Heteroatom Chemistry
Volume 3, Number 5/6, 1992

# Synthesis and Reactions of Optically Active Phosphine-Boranes

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*Received 14 July 1992*

## ABSTRACT

*Synthesis and reactions of optically active phosphine-boranes have been investigated. Optically active secondary phosphine-boranes, ($S_P$)-and ($R_P$)-menthyloxyphenylphosphine-boranes, and (S)-methylphenylphosphine-borane underwent palladium(0)-catalyzed electrophilic arylation with o-, m-, or p-iodoanisole. The stereochemistry of this arylation was largely dependent on the solvent and the base used. The reaction in acetonitrile proceeded with almost complete retention of configuration at the chiral phosphorus, whereas inversion of configuration was observed in ethereal solvents or toluene. The phosphorus-oxygen bond of ($R_P$)-menthyloxy (methyl)phenylphosphine-borane and ($S_P$)-menthyloxy(o-methoxyphenyl)phenylphosphine-borane was reductively cleaved at −78°C by lithium naphthalenide or Li/$NH_3$ with virtually net retention of configuration at phosphorus, providing secondary or tertiary phosphine-boranes in excellent yields. New synthetic routes to optically pure $C_2$-symmetric bisphosphine-boranes possessing chirality at phosphorus have been developed on the basis of these stereochemical studies.*

Phosphine-boranes, adducts of phosphines with boranes, constitute a unique class of organophosphorus compounds because of their unique chemical properties. The properties of phosphine-boranes have attracted the attention of many chemists, and a number of investigations on these compounds have been made so far, revealing the inherent nature of the phosphorus-boron bond [1,2]. We have been interested in the characteristic properties of phosphine-boranes and have investigated the syntheses and reactions of this class of compounds from the viewpoint of organic synthesis [3–5].

It is known that optically active phosphorus compounds possessing a chiral center at phosphorus occupy a central position in the study of the stereochemistry of reactions occurring at phosphorus [6]. Previous investigations in this area have utilized a great number of chiral phosphorus compounds. However, little attention has been paid to optically active phosphine-boranes. Recently, we have initiated the syntheses and stereochemical studies of optically active phosphine-boranes [7]. In this article, we describe new stereochemical aspects of reactions occurring at a chiral phosphorus as well as novel synthetic routes to optically pure $C_2$-symmetric bisphosphine-boranes [8].

## *RESULTS AND DISCUSSION*

### *Palladium-Catalyzed Cross-Coupling Reactions of Secondary Phosphine-Boranes with Iodoanisoles*

Recently, Xu *et al.* reported that palladium-catalyzed cross-coupling reactions of optically pure phosphinates with aromatic or vinylic halides proceed with almost complete retention of configuration [9]. We have been interested in palladium-catalyzed phosphorus-carbon bond forming reactions and have studied the reactions of optically active secondary phosphine-boranes and related substrates. Our initial experiments were conducted with the reactions of diastereomerically pure

Dedicated to Prof. Yao-Zeng Huang on the occasion of his eightieth birthday.

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1042-7163/92/$3.50 + .25

($S_P$)-menthyloxyphenylphosphine-boranes ($\mathbf{1}_s$) [7] with *o*-iodoanisole (Scheme 1), since the expected arylation products ($\mathbf{2}_S$ or $\mathbf{2}_R$) are key intermediates to optically pure 1,2-bis[(*o*-methoxyphenyl)phenylphosphino]ethanes (diPAMP) which are among the most useful phosphine ligands in catalytic asymmetric hydrogenation [10].

The reactions were carried out under various conditions. The results are summarized in Table 1. It was found that $\mathbf{1}_S$ reacted smoothly with *o*-iodoanisole in the presence of a catalytic amount of palladium(0) complex in acetonitrile. Divalent palladium salts, $PdCl_2$, $PdCl_2(PhCN)_2$, and $Pd(OAc)_2$, also catalyzed the reaction, although the chemical yields of the product were not satisfactory (entries 7–10) in comparison with the reactions brought about by the use of Pd(0) catalysts, such as $Pd(Ph_3P)_4$ or $Pd_2(dba)_3 \cdot CHCl_3$. Use of *o*-bromoanisole or *o*-methoxyphenyl trifluoromethanesulfonate instead of *o*-iodoanisole provided no trace of the cross-coupling product under these conditions (entries 13, 17, 18, and 39).

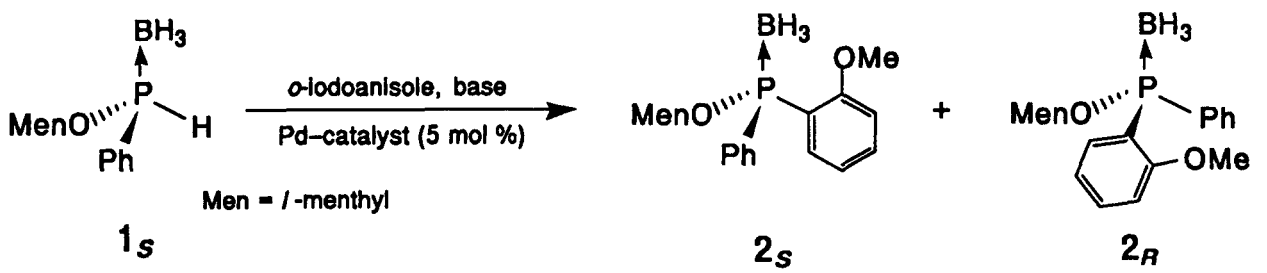
It is noted that retention of configuration at chiral phosphorus was observed with acetonitrile as the solvent. These results are in accordance with previously reported results of palladium-catalyzed reactions of optically active isopropyl methylphosphinate with aromatic or vinylic halides [9]. The optical purity of the product depended on the reaction temperature. Complete retention of configuration was observed at 50°C (entries 1, 5, 6, 10, and 11), while the optical purity of the product was slightly decreased at higher temperatures (entries 2–4).

The reactions in other solvents were also examined. Retention of configuration was also observed for the reaction carried out in *N*,*N*-dimethylformamide (DMF) although the yield was moderate (entry 16). The reaction in methanol resulted in the formation of a complex mixture. In sharp contrast, the use of ethereal solvents, such as tetrahydrofuran (THF), tetrahydropyran (THP), dioxane, and 1,2-dimethoxyethane (DME), caused a completely different stereochemical course; thus, the reactions in these solvents proceeded with inversion of configuration with a high degree of stereospecificity. It is particularly worthy to mention that the cross-coupling product $\mathbf{2}_R$ with 92% de was obtained in THF (entry 22). This unexpected stereochemical outcome was also observed when a hydrocarbon solvent, such as toluene, was used (entry 40).

It is noted that stereospecificity in less polar solvents is largely dependent on the base used. Reactions in THF in the presence of $K_2CO_3$ or $CH_3CO_2K$ proceeded with a remarkably high degree of stereospecificity, while the use of a stronger base, such as $K_3PO_4$ or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), resulted in lower levels of specificity (entries 28 and 31). Overall retention of configuration occurred when NaH or $Ag_2CO_3$ was employed (entries 30 and 32).

In order to examine the ability of the *l*-menthyl group to affect the stereospecificity, another diastereomer, ($R_P$)-menthyloxyphenylphosphine-borane ($\mathbf{1}_R$), was allowed to react with *o*-iodoanisole in acetonitrile or THF. The results are shown in Scheme 2. Complete retention occurred in acetonitrile, whereas nearly complete inversion was observed in THF. These results, which are almost the same as those of the reaction of $\mathbf{1}_S$, clearly indicate that the stereochemistry of the reaction is not affected by the chirality of the *l*-menthyl group.

