



JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc., 1996, 118(26), 6325-6326, DOI:[10.1021/ja9609112](https://doi.org/10.1021/ja9609112)

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1996 American Chemical Society

SUPPLEMENTARY MATERIAL

Role of Electronic Asymmetry in the Design of New Ligands: The Asymmetric Hydrocyanation Reaction

T. V. RajanBabu,* Albert L. Casalnuovo*

(Contribution from the Department of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, OH 43210, and Central Research and Development, Experimental Station, The DuPont Company, Wilmington, DE 19880)

General methods. Details of the hydrocyanation protocols and analytical methods have been described before.¹

Synthesis of Fructose-Derived Ligands.

Methyl 1,6-O-bis-(triphenylmethyl)- α and β -D-fructofuranosides. (3a and 3b) These compounds were prepared by tritylation of a mixture of methyl α and β -fructofuranosides with trityl chloride in pyridine at 50 °C and separating the α and β -isomers by column chromatography on silica gel using 10 - 30 % ethyl acetate in hexane as eluant. The faster moving isomer was assigned the α - anomeric structure **3a**. The α -anomer: mp 92-93 °C; ¹H NMR 3.05 (s, 3 H), 3.07 (d, J = 10 , 1 H), 3.24, 3.48 (ABX dq, J = 10, 2 H), 3.34, 3.50 (AB J = 10 , 2 H), 3.57 (d, J = 10 Hz, 1 H), 3.87 (d, br, J = 11, 1 H) 4.05 (m, 1 H), 4.19 (d, J = 10, 1 H), 7.20 - 7.60 (m, aromatic); Anal. C 78.85 ; H 6.37. Calcd C 79.62; H 6.24 The β -anomer (**3b**): mp 195-199 °C; 2.15 (d, J= 4, 1 H, exch with D₂O), 2.65 (d, br, J = 8, exch with D₂O, 1 H), 3.05 (s, 3 H), 3.07 - 3.27 (m, 4 H), 3.97 (m, 1 H), 4.17 - 4.22 (m, 2 H), 7.20 - 7.55 (m, aromatic); Anal. C 78.85; H 6.36. Calcd C 79.62; H 6.24.

The stereochemistry of the two fructosides were established by converting them to the know² methyl 3,4-anhydro-derivatives by Mitsunobu reaction and studying the ¹³C NMR spectrum. For the α -anomer the methoxy signal consistently has the lower chemical shift. In the case of the triphenylmethyl fructofuranosides, the α -methoxy carbon appears at δ 49.20 and the β -derivative at 52.30 (CDCl₃).

Methyl 1,6-O-bis-(triphenylmethyl)-3,4-O-bis-(diphenylphosphino)- α -D-fructofuranoside (5a). ¹H NMR (C₆D₆) 3.10 (s, 3 H), 3.35, 3.45 (ABX, J = 10, 7, 6, 2 H), 3.60, 3.78 (AB, J = 10, 2 H), 4.50 (ddm, br, 1 H), 4.88 (m, 1 H), 5.00 (d, J = 10, 1 H), 6.80 - 7.80 (m, aromatic); ³¹P NMR (C₆D₆) 114.2, 115.1 (AB J = 9).

Methyl 1,6-O-bis-(triphenylmethyl)-3,4-O-bis-di[bis-(3,5-trifluoromethylphenyl)phosphino]- α -D-fructofuranoside. (5b) This compound was prepared by the standard procedure and was purified by column chromatography using 5 % ether/hexane on silica gel. ^1H NMR (C_6D_6) 3.10 (s, 3 H), 3.30 - 3.46 (m, 4 H), 4.20 (q, J = 6), 4.90 (dd, J = 10, 3, 1 H), 5.05 (m, 1 H), 6.90 -7.90 (m, aromatic); ^{31}P NMR (C_6D_6) 106.4, 115.1

