–152°C; $[\alpha]_D^{24}=-43.8$ (c 1.0, CH_2Cl_2); yield 5.5 g (77%). ^{31}P NMR (THF-d_8) δ=137.1 (J_{PH}=9.0), 137.8 (J_{PH}=9.1). ^{1}H NMR (C_6D_6) δ=2.61 (ddd, $J_{56'}$=4.9, J_{56}=9.9, J_{54}=9.5, H-5), 2.97 (dd, 0.5|J_{43}+J_{45}|=9.3, H-4), 3.16 (dd, 0.5|J_{65}+$J_{66'}$|=10.2, H-6), 3.82 (dd, $J_{56'}$=5.0, $J_{66'}$=10.4, H-6′), 3.95 (ddd, $J\approx$8.5–9.0, H-2 or H-3), 4.08 (ddd, $J\approx$7.6–9.0, H-3 or H-2), 4.74 (d, J_{12}=7.4, H-1), 5.38 (s, H-b), 7.18–8.10 (m, 22H-aromatic). MS m/z 720 (M^+). Anal. found C 64.98, H 4.26, P 8.63; calcd for $C_{39}H_{30}O_{10}P_2$ (720.58) C 65.00, H 4.20, P 8.60.

2.7.3. Phenyl 4,6-O-benzylidene-2,3-O-bis(naphtho[1,8-de][1,3,2]dioxaphosphorinyl-2)-β-D-glucopyranoside ***2c***

Colorless solid; recrystallized from benzene; m.p. 226–227°C; $[\alpha]_D^{24}=-115.5$ (c 1.0, CH_2Cl_2); yield 5 g (69%). ^{31}P NMR (C_6D_6) δ=113.7 (J_{PH}=7.9), 114.4 (J_{PH}=8.1). ^{1}H NMR (C_6D_6) δ=2.68 (ddd, $J_{56'}$=4.8, J_{56}=9.7, J_{54}=9.5, H-5), 2.75 (dd, 0.5|J_{43}+J_{45}|=9.1, H-4), 3.16 (dd, 0.5|J_{65}+$J_{66'}$|=10.0, H-6), 3.84 (dd, $J_{56'}$=4.8, $J_{66'}$=10.4, H-6′), 3.93 (ddd, $J\approx$8.5–9.0, H-3), 4.07 (ddd, $J\approx$7.6–9.0, H-2), 4.33 (d, J_{12}=7.5, H-1), 5.01 (s, H-b), 6.5–7.8 (m, 22H-aromatic). ^{13}C NMR (C_6D_6) δ=66.0, 68.2, 76.4 (d, J_{PC}=22.3), 77.4 (d, J_{PC}=19.0), 78.3, 100.1, 101.1, 112.1, 112.8 (d, J_{PC}=8.6), 117.6, 122.2, 122.3, 123.3, 126.6–129.5, 138.0, 144.8 (dd, J_{PC}=7.9, J_{PC}=3.7), 144.9 (dd, J_{PC}=5.8, J_{PC}=3.7), 157.6. MS m/z 720 (M^+). Anal. found C 64.55, H 4.17, P 8.63; calcd for $C_{39}H_{30}O_{10}P_2$ (720.58) C 65.00, H 4.20, P 8.60.

2.7.4. Phenyl 2,3-O-bis(dibenzo[df][1,3,2]dioxaphosphepinyl-2)-4,6-O-benzylidene-β-D-glucopyranoside ***2d***

Colorless solid; extracted with ether and recrystallized from acetone; m.p. 215–216°C; $[\alpha]_D^{24}=-29.3$ (c 1.0, CH_2Cl_2); yield 5.5 g (71%). ^{31}P NMR ($CDCl_3$) δ=153.1 (J_{PH}=7.3), 153.5 (J_{PH}=8.0). ^{1}H NMR ($CDCl_3$) δ=3.54 (ddd, $J_{56'}$=5.0, J_{56}=9.9, J_{54}=9.5, H-5), 3.74 (dd, 0.5|J_{43}+J_{45}|=9.2, H-4), 3.78 (dd, 0.5|J_{65}+$J_{66'}$|=10.3, H-6), 4.36 (dd, $J_{56'}$=5.0, $J_{66'}$=10.5, H-6′), 4.50 (ddd, J=7.6, J=8.2, J=8.4, H-3 or

