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Preparation of Chiral Diphenylphosphines from D-Glucose and Enantioselective Hydrogenation with Their Rh(I) Complexes

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(2*R*,3*S*)-2-Methylsulfonyloxymethyl-3-methylsulfonyloxy-tetrahydropyran (*4*), derived from D-glucose, is diphenylphosphinated to (2*R*,3*R*)-2-diphenylphosphinomethyl-3-diphenylphosphino-tetrahydropyran (*7*), which is formed as a minor product. Compound *8* is the predominant product, formed on 3,4-elimination. Preparation and characterization of the rhodium(I) complexes *10—12* is described. Complex *10* of bidentate ligand *7* exhibits in hydrogenation of *Z*-α-N-acetylaminocinnamic acid enantioselectivity comparable to that obtained with rhodium(I) complex of (-)-DIOP (~70% e. e.). Saturated monophosphine, (2*S*)-2-diphenylphosphinomethyl-tetrahydropyran (*9*) affords mixed rhodium(I) complex (*11, 12*), which exhibits low enantioselectivity.

INTRODUCTION

The asymmetric catalytic hydrogenation of prochiral olefins constitutes one of the most impressive achievements to date in catalytic selectivity. Many reviews on this topic are available.[1–7] Previously, we investigated the homogeneous catalytic hydrogenation of various prochiral substrates, catalyzed by some known or newly developed rhodium(I) complexes of chiral diphenylphosphines or diphenylphosphinites.[8–11] We wish to describe here the investigation of preparation and enantioselective hydrogenation with chiral diphenylphosphines derived from D-glucose, the most widespread monosaccharide in nature. These results are of interest in view of the known difficulties encountered by others in preparation of bis-diphenylphosphines derived from cyclic diols by nucleophilic substitution of their activated esters, usually tosylates or mesylates. To our best knowledge no examples of preparation of bis-diphenylphosphines by direct nucleophilic substitution at *sec.* carbon atoms of a six-membered ring have been described. The only example of double substitution refers to five-membered pyrrolidine derivative,[12] while many examples of diphosphines derived from C(3)-hydroxy prolinol by substitution on the ring and on the side chain are known.[13,14] Severe steric hindrance seems to be the reason for the unsuccessful attempts at substitution of the tosyl group at *sec.* carbon in some monosaccharide derivatives.[15,16] In

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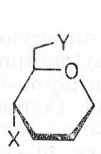
one example, where an exocyclic double bond was created at C(3) of 1,2-*O*-isopropylidene-2-D-xylose derivative, subsequent addition of diphenylphosphide anion afforded bis-diphenylphosphine ligand derived from D-xylofuranose.[16]

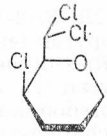
Carbocyclic bis-diphenylphosphines with both phosphine groups attached to the ring carbons were obtained only by cycloadditions to the unsaturated precursors, cyclopentene[17] or cyclopentadiene[18], with an obvious need for resolution of the racemic products. With the chiral starting diene the resolution step can be avoided, as recently demonstrated by Samuel *et al.*[19]

RESULTS AND DISCUSSION

Our synthetic targets were new bis-phenyl-phosphine *7* and its $[Rh(NBD)_2]ClO_4$ (NBD=norbornadiene) complex *10*. To this end, chiral diol *1*,[20] was transformed into active esters *2*—*4*.



	X, Y
1	OH
2	p-Tosyl
3	OSO_2CF_3
4	OSO_2CH_3
5	OSO_2CH_3, Cl



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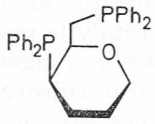

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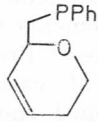

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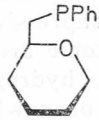

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Ditosylate *2* was diphenylphospinated in THF, screening the temperature interval —4° to 60 °C. Extensive decomposition took place in the whole temperature range. When the more soluble and reactive ditriflate *3* was used, decomposition was partly prohibited at —15° to —20 °C, but minor amounts of only the unsaturated monophosphine *8* were identified. Dimesylate *5* turned out to be the optimal starting material, being stable enough and more reactive than ditosylate.[21,22] As Table I shows, phosphination under various conditions afforded only 7—8% of *7* and up to *ca.* 60% of the unsaturated product *8*.