Methyl 1,6-O-bis-(triphenylmethyl)-3,4-O-bis-di[bis-(3,5-trifluoromethylphenyl)phosphino]- β -D-fructofuranoside. ^1H NMR (C_6D_6) 2.80 (d, J = 8 Hz, 1 H), 3.04 (s, 3 H), 3.25, 3.30 (ABX, J = 12, 4, 2 H), 3.75 (d, J = 10, 1 H), 4.55 (m, 1 H), 5.41 (q, J = 8, 1 H), 5.60 (t, J = 9, 1 H), 6.60 -8.00 (m, aromatic); ^{31}P NMR (C_6D_6) 107.8, 109.3.

Methyl 1,6-O-(bis-triphenylmethyl)-3,4-O-bis-di[(3,5-dimethylphenyl)phosphino]- α -D-fructofuranoside. (5h) ^1H NMR (C_6D_6) 1.85, 1.91, 1.94, 2.05 (4 s, 3 H each), 3.10 (s, 3 H), 3.45 - 3.60 (ABX, J = 9, 5, 5, 2 H), 3.67, 3.80 (AB J = 10, 2 H), 4.47 (qm, br, 1 H), 5.12 (d, J = 11, 1 H), 5.20 (m, 1 H), 6.50 - 7.80 (m, aromatic); ^{31}P NMR (C_6D_6), 116.41 (d, J_{pp} = 8, 1 P), 118.53 (d, J_{pp} = 8, 1 P).

Methyl 1,6-O-(bis-triphenylmethyl)-3,4-O-bis-di[(3,5-difluorophenyl)phosphino]- α -D-fructofuranoside. (5j) ^1H NMR (C_6D_6) 3.10 (s, 3 H), 3.30, 3.40 (ABX, qd, J = 10, 4, 4, 2 H), 3.40, 3.61 (AB q, J = 9, 2 H), 4.28 (ddd, 5, 5, 5, 1 H), 4.68 (m, br, 1 H), 4.81 (qd, br, J = 10, 1 H), 6.15 - 7.60 (m, aromatic); ^{31}P (C_6D_6) 112.10, (J_{PP} = 6, 1 P), 107.95 (d, J_{PP} = 6, 1 P)

Methyl 1,6-O-bis-(triphenylmethyl)-4-O-[bis-3,5-difluoro-phenylphosphino]- α -D-fructofuranoside (4c) ^1H NMR (C_6D_6) 3.00 (d, J = 6 Hz, 1 H), 3.10 (s, 3 H), 3.28, 3.45 (ABX, J = 11, 5, 4, 2 H), 3.55 (AB, J = 10, 2 H), 4.18 (ddd, J = 5, 5, 5, 1 H), 4.50 (ddd, J = 9, 5, 2, 1 H), 4.61 (d br, J = 6, 1 H), 6.25 (2 H), 6.70 - 7.60 (m, aromatic); ^{31}P NMR 106.2.

Methyl 1,6-O-bis-(triphenylmethyl)-4-O-[bis-3,5-difluoro-phenylphosphino]-3-O-diphenylphosphino- α -D-fructofuranoside (5l) ^1H NMR(C_6D_6) 3.08 (s, 3 H), 3.35, 3.45 (ABX, J = 10, 6, 6, 2 H), 3.61, 3.75 (AB, J = 10, 2 H), 4.35 (q, br, J = 4 Hz, 1 H), 4.75 (m, 1 H), 4.90 (d, J = 10, 1 H), 6.27 (m, 2 H), 6.70- 7.70 (m, aromatic).; ^{31}P NMR (C_6D_6) 106.1, 115.5.

