Pergamon

Tetrahedron Vol. 51, No. 28, pp. 7655-7666, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00390-8

An Efficient Procedure for the Synthesis of C-Chiral Bisphosphines.

Lydia McKinstry and Tom Livinghouse*[1]

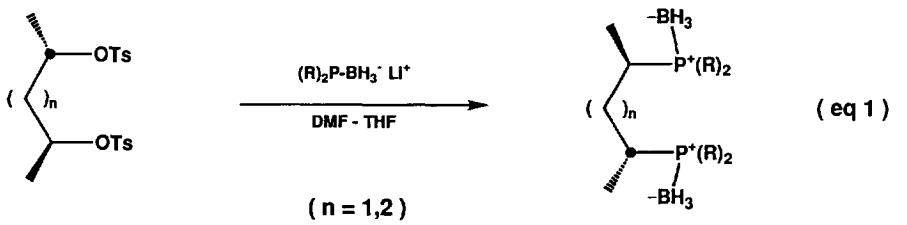
Department of Chemistry and Biochemistry
Montana State University
Bozeman, MT 59717
U.S.A.

Abstract: A practical method for the synthesis of bisphosphines containing homochiral carbon backbones is described. This procedure entails sequential reaction of a homochiral ditosylate with the appropriate dialkyl- or diarylphosphine-borane anion followed by BH_3 decomplexation mediated by $HBF_4{\cdot}OMe_2$.

Homochiral phosphines that form stereodifferentiated chelate complexes with transition metals have become indispensable tools for asymmetric catalysis.[2] At the present time there is a noteworthy deficiency of *general* methods for the enantioselective synthesis of P-chiral phosphines.[3] In consequence, the largest existing family of phosphines that have been developed for asymmetric catalysis comprises molecules in which steric differentiation at phosphorus is imparted by homochiral carbon backbones.[4] The most commonly utilized procedure for the synthesis of many of these phosphines involves the alkylation of *strongly basic* diaryl or dialkyl metallophosphides with the appropriate homochiral disulfonate.[5] Unfortunately, this method is not always reliable in that diminished yields of the desired substitution product can result as a consequence of competing side reactions such as base mediated elimination, electron transfer processes, etc. Intervening reactions of this variety are particularly problematic when very basic metallo derivatives of sterically hindered *dialkyl* phosphines are used as nucleophiles. For these species, efficient carbon-phosphorus bond formation is most effectively achieved by using a homochiral *difluoride* as the substrate.[6,7]

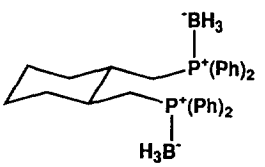
Over the past few years, Imamoto and co-workers have published a series of important papers on the synthetic utility of phosphine-borane complexes.[8] The nucleophilic but *mildly basic* anions derived from secondary phosphine-boranes have been shown to undergo alkylation, 1,4-addition and Pd(0) catalyzed cross-coupling reactions with a wide variety of common substrates.[8] It is therefore surprising that the potential utility of these complexes for the synthesis of bisphosphines containing homochiral carbon backbones has been largely overlooked.[9] We have previously communicated a versatile method for the synthesis of C-chiral bisphosphines that relies on the alkylation of phosphine-borane anions with homochiral ditosylates.[10] Herein we provide a more detailed account of this method.

The general procedure that was routinely employed for the synthesis of C-chiral bisphosphine-borane intermediates involves the deprotonation of the requisite monophosphine-borane adduct[8b] using "*alkoxide free*" *n*-BuLi[11] (THF, -78 °C) followed by the addition of a DMF solution of the homochiral ditosylate of interest (-40 °C). Typically, the reaction mixture is then stirred under argon at ambient temperature until bis-alkylation has been achieved (Scheme 1).[12,13] A series of bisphosphine-borane complexes that have been synthesized in this manner is shown in Table I. The preparative generality of the above procedure can be inferred from the high yields obtained for the α,α′-branched cyclohexyl bearing bisphosphine-boranes **2d** and **2c** as well as for the sterically congested bis(diarylphosphine-borane) analog **2f**.

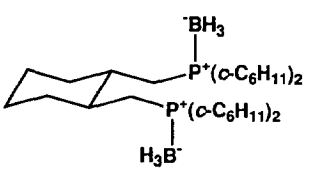


1 **2**

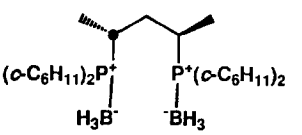
Table I. Synthesis of Representative Bisphosphine-boranes via Nucleophilic Displacement with Phosphine-borane Anions.



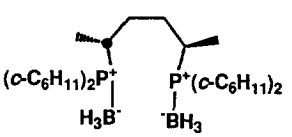
2a (93 %)



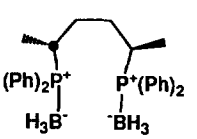
2b (89 %)



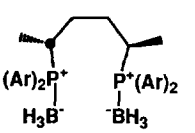
2c (91 %)



2d (86 %)



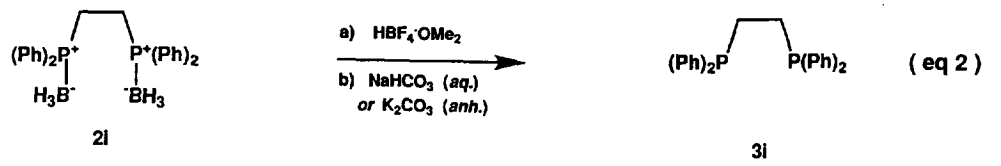
2e (88 %)



2f (82 %)

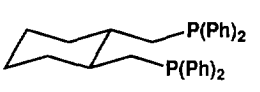
[Ar = 2-CH_3-4-(CH_3O)C_6H_3]