It also revealed surprising the result that lowering the reaction temperature by 110 °C only increased the yield of the unsaturated monophosphine *8* by *ca.* 12%, while the yield of disubstituted product (7) remained practically unchanged.

TABLE I

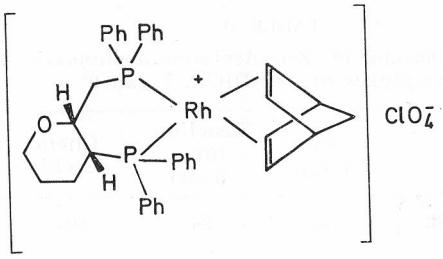
Preparation of Diphenylphosphines 7 and 8 from Dimesylate 5

Run	Solvent	Temperature °C	Yield %[a]	
			7	8
1	THF	60	7	45.6
2	THF	—5	7.3	55.6
3	THF/DMF	—50	8.3	58.1

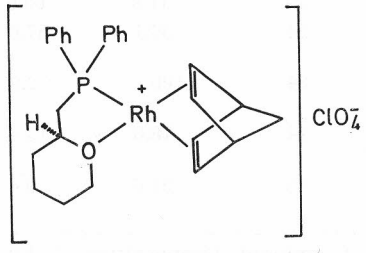
[a] After quantitative separation by chromatography on silica gel column.

Prompted by the report[23] on improved synthesis of (—)-DIOP from its dichloro precursor obtained by nucleophilic exchange of tosyl groups for chlorine, we attempted preparation of dichloro congener from *4*. Under mild conditions, compound *4* was quantitatively chlorinated into *5*. Dichloro compound was not formed even after a prolonged reaction time (days), while at elevated temperatures extensive decomposition took place. The cited method[22] seems to be applicable to substitution of active esters of primary alcohols only.

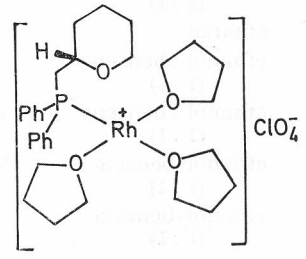
Following the report of Jennings *et al.*,[24] who isolated the anomeric mixture of 1,4,6-trichloro-2,3-bis-*O*-chlorosulfonyl-D-glucose was treated with sulfuryl chloride, we carried out chlorination of diol *1*. Trichloro-derivative *6* was the only product, isolated in a limited amount, whose unexpected structure was confirmed by spectral and analytical data.



10



11



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The structure of *8*, in the particular position of double bond, was mainly deduced from the ^{13}C-NMR spectra. In view of the easy 5,6-elimination and formation of an exocyclic double bond in D-glucose series,[25] formation of endocyclic double bond in 3,4-position of *8* was unexpected. Carbon atoms C(2'), C(2) and C(3), in α-, β- and γ-position to phosphorus atom, continued to exhibit doubled signals after decoupling to protons because of the long--range coupling to phosphorus, while more distant carbon atoms, C(4), C(5) and C(6), exhibited simple decoupled signals in the off-resonance spectrum.