Methyl 1,6-O-bis-(triphenylmethyl)-3-O-bis-(3,5-di-trifluoromethylphenyl)phosphino]-4-O-bis(3,5-difluorophenylphosphino)- α -D-fructofuranoside. (5m)

^1H NMR (C_6D_6) 3.05 (s, 3 H), 3.15, 3.30 (AB, $J = 9$, 2 H), 3.35 (d, br, 2 H), 4.15 (q, br, 1 H), 4.75 - 4.95 (m, 2 H), 6.10 (m, 2 H), 6.50- 7.80 (m. aromatic); ^{31}P NMR (C_6D_6) 109.8 (1 P), 115.3 (d, $J_{\text{PP}} = 5$, 1 P). The only contaminant in this sample is ~ 8 % of the symmetrical bis- CF_3 -phenylphosphinite, presumably formed by an exchange reaction during step 2. This was identified by the ^{31}P NMR peaks at δ 105.4 and 113.9.

Methyl 1,6-O-bis-(triphenylmethyl)-3-O-(3,5-di-fluorophenyl)phosphino]-4-O-(diphenylphosphino)- α -D-fructofuranoside. (5k)

^1H NMR(C_6D_6) 3.15(s, 3 H), 3.40(ABX, 2 H), 3.45, 3.66(AB, $J = 10$, 2 H), 4.45(q, br, $J = 5$, 1 H), 4.80 (m, br, 1 H), 4.93(dd, $J = 10$, 2, 1 H), 6.20- 7.70 (aromatic). An additional methyl signal at δ 3.12(ca. 20 %) indicates the presence of symmetrical diphosphinite. Other corresponding signals were also observed. See also the ^{31}P spectrum reported below. ^{31}P NMR (C_6D_6) 110.4 (s, 1 P), 115.3 (d, $J = 9$, 1 P). Also present two peaks (δ 108.0 and 112.1, ca. 20 % of the signal from the major component) corresponding to the symmetric 3,4-diphosphinite formed by exchange with the slight excess of the bis-(3,5-difluorophenyl)chlorophosphine used in the second step.

Methyl 1,6-O-bis-(triphenylmethyl)-3,4-O-bis[di-(4-methoxyphenyl)phosphino]- α -D-fructofuranoside. (5e) ^1H NMR (C_6D_6) 3.05 - 3.30 (4 s 15 H), 3.40, 3.50 (ABX, $J = 10$, 7, 6, 2 H), 3.61, 3.79 (AB, $J = 10$, 2 H), 4.58 (ddm, br, 1 H), 4.90 (m, 1 H), 5.05 (d, $J = 10$, 1 H), 6.42 - 7.61 (m, aromatic); ^{31}P NMR (C_6D_6) 115.0, 115.2 (AB, $J = 7$).

Methyl 1,6-O-bis-(triphenylmethyl)-4-O-[diphenylphosphino]- α -D-fructofuranoside (4a) and Methyl 1,6-O-bis-(triphenylmethyl)-3-O-[diphenylphosphino]- α -D-fructofuranoside.

In a nitrogen-filled dry box, 136 mg (0.2 mmol) of the diol and 3 mg of 4-DMAP were dissolved in 1 mL of CH_2Cl_2 and 1 mL of pyridine. In another vial 47 mg (0.21 mmol) of chlorodiphenylphosphine was dissolved in 1 mL of CH_2Cl_2 . Both vials were chilled to -10°C and the chlorophosphine solution was slowly added to the sugar solution at -10°C . Additional 1 mL of CH_2Cl_2 was used to facilitate quantitative transfer of the chlorophosphine. The reaction was warmed to room temperature and stirred overnight. The solvents and other low boilers were pumped off and a tlc (10 % ether/hexane) and NMR were run. The product was identified as a mixture of three phosphinites formed in a ratio of 23:70:7. In elution order they were: (1) 3,4-diphosphinite, (5a) 23 % (2) the 4-monophosphinite, (4a) 70 % (3) the 3-monophosphinite, 7 %. The relative amounts were determined by ^{31}P signal intensity. The compound 5a was identified by comparison of spectral properties with those of an authentic