H-2), 4.58 (ddd, J=7.5, J=8.8, J=9.0, H-2 or H-3), 5.11 (d, J_{12}=7.4, H-1), 5.56 (s, H-b), 6.74–7.66 (m, 26H-aromatic). ^{13}C NMR ($CDCl_3$) δ=66.2 (CH), 68.4 (CH_2), 76.1 (dd, J_{PC}=23.3, J_{PC}=2.9, CH), 77.2 (dd, J_{PC}=21.5, J_{PC}=3.3, CH), 78.9, 100.3, 101.4, 117.1, 122.0, 122.1, 122.4, 123.4, 125.2, 126.2, 128.3, 129.0–129.7 (CH), 130.9, 131.3 (d, J_{PC}=3.0), 131.4 (d, J_{PC}=3.3), 136.8, 149.0 (dd, $0.5|J_{PC}+J_{PC}|$=5.0), 149.4 (dd, J_{PC}=5.8, J_{PC}=7.8), 156.6 (C). MS m/z 772 (M^+). Anal. found C 66.89, H 4.37, P 8.63; calcd for $C_{43}H_{34}O_{10}P_2$ (772.65) C 66.84, H 4.44, P 8.02.

2.7.5. Phenyl 4,6-O-benzylidene-2,3-O-bis[2,9-diphenyl-(dibenzo[df][1,3,2]dioxaphosphepinyl-11)]-β-D-glucopyranoside 2e

Colorless solid; purified by column chromatography (silica gel, 1% NEt_3 in toluene); m.p. 127–129°C; $[\alpha]_D^{24}$=6.7 (c 1.0, acetone); yield 4.7 g (44%). ^{31}P NMR ($CDCl_3$) δ=148.2 (J_{PH}=6.7), 149.6 (J_{PH}=3.0). ^{1}H NMR ($CDCl_3$) δ=2.35 (dd, $0.5|J_{43}+J_{45}|$=9.2, H-4), 2.88 (ddd, $J_{56'}$=4.9, J_{56}=9.9, J_{54}=9.8, H-5), 3.36 (dd, $0.5|J_{65}+J_{66'}|$=10.3, H-6), 3.38–3.45 (m, H-2 and H-3), 3.71 (d, J_{12}=6.3, H-1), 4.13 (dd, $J_{56'}$=4.9, $J_{66'}$=10.3, H-6′), 4.90 (s, H-b), 6.7–7.5 (m, 42H-aromatic). ^{13}C NMR ($CDCl_3$) δ=65.8 (CH), 68.4 (CH_2), 76.3 (dd, J_{PC}=22.6, J_{PC}=2.6, CH), 76.4 (dd, J_{PC}=22.9, J_{PC}=3.6, CH), 78.4, 100.4, 101.7, 118.1, 123.6, 124.7, 124.8, 125.68, 125.74, 126.2, 127.2, 127.4, 127.6, 127.7, 128.2, 128.49, 138.60, 128.68, 129.1, 129.4, 129.7, 130.0, 130.24, 130.37, 130.54, 130.62, 131.1, 131.4 (CH), 133.58 (d, J_{PC}=3.8), 133.67 (d, J_{PC}=3.8), 135.3, 135.7, 137.28, 137.38, 137.48, 138.95, 140.0, 145.8 (d, J_{PC}=8.1), 147.5 (d, J_{PC}=8.1), 157.0 (C). MS m/z 1077 (M^+). Anal. found C 74.68, H 5.19; calcd for $C_{67}H_{50}O_{10}P_2$ (1077.02) C 74.71, H 4.68.