We next examined the reactions of (*S*)-methlphenylphosphine-borane (**3**) with *o*-, *m*-, or *p*-iodoanisole under various conditions in order to evaluate the generality of this method (Scheme 3). The results are summarized in Table 2. The reactions in acetonitrile using $K_2CO_3$ as the base afforded the arylation products with retention of configuration to a highly stereospecific degree regardless of the substitution pattern of the iodoanisole. On the other hand, the use of $Ag_2CO_3$ resulted in an extremely poor yield of the product. The reaction in the presence of $Cs_2CO_3$ provided virtually racemized product. The formation of racemized product may be ascribed to the rapid racemization of the starting material **3** by contact with $Cs_2CO_3$. Inversion of configuration was observed in THF when $K_2CO_3$ was employed as the base, although




SCHEME 1

**TABLE 1** Palladium-Catalyzed Cross-Coupling Reaction of $\mathbf{1}_S$ with *o*-Iodoanisole[a]

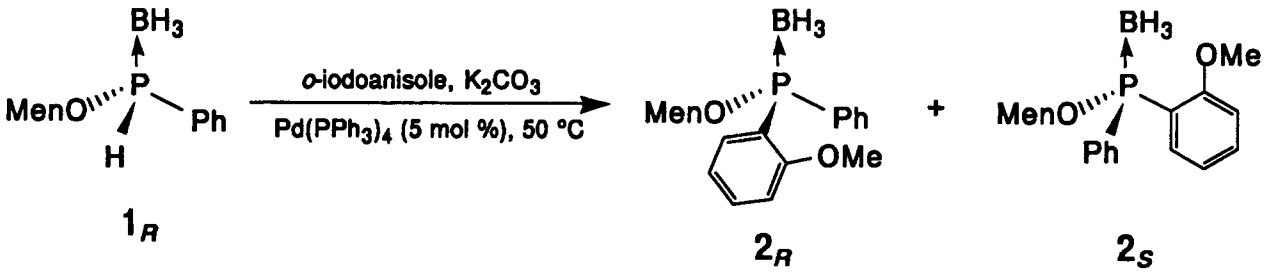
| Entry | Catalyst | Base | Solvent | Temperature (°C) | Time (hours) | Yield (%) | $2_S:2_R$[b] |
|---|---|---|---|---|---|---|---|
| 1 | $Pd(PPh_3)_4$ | $K_2CO_3$ | $CH_3CN$ | 50 | 16 | 96 | 100:0 |
| 2 | $Pd(PPh_3)_4$ | $K_2CO_3$ | $CH_3CN$ | 60 | 14 | 89 | 97:3 |
| 3 | $Pd(PPh_3)_4$ | $K_2CO_3$ | $CH_3CN$ | 70 | 8 | 78 | 94:6 |
| 4 | $Pd(PPh_3)_4$ | $K_2CO_3$ | $CH_3CN$ | 82 | 2 | 53 | 84:16 |
| 5 | $Pd_2(dba)_3 \cdot CHCl_3$ | $K_2CO_3$ | $CH_3CN$ | 50 | 16 | 50 | 100:0 |
| 6 | $Pd_2(dba)_3 \cdot CHCl_3$-8$PPh_3$ | $K_2CO_3$ | $CH_3CN$ | 50 | 16 | 63 | 100:0 |
| 7 | $PdCl_2$ | $K_2CO_3$ | $CH_3CN$ | 82 | 2 | 35 | 84:16 |
| 8 | $PdCl_2(PhCN)_2$ | $K_2CO_3$ | $CH_3CN$ | 82 | 2 | 30 | —[c] |
| 9 | $Pd(OAc)_2$ | $K_2CO_3$ | $CH_3CN$ | 82 | 2 | 29 | —[c] |
| 10 | $Pd(OAc)_2$-4$PPh_3$ | $K_2CO_3$ | $CH_3CN$ | 50 | 16 | 38 | 100:0 |
| 11 | $Pd(PPh_3)_4$ | $K_3PO_4$ | $CH_3CN$ | 50 | 16 | 72 | 100:0 |
| 12 | $Pd(PPh_3)_4$ | $K_3PO_4$ | $CH_3CN$ | 20 | 16 | 74 | 100:0 |
| 13[d] | $Pd(PPh_3)_4$ | $K_3PO_4$ | $CH_3CN$ | 50 | 16 | 0 | — |
| 14 | $Pd(PPh_3)_4$ | $Et_3N$ | $CH_3CN$ | 50 | 16 | 0 | — |
| 15 | $Pd(PPh_3)_4$ | $Ag_2CO_3$ | $CH_3CN$ | 30 | 2 | 61 | 99:1 |
| 16 | $Pd(PPh_3)_4$ | $K_2CO_3$ | DMF | 50 | 16 | 39 | 80:20 |
| 17[e] | $Pd(PPh_3)_4$ | $K_2CO_3$ | DMF | 60 | 3 | 0 | — |
| 18[e] | $Pd(PPh_3)_4$ | $Et_3N$ | DMF | 60 | 2 | 0 | — |
| 19 | $Pd(PPh_3)_4$ | $K_2CO_3$ | MeOH | 50 | 1 | 0 | — |
| 20 | $Pd(PPh_3)_4$ | $K_2CO_3$ | THF | 66 | 20 | 67 | 6:94 |
| 21 | $Pd(PPh_3)_4$ | $K_2CO_3$ | THF | 50 | 16 | 60 | 5:95 |
| 22 | $Pd(PPh_3)_4$ | $K_2CO_3$ | THF | 50 | 48 | 76 | 4:96 |
| 23[f] | $Pd(PPh_3)_4$ | $K_2CO_3$ | THF | 90 | 2 | 59 | 6:94 |
| 24 | $Pd(PPh_3)_4$ | $CH_3COOK$ | THF | 50 | 48 | 55 | 3:97 |
| 25 | $Pd(PPh_3)_4$ | $K_2CO_3$-18-C-6[g] | THF | 50 | 48 | 36 | 24:76 |
| 26 | $Pd(PPh_3)_4$ | $Li_2CO_3$ | THF | 50 | 24 | 23 | 16:84 |
| 27 | $Pd(PPh_3)_4$ | $Na_2CO_3$ | THF | 50 | 68 | 60 | 25:75 |
| 28 | $Pd(PPh_3)_4$ | $K_3PO_4$ | THF | 50 | 16 | 76 | 47:53 |
| 29 | $Pd(PPh_3)_4$ | LiH | THF | 50 | 48 | 9 | 20:80 |
| 30 | $Pd(PPh_3)_4$ | NaH | THF | 50 | 0.5 | 21 | 82:18 |
| 31 | $Pd(PPh_3)_4$ | DBU | THF | 50 | 68 | 24 | 35:65 |
| 32 | $Pd(PPh_3)_4$ | $Ag_2CO_3$ | THF | 50 | 12 | 67 | 99:1 |
| 33 | $Pd(PPh_3)_4$ | $K_2CO_3$ | THP | 50 | 48 | 56 | 13:87 |
| 34 | $Pd(PPh_3)_4$ | $K_2CO_3$ | dioxane | 50 | 16 | 61 | 10:90 |
| 35 | $Pd(PPh_3)_4$ | $K_2CO_3$ | DME | 70 | 16 | 52 | 8:92 |
| 36 | $Pd(PPh_3)_4$ | $K_2CO_3$ | DME | 50 | 16 | 22 | 9:91 |
| 37 | $Pd(PPh_3)_4$ | $K_2CO_3$ | diglyme | 50 | 16 | trace | — |
| 38 | $Pd(PPh_3)_4$ | $K_2CO_3$ | toluene | 111 | 2 | 41 | 45:55 |
| 39[e] | $Pd(PPh_3)_4$ | $K_2CO_3$ | toluene | 90 | 24 | 0 | — |
| 40 | $Pd(PPh_3)_4$ | $K_2CO_3$ | toluene | 50 | 16 | 17 | 22:78 |
| 41 | $Pd(PPh_3)_4$ | $Ag_2CO_3$ | toluene | 40 | 4 | 56 | 100:0 |

[a]All reactions were carried out with a molar ratio of $\mathbf{1}_S$:*o*-iodoanisole:base:catalyst = 1:2:2:0.05, unless otherwise stated. [b]The product ratios were determined by the HPLC analysis of (*o*-methoxyphenyl)methylphenylphosphine-borane, which was obtained by the reaction of the arylation product with MeLi. See Experimental section. [c]The substrate was a diastereomer mixture. The isomer ratio was not determined. [d]*o*-Bromoanisole was used instead of *o*-iodoanisole. [e]*o*-Methoxyphenyl trifluoromethanesulfonate was used instead of *o*-iodoanisole. [f]The reaction was carried out in a sealed tube. [g]$K_2CO_3$:18-crown-6 = 1:2.

the degree of stereospecificity was not high (entries 7 and 8). Use of stronger bases in THF resulted in predominant retention of configuration (entries 10–12).