sample prepared using 2 equivalents of the chlorophosphine. **4a**: ^1H NMR (C_6D_6) 2.80 (d, $J = 6$ Hz, 1 H), 3.12 (s, 3 H), 3.35, 3.50 (ABX, $J = 11, 5, 2, 2$ H), 3.50, 3.60 (AB, $J = 10, 2$ H), 4.40 (ddd, $J = 5, 5, 5, 1$ H), 4.64 (dddd, $J = 6, 5, 2, 1$ H), 4.75 (dd, $J = 6, 2, 1$ H), 6.80 - 7.80 (m, aromatic); ^{31}P NMR 114.6.

Methyl 1,6-O-bis-(triphenylmethyl)-3-O-[diphenylphosphino]- α -D-fructofuranoside: ^1H NMR (C_6D_6) 2.82 (s, 3 H), 2.95 (d, $J = 12, 1$ H), 3.08 (dd, $J = 8, 5, 1$ H), 3.60 (dd, $J = 8, 8, 1$ H), 3.68 (AB, $J = 11, 2$ H), 4.00 (d, br $J = 12, 1$ H), 4.38 (m, 1 H), 4.77 (dd $J = 12, 1, 1$ H), 6.80 - 7.8 (m, aromatic); ^{31}P NMR 115.5.

Methyl 1,6-bis-O-(triphenylmethyl)-3-O-[bis-(3,5-di-trifluoromethylphenyl)phosphino]-4-O-(diphenylphosphino)- α -D-fructofuranoside. (5c) To 31 mg (0.036 mmol) of the **4a** dissolved in 0.60 mL of CH_2Cl_2 and 0.30 mL of pyridine was added 1 mg of 4-DMAP. To this solution was added, at room temperature, 26 mg (0.40 mmol) of chloro-di-(bis-3,5-trifluoromethylphenyl)phosphine dissolved in CH_2Cl_2 . The reaction mixture was stirred overnight and the low-boiling components were removed on the vacuum pump. The expected diphosphinite (**5c**, 10 mg) was isolated by column chromatography on silica gel inside the box using 3 % ether/hexane. ^1H NMR (C_6D_6) 3.10 (s, 3 H); 3.30, 3.41 (AB, $J = 10, 2$ H), 3.48 (ABX, $J = 9, 4, 4, 2$ H), 4.45 (m, 1 H), 5.00 (m, 2 H), 6.80 - 7.80 (m, aromatic); ^{31}P NMR 114.49 (d, $J_{\text{pp}} = 5, 1$ P), 117.83 (d, $J_{\text{pp}} = 5, 1$ P).

Methyl 1,6-bis-O-(triphenylmethyl)-3-O-(diphenylphosphino)-4-O-[bis-(3,5-di-trifluoromethylphenyl)phosphino]- α -D-fructofuranoside. (5d). Methyl 3-O-diphenylphosphino- α -D-fructofuranoside was reacted with chloro-di-(bis-3,5-trifluoromethylphenyl)phosphine as outlined in the previous experiment to produce the title compound. Recorded below is an alternate synthesis and characterization of this compound starting from the 4-O-[bis-(3,5-di-trifluoromethylphenyl)phosphino] compound **4b**.

Methyl 1,6-O-(triphenylmethyl)-4-O-[di-(3,5-bis-trifluoromethylphenyl)phosphino]- α -D-fructofuranoside (4b). To 0.240 g (0.30 mmol) of the diol **3a** and 3 mg of 4-DMAP dissolved in 1 mL of pyridine and 1 mL of methylene chloride was added bis(3,5-di-trifluoromethylphenyl)chlorophosphine (0.163g, 0.33 mmol) in 1 mL of methylene chloride at ~ -10 °C in side a dry box. The reaction was maintained at -20 °C for 6 h and was subsequently brought to room temperature and stirring was continued for 16 h. The low-boiling components were pumped off using a high vacuum and the residue was dissolved in 2

mL of benzene. The precipitated salts were filtered off with the aid of a disposable pipette with a cotton plug at the bottom. The pure product (**4b**, 0.240 g, 71 %) was isolated by column chromatography inside the box using a short column (8" X 1 ") of silica using 10-15 % ether hexane as the eluant. ^{31}P NMR (CDCl_3) 104.8. A minor peak (<4 %) at 110.2 was also noticed. The major product (**4b**) was used for the preparation of the unsymmetrical vicinal phosphinites as described below.