Preparation of the catalytic complex *10* followed the known route.[9,26] Preparation of catalytic complex of *9*, tentatively bidentate (P, O) ligand,[27–29] was attempted as well. Although it is conceivable that the unsaturated monophosphine *8* after complexation with $[Rh(NBD)_2]ClO_4$ and subsequent hydrogenation would *in situ* give the saturated ligand *9*, we have prepared compound *9* by autocatalyzed hydrogenation of *8*. It afforded on complexation with $[Rh(NBD)_2]ClO_4$ a non-uniform product which according to ^{1}H and ^{13}C-NMR spectra and elemental analysis data could tentatively be defined as the mixture of NBD-complex with *9* as bidentate ligand (*11*) and a complex with three THF molecules in the coordination sphere of rhodium(I) (*12*). The ^{1}H-NMR spectrum reveals characteristic multiplets for the coordinated norbornadiene at 5.20, 4.45 and 1.87 ppm, while in the ^{13}C-NMR spectrum characteristic signals at 85.55, 85.27 (unsaturated carbons) 64.79 (*tert.* carbons) and 52.49 ppm (*sec.* carbon atom) are present. Bound THF molecules exhibit characteristic signals at 3.74 and 1.85 ppm in ^{1}H-NMR spectrum, and at 67.95 and 25.62 ppm in ^{13}C-NMR spectrum. Ratio of the aliphatic *vs.* aromatic protons of diphenylphosphinic subunit indicated, while the elemental analysis data confirmed, the presence of ca. 1 : 1 mixture of *11* and *12*.

TABLE II

Enantioselective Hydrogenation of Z-α-Acetylaminocinnamic Acid with Rh(I) Complexes of (—)-DIOP, 7 and 9[a]

Chiral Phosphine	Solvent	p_{H_2} (atm)	Reaction time (hour)	Chem. Yield	e. e.[b] (%)	Configuration
(—)-DIOP	ethanol : benezne (1 : 1)	1.5	24	100	71.7	*R*
7	ethanol : benzene (1 : 1)	1.5	24	23.1	52.9	*S*
7	ethanol : benzene (2 : 1)	1.5	24	57.5	51.1	*S*
7	ethanol	1.5	24	71.9	65.6	*S*
7	ethanol : benzene (1 : 1)	5.0	24	59.1	57.8	*S*
7	ethanol : benzene (1 : 1)	10.0	24	100	72.9	*S*
9	ethanol-benzene (1 : 1)	70.0	24	18.6	13.4	*R*
9	ethanol-benzene (1 : 1)	50.0	68	51.6	9.4	*R*

[a] Catalyst-to-substrate ratio was 1 : 100, at ambient temperature. [b] Enantiomeric excesses were calculated with the $[\alpha]_D + 46.0^\circ$ C = 1.0 in EtOH for optically pure *R*-*N*-acetylphenylalanine.

We looked at the catalytic activity of the complexes obtained from both 7 and 9 in enantioselective hydrogenation of Z-α-acetylaminocinnamic acid, and compared them with the well known complex of (—)-DIOP,[30,31] (Table II).

We observed a somewhat lower catalytic activity of the complex *10* as compared to complex of (—)-DIOP, but nearly the same enantioselectivity (e. e. ~ 70%); Kagan *et al.*[30] achieved 84% e. e. with the latter complex. Complex mixture formed from *9*, although presumably transformed into single complex on oxidative addition of hydrogen, was significantly less enantioselective (e. e. ~ 10%). This result compares with that recently obtained by Johnson,[32] who obtained 22% e. e. of *S*-N-acetylphenylalanine on hydrogenation of the same substrate with a monophosphine derived from (—)-menthol, which also posses one oxygen atom in β-position to phosphorus atom.

In conclusion, it could be stated that bidentate ligand 7, derived from D-glucose was prepared, though in low yield, by double nucleophilic substitution of a cyclic precursor (*4*). This represents the first preparation of a diphosphine *via* substitution on a six-membered ring. Rhodium(I) complex (*10*) exhibited high enantioselectivity in hydrogenation of Z-α-N-acetylaminocinnamic acid as model substrate.

EXPERIMENTAL

Melting points were determined on Büchi mp apparatus (nach Tottoli) and are not corrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a JOEL FX 90Q, Fourier--transform spectrometer. Chemical shifts are given in δ values downfiled from TMS as an internal standard. IR spectra were obtained with a Perkin-Elmer M 137 spectrometer. Optical rotations were measured with a Perkin-Elmer M 141 polarimeter at ambient temperature, using 1 dm cells. TLC was performed on Merck's DC-alufolien with Kieselgel 60F—254. Flash column chromatography was performed with dry nitrogen as pressurizing gas, and using silica gel Merck, 0.040—0.063 mm (230—400 mesh ASTM). Solvents used for flash chromatography were dried, and prior to use deaerated by continuous flushing with dry nitrogen for 20 min.