We were deeply interested in the unprecedented stereochemistry observed in this study, and tested the stereochemistry of the reaction of ($R_P$)-menthyl phenylphosphinate (**5**) whose structure closely resembles $\mathbf{1}_S$. Compound **5** [11] was allowed to react with *o*-iodoanisole (2 equiv) under the same conditions as shown in entry 23 in Table 1. The $^1H$ NMR (500 MHz) analysis of the product (**6**) by comparison with the spectra of authentic samples indicated that the reaction proceeded with retention of configuration at phosphorus (Scheme 4). This result is in accordance with the previously reported results of the palladium-catalyzed reaction of optically active isopropyl methylphosphinate with aromatic or vinylic halides [9].

Inversion of configuration and dramatic solvent effects found in this study are characteristic reactivities of phosphine-boranes. The mechanism




$1_R$ $2_R$ $2_S$

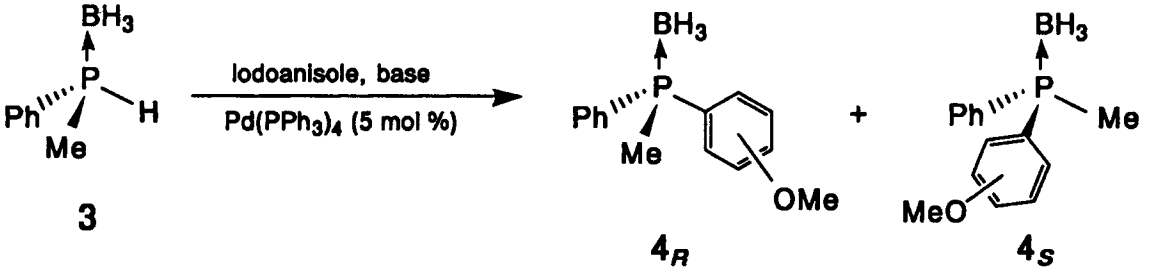
| Solvent | Time (h) | Yield (%) | $2_R$ : $2_S$ |
|---|---|---|---|
| $CH_3CN$ | 16 | 98 | 100 : 0 |
| THF | 48 | 67 | 4 : 96 |

**SCHEME 2**

**TABLE 2** Palladium-Catalyzed Reaction of (*S*)-Methylphenylphosphine-Borane (**3**) with Iodoanisole[a]

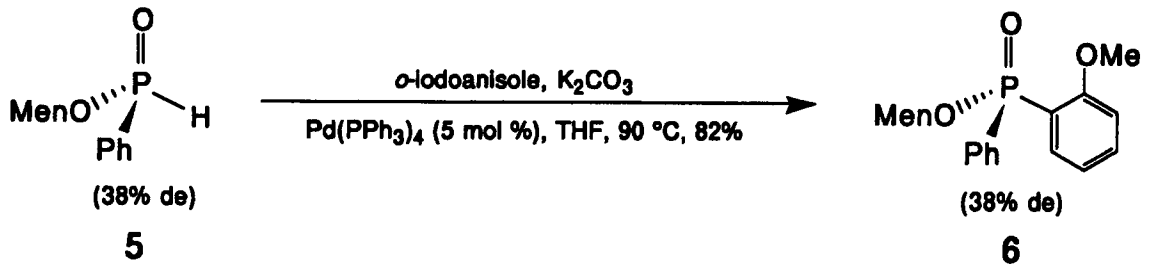
| *Entry* | *Iodoanisole* | *Base* | *Solvent* | *Temperature (°C)* | *Time (hours)* | *Yield (%)* | $4_R$:$4_S$[b] |
|---|---|---|---|---|---|---|---|
| 1 | ortho | $K_2CO_3$ | $CH_3CN$ | 40 | 6 | 77 | 99:1 |
| 2 | meta | $K_2CO_3$ | $CH_3CN$ | 40 | 6 | 51 | 98:2 |
| 3 | para | $K_2CO_3$ | $CH_3CN$ | 40 | 8 | 73 | 99:1 |
| 4 | ortho | CsF | $CH_3CN$ | 40 | 4 | 89 | 99:1 |
| 5 | ortho | $Ag_2CO_3$ | $CH_3CN$ | 40 | 14 | 1 | 94:6 |
| 6 | ortho | $Cs_2CO_3$ | $CH_3CN$ | 40 | 1 | 57 | 52:48 |
| 7 | ortho | $K_2CO_3$ | THF | 40 | 14 | 79 | 19:81 |
| 8 | meta | $K_2CO_3$ | THF | 40 | 15 | 82 | 40:60 |
| 9 | para | $K_2CO_3$ | THF | 40 | 24 | 65 | 26:74 |
| 10 | ortho | $Ag_2CO_3$ | THF | 15 | 24 | 15 | 98:2 |
| 11 | ortho | $Tl_2CO_3$ | THF | 15 | 48 | 64 | 87:13 |
| 12 | ortho | $Cs_2CO_3$ | THF | 40 | 18 | 48 | 60:40 |
| 13 | ortho | CsF | THF | 40 | 24 | 59 | 42:58 |
| 14 | ortho | *n*-$Bu_4NF$ | THF | 40 | 15 | 3 | 51:49 |
| 15 | ortho | $K_2CO_3$ | DME | 40 | 48 | 57 | 25:75 |

[a]All reactions were carried out with a molar ratio of **3**:iodoanisole:base:$Pd(PPh_3)_4$ = 1:2:2:0.05. [b]The enantiomeric excess was determined by HPLC analysis using a chiral column. The ratio was corrected based on the enantiomeric excess (98% ee) of starting material **3**.




**3** $4_R$ $4_S$

**SCHEME 3**

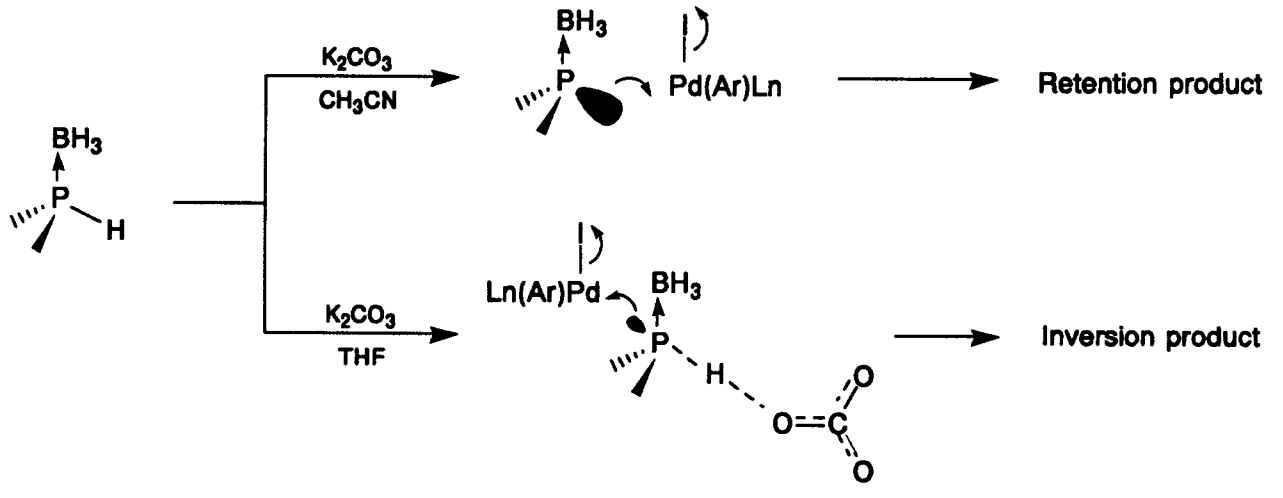



**SCHEME 4**

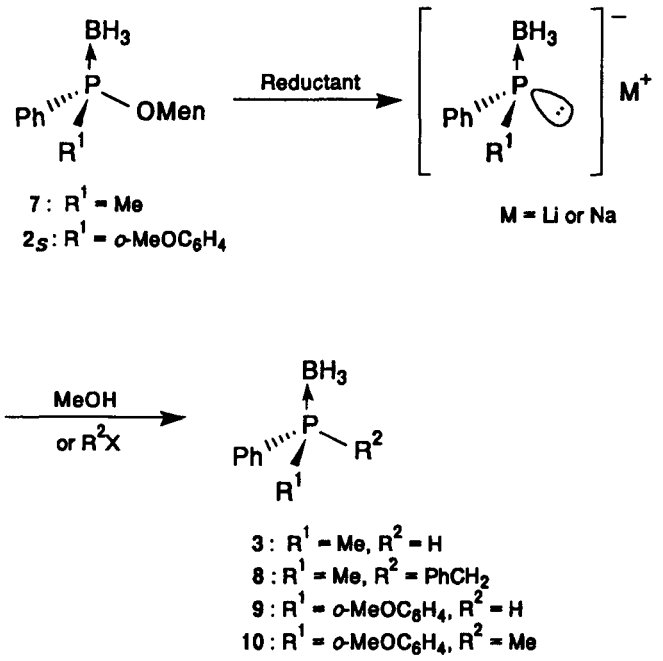
accounting for the observed stereochemical outcome is not yet fully understood, but we suppose that the stereochemistry of the product is determined at the transmetallation step in the catalytic cycle. Thus, as is shown in Scheme 5, in a polar solvent, acetonitrile, the proton abstraction from the secondary phosphine-borane by $K_2CO_3$ occurs readily and the generated naked phosphorus anion attacks the palladium atom with retention of configuration at phosphorus. On the contrary, in a less polar solvent, THF, the proton abstraction and attack on the palladium atom occur simultaneously with inversion.