Methyl 1,6-bis-O-(triphenylmethyl)-3-O-(diphenylphosphino)-4-O-[bis-(3,5-difluoromethylphenyl)phosphino]- α -D-fructofuranoside (5d). The procedure reported in the previous experiment was repeated with **4b** and chlorodiphenylphosphine as the starting materials. The product was purified by column chromatography on silica gel inside the dry box using 10 % ether / hexane as the solvent. ^1H NMR(C_6D_6) 3.10 (s, 3 H), 3.32, 3.49 (ABX, J = 10, 6, 6, 2 H), 3.62, 3.75 (AB, J = 10, 2 H), 4.39 (m, br, 1 H), 4.80 (d m, J = 10, 1 H), 4.82 (d m, J = 10, 1 H), 6.56 - 7.90 (m, aromatic); ^{31}P NMR 103.74 (d, J = 8, 1 P), 116.51 (d, J = 8, 1 P).

The following compounds were prepared using the same procedure. All compounds were purified by column chromatography on silica gel inside the dry box using ether / hexanes as the solvent. As judged by proton NMR, the estimated purity of these compounds were > 95 %. Only ^{31}P signals observed (δ 200 to -100) were due to the expected products.

Methyl 1,6-O-bis-(triphenylmethyl)-3-O-bis(di-3,5-dimethylphenylphosphino)-4-O-[bis-(3,5-difluoromethylphenyl)phosphino]- α -D-fructofuranoside (5i). ^1H NMR (C_6D_6) 1.84 (s, 6 H), 1.90 (s, 6 H), 3.03 (s, 3 H), 3.41, 3.50 (ABX, J = 10, 6, 6, 2 H), 3.74 (AB, J = 10, 2 H), 4.22 (m br, 1 H), 4.90 (d, J = 11, 1 H), 5.14 (dd, br, J = 10, 4, 1 H), 6.60- 7.95 (m, aromatic); ^{31}P NMR 104.12 (d, J = 8, 1 P), 120.03 (d, J = 8, 1 P).

Methyl 1,6-O-bis-(triphenylmethyl)-3-O-bis(4-fluorophenylphosphino)-4-O-[bis-(3,5-difluoromethylphenyl)phosphino]- α -D-fructofuranoside (5g) ^1H NMR (C_6D_6) 3.10 (s, 3 H), 3.25, 3.46 (ABX, J = 10, 6, 6, 2 H), 3.49, 3.70 (AB, J = 10, 2 H), 4.40 (m br, 1 H), 4.72 (d m, J = 9, 1 H), 4.77 (d, J = 10, 1 H), 6.50 - 7.95 (m, aromatic); ^{31}P NMR 104.15 (d, J = 8, 1 P), 114.06 (t, J = 3, 1P).

Methyl 1,6-O-bis-(triphenylmethyl)-3-O-di(4-methoxyphenyl)phosphino-4-O-bis-[(3,5-difluoromethylphenyl)phosphino]- α -D-fructofuranoside (5f) ^1H NMR (C_6D_6) 3.10 (s, 3 H), 3.18 (s, 3 H), 3.20 (s, 3 H), 3.30, 3.51 (ABX, J = 10, 6, 5, 2 H), 3.52, 3.63 (AB, J = 10, 2 H), 4.41 (m, br, 1 H), 4.81 (d m, J = 10, 1 H), 4.88 (d, J = 10, 1 H), 6.50- 8.00 (m, aromatic); ^{31}P NMR 103.15 (d, J = 9, 1 P), 116.58 (d, J = 9, 1 P).