Manipulations involving air sensitive solutions were carried out under dry nitrogen atmosphere, glassware was dried 12 hrs at 150 °C before assembling. Organic extracts during usual work-up were dried over Na_2SO_4 and evaporated *in vacuo*.

Preparations of diol *1* and ditosylate *2* are described in our recent papers.[10,11] Z-α-*N*-acetylaminocinnamic acid (Aldrich) was recrystallized twice from 2-propanol before use. (—)-DIOP was prepared from (+)-tartaric acid according to the described method.[30]

(2R,3S)-2-Trifluoromethanesulfonyloxymethyl-3-trifluoromethanesulfonyloxy--tetrahydropyran (3)

To the mixture of trifluoromethanesulfonic acid anhydride (5.9 ml; 10.0 g, 35.5 mmol) and dry dichloromethane (10 ml), cooled to —10 °C, a solution of diol *1* (2.36 g, 17.9 mmol) in dry pyridine (2.9 ml; 2.8 g, 35.5 mmol) was added dropwise over a period of 1.5 hours. The reaction mixture was deposited on ice for 24 hours, then poured on crushed ice, and extracted with chloroform (3 × 100 ml). Combined organic extracts were washed (3 × 100 ml), dried and evaporated, affording 5.92 g (83.6%) of the crude *3*, as dark oil, spot with R_f 0.38 (in chloroform).

Chromatography on 120 g silicagel, eluation with chloroform, yielded 2.71 g (45.8%) of the pure *3*, colourless oil that solidifies in refrigerator. IR(KBr): 2980 2940, 2880, 2860, 1415, 1340, 1315, 1265, 1250, 1200, 1140, 1110, 1055, 970, 940, 915, 890,

865, 835, 800, 760, 660, 610 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.82—1.88 (m, 3H), 2.2—2.6 (m, 1H), 3.4—3.74 (m, 2H). 3.8—4.1 (m, 1H), 4.45—4.84 (m, 3H). ^{13}C-NMR ($CDCl_3$): 25.35 C(5), 30.47 C(4), 68.06 C(6), 73.82 C(2'), 76.13 C(2), 81.66 C(3), 118.77 (CF_3COO C(2'), q, J = 318 Hz). 119.05 (CF_3COO C(3), q, J = 318 Hz).

(2R,3S)-2-Methanesulfonyloxymethyl-3-methanesulfonyloxy--tetrahydropyran (4).

To the solution of diol *1* (5.0 g, 37.8 mmol) in dry pyridine (50 ml), cooled to 0 °C, methanesulfonylchloride (8.85 ml; 13.0 g, 113.5 mmol) was added over 40 minutes. After 4 hours stirring at the same temperature, the reaction mixture was deposited on ice overnight. Usual work-up afforded 11.54 g of crude product, which crystallized on addition of methanol (8.45 g, 73%). Recrystallization from the same solvent afforded the analytically pure product, *mp.* 92—94 °C. ^{1}H-NMR (Py-d_5): 1.71—1.95 (m, 1H), 2.0—2.4 (m, 1H), 3.18 and 3.20 (two s, $2CH_3$, 6H), 3.3—3.6 (m, 1H), 3.8—4.0 (m, 2H), 4.18 (s, 3H), 4.49 (s, 1H), 4.55 (d, J = 1.22 Hz, 1H). ^{13}C-NMR (Py-d_5): 20.09 C(5), 28.50 C(4), 37.25 ($CH_3SO_2OC(2')$), 38.49 ($CH_3SO_2OC(3)$), 67.72 C(6), 69.81 C(2'), 74.95 C(2), 75.96 C(3). *Anal.* Calc'd for $C_8H_{16}O_7S_2$ (288.34); C 33.43, H 5.59%. Found: C 33.57, H 5.59%.