### *Stereospecific Reduction of Menthyloxyphosphine-Boranes*

Chiral tetracoordinate organophosphorus compounds containing a leaving group are well-known to undergo nucleophilic substitution reactions, and numerous examples of this kind of reaction have been described in the literature [6]. However, comparatively little work has been done on the reductive removal of the leaving group [12], and a stereospecific cleavage of the bond between phosphorus and on alkoxy group has not yet been reported. We envisioned that diastereomerically pure menthyloxyphosphine-boranes might be converted into optically active secondary phosphine-boranes by reductive removal of the menthyloxy group. The initial trial was undertaken by treatment of diastereomerically pure ($R_P$)-menthyloxy(methyl) phenylphosphine-borane (**7**) and ($S_P$)-menthyloxy (*o*-methoxyphenyl)phenylphosphine-borane (**2$_S$**) with various reducing agents, and it was found that the desired reductions could be accomplished by the use of one-electron reductants, such as lithium naphthalenide, sodium naphthalenide, lithium 4,4'-di-*tert*-butylbiphenylide (LDBB) [13], and lithium in liquid ammonia [14]. Thus, the reductions proceeded rapidly at −78°C, and subsequent treatment with methanol or alkyl halides at the same temperature afforded optically active secondary or tertiary phosphine-boranes (Scheme 6) [15]. The results obtained under various reaction conditions are summarized in Table 3.




**SCHEME 5**




**SCHEME 6**

The reductions of $\mathbf{2_S}$ and **7** with lithium naphthalenide or $Li/NH_3$ provided products (**3, 8, 9, 10**) in almost quantitative yields with an excellent degree of stereospecificity (entries 1–3 and 13–15). Use of LDBB and lithium biphenylide, which possess reducing power stronger than that of lithium naphthalenide, resulted in a slightly diminished degree of stereospecificity (entries 8, 9). Sodium naphthalenide also reduced these substrates in essentially quantitative yield, while the optical purities of the products were slightly lower than the ones obtained by the use of lithium naphthalenide (entries 12 and 17).

On the other hand, the reactions at elevated temperatures provided products with almost complete racemization (entries 4, 5, and 16). Racemized products were obtained also when reactions were carried out under the conditions of entries 6 and 7. These results indicate that the intermediate tricoordinate phosphorus species were readily racemized at elevated temperatures.

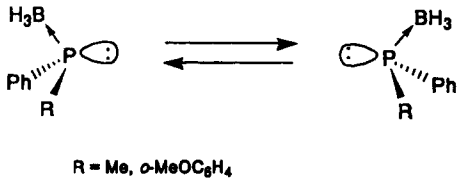
The following two mechanisms may be proposed for the racemization. Scheme 7 illustrates a conceivable racemization process via pyramidal inversion. The other possible racemization pathway, which involves intermolecular borane transfer, is depicted in Scheme 8.

In order to determine the mechanism of the racemization, ($R_P$)-menthyloxy[methyl($d_3$)]phenylphosphine-borane($d_3$) (**11**) was prepared from ($S_P$)-menthyloxyphenylphosphine-borane($d_3$). This compound was mixed with compound **7** in a 1:1 molar ratio, and the mixture was allowed to react with lithium naphthalenide at 25°C for 5 minutes, followed by treatment with benzyl bromide. The product was analyzed by field desorption (FD) mass spectroscopy [16]. The mass spectrum showed that the product consisted of compounds **8** [*m/e* 229 ($M^+$+1)] and **12** [*m/e* 235 ($M^+$+1)]; no traces of crossover compounds **13** [*m/e* 232 ($M^+$+1)] and **14**

**TABLE 3** Stereospecific Reduction of Menthyloxyphosphine-Boranes with One-Electron Reducing Agents[a]

| Entry | Substrate | Reductant | Temperature (°C) | Electrophile | Product | Yield (%) | ee (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | **7** | $Li^+[C_{10}H_8]^-$ | −78 | MeOH | **3** | 95 | 95 |
| 2 | **7** | Li-$NH_3$ | −78 | MeOH | **3** | 94 | 98 |
| 3 | **7** | $Li^+[C_{10}H_8]^-$ | −78 | $PhCH_2Br$ | **8** | 100 | 95 |
| 4 | **7** | $Li^+[C_{10}H_8]^-$ | 25 | $PhCH_2Br$ | **8** | 93 | 3 |
| 5 | **7** | $Li^+[C_{10}H_8]^-$ | 65 | $PhCH_2Br$ | **8** | 76 | 2 |
| 6 | **7** | $Li^+[C_{10}H_8]^-$ | −78; 65[c] | $PhCH_2Br$ | **8** | 92 | 5 |
| 7 | **7** | $Li^+[C_{10}H_8]^-$ | 65; −78[d] | $PhCH_2Br$ | **8** | 92 | 3 |
| 8 | **7** | LDBB[e] | −78 | $PhCH_2Br$ | **8** | 100 | 81 |
| 9 | **7** | LDBB[e] | −95 | $PhCH_2Br$ | **8** | 100 | 88 |
| 10 | **7** | LB[f] | −78 | $PhCH_2Br$ | **8** | 100 | 85 |
| 11 | **7** | LA[g] | −78 | $PhCH_2Br$ | **8** | trace | — |
| 12 | **7** | $Na^+[C_{10}H_8]^-$ | −78 | $PhCH_2Br$ | **8** | 100 | 93 |
| 13 | $\mathbf{2_S}$ | $Li^+[C_{10}H_8]^-$ | −78 | MeOH | **9** | 100 | 93 |
| 14 | $\mathbf{2_S}$ | $Li^+[C_{10}H_8]^-$ | −95 | MeI | **10** | 97 | 94 |
| 15 | $\mathbf{2_S}$ | $Li^+[C_{10}H_8]^-$ | −78 | MeI | **10** | 100 | 93 |
| 16 | $\mathbf{2_S}$ | $Li^+[C_{10}H_8]^-$ | 65 | MeI | **10** | 66 | 3 |
| 17 | $\mathbf{2_S}$ | $Na^+[C_{10}H_8]^-$ | −78 | MeI | **10** | 96 | 88 |

[a]All reactions were carried out in THF. [b]Enantiomeric excesses were determined by HPLC analysis with a chiral column. [c]The reduction was carried out at −78°C, the mixture was warmed to 65°C, and then benzyl bromide was added. [d]The reduction was carried out at 65°C, the mixture was cooled to −78°C, and then benzyl bromide was added. [e]Lithium 4,4′-di-*tert*-butylbiphenylide. [f]Lithium biphenylide. [g]Lithium anthracenide.