Methyl 1,6-O-bis-(triphenylmethyl)-3-O-bis(3,5-di-fluorophenylphosphino)-4-O-[bis-(3,5-di-trifluoromethylphenyl)phosphino]- α -D-fructofuranoside. (5n) ^1H NMR (C_6D_6) 3.15 (s, 1 H), 3.28, 3.45 (ABX, dq, $J_{\text{AB}} = 10$, $J_{\text{AX}} = J_{\text{BX}} = 6$, 2 H), 3.35, 3.65 (ABq, $J_{\text{AB}} = 10$, 2 H), 4.31 (q, br, $J = 4$, 1 H), 4.75 (dd, br, $J = 8$, 4, 1 H), 4.80 (d, $J = 12$, 1 H), 6.25 (m, 2 H), 6.52 (m, 2 H), 6.75 (m, 2 H), 6.85 - 7.15 (m, aromatic), 7.35 - 7.60 (m, aromatic), 7.78 (d, $J = 7$, 2 H), 7.93 (d, $J = 7$, 2 H); ^{31}P NMR (C_6D_6) 104.9 (d, $J = 5$, 1 P), 112.8 (d, $J = 5$, 1 P).

Tartranil [(2R,3R)-N-phenyltartramide, ($\text{C}_6\text{H}_5\text{N}(\text{C}(=\text{O})\text{CHOH})_2$)]. (6) Tartranil was prepared by an adaptation of the method of Barrow and Atkinso³. Aniline (18.60 g, 0.200 mol) was added dropwise to a refluxing slurry of L-(2R,3R)-tartaric acid (30.00 g, 0.200 mol) in 300 mL of THF. After 45 minutes, the slurry was cooled to room temperature and stirred for an additional 48 h. The resulting white solids were filtered and dried in vacuo. Yield 42 g.

5.01 g of this solid was heated at 150°C in the solid state. After 8 h, the resulting yellow solids were slurried in methanol and filtered (50 mL, 3x). Concentration of the methanol filtrate afforded 0.848 g of off-yellow solids after 18 h. ^1H NMR analysis of this material (CD_3OD) showed a 96:4 mixture of tartranil and the dianilide ($\text{C}_6\text{H}_5\text{NHC}(=\text{O})\text{CHOH})_2$. Further concentration of the methanol filtrate afforded an additional 0.380 g of tartranil. ^1H (DMF- d_7): 4.66 (d, $J = 4$, 2H), 6.48 (s, br, 2H), 7.2-7.5 (m, 5H).

(2R,3R)-2,3-O-bis(diphenylphosphino)-N-phenyltartramide, (8a).⁴ A solution of diphenylchlorophosphine (0.551 g, 2.50 mmol) in 5 mL of Et_2O was added dropwise to a solution of tartranil (0.207 g, 1.00 mmol) and triethylamine (0.252 g, 2.50 mmol) in 10 mL of DMF at -50°C. The solution was warmed to -15°C, stirred for 1 h, and then concentrated to dryness in vacuo (< 1 millitorr) at room temperature. The residue was slurried in benzene and filtered. The resulting white solids were dissolved in THF and filtered to remove $[\text{Et}_3\text{NH}]\text{Cl}$. Concentration of the filtrate in vacuo gave 0.420 g (73%) of a white solid. ^1H (THF- d_8): 5.24 (m, 2H), 7.1-7.6 (m, 25H). ^{31}P (THF- d_8): 125.3 (s).