(2R,3S)-2-Chloromethyl-3-methanesulfonyloxy-tetrahydropyran (5)

To the solution of dimesylate *4* (0.50 g, 1.7 mmol) in dry DMSO (5 ml) lithium chloride (0.22 g, 5.2 mmol; dried *in vacuo* over open flame) was added, and reaction mixture stirred in nitrogen atmosphere at 70 °C. After 3 hours, the starting compound (*Rf* 0.27, chloroform) turned quantitatively into a product (*Rf* 0.53) which was isolated by pouring the reaction mixture on crushed ice, and the usual extractive work-up. Crude product *5* (0.30 g, 75.6%, yellow oil) was purified by distillation, *b.p.* 115—125 °C/0.005 mm Hg. IR(KBr): 3030, 2950, 2860, 1460, 1455, 1435, 1360, 1340, 1180, 1095, 965, 920, 835, 745, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.7—1.8 (m, 3H), 2.0—2.7 (m, 1H), 3.09 (s, 3H), 3.12—3.96 (m, 5H), 4.1—4.7 (m, 1H). ^{13}C-NMR ($CDCl_3$): 24.94 (C(5), -triplet in off resonance), 30.54 (C(4), t), 38.71 (CH_3SO_2O, q), 44.13 (C(2'), t), 67.83 (C(6), t), 75.85 (C(2), d), 78.05 (C(3), d). *Anal.* Calc'd for $C_7H_{13}O_4SCl$ (228.69); C 36.77, H 5.73%. Found: C 36.96, H 5.96%.

(2R,3S)-2-Dichloromethyl-3-chloro-tetrahydropyran (6)

To the solution of diol *1* (1.5 g, 11.4 mmol, dried over P_2O_5 *in vacuo*) in a chloroform-pyridine mixture (25 + 10 ml), the freshly distilled sulfuryl chloride (4.6 g, 34.0 mml) was added dropwise at —55 °C, under nitrogen and vigorous stirring. After additional 2 hours stirring at ambient temperature the precipitate was filtered off, washed with chloroform (3 × 20 ml), and the collected filtrates were washed with 10% sodium bicarbonate, then water. The organic phase was dried, evaporated and the residual mixture of products (1.73 g, yellow oil) was separated on silicagel column (70 g), using chloroform-light petroleum (2 : 1) as eluant. In fractions 10—41 (5 ml pro fraction), 202 mg (8.8%) of crude *6* were obtained, *b.p.* 70—80 °C/25 mm Hg. IR(KBr): 2960, 2930, 2870, 1465, 1445, 1425, 1325, 1290, 1270, 1250, 1205, 1115, 1100, 1070, 1050, 1035, 900, 760, 745, 640 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.26 (s, 1H), 1.6—1.8 (m, 1H), 2.4—2.8 (m, 1H), 3.54 (d, J = 1.8 Hz, 1H), 3.61 (s, 1H), 3.90 (d, J = 1.80 Hz, 1H), 4.0 (t, J = 2.2 Hz, 1H), 4.2—4.35 (m, 2H), 4.53 (q, J = 2.9 Hz, 1H). ^{13}C-NMR ($CDCl_3$): 27.20 (C(5)-t in ORS), 42.95 (C(4)-t in ORS), 56.90 (C(3)-d in ORS), 58.02 (C(2')-d in ORS), 72.70 (C(6)-t in ORS), 75.45 (C(2)-d in ORS). *Anal.* Calc'd for $C_6H_9OCl_3$ (203.50): C 35.41, H 4.46, Cl 52.27%. Found: C 35.43, H 4.52, Cl 51.97%.