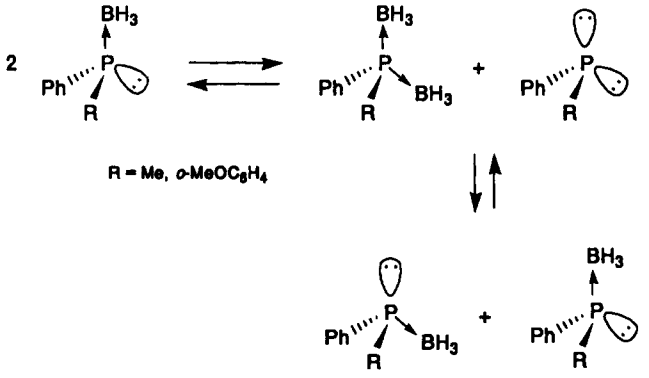



**SCHEME 7**

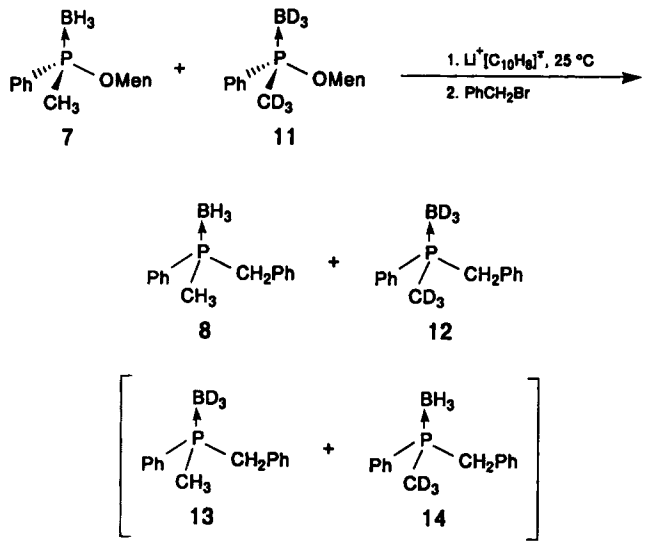
[*m/e* 232 ($M^+$+1)] were detected in the spectrum (Scheme 9). These results demonstrate that intermolecular borane transfer does not take place under these conditions, and they strongly suggest that the racemization occurs via pyramidal inversion.

### *Synthesis of Optically Pure $C_2$-Symmetric Bis(phosphine-boranes)*

Based on the stereochemical studies described earlier, we have explored new synthetic routes to optically pure $C_2$-symmetric bis(phosphine-boranes), since they are excellent precursors to chiral bidentate phosphine ligands [7]. Our synthetic routes to compounds **16a–c**, **18a–c**, **19a–c**, and **20a–c** are illustrated in Scheme 10.




**SCHEME 8**




**SCHEME 9**

The key intermediates **15a–c** were derived from compound $\mathbf{1}_S$. The reaction of $\mathbf{1}_S$ with 1,3-diiodopropane and 1,4-diiodobutane in the presence of NaH afforded **15b** and **15c** in 66% and 85% yield, respectively. Synthesis of **15a** was accomplished via compound **7** [7]. Thus, the metallation of **7** with *sec*-butyllithium, followed by oxidative coupling by copper(II) chloride, afforded **15a** in 73% yield.

The nucleophilic substitution reactions of **15a–c** with methyllithium in benzene proceeded with complete inversion of configuration to give **16a–c** in 57%, 57%, and 82% yield, respectively.

Compounds **15a–c** were converted to other intermediates **17a–c** by the reduction with lithium naphthalenide at −78°C. The secondary phosphine-boranes obtained were readily subjected to electrophilic alkylation. Thus, treatment of **17a–c** with iodomethane in the presence of NaH afforded **18a–c** in good yields. It is noted that these compounds are enantiomers of **16a–c**. Similarly, compounds **19a–c** were synthesized in reasonable yields by the reactions with 1-iodo-2-methoxyethane. However, the ease of arylation with *o*-iodoanisole in the presence of $Pd(PPh_3)_4$ was largely dependent on the structure of **17**. The reaction of **17a** in the presence of $K_2CO_3$ in acetonitrile afforded no trace of the expected compound **20a**, although the starting material was completely consumed [17]. Under similar conditions, **17b** and **17c** were converted to **20b** and **20c** in 19% and 71% yield, respectively. This method is advantageous over the previously existing one [7] in the overall yield [18].

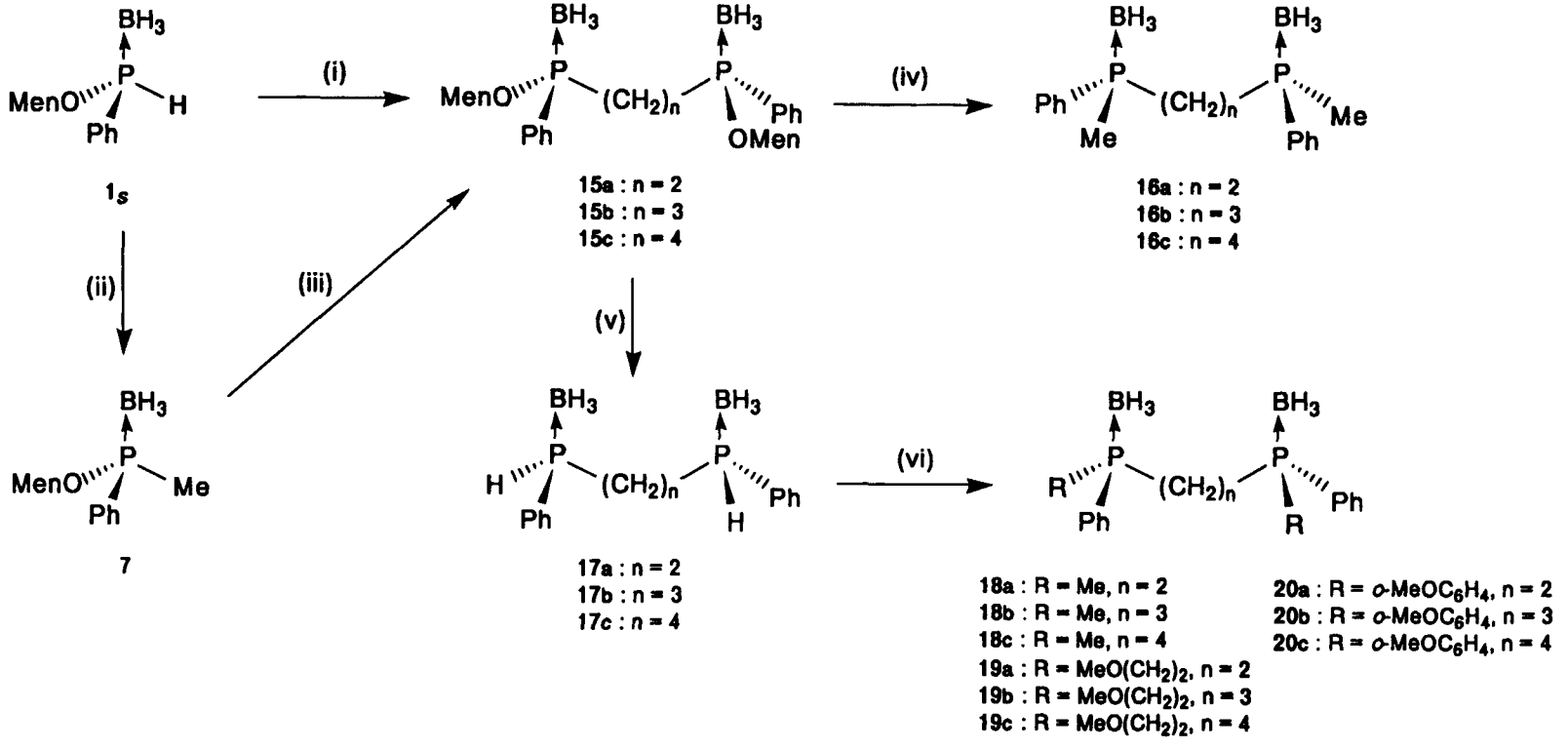
In summary, we have established a new method for the synthesis of optically pure $C_2$-symmetric bis(phosphine-boranes) by utilizing stereospecific reactions occurring at chiral phosphorus. This method is applicable to the synthesis of other analogous phosphine-boranes and phosphine ligands.