The reported procedures for converting phosphine-boranes to the corresponding free phosphines involve heating the parent complexes with a *large excess* of a secondary amine (e.g., morpholine or diethyl amine)[8b] or DABCO.[9b] Although **2e** could be converted to bisphosphine **3e** by either of the published procedures, the bisborane complexes **2b**, **2c** and **2d** proved remarkably resistant toward amine mediated BH_3 exchange. Even at elevated temperatures (e.g., 100 °C), these complexes were incompletely converted (~70-80%) to the corresponding bisphosphines. An examination of other borane adducts of hindered, electron rich phosphines further indicated that BH_3 decomplexation by amine exchange can be an inefficient process. Presumably, the enhanced strength of the P-B bond in borane complexes of *electron rich* phosphines is responsible for the observed lethargy of **2b**, **2c**, **2d** and other hindered BH_3 adducts toward aminolysis. In light of this apparent limitation, we set out to develop an alternative and *complementary* method for phosphine-borane decomplexation.[14] Imamoto has reported that representative sulfonic acids react with phosphine-boranes in aprotic media to provide the corresponding borane sulfonate derivatives.[8a] In a preliminary study to determine if this type of reaction could serve as a basis for phosphine deprotection, DPPE•$(BH_3)_2$ (**2i**) was treated with a variety of acids (i.e., CH_3SO_3H, CF_3SO_3H, HBF_4•OMe_2, etc., CH_2Cl_2, -5 °C → 25 °C) and subsequently hydrolyzed [$NaHCO_3$ *aq.*, 0 °C (10 min under Ar) *or* K_2CO_3 *anh.*, 25 °C (6.5 h under Ar)]. A rough measure of the efficiency of decomplexation was obtained by TLC analyses of reaction aliquots. This procedure readily revealed the stepwise conversion of **2i** to DPPE (**3i**) (**Scheme 2**).[15] Of the various acids that were examined, commercial HBF_4•OMe_2 proved the most efficacious in terms of rate as well as isolated yield of free phosphine.[16] Although reaction conditions custom tailored to a given phosphine-borane could be readily derived, the *standard* conditions that were used for *all* of the examples described here involve treatment with HBF_4•OMe_2 [(5 equiv/P•BH_3 moiety), CH_2Cl_2, -5 °C → 25 °C, 12 h] followed by hydrolysis ($NaHCO_3$ *aq.*, 0 °C). The results obtained for the decomplexation of a range of phosphine-boranes are illustrated in **Table II.**

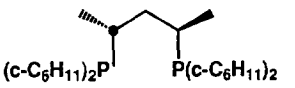


2i **3i** (eq 2)

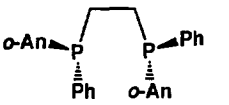
Table II. $HBF_4 \cdot OMe_2$ Mediated Decomplexation of Representative Bisphosphine-boranes.



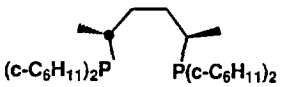
3a (97 %)



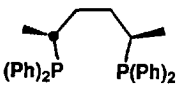
3c (91 %)



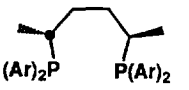
3j (98 %)



3d (91 %)

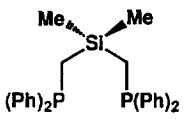


3e (99 %)

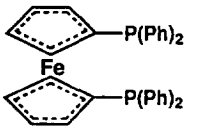


3f (96 %)

[Ar = 2-CH_3-4-(CH_3O)C_6H_3]



3g (89 %)



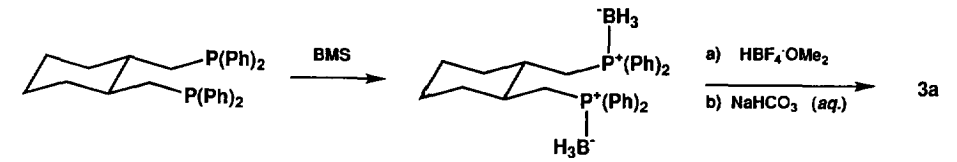
3h (94 %)

3l (92 %)

To gain insight into the prospective mechanism of decomplexation, methyldiphenylphosphine-borane (**4**) was treated with $HBF_4 \cdot OMe_2$ (1 equiv) in $CDCl_3$. ^1H NMR analysis revealed consumption of **4** with concomitant formation of a product possessing a down field shifted methyl doublet of doublets at 2.41 ppm ($J_{H\text{-}P}$ = 15.22 Hz and $J_{H\text{-}F}$ = 5.82 Hz). In addition, ^{31}P NMR analysis revealed an up field shifted signal at 1.98 ppm (doublet of multiplets, $J_{P\text{-}F}$ = 521 Hz). The appearance of these new resonances is consistent with the intermediacy of the phosphine-fluoroborane complex **5** (eq 3).

4 5 (eq 3)

As is evident from the examples presented above, the $HBF_4 \cdot OMe_2$ decomplexation procedure can facilitate rapid access to certain *electron rich* homochiral bisphosphines that are otherwise very difficult to prepare. In addition, the conditions for decomplexation are sufficiently mild to permit the survival of the C-Si and ferrocenyl linkages of ligands **3g** and **3h**.[17] It is also noteworthy that highly impure samples of valuable phosphines can be conveniently purified via the corresponding BH_3 adducts. For example, treatment of impure (1*S*,2*S*)-1,2-bis(diphenylphosphinomethyl)cyclohexane (**3a**) (of 80% purity) with $BH_3 \cdot SMe_2$ (2.1 equiv) followed by trituration with methanol gave the highly crystalline bisborane adduct. Decomplexation of this material in the usual manner returned pure **3a**.



(eq 4)

The efficient route to homochiral bisphosphine-boranes delineated here, when utilized in tandem with the convenient $HBF_4 \cdot OMe_2$ decomplexation procedure, is expected to facilitate the preparation of a wide range of stereochemically varied phosphine ligands. The synthesis and utilization of these new chiral modifiers for asymmetric catalysis will be described in upcoming accounts from these laboratories.

Acknowledgements. Generous support for this research by grants from the National Institute of Health and the National Science Foundation is gratefully acknowledged.