Preparation of Diphenylphosphines 7 *and* 8

To the solution of triphenylphosphine (19.1 g, 72.8 mmol) in 25 ml of dry THF, freshly coined, thin lithium plates (1.01 g, 145 mmol) were added, and

allowed to react under vigorous stirring and without cooling for 2 hours. The resulting warm solution (55 °C) was cooled to ambient temperature, then 5.26 g (56.8 mmol) of freshly distilled *tert.* butyl chloride was added. The temperature was raised to *ca* 60 °C, then the pale-red solution was cooled to —50 °C and dimesylate *4* (3.0 g, 10.4 mmol) dissolved in 10 ml of dry DMF was added dropwise over 20 minutes. Stirring under nitrogen atmosphere proceeded for 24 hours, then the reaction mixture was poured in 300 ml of deaerated water. Organic solvents were partially evaporated *in vacuo* and aqueous phase was extracted with ether (3 × 200 ml). Combined organic extracts afforded, after standard work-up procedure, 14.2 g of the crude product mixture, which was purified by chromatography on 150 g of silica gel using light petroleum-chloroform-ether (30 : 10 : 1) as eluant. In fractions 19—30 (10 ml pro fraction) 9.0 g of diphenylphosphine and other oxidation products was separated, in fractions 32—52 1.71 g (58.1%) of *8* was obtained.

(2S)-2-Diphenylphosphinomethyl-pyr-3,4-en (8)*

Pure product *8* was obtained on distillation, *b.p.* 130—140 °C/0.01 mm Hg. IR(KBr): 3080, 3060, 3040, 2960, 2920, 2860, 1590, 1485, 1440, 1375, 1275, 1210, 1185, 1080, 1030, 915, 740, 710 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.75—2.56 (m, 4H), 3.4—3.7 (m, 1H), 3.9—4.2 (m, 2H), 5.78 (s, 2H), 7.2—7.55 (m, 10 H). ^{13}C-NMR ($CDCl_3$): 25.06 (s, C(5)-t, in the off-resonance spectrum (ORS)), 35.27 (d, J = 15.2 Hz, C(2')-2×t in ORS), 62.98 (s, C(6)-t in ORS), 71.53 (d, J = 16.5 Hz, C(2), 2×d in ORS), 124.61 (s, C(4)-d in ORS), 130.34 (d, J = 8.90 Hz, C(3)-2×d in ORS), 128.19 (d, J = 7.0 Hz), 132.20 (d, J = 3.8 Hz), 133.04 (d, J = 3.82 Hz), 138.49 (d, J = 2.54 Hz), 139.08, (d, J = 3.82 Hz). *Anal.* Calc'd $C_{18}H_{19}OP$ (282.32); C 76.58, H 6.78%. Found: C 76.59, H 7.03%.

In fractions 7—110, 0.40 g (8.3%) of *7* was obtained, colourless, densy oil, one spot on TLC, *Rf* 0.22 (chloroform).

(2R,3R)-2-Dihpenylphosphinomethyl-3-diphenylphosphino-tetrahydropyran (7)

Colourless oil, spot at *Rf* 0.22 (chloroform). IR(KBr): 3080, 3060, 2940, 2860, 1585, 1570, 1480, 1435, 1100, 1080, 1070, 1060, 1020, 1000, 740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.43—1.80 (m, 5H), 2.21—2.86 (m, 3H), 3.40—3.82 (m, 2H), 7.09—7.64 (m, 20H). ^{13}C-NMR H($CDCl_3$): 22.48 (d, J = 14.6 Hz, C(5)), 25.40 (d, J = 8.8 Hz, C(4)), 28.03 (t, J = 12.5 Hz, C(2')) 38.56 (q, J_1 = 12.5 Hz, J_2 = 5.12 Hz, C(3)), 61.66 (s, C(6)), 72.11 (q, J_1 = 13.2 Hz, J_2 = 10.2 C(2)), 127.81, 128.16, 128.51, 128.69, 128.98, 131.60, 132.36, 133.18, 133.82, 133.94, 133.76, 135.22, 136.81, 136.39 136.86, 139.02, 139.55.