2.7.6. Phenyl 4,6-O-benzylidene-2,3-O-bis(4,4,5,5-tetramethyl-1,3,2-dioxaphospholyl-2)-β-D-glucopyranoside 2f

Colorless solid; recrystallized from petroleum ether; m.p. 40–44°C; $[\alpha]_D^{24}$=−45.7 (c 1.0, THF); yield 2 g (31%). ^{31}P NMR (C_6D_6) δ=148.2 (J_{PH}=8.3), 149.2 (J_{PH}=8.8). ^{1}H NMR (C_6D_6) δ=1.16 (s, 3H), 1.21 (s, 3H), 1.24 (s, 3H), 1.26 (s, 3H), 1.28 (s, 3H), 1.43 (s, 3H), 1.52 (s, 3H), 1.60 (s, 3H), 3.23 (ddd, $J_{56'}$=4.9, J_{56}=10.0, J_{54}=9.3, H-5), 3.52 (dd, $0.5|J_{43}+J_{45}|$=9.4, H-4), 3.53 (dd, $0.5|J_{65}+J_{66'}|$=10.2, H-6), 4.17 (dd, $J_{56'}$=4.9, $J_{66'}$=10.3, H-6′), 4.46 (ddd, $J\approx$8.7–9.6, H-3 or H-2), 4.55 (ddd, $J\approx$7.2–9.0, H-2 or H-3), 4.96 (d, J_{12}=7.3, H-1), 5.36 (s, H-b), 7.0–7.9 (m, 10H-aromatic). MS m/z 636 (M^+). Anal. found C 54.42, H 6.68, P 9.48; calcd for $C_{31}H_{42}O_{10}P_2$ (636.6) C 58.49, H 6.65, P 9.73.

2.7.7. Phenyl 4,6-O-benzylidene-2,3-O-bis(4,5-diphenyl-1,3,2-dioxaphospholyl-2)-β-D-glucopyranoside 2g

Colorless solid; recrystallized from benzene; m.p. 71–74°C; $[\alpha]_D^{24}$=−2.9 (c 1.0, THF); yield 5.3 g (64%). ^{31}P NMR (C_6D_6) δ=140.0 (J_{PH}=9.0), 141.6 (J_{PH}=9.6). ^{1}H NMR (C_6D_6) δ=3.36 (ddd, $J_{56'}$=4.8, J_{56}=9.7, J_{54}=10.3, H-5), 3.62 (dd, $0.5|J_{65}+J_{66'}|$=10.0, H-6), 3.73 (dd, $0.5|J_{43}+J_{45}|$=9.0, H-4), 4.23 (dd, $J_{56'}$=4.8, $J_{66'}$=10.2, H-6′), 4.73 (ddd, $J\approx$8.5–9.0, H-3 or H-2), 4.83 (ddd, $J\approx$8.3–9.0, H-2 or H-3), 5.16 (d, J_{12}=7.2, H-1), 5.45 (s, H-b), 5.89 (d, J_{PH}=7.3, 1H), 6.04 (br., 3H), 6.9–7.9 (m, 30H-aromatic). ^{13}C NMR (C_6D_6) δ=67.5, 69.2, 75.7 (d, J_{PC}=12.8), 76.7 (d, J_{PC}=13.8), 80.5, 82.5, 82.6, 82.7, 83.6, 102.1, 102.5, 118.6, 124.2–130.5, 137.3 (d, J_{PC}=3.3), 137.4 (d, J_{PC}=4.0), 137.5 (d, J_{PC}=1.8), 138.6, 158.8. MS m/z 828 (M^+). Anal. found C 69.68, H 5.33, P 7.13; calcd for $C_{47}H_{42}O_{10}P_2$ (828.76) C 68.11, H 5.12, P 7.49.