EXPERIMENTAL SECTION

General procedures. All reactions were performed in either oven-dried or flame-dried round- bottom flasks fitted with rubber septa, under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation at ~25 Torr (water aspirator) with a Buchi rotary evaporator. Analytical gas chromatography was performed on a Varian Model 3700 Gas Chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3390A reporting integrator and a

15 m X 0.54 mm ID column with DB5 (or SE-45 or equivalent) bonded phase. Preparative gas chromatography was performed on a Varian Model 3300 Gas Chromatograph equipped with a thermal conductivity detector, a Hewlett-Packard 3390A reporting integrator and a 1.8 m X 4 mm column with a 10% silicone OV-17 chromosorb adsorbent phase. High Performance Liquid Chromatography was performed on an IBM LC/9533 Ternary Gradient Liquid Chromatograph equipped with an IBM LC/9523 Variable UV Detector. For general analytical separations an IBM 250 mm X 4.5 mm ID column packed with IBM 5 μm spherical silica was used in conjunction with a Linear Model 156 chart recorder. Flash column chromatography was performed as described by Still[18] employing E. Merck 230-400 ASTM mesh, 0.040-0.063 mm particle size, silica gel 60. Solvent systems used for elution are reported in % volume/volume. Analytical thin-layer chromatography was performed using K42-G plates supplied by Alltech Associates.

Materials. Commercial reagents and solvents were used as received with the following exceptions. Tetrahydrofuran, 1,2-dimethoxyethane, benzene, heptane and hexane were distilled from potassium. Diethyl ether was distilled from sodium-benzophenone ketyl. *N,N*-dimethylformamide and hexamethylphosphoric triamide were distilled from calcium hydride at 20 Torr, while dichloromethane, acetonitrile, toluene and 2-butanol were distilled from calcium hydride at atmospheric pressure under an inert atmosphere of argon or nitrogen. Purification of methanol was accomplished by distillation from magnesium dimethoxide under an atmosphere of argon. The molarities indicated for organolithium reagents were established by titration with a standard solution of 2-butanol in xylene using 1,10-phenanthroline as indicator. Grignard reagents were titrated in the same manner. Periodically these reagents were titrated for total base content with a standard solution of potassium biphthalate using phenolphthalein as indicator.

Instrumentation. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were measured at 300 and 75 MHz, respectively, with a Bruker AC-300 spectrometer. Phosphorus nuclear magnetic resonance (^{31}P NMR) spectra were measured at 202 MHz with a Bruker AM-500 spectrometer. Proton chemical shifts are reported as δ values in parts per million down field from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.24, C_6HD_5: δ 7.15). Carbon chemical shifts are reported as δ values in parts per million down field from tetramethylsilane and are referenced to the ^{13}C in the NMR solvent ($CDCl_3$: δ 77.0, C_6D_6: δ 128.0). Phosphorus chemical shifts are reported as δ values in parts per million down field from 85% aqueous phosphoric acid and are referenced internally to the ^{31}P signal in triphenyl phosphine (δ -6.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant in Hertz (Hz) and assignment. High resolution mass spectra were measured on a VG Analytical 7070E spectrometer by Dr. L. J. Sears. Infrared spectra were recorded with either a Bruker IFS 25 IR, a Perkin-Elmer 1800 FTIR or a Perkin-Elmer 237B grating IR. Melting points were determined with either a Fisher-Johns or a

Mel-Temp II melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 C polarimeter. Elemental analysis was performed by Desert Analytics, Tucson, AZ.

(Dicyclohexylphosphine)trihydroboron (6a). An oven-dried, round-bottomed flask fitted with a rubber septum and a magnetic stirring bar was charged with dicyclohexylphosphine (431 mg, 2.22 mmol, 1 equiv), diethyl ether (3.0 mL) and purged with argon. The solution was cooled to 0 °C, whereupon borane methyl sulfide (0.330 mL of a 10.1 M solution, 3.33 mmol, 1.5 equiv) was added slowly by syringe. The reaction mixture was warmed slowly to 25 °C and subsequently stirred at this temperature for an additional 2 h. The solvents were evaporated under reduced pressure and the resulting residue was triturated with three 2-mL portions of diethyl ether to give 456 mg (99%) of **6a** as a white solid: mp 78.6-80.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.11 (app d sx, J = 4.9 Hz, $J_{H\text{-}P}$ = 351 Hz, P-*H*), 1.80 (m, 10H, CH_2), 1.71 (br m, 2H, P-C*H*), 1.25 (m, 10H, CH_2), 0.40 (br q, $J_{H\text{-}B}$ = 94.7 Hz, 3H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 29.4, 29.2, 28.8, 28.6, 27.7, 26.7, 26.5, 26.3, 25.7; ^{31}P NMR (202 MHz, $CDCl_3$) δ 17.3 (br d, $J_{P\text{-}H}$ = 351 Hz); IR (film) 2929, 2853, 2382, 2350, 1449, 1062 cm^{-1}. Anal. Calcd. for $C_{12}H_{26}BP$: C, 67.93; H, 12.36; P, 14.61. Found: C, 68.14; H, 12.02; P, 14.50.

(Diphenylphosphine)trihydroboron (6b). The reaction of diphenylphosphine (1.86 g, 10.0 mmol, 1 equiv) with borane methyl sulfide (1.08 mL of a 10.2 M solution, 11.0 mmol, 1.1 equiv) was carried out as described for **6a**. (Diphenylphosphine)trihydroboron (**6b**) was isolated (1.96 g, 98%) as a viscous clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.61 (m, 2H, Ph-*H*), 7.50-7.41 (m, 8H, Ph-*H*), 6.29 (dq, J = 6.9 Hz, $J_{H\text{-}P}$ = 378 Hz, 1H, P-*H*), 1.07 (br q, $J_{H\text{-}B}$ = 97.3 Hz, 3H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 133.1 (*C*H), 132.9 (*C*H), 131.6 (*C*H), 129.2 (*C*H), 129.0 (*C*H), 128.5 (*C*); ^{31}P NMR (202 MHz, $CDCl_3$) δ 0.8 (d, $J_{P\text{-}H}$ = 337 Hz); IR (film) 2388, 1483, 1438, 1109, 1059 cm^{-1}.

4-Lithio-3-methylanisole. An oven-dried, 250 mL, three-necked, round-bottomed flask was fitted with a pressure equalizing addition funnel, glass stopper, condenser, magnetic stirring bar and glass beads. The vessel was purged with argon and charged with diethyl ether (20 mL). The stopper was removed and replaced with a conical funnel while a constant flow of argon was passed through the flask. Lithium wire, alloyed with 1% sodium [0.385 g, 55.0 mmol, 2.2 equiv (prewashed with toluene)], was held with forceps over the funnel and cut with clean scissors into 2 mm pieces so that they dropped directly into the ether. A solution of 4-bromo-3-methylanisole[19] (5.02 g, 25.0 mmol, 1 equiv) in diethyl ether (50 mL) was added slowly to the lithium suspension via addition funnel, such that the reaction mixture was maintained at reflux. Upon completion of the addition, the yellow solution was stirred vigorously at 25 °C for an additional 3 h.