(2S)-2-Diphenylphosphinomethyl-tetrahydropyran (9)

The solution of *8* (1.71 g, 6.1 mmol) and $[Rh(NBD)_2]ClO_4$ (31.5 mg, 0.08 mmol) in 8 ml of deaerated, abs. benzene-ethanol was submitted to hydrogenation at 5 atm for 24 hours. After evaporation the crude product was isolated by chromatography on 15 g silica gel, using light-petroleum-chloroform-ether (30 : 10 : 1) as eluant. In fractions 4—10 (10 ml pro fraction) 1.24 g (72.1%) of pure *9* was obtained, *b.p.* 160—170 °C/0.9 mm Hg. IR(KBr): 3070, 3060, 2940, 2840, 1585, 1480, 1430, 1375, 1280, 1190, 1180, 1090, 1050, 1025, 908, 895, 740, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.3—1.8 (m, 6H), 2.0—2.5 (m, 2H), 3.3 (m, 2H), 3.9 (m, 1H), 7.2—7.5 (m, 10 H). ^{13}C-NMR ($CDCl_3$): 23.52 (s, C(4)), 25.90 (s, C(5)), 33.30 (d, J = 7.6 Hz C(3)), 36.26 (d, J = 14.0 (C(2')), 68.57 (s, C(6)), 75.68 (d, J = 17.8 Hz, C(2)), 128.33, 128.40, 132.57, 132.99, 138.89, 139.17. *Anal.* Calc'd for $C_{18}H_2OP$ (282.34); C 76.04, H 7.44%. Found: C 75.82, H 7.18%.

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* *Note:* According to CPI-nomenclature descriptor at C(2) changes from *R* to *S*, although absolute configuration remains unaltered!

Rh(Norbornadiene) (2R,3R)-2-diphenylphosphinomethyl-3-diphenylphosphino--tetrahydropyran perchlorate (10)

To the solution of bis-diphenylphosphine 7 (356 mg, 0.76 mmol) in 15 ml of degassed THF, $[Rh(NBD)_2]ClO_4$ (294 mg, 0.76 mmol) was added under stirring. The reaction mixture was stirred at ambient temperature for 1 hour, over which period a yellow-brown precipitate was separated. Then, 40 ml of degassed *n*-hexane was added, and stirring was continued at 0 °C for an additional hour. The precipitate was collected on filter, washed with cold *n*-hexane (3 × 100 ml), and the crude product (0.55 g, 94.9%) was crystallized from chloroform-ether (*ca.* 2 : 1), affording red crystals, *m.p.*, decc. above 180 °C. IR(KBr): 3060, 3020, 2960, 2920, 2870, 1585, 1570, 1480, 1460, 1435, 1410, 1360, 1310, 1270, 1220, 1190, 1090, 1035, 1020, 995, 970, 930, 900, 875, 850, 830, 795, 740, 690, 620 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.5—1.7 (m, CH_2 in NBD), 1.7—1.9 (m, 4H), 2.2—2.9 (m, 2H), 3.3—3.8 (m, 4H), 3.8—3.9 (m, 2x CH in NBD), 4.0—4.2 (m, —CH=CH— in NBD), 4.65—5.2 (m, —CH=CH— in NBD), 7.12—7.9 (m, 20 H, 4xphenyl). ^{13}C NMR ($CDCl_3$): 20.28 (s, C(5)), 24.68 (q, J_1 = 25.6 Hz, J_2 = 4.9 Hz, C(4)), 26.02 (d, J = 7.3 Hz, C(2')), 37.23 (d, J = 20.7 Hz, C(3)), 60.85 (s, C(6)), 70.82 t, J_1 = 10.13 Hz, J_2 = 8.25 Hz, C(2)), 53.99 (2x CH, in NBD), 69.95 (CH_2 in NBD), 87.36 (2x CH=CH in NBD), 127.92; 128.21; 128.41; 128.75; 129.09; 129.48; 129.77; 129.87; 130.40; 130.79; 131.52; 132.84; 132.98; 133.27; 133.42; 133.66; 134.15. *Anal.* Calc'd for $C_{37}H_{38}O_5P_2ClRh \times 1/2\ CHCl_3$ (322.704): Calc'd: C 54.75, H 4.72%; Found: C 55.05, H 4.58%.