2.7.8. Phenyl 4,6-O-benzylidene-2,3-O-bis((4R,5R)-dicarbomethoxy-1,3,2-dioxaphospholyl-2)-β-D-glucopyranoside ***2h***

Colorless solid; recrystallized from ether; m.p. 96–99°C; $[\alpha]_D^{24}=-104.6$ (c 1.0, THF); yield 3 g (56%). ^{31}P NMR (C_6D_6) δ=147.5 (dd, J_{PH}=8.8, $J_{PH}\approx$8.6), 146.6 (dd, J_{PH}=9.3, J_{PH}=7.4). ^1H NMR (C_6D_6) δ=3.01 (ddd, $J_{56'}\approx5$, $J_{56}\approx10$, J_{54}=9.8, H-5), 3.20, 3.23, 3.41, 3.48 (s, 4×3H), 3.27–3.40 (m, H-4, H-6), 4.00 (dd, $J_{56'}$=5.0, $J_{66'}$=10.3, H-6′), 4.30 (ddd, J_{12}=7.2, J_{23}=9.0, J_{2P}=8.7, H-2), 4.39 (ddd, J_{34}=7.8, J_{23}=9.0, J_{3P}=8.1, H-3), 4.78 (d, J_{12}=7.2, H-1), 4.82 (dd, J_{HH}=5.9, J_{PH}=9.7, 1H), 4.89 (dd, J_{HH}=6.0, J_{PH}=9.8, 1H), 5.23 (s, H-b), 5.47 (d, J_{HH}=5.8, 1H), 5.64 (d, J_{HH}=5.9, 1H), 6.9–7.9 (m, 10H-aromatic). MS m/z 756 (M^+), 725, 663. Anal. found C 49.33, H 4.47, P 7.49; calcd for $C_{31}H_{34}O_{18}P_2$ (756.53) C 49.21, H 4.53, P 8.19.

2.7.9. Phenyl 4,6-O-benzylidene-2,3-O-bis((4S,5S)-dicarbomethoxy-1,3,2-dioxaphospholyl-2)-β-D-glucopyranoside ***2i***

Colorless solid; recrystallized from ether; m.p. 107–110°C; $[\alpha]_D^{24}$=19.4 (c 1.0, THF); yield 6.26 g (83%). ^{31}P NMR (C_6D_6) δ=143.4 (dd, $J_{PH}\approx$7.8, $J_{PH}\approx$6.6), 146.4 (dd, $J_{PH}\approx$8.1, $J_{PH}\approx$8.2). ^1H NMR (C_6D_6) δ=3.22 (ddd, $J_{56'}$=4.9, J_{56}=10.1, J_{54}=9.3, H-5), 3.33, 3.38, 3.39, 3.46 (s, 4×3H), 3.56 (dd, J_{56}=10.1, $J_{66'}$=10.3, H-6), 3.70 (dd, J_{54}=9.3, J_{34}=9.3, H-4), 4.16 (dd, $J_{56'}$=4.9, $J_{66'}$=10.3, H-6′), 4.36–4.49 (m, H-2, H-3), 4.87 (dd, J_{HH}=6.0, J_{PH}=9.2, 1H), 4.89 (dd, J_{HH}=6.4, J_{PH}=8.6, 1H), 5.04 (d, J_{12}=7.2, H-1), 5.51 (s, H-b), 5.69 (d, J_{HH}=6.4, 1H), 5.70 (d, J_{HH}=6.0, 1H), 6.9–7.9 (m, 10H-aromatic). MS m/z 756 (M^+), 725, 663. Anal. found C 48.42, H 4.24, P 8.16; calcd for $C_{31}H_{34}O_{18}P_2$ (756.53) C 49.21, H 4.53, P 8.19.

2.7.10. Phenyl 4,6-O-benzylidene-2,3-O-bis((4R,5R)-dicarboethoxy-1,3,2-dioxaphospholyl-2)-β-D-glucopyranoside ***2j***

Colorless solid; recrystallized from ether/hexane; m.p. 71–74°C; $[\alpha]_D^{24}=-114.9$ (c 1.0, THF); yield 5.7 g (70%). ^{31}P NMR (C_6D_6) δ=146.7 (dd, J_{PH}=8.0, J_{PH} 7.6), 147.5 (dd, J_{PH}=8.1, J_{PH}=8.2). ^1H NMR (C_6D_6) δ=0.90 (t, J=7.0, 3H), 0.92 (t, J=7.3, 3H), 1.06 (t, J=7.0, 3H), 1.12 (t, J=7.0, 3H), 3.12 (ddd, $J_{56'}$=5.0, J_{56}=10.1, J_{54}=9.3, H-5), 3.43 (dd, J_{56}=10.1, $J_{66'}$=10.3, H-6), 3.44 (dd, J_{54}=9.3, J_{34}=9.0, H-4), 3.91 (q, J=7.1, 1H), 3.92 (q, J=7.2, 1H), 3.94 (q, J=6.9, 2H), 4.09 (q, J=7.3, 1H), 4.09 (q, J=6.8, 1H), 4.10 (dd, $J_{56'}\approx5$, $J_{66'}\approx10$, H-6′), 4.16 (q, J=6.9, 1H), 4.17 (q, J=7.3, 1H), 4.40–4.57 (m, H-2, H-3), 4.89 (d, J_{12}=7.2, H-1), 4.97 (dd, J_{HH}=6.2, J_{PH}=9.1, 1H), 5.01 (dd, J_{HH}=6.3, J_{PH}=9.4, 1H), 5.31 (s, H-b), 5.56 (d, J_{HH}=6.2, 1H), 5.73 (d, J_{HH}=6.3, 1H), 7.2–8.2 (m, 10H-aromatic). MS m/z 812 (M^+), 767, 719. Anal. found C 51.85, H 5.21, P 7.77; calcd for $C_{35}H_{42}O_{18}P_2$ (812.64) C 51.73, H 5.21, P 7.62.