Bis(4-methoxy-2-methylphenyl)-*N*,*N*-dimethylaminophosphine (7). An oven-dried, 250 mL, three-necked, round-bottomed flask was fitted with a pressure equalizing addition funnel, 2 glass stoppers and a magnetic stirring bar. The vessel was purged with argon, charged with dichloro-*N*,*N*-dimethylaminophosphine[20] (1.83 g, 12.5 mmol, 1 equiv) in diethyl ether (50 mL) and cooled to -78 °C. A solution of 4-lithio-3-methylanisole (70.0 mL of a 0.357 M solution in diethyl ether, 25.0 mmol, 2 equiv) was added slowly via addition funnel. Upon completion of the addition, the mixture was warmed slowly to 25 °C over a period of 1 h. After dilution with anhydrous diethyl ether (20 mL), the mixture was filtered through activity II neutral alumina under a constant flow of argon and concentrated in vacuo. The resulting residue was purified by distillation (160-165 °C, 5 μTorr) to afford 3.33 g (84%) of **7** as a highly viscous colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (dd, J = 3.9, 8.4 Hz, 2H, Ar-*H*), 6.70 (m, 4H, Ar-*H*), 3.78 (s, 6H, OCH_3), 2.65 (d, J = 8.2 Hz, 6H, N(CH_3)$_2$), 2.27 (s, 6H, CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 49.7 (s).

[Bis(4-methoxy-2-methylphenyl)phosphine]trihydroboron (6c). An oven-dried, 250 mL, three-necked, round-bottomed flask was fitted with a glass stopper, a gas-inlet adapter and a magnetic stirring bar. The vessel was purged with argon, charged with **7** (0.850 g, 2.68 mmol, 1 equiv) in diethyl ether (107 mL) and cooled to 0 °C. Anhydrous hydrogen chloride (0.219 g, 6.00 mmol, 2.2 equiv) was *slowly* bubbled into the solution whereupon a white precipitate formed. The reaction mixture was warmed to 25 °C and stirred

for 5 h. The precipitated dimethylamine hydrochloride was filtered under a stream of argon and the filtrate was concentrated in vacuo. The resulting bis(4-methoxy-2-methylphenyl)chlorophosphine was redissolved in tetrahydrofuran (1.5 mL) and added *slowly*, via addition funnel, to an oven-dried, round-bottomed flask containing lithium aluminum hydride (0.122 g, 3.20 mmol, 1.19 equiv), borane methyl sulfide (0.320 mL of a 10.2 M solution, 3.25 mmol, 1.25 equiv) and tetrahydrofuran (2.0 mL), at 0 °C. Upon completion of the addition, the mixture was warmed to 25 °C and stirred for an additional 2 h. Excess lithium aluminum hydride was quenched with aqueous hydrochloric acid (5 N, 1.5 mL) and ice (3.0 g), and the biphasic mixture was diluted with diethyl ether (4.0 mL). The organic phase was separated and the aqueous phase was extracted further with two 2-mL portions of diethyl ether. The organic layers were combined, washed with brine (5.0 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting viscous beige residue was purified by flash chromatography on silica gel (20% ethyl acetate-hexane for elution) to give 317 mg (42%) of **6c** as a white crystalline solid: mp 97.3-99.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, J = 8.9, 13.6 Hz, 2H, Ar-*H*), 6.76 (br s, 4H, Ar-*H*), 6.39 (dq, J = 6.5 Hz, $J_{H\text{-}P}$ = 376 Hz, 1H, P-*H*), 3.79 (s, 6H, OCH_3), 2.28 (s, 6H, CH_3), 1.54-0.38 (br envelope, 3H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 162.3 (*C*), 143.9 (*C*), 143.7 (*C*), 135.8 (*C*H), 135.6 (*C*H), 117.1 (*C*H), 117.0 (*C*H), 111.8 (*C*H), 111.6 (*C*H), 75.2 (*C*), 70.3 (*C*), 55.2 (CH_3), 21.1 (CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.0 (d, $J_{P\text{-}H}$ = 415 Hz); IR (film) 2358, 1599, 1564, 1489, 1455, 1303, 1242, 1079 cm^{-1}; high resolution mass spectrum calcd. for $C_{16}H_{19}O_2P$ ($M^+ - BH_3$) 274.1124, found 274.1122.

(2*S*,5*S*)-2,5-Hexanediol (8). The title compound was prepared from acetonylacetone (5.71 g, 50.0 mmol, 1 equiv) according to the method of Lieser.[21a] The mixture was filtered through celite and the solids were rinsed with four 50-mL portions of ethyl acetate. The organic portion of the filtrate was separated and the aqueous layer was subjected to continuous extraction with ethyl acetate for 3 days. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to yield a viscous beige oil. Purification of this material was accomplished by column chromatography on silica gel (ethyl acetate for elution) to yield 4.49 g (75%) of **8** as a white solid. Recrystallization from *t*-butyl-methyl ether afforded 3.96 g (67%) of **8** as a white crystalline solid: mp 50.4-53.2 °C; $[\alpha]_D^{25}$ + 35.2° (c=14.7, $CHCl_3$), lit.[21b] $[\alpha]_D^{24}$ + 34.9° (c=9.48, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (m, 2H, C*H*), 3.15 (br s, 2H, O*H*), 1.53 (m, 4H, CH_2), 1.17 (d, J = 6.2 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 68.1 (*C*H), 35.9 (CH_2), 23.6 (CH_3).