(2R,3R)-2,3-O-bis(di(3,5-bis-trifluoromethylphenyl)phosphino)-N-phenyltartramide, (8b). This compound was prepared as described for 8a using 0.031 g of tartranil (0.15 mmol), 0.038 g of triethylamine (0.375 mmol) and 0.185 g of di(3,5-bistrifluoromethylphenyl)chlorophosphine (0.375 mmol). After the reaction mixture was concentrated under high vacuum, the residue was slurried with 5 mL of hexane. The hexane mother liquor was decanted from the insoluble residues and concentrated to about 1 mL in vacuo. After 18 h, white crystals (0.070 g, 42%)

precipitated from the solution. $^1\text{H}(\text{C}_6\text{D}_6)$: 3.93 (m, 2H), 6.8-7.1 (m, 3H), 7.40 (m, 2H), 7.49 (s, 2H), 7.56 (s, 2H), 7.66 (dd, $J = 1.0, 6.4$, 4H), 7.99 (d, 6.6 Hz, 4H). $^{31}\text{P}(\text{C}_6\text{D}_6)$: 118.9 (s).

(2*R*,3*R*)-2-*O*-diphenylphosphino-*N*-phenyltartramide, (**7a**). A solution of diphenylchlorophosphine (0.242 g, 1.1 mmol) in 4 mL of Et₂O was added dropwise to a solution of tartranil (0.207 g, 1.00 mmol) and triethylamine (0.151 g, 1.5 mmol) in 10 mL of DMF as described for **8a**. After the reaction mixture was concentrated under high vacuum, the residue was slurried with 3 mL of benzene and then filtered. The filtrate was concentrated to dryness in vacuo. ^1H NMR analysis showed that the benzene insoluble solids (0.273 g) contained **8a** as the major compound whereas the filtrate contained most of the monosubstituted compound **7a**. Flash chromatography of the filtrate residue (hexane (68.5%)/ethyl acetate (29%)/THF (2.5%)) on silica gel gave 0.014 g (4%) of **7a**. $^1\text{H}(\text{THF-d}_8)$: 4.71 (m, 1H), 4.96 (m, 1H), 5.74 (s (br), 1H), 7.1-7.6 (m, 15H). $^{31}\text{P}(\text{THF-d}_8)$: 125.0 (s).

(2*R*,3*R*)-2-*O*-di(3,5-bis-trifluoromethylphenyl)phosphino-3-*O*-diphenylphosphino-*N*-phenyltartramide, **8c**. A solution of di(3,5-bis-trifluoromethylphenyl)chlorophosphine (0.020 g, 0.041 mmol) in 2 mL of Et₂O was added dropwise to solution of **7a** (0.014 g, 0.036 mmol) and triethylamine (0.005 g, 0.050 mmol) in 2 mL of DMF at -10°C . The reaction mixture was warmed to room temperature for 5 minutes and then stored at -10°C . After 18 h, the reaction mixture was concentrated to dryness in vacuo. Flash chromatography of the residue on silica gel (90/10 hexane/ethyl acetate) gave 0.013 g (43%) of **8c** (about 95% pure by ^{31}P NMR). $^1\text{H}(\text{C}_6\text{D}_6)$: 4.27 (m, 2H), 6.8-7.1 (m, 4H), 7.2-7.4 (m, 9H) 7.55 (m, 2H), 7.63 (m, 2H), 7.78 (d, $J = 6.6$, 2H), 8.00 (d, 6.5, 2H). $^{31}\text{P}(\text{C}_6\text{D}_6)$: 117.4 (s, 1P), 128.3 (s, 1P).

REFERENCES

- (1) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. *J. Am. Chem. Soc.* **1994**, 116, 9869.
- (2) (a) Guthrie, R. D.; Jenkins, I. D.; Yamasaki, R. *J. Chem. Soc., Perkin Trans. I*, **1981**, 2328. (b) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.*, **1994**, 116, 986.
- (3) Barrow, F.; Atkinson, R. G. *J. Chem. Soc.*, **1939**, 638.
- (4) Bourson, J.; Laureano, O. *J. Organomet. Chem.*, **1982**, 229, 77.