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Synthesis of novel diphosphines from D-(+)-glucose. Use in asymmetric hydrogenation

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Abstract

A new family of bidentate diphosphine ligands which contain a glucofuranoside as a simple but highly effective chiral backbone are reported. These ligands are prepared in a few steps from readily available D-(+)-glucose. These new ligands have been applied to the rhodium-catalysed hydrogenation of α,β–unsaturated carboxylic acid derivatives under very mild reaction conditions, with enantiomeric excesses of up to 98%.

1. Introduction

The enantioselective hydrogenation of prochiral substrates is one the most important applications of asymmetric catalysis.[1] Although the use of numerous chiral diphosphines in asymmetric hydrogenation has been successfully reported,[2] the design and synthesis of new readily available, highly active and enantioselective chiral ligands continues to be an active field of research.

One of the simplest methods of obtaining chiral ligands is the transformation of readily available natural homochiral compounds (the so-called chiral pool). Despite the accessibility at low cost of the carbohydrate synthons and the excellent enantioselectivities obtained in different processes,[3] the full potential of the carbohydrate chiral pool to provide ligands has not been fully exploited.

In the context of our studies on furanoside ligands,[4–6] we have described the synthesis of a new diphosphine derived from xylose (Scheme 1, xylophos) and its successful use in the Rh-asymmetric hydrogenation of alkenes with enantioselectivities of up to 98%.[5] Moreover, we have recently shown that the rate and enantioselectivity in the Rh-asymmetric hydroformylation of styrene with the furanoside diphosphite **1** (Scheme 1, ee = 61%)[6a] was notably improved by

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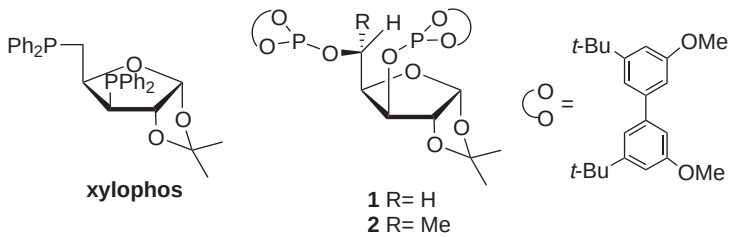
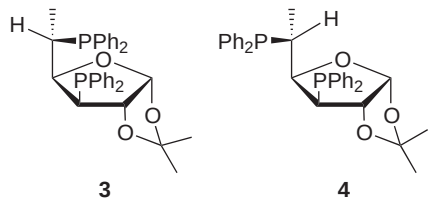
introducing a new stereocentre at the C-5 position[6] (Scheme 1, **2**, ee = 90%).[6b] These results suggested that diphosphine ligands related to xylophos, but with a new stereocentre at C-5, could also provide more active and enantioselective hydrogenation catalytic systems.



Scheme 1.

In this context we now report the synthesis of the new diphosphines 3,5,6-trideoxy-3,5-bis-diphenylphosphine-1,2-*O*-isopropylidene-α-D-glucofuranose **3** and 3,5,6-trideoxy-3,5-bis-diphenylphosphine-1,2-*O*-isopropylidene-α-D-glucofuranose **4** (Scheme 2) and their use in the Rh-catalysed enantioselective hydrogenation of prochiral α,β-unsaturated carboxylic acid derivatives. With these two diastereomers we can explore the effects of the stereogenic C-5 atom, whose configuration is expected to be important for the course of the catalytic reaction because of its proximity to the metal. In addition, these ligands are particularly interesting from a practical point of view since they can be prepared in very few steps from available D-(+)-glucose.