(2*S*,5*S*)-2,5-Hexanediol di-*p*-toluenesulfonate (1a). An oven-dried, round-bottomed flask equipped with a rubber septum and a magnetic stirring bar was charged with (2*S*,5*S*)-2,5-hexanediol (1.18 g, 10.0 mmol, 1 equiv), dichloromethane (30 mL) and pyridine (1.58 g, 20.0 mmol, 2 equiv). The solution was cooled to 0 °C and then *p*-toluenesulfonyl chloride (3.80 g, 20.0 mmol, 2 equiv) was added in several small portions over a period of 1 h. The mixture was stirred at 0 °C for an additional 19 h. The resulting white suspension was diluted with dichloromethane (15 mL) and partitioned between 10% aqueous hydrochloric acid solution (10 mL) and dichloromethane (5 mL). The organic layer was separated and the aqueous layer was extracted further with two 10-mL portions of dichloromethane. The combined organic layers were washed with another 10-mL portion of 10% aqueous hydrochloric acid solution, two 10-mL portions of saturated aqueous sodium bicarbonate solution and dried (Na_2SO_4). The solvents were evaporated under reduced pressure and the resulting white solid was purified by recrystallization from 10% heptane in methylcyclohexane to yield 3.54 g (83%) of **1a** as a white crystalline solid: mp 94.5-97.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 4H, Ar-*H*), 7.32 (d, J = 8.2 Hz, 4H, Ar-*H*), 4.50 (m, 2H, C*H*), 2.43 (s, 6H, Ar-CH_3), 1.54 (m, 4H, CH_2), 1.11 (d, J = 6.3 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 144.6 (*C*), 134.8 (*C*), 129.8 (*C*H), 127.7 (*C*H), 79.0 (*C*H), 31.7 (CH_3), 21.6 (CH_2), 20.8 (CH_3); IR (KBr) 3004, 2980, 2954, 2930, 1598, 1450, 1438, 1378, 1323, 1308, 1294, 1189, 1171, 1096, 892, 852, 820, 758, 688, 578, 544, 522 cm^{-1}.

(1*S*,2*S*)-1,2-Bis[(diphenylphosphino)methyl]cyclohexane-P:P′-hexahydrodiboron (2a). An oven-dried round bottomed flask equipped with a magnetic stirring bar was charged with (diphenylphosphine)trihydroboron (**6b**) (0.928 g, 4.64 mmol, 2.1 equiv) and purged with argon. The

reaction mixture was cooled to -78 °C and *n*-butyllithium (1.07 mL of a 4.50 M solution in heptane, 4.68 mmol, 2.12 equiv) was added dropwise via syringe over a period of 10 minutes. The reaction mixture was stirred at -78 °C for an additional 10 minutes and then warmed to 25 °C for 10 min. The reaction mixture was then cooled to -40 °C and a solution of (1*S*,2*S*)-1,2-di(*p*-tosyloxymethyl)cyclohexane[23] (1.00 g, 2.21 mmol, 1 equiv) in *N*,*N*-dimethylformamide (9.2 mL) was added slowly via syringe. Upon completion of the addition, the mixture was warmed slowly to 25 °C and stirred for an additional 9 h. The mixture was partitioned between diethyl ether (20 mL) and 10% aqueous hydrochloric acid solution (25 mL). The organic layer was separated and the aqueous layer was extracted further with two 20 mL portions of diethyl ether. The organic layers were combined, washed with two 20 mL portions of water and one 20 mL portion of brine, dried ($MgSO_4$) and concentrated in vacuo. The resulting colorless residue was purified by flash chromatography on silica gel (40% ethyl acetate-hexanes for elution) to yield 1.02 g (93%) of **2a** as a colorless solid. mp 184-189 °C $[\alpha]_D^{23}$ + 15.6 °(C 0.027, $CHCl_3$) ^1H NMR (75 MHz, $CDCl_3$) δ 0.5-1.6 (br envelope, 16H, Cy-*H*, CH_2 and BH_3); 1.85 (ddd, 2H, *J*=14.2, 7.1, 6.7, P-CH*H*); 2.19 (app t, 2H, P-CH*H*); 7.26-7.47 (m, 12H, Ar*H*); 7.54-7.60 (m, 4H, Ar*H*); 7.65-7.71 (m, 4H, Ar*H*); ^{13}C NMR (300 MHz, $CDCl_3$, ^1H decoupled) δ 25.4, 29.5, 29.9, 34.7, 38.3, 38.4, 128.7, 128.8, 130.2, 130.3, 130.9, 131.0, 131.2, 132.1, 132.2, 132.4, 132.5; ^{31}P NMR (202, $CDCl_3$) δ 13.96(S); IR (CCl_4) 3080, 3061, 3026, 3010, 2932, 2856, 2384, 2344, 2254, 1958, 1895, 1814, 1736, 1485, 1437, 1408, 1261, 1186, 1131, 1108, 1060, 1028, 1000, 958, 909, 866; high resolution mass spectrum calcd for $C_{32}H_{36}PB_2$ (M^+-BH_4) 493.4293, found 493.4290.

(1*S*,2*S*)-1,2-Bis[(dicyclohexylphosphino)methyl]cyclohexane-P:P'-hexahydrodiboron (2b). The reaction of the lithium derivative of (dicyclohexylphosphine)trihydroboron (**6a**) (56.1 mg, 0.263 mmol, 2.1 equiv) with (1*S*,2*S*)-1,2-di(*p*-tosyloxymethyl)cyclohexane[23] (56.5 mg, 0.125 mmol, 1 equiv) in tetrahydrofuran (2.0 mL) was carried out as described for **2e**. After the described workup, evaporation of the solvents under reduced pressure yielded 59.2 mg (89%) of **2b** as a white residue. Purification by recrystallization from heptane afforded a white crystalline solid: mp 93.6-96.2 °C; $[\alpha]_D^{23}$ +10.7° (c = 0.06, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 2.00-1.46 (br envelope, 34H, Cy-*H* and CH_2), 1.45-1.00 (br envelope, 28H, Cy-*H* and CH_2), 0.90-0.40 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^1H decoupled) δ 38.7, 38.6, 33.9, 33.2, 33.1, 32.7, 32.6, 27.8, 27.1, 27.0, 26.9, 26.6, 26.1, 25.8, 24.9, 23.8, 23.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.8 (s); IR (film) 2927, 2853, 2372, 1447, 1063 cm^{-1}; high resolution mass spectrum calcd. for $C_{32}H_{60}BP_2(M^+-BH_4)$ 517.4293, found 517.4248.