Attempt at Preparation of Rh(norbornadiene) (2S)-2-Diphenylphosphino-methyl Tetrahydropyran Perchlorate (11)

Starting from 300 mg (1.1 mmol) of monophosphine *9* and 410 mg (1.1 mmol) of $[Rh(NBD)_2]ClO_4$, preparation was performed as described for *10*. The product mixture (630 mg, 103% calc'd. on *11*), had *m.p.* 216—218 °C (decc.). The following spectroscopic and analytical data indicated *ca. 1 : 1* mixture of *11* and *12*. IR(KBr): 2970, 2950, 2890, 1580, 1490, 1440, 1385, 1320, 1185, 1150, 1100, 1035, 1005, 905, 760, 750, 700, 630 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.8 (m, NBD). 1.85 (m, THF), 1.2—2.5 (m, protons in tetrahydropyran ring), 3.1—3.2 (m, protons in tetrahydropyran ring), 3.74 (m, THF), 3.8—4.3 (m, protons in tetrahydropyran ring), 4.45 (m, NBD), 5.20 (m, NBD), 7.2—7.9 (m, 2x phenyl). ^{13}C-NMR ($CDCl_3$): 22.63 C(4), 25.62 (C(5) and C(2) C(2') of THF), 32.85, 33.46 (C(3) in two species *11, 12*), 39.90 C(2'), 52.48 (CH_2 of NBD), 64.79 (CH of NBD), 67.95 (C(6) and C(1), C(1') of THF), 74.44, 75.34 (C(2) in two species *11, 12*) 85.27, 85.55 (2x CH=CH in NBD), 127.32, 128.67, 129.12, 129.29, 129.57, 129.80, 130.82, 131.27, 131.43, 131.95, 132.51, 133.41, 133.81, 133.98, 134.20, 134.60, 134.82. *Anal.* for *11*: $C_{25}H_{29}O_5PClRh$ (578.83). Calc'd C 51.88, H 5.05%. *Anal.* for *12* $C_{30}H_{45}O_8PClRh$ (763.01). Calc'd: C 51.26, H 6.45%. Found (two determinations) C 51.97, 52,42%, H 6.34, 6.06%.

Hydrogenation Experiments

To a 25 ml probe tube, joined to a three-way glass stopock, and thus alternatively connected to a respiratory pump or nitrogen source, solvent (8 ml) was placed, and dearated by alternative evacuation and flushing with nitrogen. Then, the catalyst (0.1 mmol) was added, and the yelloworange-solution was stirred for 30 minutes under nitrogen. Subsequently, diethylamine (0.015 mmol) and *Z-α-N*-acetylaminocinnamic acid were added, and the resulting mixture was stirred and repeatedly spilled with hydrogen. The probe tube was then placed into Parr-hydrogenation bomb (40 ml), and hydrogen controled at working pressure. The work-up of the reaction mixture, ^{1}H-NMR control of the conversion, and determination of e.e. (%) were performed as described.[10] The results are summed up in the Table II.

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SAŽETAK

Priprava kiralnih difenilfosfina iz D-glukoze i enantioselektivna hidrogenacija s njihovim Rh(I) kompleksima

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(*2R,3S*)-2-Metilsulfoniloksimetil-3-metilsulfoniloksi-tetrahidropiran (*4*), izveden od D-glukoze, difenilfosfoniran je u (*2R,3R*)-2-difenilfosfinometil-*3*-difenilfosfino-tetrahidropiran (*7*), koji je nastao kao sporedni produkt, dok je pretežno nastao spoj *8* kao rezultat C(3), C(4)-eliminacije i monofosfinacije na C(2'). Opisana je priprava i karakterizacija rodij(I)-kompleksa *10—12*. Kompleks *10*, izveden od bidentatnog liganda *7*, pokazao je u hidrogenaciji Z-α-acetamidocimetne kiseline enantioselektivnost usporedivu s onom dobivenom za kompleks (—)-DIOPa (~70% e. v.). Zasićeni monofosfin (*2S*)-2-difenilfosfinilmetil-tetrahidropiran (*9*) dao je nejedinstven rodij(I)-kompleks (*11, 12*), koji je pokazao nisku enantioselektivnost.