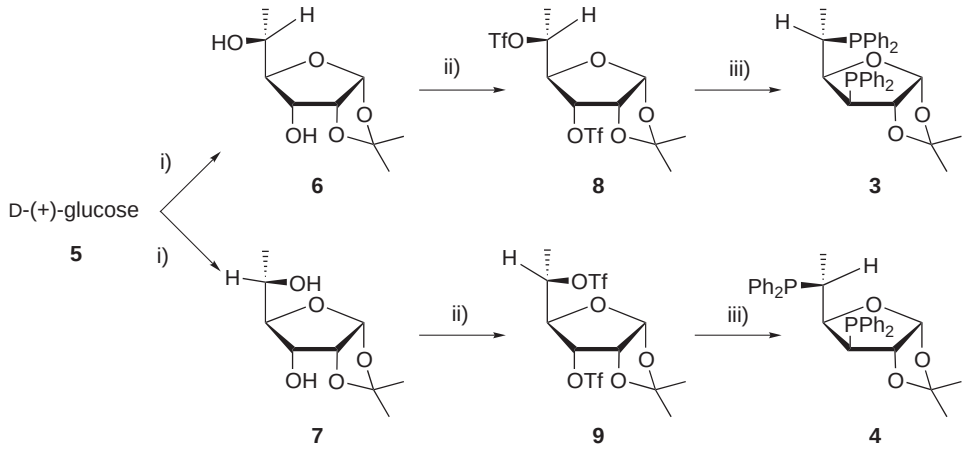


Scheme 2.

2. Results and discussion

2.1. Synthesis of diphosphines

The new C_1-symmetrical homochiral diphosphines **3** and **4** were synthesised very efficiently in two steps from the corresponding alcohols 6-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose **6** and 6-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose **7**, as shown in Scheme 3. These diols were readily prepared from natural D-(+)-glucose **5**.[7] The reaction of **6** and **7** with trifluoromethanesulfonic anhydride in the presence of pyridine afforded the ditriflate compounds **8** and **9**, respectively. Subsequent addition of a slight excess of potassium diphenylphosphide in THF provided easy access to the desired diphosphines **3** and **4**.



Scheme 3. Synthesis of diphosphine ligands **3** and **4.** (i) Ref. 7. (ii) Tf_2O, Py, CH_2Cl_2, −20 to 25°C. (iii) $KPPh_2$, THF, −78 to 25°C.

Diphosphines **3** and **4** were isolated in good yields by flash chromatography under argon atmosphere as white crystalline solids that are stable at air in solid state. The elemental analysis and mass spectrometry data were in agreement with the assigned structure. The ^{31}P, ^{13}C and ^{1}H NMR spectra provided further unequivocal evidence to identity the compounds (see Section 4).

The ^{31}P NMR spectrum of **4** displays a large phosphorus–phosphorus coupling constant ($^4J_{P-P}$) of 34.7 Hz. In the ^{13}C NMR spectrum, double doublets due to the coupling with both non-equivalent phosphorus atoms were observed for the furanoside carbon atoms C-3 and C-5 with J_{P-C} between 7 and 22 Hz. Unlike the ^{31}P NMR spectrum of **4**, no phosphorus–phosphorus coupling constant was observed for diphosphine **3**. The inverse configuration at C-5 of the sugar backbone gave rise to a solution structure without the correct conformation to appreciable phosphorus–phosphorus coupling.[8]

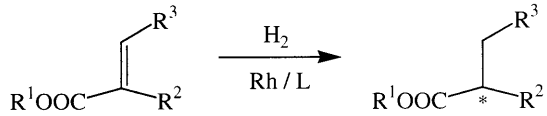
2.2. Hydrogenation of prochiral olefins

Diphosphine ligands **3** and **4** were tested in the Rh-catalysed asymmetric hydrogenation of a variety of prochiral α,β-unsaturated carboxylic acid derivatives **10–13** under mild reaction conditions (1 bar of H_2). The results are shown in Table 1.

Reaction of the prochiral olefin *Z*-α-acetamidocinnamic **10** using the catalyst precursor containing ligand **3** afforded a quantitative yield of hydrogenation product with 52% ee (entry 1). The related ester 2-acetoamidomethacrylate **11** and substrate **12** gave similar results at room temperature (entries 2–3). When itaconic acid **13** was used as a substrate the enantioselectivity substantially decreased (23% ee, entry 4). This is in line with the lower substrate acceptability of the six-membered ring Rh–diphosphine catalysts.[1,9] Catalytic precursor containing ligand **4** hydrogenated substrates **10–12** with higher enantioselectivities (up to 93% ee, entries 5–7). Decreasing the reaction temperature to 0°C enhanced the enantioselectivity (up to 98%, entries 9 and 10).