(2*R*,4*R*)-2,4-Bis(dicyclohexylphosphino)pentane-P:P'-hexahydrodiboron (2c). An oven-dried, round-bottomed flask equipped with a magnetic stirring bar and a rubber septum was charged with (dicyclohexylphosphine)trihydroboron (**6a**) (54.7 mg, 0.263 mmol, 2.1 equiv), tetrahydrofuran (0.5 mL) and purged with argon. Upon cooling to -78 °C, *n*-butyllithium (40.3 μL of a 7.17 M solution in heptane, 0.289 mmol, 2.3 equiv) was added dropwise via syringe over a period of 10 min, followed by the addition of hexamethyl phosphoric triamide (0.5 mL) to the reaction flask. The mixture was stirred at -78 °C for 30 min then warmed to 0 °C for 20 min. After cooling to -40 °C, a solution of (2*S*,4*S*)-2,4-pentanediol di-*p*-toluenesulfonate **9**[22] (51.5 mg, 0.125 mmol, 1 equiv) in *N*,*N*-dimethylformamide (0.5 mL) was added dropwise via syringe. Upon completion of the addition, the mixture was warmed slowly to 25 °C and stirred for an additional 3 h. The mixture was partitioned between diethyl ether (1.0 mL) and 10% aqueous hydrochloric acid solution (1.5 mL). The organic layer was separated and the aqueous layer was extracted further with four 1-mL portions of diethyl ether. The organic layers were combined, washed with two 2-mL portions of water and one 2-mL portion of brine, dried ($MgSO_4$) and concentrated in vacuo. The resulting beige residue was purified by flash column chromatography on silica gel (10% ethyl acetate-hexane for elution) and the material that was obtained in this way was recrystallized from hexane at 0 °C to yield 58 mg (91%) of **2c** as a white solid: mp 92.1-94.6 °C; $[\alpha]_D^{23}$ -11.4° (c = 0.06, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 2.04-1.57 (br envelope, 24H, C*H* and Cy-*H*), 1.50-1.12 (br envelope, 24H, CH_2 and Cy-*H*), 1.14 (dd, *J* = 7.1, 13.4 Hz, 6H, CH_3), 1.01--0.20 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^1H decoupled) δ 34.9, 34.5, 26.5, 26.4, 25.9, 25.7, 24.8, 22.3, 13.9; ^{31}P NMR (202 MHz, $CDCl_3$) δ 24.1 (s);

IR (film) 2929, 2852, 2365, 1449, 889 cm^{-1}; high resolution mass spectrum calcd. for $C_{29}H_{56}BP_2(M^+-BH_4)$ 477.3950, found 477.3949.

(2*R*,5*R*)-2,5-Bis(dicyclohexylphosphino)hexane-P:P'-hexahydrodiboron (2d). The reaction of the lithium derivative of (dicyclohexylphosphine)trihydroboron (**6a**) (112 mg, 0.525 mmol, 2.1 equiv) with **1a** (107 mg, 0.250 mmol, 1 equiv) was carried out as described for **2e**. After the described workup, evaporation of the solvents under reduced pressure yielded a white solid. This material was purified by crystallization from 10% ethyl acetate in hexanes to yield 107 mg (86%) of **2d** as a white crystalline solid: mp 203.2-205.4 °C; $[\alpha]_D^{23}$ -19.5° (c = 0.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.95-1.60 (m, 35H, Cy-*H* envelope), 1.55-1.20 (m, 15H, C*H*, CH_2 and Cy-*H* envelope), 1.17 (dd, *J* = 7.0, 13.3 Hz, 6H, CH_3), 0.77--2.30 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^1H decoupled) δ 31.6, 31.5, 31.2, 31.1, 30.5, 30.4, 28.2, 27.9, 27.8, 27.7, 27.3, 27.2, 26.1, 25.4, 25.0, 14.6; ^{31}P NMR (202 MHz, $CDCl_3$) δ 31.1 (br s); IR (film) 2927, 2853, 2362, 2342, 1067 cm^{-1}; high resolution mass spectrum calcd. for $C_{30}H_{59}BP_2(M^+-BH_3)$ 492.4185, found 492.4210.

(2*R*,5*R*)-2,5-Bis(diphenylphosphino)hexane-P:P'-hexahydrodiboron (2e). An oven-dried, round-bottomed flask equipped with a magnetic stirring bar and a rubber septum was charged with (diphenylphosphine)trihydroboron (**6b**) (100 mg, 0.50 mmol, 2.1 equiv), tetrahydrofuran (1.5 mL) and purged with argon. Upon cooling to -78 °C, *n*-butyllithium (88.0 μL of a 5.80 M solution in heptane, 0.51 mmol, 2.12 equiv) was added dropwise via syringe over a period of 10 min. The reaction mixture was stirred at -78 °C for an additional 10 min and then warmed to 25 °C for 10 min. Upon cooling to -40 °C, a solution of **1a** (102 mg, 0.24 mmol, 1 equiv) in *N*,*N*-dimethylformamide (1.0 mL) was added slowly via syringe. Upon completion of the addition, the mixture was warmed slowly to 25 °C and stirred for an additional 9 h. The mixture was partitioned between diethyl ether (2.0 mL) and 10% aqueous hydrochloric acid solution (3.0 mL). The organic layer was separated and the aqueous layer was extracted further with four 2-mL portions of diethyl ether. The organic layers were combined, washed with two 2-mL portions of water and one 2-mL portion of brine, dried ($MgSO_4$) and concentrated in vacuo. The resulting beige residue was purified by flash column chromatography on silica gel (20% ethyl acetate-hexane for elution) to yield 102 mg (88%) of **2e** as a white solid: mp 153.4-154.8 °C; $[\alpha]_D^{23}$ + 35.2° (c=14.7, $CHCl_3$), lit.21b $[\alpha]^3$ -9.5° (c = 0.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.68-7.62 (m, 8H, Ph-*H*), 7.47-7.36 (m, 12H, Ph-*H*), 2.37 (app sept., *J* = 7.4 Hz, 2H, C*H*), 1.52 (m, 4H, CH_2), 1.01 (dd, *J* = 6.9, 16.5 Hz, 6H, CH_3), 1.45-0.20 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^1H decoupled) δ 132.7 (*C*H), 132.6 (*C*H), 132.5 (*C*H), 132.4 (*C*H), 131.1 (*C*H), 128.9 (*C*), 128.8 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 128.3 (*C*), 29.5 (*C*H), 29.4 (*C*H), 28.7 (CH_2), 28.2 (CH_2), 13.7 (CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.9 (s); IR (film) 2928, 2385, 1436, 1107, 1064 cm^{-1}; high resolution mass spectrum calcd. for $C_{30}H_{32}P_2(M^+-B_2H_6)$ 454.1982, found 454.1980.