## *EXPERIMENTAL SECTION*

### *General*

The NMR spectra were recorded on JEOL GX-270 ($^1$H NMR at 270 MHz and $^{13}$C NMR at 68 MHz), Varian VXR-300 ($^{11}$B NMR at 96 MHz and $^{31}$P NMR at 121 MHz), JEOL JNM-GSX-400 ($^1$H NMR at 400 MHz), and JEOL JNM-GSX-500 ($^1$H NMR at 500 MHz and $^{13}$C NMR at 126 MHz) spectrometers. Chemical shifts ($\delta$) are expressed in parts per million relative to tetramethylsilane ($CDCl_3$). The chemical shifts of $^{11}$B and $^{31}$P NMR spectra are quoted relative to external $(CH_3O)_3B$ and $(PhO)_3PO$, respectively. The IR spectra were recorded on a Hitachi-IR215 spectrophotometer. Optical rota-

SCHEME 10




[a]Reagents and conditions: (i) $I(CH_2)_nI$ (n=3, 4), NaH, THF; (ii) MeI, NaH, THF; (iii) *sec*-BuLi, THF, –78 °C, then $CuCl_2$, –78 °C to 0 °C; (iv) MeLi, benzene; (v) $C_{10}H_8$–Li, THF, –78 °C; (vi) RI (R=Me, $MeO(CH_2)_2$), NaH, THF or *o*-$MeOC_6H_4I$, $K_2CO_3$, $Pd(PPh_3)_4$, MeCN

tions were measured with a JASCO DIP-370 digital polarimeter with a 10-cm-long cell. Analytical high-performance liquid chromatography (HPLC) was performed on a Hitachi L-6000 pump and Hitachi L-4000 UV detector. Mass spectra were obtained on JEOL JMS-HX110 and JEOL JMS-DX-300 (FD-Mass) instruments. Microanalyses were performed on a Perkin-Elmer 240B instrument at the Chemical Analysis Center of Chiba University. Tetrahydrofuran and DME were distilled from potassium benzophenone ketyl under argon prior to use. Ether was distilled from $LiAlH_4$ under argon prior to use. Acetonitrile, benzene, diethylene glycol dimethyl ether (diglyme), and dioxane were distilled from $CaH_2$ and stored over 4-Å molecular sieves. All experiments were carried out under an argon atmosphere. The products were isolated by preparative TLC on silica gel (Wakogel B-5F) or column chromatography on silica gel (Wakogel C-200 or C-300).

### *Materials*

$PdCl_2$ and $Pd(OAc)_2$ were commercial products. $PdCl_2(PhCN)_2$ [19], $Pd(PPh_3)_4$ [20], and $Pd_2(dba)_3 \cdot CHCl_3$ [21] were prepared according to the reported procedures. *o*-Methoxyphenyl trifluoromethanesulfonate was prepared from *o*-methoxyphenol and trifluoromethanesulfonic anhydride according to the procedure described in the literature [22]. 4,4'-Di-*tert*-butylbiphenyl (DBB) was prepared according to the literature procedure [23]. ($S_P$)-Menthyloxyphenylphosphine-borane (**1**$_S$) and ($R_P$) menthyloxyphenylphosphine-borane (**1**$_R$) were prepared according to the procedure described in the previous article [7].

### *Reaction of ($S_P$)-Menthyloxyphenylphosphine-Borane (**1**$_S$) with o-Iodoanisole in the Presence of $Pd(PPh_3)_4$ and Determination of the Diastereomeric Excess of the Product*

A mixture of finely powdered, anhydrous $K_2CO_3$ (1.0 g, 7.2 mmol), ($S_P$)-menthyloxyphenylphosphine-borane (**1**$_S$) (1.00 g, 3.59 mmol), $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol, 5 mol %), *o*-iodoanisole (1.68 g, 7.2 mmol), and acetonitrile (10 mL) was stirred at 50°C under argon for 16 hours. The reaction mixture was acidified with 1 M HCl and extracted with ether. The combined extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residual oil was purified by column chromatography on silica gel using hexane-acetone (9:1) to give diastereomerically pure ($S_P$)-menthyloxy(*o*-methoxyphenyl)phenylphosphine-borane (**2**$_S$) as a white powder (1.32 g, 96% yield).

The coupled product was transformed via complete inversion of configuration to *o*-(methoxyphenyl)methylphenylphosphine-borane by treatment with excess methyllithium. Thus, a flame-dried 20 mL, two-necked flask equipped with a magnetic stirrer was flushed with argon and charged with the coupled product (77 mg, 0.2 mmol) and dry benzene (2 mL). Methyllithium (0.6 mmol, 0.4 mL of 1.5 M diethyl ether solution) was added to the resulting solution. The solution was stirred at room temperature for more than 2 hours until the reaction was complete. The mixture was treated with 1 M HCl (5 mL) and was extracted with ether. The combined extracts were dried over $MgSO_4$ and concentrated. The residual oil was purified by preparative thin layer chromatography on silica gel using benzene-hexane (2:1). The enantiomeric excess of the product was determined by HPLC analysis (column, CHIRALCEL OJ (Daicel Chemical Industries, Ltd); eluent, hexane-2-propanol (9:1); flow rate, 1.0 mL/min; detection, UV 254 nm). The absolute configuration was determined according to the literature [3].

### *Reduction of ($R_P$)-Menthyloxy(methyl)phenylphosphine-Borane (**7**) and ($S_P$)-Menthyloxy(o-methoxyphenyl)phenylphosphine-Borane (**2**$_S$) with a Radical Anion. Synthesis of (S)-Benzylmethylphenylphosphine-Borane (**8**) and (R)-o-Methoxyphenyl(phenyl)phosphine-Borane (**9**)*

A solution of compound **7** (146 mg, 0.5 mmol) in THF (2.5 mL) was added dropwise with vigorous stirring to a preformed solution of lithium naphthalenide (2 mmol) in THF (10 mL) at −78°C. After 5 minutes, benzyl bromide (180 μL, 1.5 mmol) was added at the same temperature and the stirring was continued for an additional 5 minutes. The reaction was quenched with 1 M HCl, and the mixture was extracted with ether. The combined extracts were dried over $MgSO_4$ and concentrated on an evaporator. The residue was passed through a short column of silica gel using hexane-benzene as the eluent to remove naphthalene. The crude product obtained was subjected to preparative TLC [benzene-hexane (2:1)] to give **8** (114 mg, 100%). Mp 85–86°C; $[\alpha]_D^{27}$ −13.5° (*c* 1.00, $CH_3OH$) (98% ee). IR (KBr): 3010, 2350, 1490, 1430, 1290, 1060, 910 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ 1.50 (d, *J* = 10.1 Hz, 3H), 3.23 (d, *J* = 11.2 Hz, 2H), 6.85–7.93 (m, 10H). MS (70 eV), *m/e* 214 ($M^+-BH_3$); FD-MS *m/e* 229 ($M^+$+1). Anal.: Calcd for $C_{14}H_{18}BP$: C, 73.73; H, 7.95; Found: C, 73.93; H, 7.80. Enantiomeric excess of this compound was determined by HPLC analysis (column, CHIRALCEL OJ; eluent, hexane-2-propanol (9:1); flow rate, 1.0 mL/min; detection, UV 254 nm).

In a similar manner, compound **9** was prepared in 95–100% yield. Mp 67–69°C; $[\alpha]_D$ 99.8° (*c* 1.0, $C_6H_6$). This compound underwent racemization gradually on standing at room temperature.

*Reduction of ($R_P$)-Menthyloxy(methyl)phenylphosphine-Borane (**7**) with Lithium-Ammonia. Synthesis of (R)-Methylphenylphosphine-Borane (**3**)*

A solution of optically pure **7** (600 mg, 2.05 mmol) in THF (4 mL) was added dropwise to a preformed solution of lithium/ammonia in THF (2 mL) with vigorous stirring at −78°C. The mixture was stirred for 5 minutes at −78°C, and methanol (1.5 mL) was then added. After having been stirred for an additional 5 minutes, 2 M HCl (10 mL) and 6 M HCl (5 mL) were added successively. After the usual workup, the residue was subjected to short column chromatography using benzene as the eluent to give practically pure **3** (245 mg, 94%). The enantiomeric excess of this compound was determined to be 98% by HPLC analysis (column, CHIRALCEL OJ; eluent, hexane-2-propanol (9:1); flow rate, 1.0 mL/min; detection, UV 254 nm).