The data demonstrate that the enantiomeric excesses are strongly dependent on the absolute configuration of the C-5 stereogenic centre of the carbohydrate backbone, while the activity and

Table 1
Asymmetric hydrogenation of α,β-unsaturated carboxylic derivatives **10**–**13**[a]



10: R^1=H; R^2=NH(CO)CH_3; R^3=Ph **11:** R^1=CH_3; R^2=NH(CO)CH_3; R^3=Ph

12: R^1=CH_3; R^2=NH(CO)CH_3; R^3=H **13:** R^1=H; R^2=CH_2COOH; R^3=H

Entry	Substrate	Ligand	*t* (h)	Conv. (%)	ee (%)
1	**10**[c]	3	2	100	52 (*S*)
2	**11**[b]	3	2	100	53 (*S*)
3	**12**[b]	3	1	75	54 (*S*)
4	**13**[e]	3	2	100	23 (*R*)
5	**10**[c]	4	2	100	92 (*S*)
6	**11**[b]	4	2	100	91 (*S*)
7	**12**[b]	4	1	80	93 (*S*)
8	**13**[c]	4	2	100	59 (*R*)
9[d]	**11**[b]	4	6	95	98 (*S*)
10[d]	**12**[b]	4	5	100	98 (*S*)
11	**12**[b]	–[e]	1	50	92 (*S*)

[a] Cat./substrate = 1/100, substrate = 1 mmol, solvent = methanol (6 ml), T = 20°C, P = 1 atm.
[b] Conversions and enantiomeric excesses measured by GC.
[c] Conversions measured by ^{1}H NMR and enantiomeric excesses measured by polarimetry.
[d] T = 0°C.
[e] Hydrogenation of **12** using catalyst precursor [Rh(cod)(xylophos)]BF_4 (**14**).

the sense of the asymmetric induction are not affected (entries 1–4 versus 5–8). Thus, the best enantioselectivities are obtained by using the catalytic precursor containing the diphosphine ligand with a (*R*)-configuration in the C-5 (up to 98%).

As with the related diphosphite ligands,[6] introducing the methyl substituent in the carbohydrate backbone considerably enhanced the rate (entries 3 and 7 versus 11). The fact that the conversions were better with the catalyst containing more hindered and slightly basic ligands **3** and **4** than with the Rh–xylophos catalyst precursor **14** could suggest that the rate-determining step is the addition of H_2.

The results obtained in the enantioselective Rh-catalysed hydrogenation compete favourably with the most efficient diphosphine with five- to seven-membered chelate rings previously reported in the literature.[1] Moreover, the Rh-catalyst containing ligand **4** is one of the few examples of six-membered chelate rings that have led to enantioselectivities of above 90% (Skewphos,[10] Josiphos,[2g] xylophos[5]).

3. Conclusion

A new family of C_1 diphosphine ligands has been easily prepared in a few steps from the readily available D-glucose. Initial studies directed towards their use as chiral ligands in the

asymmetric hydrogenation of α,β-unsaturated carboxylic acid derivatives revealed high enantioselectivities (up to 98%) under very mild reaction conditions.

The configuration of carbon C-5 strongly influences the enantioselectivity. The best results are obtained using ligand **4** with (*R*)-configuration in the C-5. The results also show that a methyl substituent in the carbon C-5 significantly increases the activity.

A thorough investigation of the Rh-complexes by NMR spectroscopy and theoretical calculations is currently in progress in order to determine the structure of the catalyst precursors and explain the different enantioselective efficiencies of the catalysts. The results will be reported in due course.[†]

4. Experimental

4.1. General procedures

All syntheses were performed by standard Schlenk techniques under a nitrogen or argon atmosphere. Compounds 6-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose **6** and 6-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose **7**[7] were prepared by previously described methods. Solvents were purified by standard procedures. All other reagents were used as commercially available. 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 Variant Gemini 400 MHz or 500 MHz spectrometer. Chemical shifts are 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 means of COSY, ^{31}P–^{1}H and ^{13}C–^{1}H correlation experiments. EI mass spectra were obtained on a HP 5989 A spectrometer. Gas chromatographic analyses were run on a Hewlett–Packard HP 5890A instrument (fused silica capillary column 25 m×0.25 mm Permabond L-Chirasil-Val) equipped with a Hewlett–Packard HP 3396 series II integrator. Optical rotations were measured at 25°C on a Perkin–Elmer 241 MC polarimeter. Hydrogenation reactions were performed in a previously described hydrogen–vacuum line.[11]

4.2. 6-Deoxy-1,2-O-isopropylidene-3,5-di-O-trifluoromethanesulfonyl-α-D-allofuranose **8**