2.7.11. Phenyl 4,6-O-benzylidene-2,3-O-bis((4R,5R)-dicarbo-n-butoxy-1,3,2-dioxaphospholyl-2)-β-D-glucopyranoside ***2k***

Colorless oil; $[\alpha]_D^{24}=-87.4$ (c 1.0, THF); yield 16.7 g (90%). ^{31}P {^1H} NMR (C_6D_6) δ=146.6, 147.5. ^1H NMR (C_6D_6) δ=1.02 (t, J=7.3, 3H), 1.03 (t, J=7.2, 3H), 1.07 (t, J=7.1, 3H), 1.13 (t, J=7.3, 3H), 1.25–1.86 (m, 16H), 3.39 (ddd, $J_{56'}$=5.0, J_{56}=10.1, J_{54}=9.3, H-5), 3.69 (dd, J_{56}=10.1, $J_{66'}$=10.4, H-6), 3.70 (dd, J_{54}=9.3, J_{34}=9.0, H-4), 3.91 (q, J=7.1, 1H), 3.92 (q, J=7.2, 1H), 3.94 (q, J=6.9, 2H), 4.09 (q, J=7.3, 1H), 4.09 (q, J=6.8, 1H), 4.19–4.49 (m, 9H), 4.68–4.84 (m, H-2, H-3), 5.15 (d, J_{12}=7.1, H-1), 5.24 (dd, J_{HH}=6.7, J_{PH}=8.5, 1H), 5.27 (dd, J_{HH}=6.7, J_{PH}=8.6, 1H), 5.56 (s, H-b), 5.80 (d, J_{HH}=6.7, 1H), 5.98 (d, J_{HH}=6.7, 1H), 7.2–8.2 (m, 10H-aromatic). MS m/z 924 (M^+), 831. Anal. found C 55.85, H 6.36, P 6.86; calcd for $C_{43}H_{58}O_{18}P_2$ (924.84) C 55.84, H 6.32, P 6.70.

2.7.12. [Rh(2c)(COD)]BF_4 6c

The phosphite **2c** (360 mg, 0.5 mmol) and [Rh(COD)$_2$]BF_4 (203 mg, 0.5 mmol) were dissolved in 40 ml of THF and heated to reflux. The cooled solution was clarified by filtration through Celite and evaporated to 8 ml under reduced pressure. Ether was added and a yellow precipitate was filtered, washed with ether and dried under vacuum. Yield 436 mg (86%). ^{31}P NMR ((CD$_3$)$_2$CO) δ=109.6 ($^1J_{RhP}$=255.9, $^2J_{PP}$=60.2, J_{PH}=9.7), 111.0 ($^1J_{RhP}$=259.1, $^2J_{PP}$=60.0, J_{PH}=9.3). ^{1}H NMR (CDCl$_3$) δ=2.4–2.9 (br. m, 4×CH$_2$), 3.43 (dd, J_{54}=9.2, J_{34}=9.4, H-4), 3.49 (dd, J_{56}=10.3, $J_{66'}$=10.4, H-6), 3.75 (ddd, $J_{56'}$=4.9, J_{56}=10.3, J_{54}=9.2, H-5), 4.17 (dd, $J_{56'}$=4.9, $J_{66'}$=10.4, H-6′), 4.39 (dd, J_{12}=7.4, J_{23}=8.3, J_{PH}=9.3, H-2), 4.96 (s, H-b), 5.24 (d, J_{12}=7.4, H-1), 5.46 (ddd, J_{23}=8.7, J_{34}=9.4, J_{PH}=9.6, H-3), 6.0–6.4 (br. s, 4×CH), 6.6–7.7 (m, 10H-aromatic). ^{13}C NMR ((CD$_3$)$_2$CO) δ=30.2, 30.4 (2×CH$_2$), 65.6 (CH), 67.9 (CH$_2$), 77.9 (d, J_{PC}=12.8, CH), 79.6 (d, J_{PC}=2.8, CH), 99.2 (d, J_{PC}=5.7, CH), 111.8 (br. m, CH), 112.9 (br. m, CH), 113.4 (CH), 115.6 (t, J_{PC}=14.3, C), 117.2, 123.4, 124.1, 124.4, 126.5 (CH), 128.1 (d, J_{PC}=3.8, CH), 128.19, 128.24, 128.3, 128.1, 129.4 129.5 (CH), 135.4, 135.5, 137.4 (C), 144.02 (dd, J_{PC}=24.8, J_{PC}=9.5), 144.37 (dd, J_{PC}=10.5, J_{PC}=3.8), 156.8 (C). Anal. found C 54.80, H 4.23, P 6.90; calcd for $C_{47}H_{42}BF_4O_{10}P_2Rh$ (1018.5) C 55.43, H 4.16, P 6.08.