(2*R*,2*R*)-2,5-Bis[bis(4-methoxy-2-methylphenyl)phosphino]hexane-P:P'-hexahydrodiboron (2f). The reaction of the lithium derivative of [bis(4-methoxy-2-methylphenyl)phosphine]trihydroboron (**6c**) (154 mg, 0.525 mmol, 2.1 equiv) with **1a** (107 mg, 0.250 mmol, 1 equiv) was carried out as described for **2e**. After the described workup, evaporation of the solvents under reduced pressure yielded a white solid. This material was purified by crystallization from methylcyclohexane to yield 135 mg (82%) of **2f** as a white crystalline solid: mp 149.3-153.1 °C; $[\alpha]_D^{23}$ -20.4° (c = 0.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 11.5, 10.5 Hz, 2H, Ar-*H*), 7.49 (app t, *J* = 10.5 Hz, 2H, Ar-*H*), 6.77 (app d, *J* = 8.5 Hz, 4H, Ar-*H*), 6.66 (app d, *J* = 17.2 Hz, 4H, Ar-*H*), 3.81 (s, 6H, OCH_3), 3.79 (s, 6H, OCH_3), 2.54 (m, 2H, C*H*), 2.08 (s, 6H, CH_3), 1.99 (s, 6H, CH_3), 1.76 (m, 4H, CH_2), 1.07 (dd, *J* = 6.8, 16.5 Hz, 6H, CH_3), 1.9-0.2 (br envelope, 6H, BH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^1H decoupled) δ 161.7, 161.0, 144.7, 144.2, 135.8, 135.3, 134.1, 133.6, 129.7, 127.6, 117.6, 111.1, 79.5, 55.0, 28.1, 27.7, 21.7, 20.3, 14.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.4 (s); IR (film) 2933, 2383, 1598, 1565, 1489, 1464, 1302, 1237, 1075 cm^{-1}; high resolution mass spectrum calcd. for $C_{38}H_{48}O_2P_2(M^+-B_2H_6)$ 630.3030, found 630.3028.

Preparation of Bisphosphine Ligands 3d-f. Representative Procedure for Phosphine-Borane Decomplexation with $HBF_4 \cdot OMe_2$[24]: (2*R*,5*R*)-2,5-Bis(diphenylphosphino)hexane (3e). A flame-dried test tube (16 mm x 100 mm) equipped with a stirring bar and a rubber septum was charged with **2e** (48.2 mg, 0.10 mmol, 1 equiv), dichloromethane (1.0 mL) and purged with argon. Upon cooling to -5 °C, tetrafluoroboric acid dimethyl ether complex (134 mg, 1.00 mmol, 10.0 equiv) was added dropwise by syringe. An exothermic reaction ensued and gas evolved. The reaction mixture was then warmed to 25 °C and stirred for an additional 12 h. Subsequently, the mixture was diluted with degassed, anhydrous diethyl ether (2.0 mL) and added to degassed, saturated aqueous sodium bicarbonate solution (5.0 mL) contained in a small Erlenmeyer flask. The resulting biphasic mixture was stirred vigorously under argon for 10 min and then poured into a separatory funnel. The organic layer was separated and the aqueous layer was extracted (*under argon*) with two 2-mL portions of degassed, anhydrous diethyl ether. The organic layers were combined, washed with two 3-mL portions of degassed water and one 3-mL portion of brine, dried ($MgSO_4$) (*all under argon*) and concentrated in vacuo. The resulting white solid was recrystallized from degassed methylcyclohexane at 0 °C to give 45.3 mg (99%) of **3e** as a white crystalline solid: mp 179.3-183.6 °C; $[\alpha]_D^{25}$ +7.0° (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (m, 8H, Ar-*H*), 7.55-7.38 (m, 12H, Ar-*H*), 2.25 (m, 2H, C*H*), 1.61 (m, 4H, CH_2), 1.03 (dd, *J* = 7.1, 17.0 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) 131.4, 130.9, 128.4, 32.8, 32.1, 27.6, 11.9; ^{31}P NMR (202 MHz, $CDCl_3$) δ -1.8 (s); IR (KBr) 3068, 3052, 2956, 2930, 2880, 2852, 1480, 1458, 1432, 1376, 1196, 1092, 1068, 1026, 738, 696, 658, 510 cm^{-1}; high resolution mass spectrum calcd. for $C_{30}H_{32}P_2(M^+)$ 454.1982, found 454.1979.

(2*R*,4*R*)-2,4-Bis(dicyclohexylphosphino)pentane (3c): white solid; yield (91%); mp 182.3-184.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (m, 2H, C*H*), 1.95-1.64 (m, 22H, Cy-*H* envelope), 1.53 (s, 2H, CH_2), 1.47-1.15 (m, 22H, Cy-*H* envelope), 1.15 (dd, *J* = 7.1, 13.3 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 31.8, 31.1, 30.0, 28.1, 27.8, 27.5, 27.3, 27.2, 26.0, 25.4, 25.0, 15.8; ^{31}P NMR (202 MHz, C_6D_6) δ 6.5 (s); high resolution mass spectrum calcd. for $C_{29}H_{54}P_2(M^+)$ 464.3704, found 464.3700.

(2*R*,5*R*)-2,5-Bis(dicyclohexylphosphino)hexane (3d): white solid; yield (91%); mp 184.6-187.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96-1.60 (m, 35H, Cy-*H* envelope), 1.60-1.05 (m, 15H, C*H*, CH_2 and Cy-*H* envelope), 1.16 (dd, *J* = 7.2, 16.1 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 35.9, 35.1, 30.2, 29.4, 28.7, 28.5, 27.0, 26.9, 26.8, 26.6, 26.5, 26.3, 26.1, 13.3; ^{31}P NMR (202 MHz, $CDCl_3$) δ 11.1 (s); IR (film) 2929, 2852, 1449, 1157 cm^{-1}; high resolution mass spectrum calcd. for $C_{30}H_{55}P_2(M^+-H)$ 477.3783, found 477.3780.