Anhydrous pyridine was added (0.8 ml, 10 mmol) to a solution of 6-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose **6** (0.75 g, 3.7 mmol) in dichloromethane (20 ml). After 10 minutes, trifluoromethanesulfonic anhydride (1.5 ml, 8.9 mmol) was added dropwise at −20°C and the mixture was allowed to react at room temperature for 20 minutes, 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 0.97 g (56%) as a colourless liquid. ^{1}H NMR: δ: 1.21 (s, 3H, CH_3), 1.40 (d, 3H, H-6, $^{3}J_{6-5}=7.1$ Hz), 1.47 (s, 3H, CH_3), 4.17 (dd, 1H, H-4, $^{3}J_{3-4}=7.8$ Hz, $^{3}J_{4-5}=1.8$ Hz), 4.67 (dd, 1H, H-2, $^{3}J_{2-1}=3.6$ Hz, $^{3}J_{2-3}=5.1$ Hz), 4.82 (dd, 1H, H-3, $^{3}J_{3-2}=5.1$ Hz, $^{3}J_{3-4}=7.8$ Hz), 5.20 (m, 1H, H-5), 5.73 (d, 1H, H-1, $^{3}J_{1-2}=3.6$ Hz). ^{13}C NMR: δ: 16.0 (C-6), 26.6 (CH_3), 77.2 (C-2), 78.5 (C-4), 79.9 (C-3), 82.6 (C-5), 103.8 (C-1), 114.6 (CMe_2), 118.2 (q, CF_3, $^{1}J_{C-F}=316.2$ Hz), 118.6 (q, CF_3, $^{1}J_{C-F}=314.4$ Hz).

[†] Preliminary NMR results indicate that there is an equilibrium between two different conformers when ligand **3** is coordinated to rhodium. For ligand **4** only one conformer is observed. Thus, the absolute configuration of C-5 seems to influence the stability of the different possible Rh-conformers and therefore the enantioselectivity of the process.

4.3. 6-Deoxy-1,2-O-isopropylidene-3,5-di-O-trifluoromethanesulfonyl-β-L-talofuranose **9**

Treatment of 6-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose **7** (0.61 g, 3.0 mmol) with trifluoromethanesulfonic anhydride as described for compound **8** afforded ditriflate **9**, which was purified by flash chromatography (eluent: hexane:ethyl acetate, 1:1). Yield: 0.77 g (55%) of a colourless liquid. ^{1}H NMR: δ: 1.41 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.62 (d, 3H, H-6, $^3J_{6-5}=6.7$ Hz), 4.11 (m, 1H, H-4), 4.81 (m, 2H, H-2, H-3), 5.12 (m, 1H, H-5), 5.89 (d, 1H, H-1, $^3J_{1-2}=3.6$ Hz). ^{13}C NMR: δ: 17.1 (C-6), 26.4 (CH_3), 26.7 (CH_3), 77.1 (C-2), 78.3 (C-4), 80.5 (C-3), 82.3 (C-5), 103.9 (C-1), 114.7 (CMe_2), 118.5 (q, CF_3, $^1J_{C-F}=319.0$ Hz), 118.7 (q, CF_3, $^1J_{C-F}=321.1$ Hz).

4.4. 3,5,6-Trideoxy-3,5-bis(diphenylphosphine)-1,2-O-isopropylidene-β-L-idofuranose **3**