2.7.13. Reaction of 2h with [Rh(COD)$_2$]BF_4

Similarly, from phosphite **2h** (378 mg, 0.5 mmol) and [Rh(COD)$_2$]BF_4 (203 mg, 0.5 mmol) 442 mg of a yellow solid were obtained. According to the ^{31}P NMR spectrum this was a mixture of [Rh(**2h**)(COD)]BF_4 (**6h**) and probably [Rh(**2h**)$_2$]BF_4. ^{31}P{^{1}H} NMR (CDCl$_3$) δ=140.8 ($^1J_{RhP}$=250.4, $^2J_{PP}$=54.1), 144.5 ($^1J_{RhP}$=250.7, $^2J_{PP}$=54.1) and broad multiplet at 150–155 ppm. The ^{1}H NMR (CDCl$_3$) spectrum of the mixtures showed two sets of signals for ligand **2h**.

2.7.14. [Pt(2c)Cl$_2$] 7c

A solution of phosphite **2c** (288 mg, 0.4 mmol) in 3 mL of THF was added to a solution of [Pt(COD)Cl$_2$] (152 mg, 0.4 mmol) in 5 mL CH_2Cl_2 and the mixture was stirred overnight. The precipitate was filtered, washed with ether and dried under vacuum. Yield 205 mg (51%). ^{31}P NMR (CDCl$_3$) δ=62.6 ($^1J_{PtP}$=5926.5, $^2J_{PP}$=29.5, J_{PH}=9.7), 63.8 ($^1J_{PtP}$=5958.6, $^2J_{PP}$=29.5, J_{PH}=11.8). ^{1}H NMR (CDCl$_3$) δ=3.41 (ddd, $J_{56'}$=5.0, 0.5|J_{56}+J_{54}|=9.7, H-5), 3.63 (dd, 0.5|J_{65}+$J_{66'}$|=10.3, H-6), 3.67 (dd, 0.5|J_{45}+J_{43}|=9.5, H-4), 4.24 (dd, $J_{56'}$=5.0, $J_{66'}$=10.5, H-6′), 4.79 (dd, J_{12}=7.5, J_{23}=9.0, J_{PH}=11.3, H-2), 4.98 (ddd, J_{23}=9.0, J_{34}=10.5, J_{PH}=9.3, H-3), 4.99 (d, J_{12}=7.4, H-1), 5.02 (s, H-b), 6.08 (d, 2H-aromatic), 6.75 (d, 2H-aromatic), 7.00–7.46 (m, 24H-aromatic). ^{13}C NMR (CDCl$_3$) δ=66.6 (CH), 68.4 (CH$_2$), 78.2 (CH), 79.7 (d, J_{PC}=4.8, CH), 80.0 (d, J_{PC}=5.7, CH), 99.1, 102.1, 117.4, 122.7 (d, J_{PC}=8.2), 123.1, 124.1, 126.7, 127.3, 127.5, 128.65 (CH), 128.98, 129.08 (C), 129.13, 129.79, 129.87, 130.37 (d, J_{PC}=6.7), 130.51 (d, J_{PC}=11.4), 130.77 (d, J_{PC}=13.3), 131.01 (d, J_{PC}=12.4) (CH), 136.6, 148.50 (d, J_{PC}=10.5), 148.62 (d, J_{PC}=9.5), 148.69 (d, J_{PC}=10.5), 148.81 (d, J_{PC}=12.4), 156.3 (C). Anal. found C 48.12, H 3.52, P 5.83; calcd for $C_{39}H_{30}Cl_2O_{10}P_2Pt$ (986.59) C 47.48, H 3.06, P 6.28.