(2*R*,5*R*)-2,5-Bis[bis(4-methoxy-2-methylphenyl)phosphino]hexane (3f): white solid; yield (96%); mp 178.4-181.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.08 (m, 4H, Ar-*H*), 6.71-6.63 (m, 8H, Ar-*H*), 3.78 (s, 6H, OCH_3), 3.74 (s, 6H, OCH_3), 2.44 (s, 6H, CH_3), 2.37 (s, 6H, CH_3), 2.10 (m, 2H, C*H*), 1.47 (m, 4H, CH_2), 0.89 (dd, *J* = 6.8, 16.0 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 159.7, 144.8, 144.6, 133.2, 132.5, 115.7, 115.6, 111.7, 54.9, 52.0, 31.5, 30.5, 29.6, 21.4, 16.1, 15.8; ^{31}P NMR (202 MHz, $CDCl_3$) δ -32.4 (s); IR (film) 2925, 2852, 1595, 1564, 1483, 1464, 1296, 1238, 1071 cm^{-1}; high resolution mass spectrum calcd. for $C_{38}H_{48}O_4P_2(M^+)$ 630.3030, found 630.3028.

LITERATURE CITED AND FOOTNOTES

1. Fellow of the Alexander von Humboldt Foundation **1993-1995.**
2. Noyori, R. *Asymmetric Catalysis in Organic Synthesis*. John Wiley and Sons: New York, 1994.
3. Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375.
4. For a review see: Kagan, H. B.; Sasaki, M. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: New York, 1990; vol. 1, p. 51.

5. a) Kagan, H. B.; Dang, T. -P. *J. Am. Chem. Soc.* **1972**, *94*, 6429. b) Dang, T. -P.; Poulin, J. C.; Kagan, H. B. *J. Organomet. Chem.* **1975**, *91*, 105. c) Morimoto, T.; Chiba, M.; Achiwa, K. *Chem. Pharm. Bull.* **1992**, *40*, 2894 and references cited therein. d) Inoguchi, K.; Fujie, N.; Yoshikawa, K.; Achiwa, K. *Chem. Pharm. Bull.* **1992**, *40*, 2921 and references cited therein. e) McNeil, P. A.; Roberts, N. K.; Bosnich, B. *J. Am. Chem. Soc.* **1981**, *103*, 2273. f) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262. g) Hobbs, C. F.; Knowles, W. S. *J. Org. Chem.* **1981**, *46*, 4422 and references cited therein. h) Hayashi, T.; Tanaka, M.; Ogata, I. *J. Mol. Catal.* **1984**, *26*, 17. i) Ojima, I.; Kogure, T. *Chem. Lett.* **1979**, 641. j) Nagel, U. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 435. k) Bakos, J.; Toth, I.; Heil, B.; Marko, L. *J. Organomet. Chem.* **1985**, *279*, 23. l) Kagan, H. B.; Fiaud, J. C.; Hoornaert, F. C.; Meyer, D.; Poulin, J. C. *Bull. Soc. Chim. Belg.* **1979**, *88*, 923.
6. In selected instances, elimination has been minimized by the use of cyclic sulfates as substrates in displacement reactions which employ an *unhindered* lithium phosphide as a nuclephile: Burk, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 8518.
7. Tani, K.; Suwa, K.; Yamagata, T.; Otsuka, S. *Chem. Lett.* **1982**, 265.
8. a) Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655 and references therein. b) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.
9. a) During the course of this work a single example was reported in which the lithium derivative of *diphenyl*phosphine-borane was used to synthesize DIOP.[9b] b) Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, *34*, 4523.
10. McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319.
11. The use of old, alkoxide contaminated samples of *n*-BuLi for this purpose results in greatly diminished yields of the desired substitution products **2a-f**.
12. Diastereomeric purity for **2a-f** was inferred by high field ^{1}H and ^{13}C NMR analysis which indicated the absence of *meso* isomers. In addition, **2a-f** were homogeneous by HPLC and GLC.
13. All new phosphine-borane complexes were fully characterized by ^{1}H, ^{13}C and ^{31}P NMR, IR and possessed satisfactory combustion analyses or exact mass.
14. Several alternative sets of conditions intended for borane decomplexation were examined and found to be ineffective. These included: exposure of **2i** to $EtO^{-}K^{+}$ in PhMe or THF; treatment with 18-crown-6•$K^{+}CN^{-}$ in Et_2NH; and warming in the presence of "catalytic" (10 mol %) $(n\text{-}Bu)_3P$ in morpholine.
15. A transient compound [presumably the monoborane complex DPPE•(BH_3) (**10**)] was observed at intermediate stages of the reaction. An authentic sample of **10** was prepared (albeit with poor selectivity) by the exposure of **3i** (1.2 equiv) to BH_3•SMe_2 (1.0 equiv) followed by chromatographic purification.
16. As a more economical alternative, borane decomplexation could be readily effected (e.g., 25 °C, 4 h) by treatment with preformed HBF_4•OEt_2 [BF_3•OEt_2 (1 equiv) + HF_{anh} (1 equiv)]. Ether complexes of BF_3 and HBF_4 were obtained from Aldrich Chemical Co.
17. In contrast, the 1,3-dioxolane linkage present within the bisborane derivative of DIOP was degraded under the prescribed set of reaction conditions.
18. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2933.
19. 4-Bromo-3-methylanisole was prepared according to a literature procedure: Oshiki, T.; Imamoto, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3719.
20. Noth, H.; Vetter, H. -J. *Chem. Ber.* **1963**, *96*, 1109.
21. a) Lieser, J. K. *Synth. Commun.* **1983**, *13a*, 765. b) Short, R. P.; Kennedy, R. M.; Masamune, S. *J. Org. Chem.* **1989**, *54*, 1755.
22. The requisite ditosylate **9** was prepared from (2*S*,4*S*)-2,4-dihydroxypentane by treatment with *p*-toluenesulfonyl chloride in the presence of pyridine (*vide supra*).
23. Prepared and characterized by Mr. D. J. Sheehan of these laboratories.
24. Analogous decomplexation of **2a**[25] on a 1 mmol scale provided **3a** in 97% isolated yield.
25. Prepared on a *2.21 mmol scale in 93% yield* by Mr. D. Belanger of these laboratories.

(*Received in USA* 22 *December* 1994; *accepted* 9 *May* 1995)