Potassium diphenylphosphide (4.2 ml, 2.1 mmol) was slowly added at −78°C to a solution of ditriflate **8** (0.94 g, 2 mmol) in THF (10 ml). The mixture was allowed to react at room temperature for 30 minutes, after which the solvent was evaporated. The residue was purified by column chromatography (solvent: toluene) under argon to give the diphosphine 0.74 g (69%) as a white solid. ^{31}P NMR, δ: −25.7 (s, 1P), 2.0 (s, 1P). ^{1}H NMR: δ: 0.91 (ddd, 3H, H-6, $^3J_{6-5}=6.7$ Hz, $J_{6-P}=9.3$ Hz, $J_{6-P}=2.7$ Hz), 1.14 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 2.89 (d, 1H, H-3, $^3J_{3-4}=4.4$ Hz), 3.39 (m, 1H, H-5), 4.09 (m, 1H, H-4), 4.56 (dd, 1H, H-2, $^3J_{2-1}=3.6$, $J_{2-P}=6.5$ Hz), 4.65 (d, 1H, H-1, $^3J_{1-2}=3.6$ Hz), 7.32 (m, 12H, CH=), 7.61 (m, 8H, CH=). ^{13}C NMR: δ: 12.9 (t, C-6, $J_{C-P}=4.9$ Hz), 26.1 (CH_3), 26.3 (CH_3), 31.7 (t, C-5, $J_{C-P}=18.9$ Hz), 44.6 (dd, C-3, $J_{C-P}=23.1$ Hz, $J_{C-P}=6.1$ Hz), 81.5 (t, C-4, $J_{C-P}=10.9$), 83.4 (C-2), 104.3 (C-1), 110.3 (CMe_2), 127.5, 127.9, 128.2, 128.4, 128.8, 129.2, 132.5, 132.8, 133.0, 134.2, 134.5, 134.9, 135.2 (CH=). MS (70 eV, EI): m/z: 541 [$M^{+\bullet}$]; $C_{33}H_{34}O_3P_2$ (540.57) calcd: C, 73.32; H, 6.34; found: C, 73.42; H, 6.39.

4.5. 3,5,6-Trideoxy-3,5-bis(diphenylphosphine)-1,2-O-isopropylidene-α-D-glucofuranose **4**

Treatment of ditriflate **9** (0.7 g, 1.5 mmol) with potassium diphenylphosphide (3.3 ml, 1.65 mmol) as described for compound **3** afforded diphosphine **4**, which was purified by flash chromatography (eluent: toluene). Yield: 0.56 g (70%) of a white solid. ^{31}P NMR, δ: −24.3 (d, 1P, $^4J_{P-P}=34.7$ Hz), −2.0 (d, 1P, $^4J_{P-P}=34.7$ Hz). ^{1}H NMR: δ: 1.01 (t, 3H, H-6, $J=7.4$ Hz), 1.14 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 3.05 (m, 1H, H-3), 3.31 (m, 1H, H-5), 4.11 (m, 1H, H-4), 4.43 (dd, 1H, H-2, $^3J_{2-1}=3.0$, $J_{2-P}=4.6$ Hz), 4.53 (m, 1H, H-1), 7.2–7.6 (m, 20H, CH=). ^{13}C NMR: δ: 13.8 (C-6), 26.3 (CH_3), 26.5 (CH_3), 31.8 (dd, C-5, $J_{C-P}=15.1$ Hz, $J_{C-P}=20.5$ Hz), 45.1 (dd, C-3, $J_{C-P}=22.2$ Hz, $J_{C-P}=7.5$ Hz), 81.4 (dd, C-4, $J_{C-P}=18.1$, $J_{C-P}=10.9$ Hz), 84.0 (C-2), 103.9 (C-1), 114.0 (CMe_2), 127.9, 128.4, 128.8, 129.1, 129.4, 129.6, 132.4, 132.9, 133.4, 133.9, 134.2, 134.6, 135.0 (CH=). MS (70 eV, EI): m/z: 541 [$M^{+\bullet}$]; $C_{33}H_{34}O_3P_2$ (540.57) calcd: C, 73.32; H, 6.34; found: C, 73.39; H, 6.26.

4.6. Hydrogenation of prochiral olefins

In a typical run, a Schlenk was filled with a methanol solution (6 ml) of substrate (1 mmol) and catalyst precursor (8.38 mg, 0.01 mmol). It was then purged three times with H_2 and vacuum. The reaction mixture was then shaken under H_2 (1 atm) at 293 K. After the desired

reaction time, the solvent was removed. The following procedures were used to isolate the hydrogenation products:

For 2-methylsuccinic acid and *N*-acetylphenylalanine, the residue was dissolved in 0.5 M NaOH and separated from the insoluble catalyst by filtration. The filtrate was acidified with diluted HCl, extracted with ether and washed with water. The ether phase was dried over sodium sulfate and evaporated to dryness. The extent of the conversion was measured by ^{1}H NMR. The enantiomeric excesses were determined by polarimetry.[12]

For *N*-acetylalanine methyl ester and *N*-acetylphenylalanine methyl ester the residue was dissolved in CH_2Cl_2 and filtered over a plug of silica to remove the catalyst. Conversion and enantiomeric excesses were determined by gas chromatography.

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