2.7.15. [Pt(2d)Cl$_2$] 7d

A solution of phosphite **2d** (387 mg, 0.5 mmol) in 5 mL of THF was added to a solution of [Pt(COD)Cl$_2$] (187 mg, 0.5 mmol) in 5 mL CH_2Cl_2 and the mixture was stirred overnight. The solvent was evaporated in vacuum and the residue crystallized from acetone at −78°C. Yield 245 mg (47%). ^{31}P NMR (CDCl$_3$) δ=80.78 ($^1J_{PtP}$=5785.2, $^2J_{PP}$=30.5, J_{PH}=9.7), 81.08 ($^1J_{PtP}$=5773.4, $^2J_{PP}$=30.5, J_{PH}=9.7). ^{1}H NMR (CDCl$_3$) δ=3.58 (ddd, $J_{56'}$=5.0, 0.5|J_{56}+J_{54}|=9.7, H-5), 3.82 (dd, 0.5|J_{65}+$J_{66'}$|=10.2, H-6), 3.90 (dd, 0.5|J_{45}+J_{43}|=9.5, H-4), 4.40 (dd, $J_{56'}$=5.2, $J_{66'}$=10.6, H-6′), 4.97 (dd, J_{12}=7.6, J_{23}=9.5, J_{PH}=9.7, H-2), 5.12 (d, J_{12}=7.6, H-1), 5.25 (ddd, J_{23}=9.5, J_{34}=9.5, J_{PH}=9.7, H-3), 5.42 (s, H-b), 6.61 (d, 2H-

aromatic), 7.23–7.56 (m, 18H-aromatic). ^{13}C NMR (DMSO-d_6) δ=65.8 (CH), 67.8 (CH_2), 77.4 (d, J_{PC}=2.7, CH), 79.6 (d, J_{PC}=7.9, CH), 80.3 (d, J_{PC}=8.0, CH), 98.0, 100.7 (CH), 113.9–114.0 (CH), 114.1 (d, J_{PC}=5.7, CH), 114.2 (d, J_{PC}=13.9, C), 114.4 (d, J_{PC}=14.3, C), 116.7, 123.7, 125.2, 125.3, 125.4, 126.2, 128.49, 128.62, 128.69, 128.9, 129.4, 129.9 (CH), 135.4, 135.6, 137.0 (C), 143.64 (dd, J_{PC}=9.5, J_{PC}=26.7), 143.92 (dd, J_{PC}=10.0, J_{PC}=17.6), 156.2 (C). Anal. found C 50.46, H 3.64, P 6.86; calcd for $C_{43}H_{34}Cl_2O_{10}P_2Pt$ (1038.67) C 49.72, H 3.30, P 5.96.

2.8. Catalytic experiments

2.8.1. Hydrogenation

For hydrogenation at 25°C and 0.1 MPa total pressure, 1 mmol substrate was added to a catalyst solution prepared in situ from 0.01 mmol $[Rh(COD)_2]BF_4$ and 0.01 mmol phosphite in 15 ml THF under anaerobic conditions.

2.8.2. Hydroformylation

A mixture of 1 mmol substrate, 0.01 mmol of $Rh(CO)_2(acac)$ and 0.01–0.05 mmol ligand in 10 ml solvent was placed into a 40 ml autoclave (Ernst HAAGE, Mühlheim, Germany), pressurized to the appropriate initial pressure with syngas ($CO:H_2$=1:1) and heated to the reaction temperature. Conversion, selectivity and enantiomeric excess were determined by GC.

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