*($S_P$)-Menthyloxyphenylphosphine-Borane ($d_3$)*

A mixture of (−)-menthol (7.71 g, 50 mmol) and pyridine (4.2 mL, 52 mmol) in 40 mL of dry benzene was added during 3 hours to a solution of dichlorophenylphosphine (7.3 mL, 54 mmol) in dry benzene (30 mL) at room temperature. The reaction mixture was stirred for 12 hours, and it was filtered quickly to remove the pyridinium salt. The filtrate was added to a solution of $LiBD_4$ [24,25] (5.70 g, 0.222 mol) in dry ether (50 mL) at 0°C. After having been stirred at room temperature for 15 minutes, the reaction mixture was poured into a vigorously stirred mixture of concentrated HCl (5 mL), ice (ca. 20 g), and hexane (50 mL). After the usual workup, the residue was subjected to column chromatography [benzene-hexane (1:3)] to give a diastereomer mixture as a white powder. It was recrystallized from hexane twice to give a pure diastereomer **5** (0.91 g). Mp 100–101°C; $[\alpha]_D^{27}$ −115.4° (*c* 1.0, $ClCH_2CH_2Cl$) (100% de). IR (KBr): 2900, 2320, 1790, 1440, 1120, 1000 $cm^{-1}$. $^1H$ NMR (500 MHz) ($CDCl_3$) $\delta$ 0.62–1.65 (m, 7H), 0.63 (d, $J$ = 7.15 Hz, 3H), 0.886 (d, $J$ = 6.60 Hz, 3H), 0.893 (d, $J$ = 7.15 Hz, 3H), 2.01–2.08 (m, 2H), 3.85–3.93 (m, 1H), 7.48–7.60 (m, 3H), 7.77—7.81 (m, 2H). $^{13}C$ NMR (126 MHz) ($CDCl_3$) $\delta$ 15.8, 20.9, 22.0, 23.0, 25.6, 31.5, 34.0, 42.2, 48.8 (d, $J$ = 6.4 Hz), 80.1 (d, $J$ = 6.4 Hz), 128.9 (d, $J$ = 8.6 Hz), 129.5 (d, $J$ = 64.5 Hz), 132.2 (d, $J$ = 10.8 Hz), 132.6 Anal.: Calcd for $C_{16}H_{24}D_4OBP$: C, 69.08; H, 10.14; Found: C, 69.03; H, 9.93.

*($R_P$)-Menthyloxymethyl($d_3$)phenylphosphine-Borane($d_3$) (**11**)*

Sodium hydride (135 mg of 40% oil dispersion, 3.4 mmol) was added to a mixture of ($S_P$)-menthyloxyphenylphosphine-borane ($d_3$) (476 mg, 1.69 mmol) and iodomethane ($d_3$) (160 $\mu$L, 2.54 mmol) in 6 mL of THF at 0°C under argon. After having been stirred at room temperature for 1 hour; the reaction mixture was treated with water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined extracts were washed with aqueous $Na_2S_2O_3$ and dried ($Na_2SO_4$). The solvent was removed under reduced pressure, and the residual oil was subjected to preparative TLC (benzene/hexane 1:4) to give **11** as a white crystalline solid (502 mg, 100%). Mp 64–65°C; $[\alpha]_D^{26}$ −3.6° (*c* 1.0, $C_6H_6$) (100% de). IR (KBr): 2900, 2330, 1790, 1440, 1120, 1000 $cm^{-1}$. $^1H$ NMR (500 MHz) ($CDCl_3$) $\delta$ 0.40–1.80 (m, 8H), 0.77 (d, $J$ = 6.60 Hz, 3H), 0.86 (d, $J$ = 6.87 Hz, 3H), 0.94 (d, $J$ = 6.87 Hz, 3H), 2.06–2.13 (m, 1H), 4.08–4.16 (m, 1H), 7.44–7.53 (m, 3H), 7.77–7.82 (m, 2H). $^{13}C$ NMR (68 MHz) ($CDCl_3$) $\delta$ 16.0, 21.0, 22.0, 23.0, 25.8, 31.3, 34.2, 43.3, 48.9 (d, $J$ = 6.8 Hz), 79.7 (d, $J$ = 2.9 Hz), 128.5 (d, $J$ = 10.7 Hz), 130.3 (d, $J$ = 10.8 Hz), 131.6 (d, $J$ = 2.0 Hz), 134.8 (d, $J$ = 59.7 Hz). FD-MS *m/e*, 297 ($M^+$−1). Anal.: Calcd for $C_{17}H_{24}D_6OBP$: C, 68.46; H, 12.16. Found: C, 69.82; H, 10.07.

*Benzyl(methyl($d_3$))phenylphosphine-Borane($d_3$)*

mp 85–86°C; $[\alpha]_D^{27}$ −12.6° (*c* 1.0, $CH_3OH$) (97% ee). IR (KBr): 3000, 2320, 1780, 1490, 1430, 1020, 910 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 3.23 (d, $J$ = 11.2 Hz, 2H), 6.85–7.93 (m, 10H). FD-MS *m/e*, 235 ($M^+$+1).

*($R_P$, $R_P$)-1,3-Bis[boranato(menthyloxy)phenylphosphino] propane (**15b**) and ($R_P$, $R_P$)-1,4-Bis[boranato(menthyloxy)phenylphosphino] butane (**15c**)*

NaH (60% dispersion in mineral oil, 160 mg) was added with stirring at 0°C to a mixture of $\mathbf{1}_S$ (558 mg, 2 mmol) and 1,3-diiodopropane (0.9 mmol) or 1,4-diiodobutane (0.9 mmol) in THF (5 mL). After having been stirred for 10 minutes, the mixture was treated with 1 M HCl (10 mL) at 0°C, and it was extracted with ether. The combined extracts were washed with aqueous $Na_2S_2O_3$ and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the residue was subjected to preparative TLC on silica gel with benzene-hexane (1:2) to afford practically pure **15b** or **15c**. Yields of products **15b** and **15c** were 66% and 85%, respectively, based on diiodoalkanes. **15b**: mp 130–131°C; $[\alpha]_D$ −2.9° (*c* 1.2, $CHCl_3$), +2.6° (*c* 1.0, $ClCH_2CH_2Cl$). IR (KBr): 2930, 2350, 1440, 1110, 1070, 990, 970 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) $\delta$ 0.77 (d, $J$ = 6.6 Hz, 6H), 0.75–0.80 (m, 4H), 0.83 (d, $J$ = 6.9 Hz, 6H), 0.92 (d, $J$ = 6.9 Hz, 6H), 0.94–1.03 (m, 4H), 1.28–1.36 (m, 4H), 1.57–1.68 (m, 4H), 1.76–1.83 (m, 2H), 1.90–1.99 (m, 2H), 2.05–2.11 (m, 2H), 4.07–4.13 (m, 2H), 7.40–7.70 (m, 10H). Anal. Calcd for $C_{35}H_{60}B_2O_2P_2$: C, 70.48; H, 10.14; Found: C, 70.47; H, 9.86.

**15c**: mp 112–113°C; $[\alpha]_D$ −1.7° (*c* 1.2, $CHCl_3$),

+2.0 (*c* 0.9 $ClCH_2CH_2Cl$). IR (KBr): 2920, 2380, 1440, 1110, 1060, 990, 820 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) $\delta$ 0.73 (d, $J$ = 6.3 Hz, 6H), 0.76–0.82 (m, 4H), 0.84 (d, $J$ = 6.9 Hz, 6H), 0.94 (d, $J$ = 7.2 Hz, 6H), 0.97–1.00 (m, 2H), 1.29–1.46 (m, 8H), 1.58–1.76 (m, 8H), 1.82–1.87 (m, 2H), 2.08–2.12 (m, 2H), 4.08–4.13 (m, 2H), 7.41–7.72 (m, 10H). Anal.: Calcd for $C_{36}H_{62}B_2O_2P_2$: C, 70.83; H, 10.24; Found: C, 70.85; H, 9.99.

*($R_P$, $R_P$)-1,2-Bis[boranato(menthyloxy)phenylphosphino]ethane* (**15a**)

*sec*-Butyllithium (0.9 M/L cyclohexane solution, 8.2 mL) was added dropwise to a solution of **7** (1.72 g, 5.85 mmol) in THF (12 mL) at −78°C. The mixture was stirred for 2 hours, whereupon the color of the mixture turned from colorless to yellow. Finely powdered copper(II) chloride (1.18 g), which was dried prior to use in vacuo at 120°C for 1 hour, was added at −78°C with vigorous stirring. The temperature was gradually raised to 0°C during 20 minutes. The reaction was quenched with 1 M HCl (10 mL), the organic layer was separated, and the aqueous layer was extracted with ether. The combined extracts were dried over $Na_2SO_4$. The solvent was evaporated in vacuo, and the residue was subjected to column chromatography on silica gel using benzene-hexane (1:2) as the eluent to afford a white solid (1.25 g, 73%). Recrystallization from pentane gave pure product. Mp 150–153°C; $[\alpha]_D$ −9.3° (*c* 2.4, $CHCl_3$). IR (KBr): 2900, 2300, 1440, 1120, 990, 740 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) $\delta$ 0.68–1.02 (m, 10H), 0.73 (d, $J$ = 6.6 Hz, 4H), 0.87 (d, $J$ = 6.9 Hz, 6H), 0.95 (d, $J$ = 7.2 Hz, 4H), 1.25–1.38 (m, 4H), 1.58–1.68 (m, 6H), 1.81–1.87 (m, 2H), 2.04–2.14 (m, 4H), 4.07–4.13 (m, 2H), 7.41–7.72 (m, 10H). Anal.: Calcd for $C_{34}H_{58}B_2O_2P_2$: C, 70.12; H, 10.04; Found: C, 69.99; H, 9.81.

*Reduction of* **15a–c** *by Lithium Naphthalenide: Preparation of* **17a–c**

A solution of lithium naphthalenide (1.0 M/L, 4.8 mL) was added dropwise at −78°C to a solution of **15a** (124 mg, 0.2 mmol) in dry THF (4 mL) over a 10 minutes period. After having been stirred for 10 minutes, the reaction mixture was treated with 1 M HCl at the same temperature. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$. The combined extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was subjected to preparative TLC on silica gel with benzene-hexane (5:1) to afford **17a** (55 mg, 91%). In a similar manner, **17b** and **17c** were obtained in 88% and 83% yield, respectively.

*(S, S)-1,2-Bis[boranatophenylphosphino]ethane* (**17a**)

mp 97–100°C. IR (KBr): 2370, 1495, 1440, 1070, 920 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) $\delta$ 2.01–210 (m, 2H), 2.17–2.27 (m, 2H), 5.57 (d, $^2J_{P\text{-}H}$ = 373 Hz, 2H), 7.36–7.69 (m, 10H).

*(S, S)-1,3-Bis[boranatophenylphosphino]propane* (**17b**)

Oil; IR (neat) 2350, 1490, 1440, 1410, 1060, 930, 750 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) $\delta$ 1.79–1.89 (m, 2H), 1.94–2.11 (m, 4H), 5.44 (d, $^2J_{P\text{-}H}$ = 366 Hz, 2H), 7.42–7.67 (m, 10H).

*(S, S)-1,4-Bis[boranatophenylphosphino]propane* (**17c**)

Oil; IR (neat) 2370, 1495, 1440, 1120, 1070, 920 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) $\delta$ 1.61 (br s, 4H), 1.91 (br s, 4H), 5.41 (d, $^2J_{P\text{-}H}$ = 366 Hz, 2H), 7.45–7.67 (m, 10H).

*Alkylations of* **17a–c** *(General Procedure)*

Sodium hydride (60% dispersion in mineral oil, 160 mg) was added to a mixture of **17a–c** (0.5 mmol) and iodomethane (2 mmol) or 1-iodo-2-methoxyethane (2 mmol) at 0°C. After having been stirred for 10 minutes, the reaction was quenched with 1 M HCl at the same temperature. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$. The combined extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was subjected to preparative TLC on silica gel with benzene-hexane (5:1) to afford the alkylation product. Yields: **18a**, 79%; **18b**, 88%; **18c**, 89%, **19a**, 89%, **19b**, 97%, **19c**, 85%.

*(R, R)-1,2-Bis[boranato(methyl)phenylphosphino]ethane* (**18a**)

mp 170–172°C; $[\alpha]_D$ −34.7° (*c* 1.2, $CHCl_3$). IR (KBr): 2380, 1060, 920, 740 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) $\delta$ 1.55 (d, $^3J_{P\text{-}H}$ = 9.6 Hz, 6H), 1.79–1.86 (m, 2H), 1.99–2.06 (m, 2H), 7.42–7.62 (m, 10H). Anal.: Calcd for $C_{16}H_{26}B_2P_2$: C, 63.64; H, 8.68; Found: C, 63.56; H, 8.47.

*(R, R)-1,3-Bis[boranato(methyl)phenylphosphino]propane* (**18b**)

mp 66–68°C; $[\alpha]_D$ −36.5° (*c* 1.0, $CHCl_3$). IR (KBr) 2370, 1435, 1405, 1070, 760, 700 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) $\delta$ 1.53 (d, $^3J_{P\text{-}H}$ = 10.2 Hz, 6H), 1.49–1.68 (m, 2H), 1.82–1.99 (m, 4H), 7.40–7.64 (m,

10H). Anal.: Calcd for $C_{17}H_{28}B_2P_2$: C, 64.62; H, 8.93; Found: C, 64.70; H, 8.73.

### *(R, R)-1,4-Bis[boranato(methyl)phenylphosphino]butane* (**18c**)

mp 99–102°C; $[\alpha]_D$ −18.2° (*c* 1.2, $CHCl_3$). IR (KBr): 2360, 1435, 1405, 1060, 745 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) δ 1.38–1.44 (m, 2H), 1.45–1.56 (m, 2H), 1.52 (d, $^3J_{P-H}$ = 10.1 Hz, 6H), 1.74–1.84 (m, 4H), 7.42–7.68 (m, 10H). Anal.: Calcd for $C_{18}H_{30}B_2P_2$: C, 65.51; H, 9.16; Found: C, 64.56; H, 8.95.

### *(R, R)-1,2-Bis[boranato(2-methoxyethyl)phenylphosphino]ethane* (**19a**)

mp 108–109°C; $[\alpha]_D$ −28.2° (*c* 1.0, $CHCl_3$). IR (KBr): 2365, 1110, 1060, 960, 740 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) δ 1.87–1.93 (m, 2H), 2.09–2.25 (m, 6H), 3.25 (s, 6H), 3.39–3.46 (m, 2H), 3.58–3.65 (m, 2H), 7.42–7.52 (m, 10H). Anal.: Calcd for $C_{30}H_{34}B_2O_2P_2$: C, 61.59; H, 8.79; Found: C, 61.44; H, 8.63.

### *(R, R)-1,3-Bis[boranato(2-methoxyethyl)phenylphosphino]propane* (**19b**)

Oil; $[\alpha]_D$ −32.1° (*c* 1.1, $CHCl_3$). IR (neat): 2900, 2380, 1440, 1120, 960 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) δ 1.57–1.63 (m, 2H), 1.91–2.00 (m, 2H), 2.18–2.30 (m, 6H), 3.24 (s, 6H), 3.26–3.44 (m, 2H), 3.54–3.56 (m, 2H), 7.02–7.37 (m, 10H). Anal.: Calcd for $C_{31}H_{36}B_2O_2P_2$: C, 62.42; H, 8.98; Found: C, 62.68; H, 8.77.

### *($R_P$, $R_P$)-1,4-Bis[boranato(2-methoxyethyl)phenylphosphino]butane* (**19c**)

Oil; $[\alpha]_D$ −7.5° (*c* 1.4, $CHCl_3$). IR (neat): 2900, 2380, 1440, 1380, 1120, 1070 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) (500 MHz) δ 1.32–1.36 (m, 2H), 1.83–1.90 (m, 2H), 2.06–2.17 (m, 2H), 3.26 (s, 6H), 3.37–3.44 (m, 2H), 3.59–3.65 (m, 2H), 7.42–7.71 (m, 10H). Anal.: Calcd for $C_{32}H_{38}B_2O_2P_2$: C, 63.20; H, 9.16; Found: C, 63.56; H, 8.87.

## *ACKNOWLEDGMENTS*

This work was supported by Grant-in-Aid for Scientific Research on a Priority Area of Organic Unusual Valency No. 02247104 from the Ministry of Education, Science and Culture, Japan. We thank Prof. M. Yokoyama and Dr. H. Togo for valuable discussions. We are grateful to Dr. K. Ogata, Mr. T. Kuramochi, Mrs. H. Seki, Mrs. R. Hara, and Mrs. S. Imamoto (Chemical Analysis Center, Chiba University) for the measurement of high-field NMR, mass spectra, and elemental analysis.

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[15] The isolated secondary phosphine-boranes (**3** and **9**) underwent racemization slowly at room temperature.

[16] HPLC analysis using a chiral column showed that this product was racemic.

[17] Optically pure **20a** can be synthesized by oxidative dimerization of optically active *o*-methoxyphenyl(methyl)phenylphosphine-borane. See Ref. [7].

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