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Synthesis of Optically Active P-Chiral and Optically Inactive Oligophosphines

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Abstract: A series of optically active P-chiral oligophosphines (*S*,*R*,*R*,*S*)-**2**, (*S*,*R*,*S*,*S*,*R*,*S*)-**3**, (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4**, and (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5** with four, six, eight, and 12 chiral phosphorus atoms, respectively, were successfully synthesized by a step-by-step oxidative-coupling reaction from (*S*,*S*)-**1**. The corresponding optically inactive oligophosphines **1′**–**5′** were also prepared. Their properties were characterized by DSC, XRD, and optical-rotation analyses. While optically active bisphosphine (*S*,*S*)-**1** and tetraphosphine (*S*,*R*,*R*,*S*)-**2** behaved as small molecules, octaphosphine (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4** and dodecaphosphine (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5** exhibited the features of a polymer. Furthermore, DSC and XRD analyses showed that hexaphosphine (*S*,*R*,*S*,*S*,*R*,*S*)-**3** is an intermediate between a small molecule and a polymer. Comparison of optically active oligophosphines **1**–**5** with the corresponding optically inactive oligophosphines **1′**–**5′** revealed that the optically active phosphines have higher crystallinity than the optically inactive counterparts. It is considered that the properties of oligophosphines depend on the enantiomeric purity as well as the oligomer chain length.

Keywords: amorphous materials · chiral polymers · oligomers · oligophosphines · phosphorus

Introduction

Over the past three decades, optically active polymers, especially helical polymers, have been extensively studied owing to their characteristic properties such as molecular recognition, chiral amplification, chiral transcription, and conformation storage. Most naturally occurring polymers, for example, DNA and protein, are composed of chiral carbon atoms,[1] and their chiral structures are closely associated with highly sophisticated functions such as replication and repair. Artificial chiral polymers are generally prepared by polymerization of chiral monomers[2] or asymmetric polymerization of optically inactive monomers by using chiral reagents.[3] Helical induction and chiral amplification of optically inactive polymers by chiral additives are also well-acknowledged.[4] For both naturally occurring and artificial chiral polymers, their chirality is mainly derived form chiral carbon atoms or chiral axes.

The synthesis of optically active polymers that contain heteroatoms as chiral centers has rarely been reported to date in spite of remarkable progress in the synthetic strategy of chiral polymers.[5] Recently, we focused on the chiral phosphorus atom for constructing optically active polymers,[6,7] because of its potential ability to coordinate to transition metals and the application of the polymers as chiral ligands and metal sensors.[8] In our previous work, we produced optically active polymers[6] and oligomers[7] that contain a chiral bisphosphine unit by using (*S*,*S*)-1,2-bis(boranato(*tert*-butyl)methylphosphanyl)ethane ((*S*,*S*)-**1**) as the key monomer. (*S*,*S*)-**1** was produced by Imamoto et al.[9] as the chiral ligand for asymmetric hydrogenation reactions. Chiral bisphosphine (*S*,*S*)-**1** can be easily accessed with high enantiomeric excess (>99%) from trichlorophosphine. Trialkylphosphines such as (*S*,*S*)-**1** are rarely known to racemize even at considerably high temperatures.[10]

We previously prepared a series of optically active oligophosphines (*S*,*R*,*R*,*S*)-**2**,[7a] (*S*,*R*,*S*,*S*,*R*,*S*)-**3**,[7b] and (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4**[7a] (Scheme 1), which have four, six, and eight chiral phosphorus atoms, respectively. In the present work, we synthesized optically active dodecaphosphine (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5**, which has 12 chiral phosphorus atoms, and the optically inactive oligophosphines **1′**–**5′** that correspond to each chiral oligophosphine. The synthetic procedures and the properties of all the optically active oligo-

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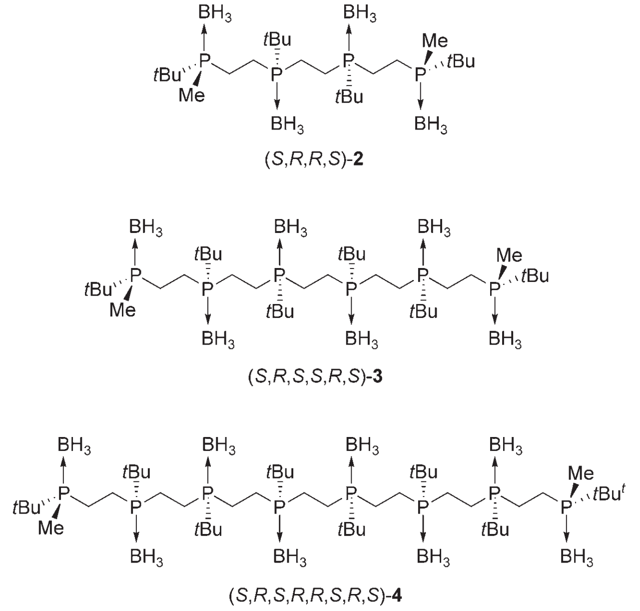


Scheme 1. The optically active oligophosphines **2**–**4** we prepared previously.[7]

phosphines **1**–**5** and optically inactive oligophosphines **1′**–**5′** are summarized and discussed in detail.

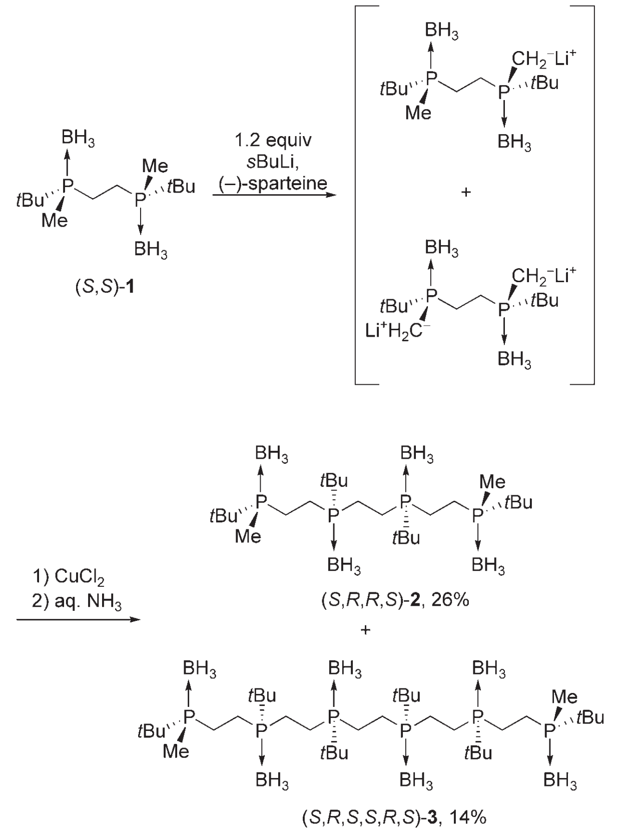
Results and Discussion

Synthesis of the Optically Active Oligophosphines

Optically active oligophosphines (*S*,*R*,*R*,*S*)-**2**[7a] and (*S*,*R*,*S*,*S*,*R*,*S*)-**3**,[7b] which contain four and six phosphorus atoms, respectively, were synthesized by an oxidative coupling reaction of (*S*,*S*)-**1** (Scheme 2). The yield of (*S*,*R*,*R*,*S*)-**2** and (*S*,*R*,*S*,*S*,*R*,*S*)-**3** depended on the amount of *sec*-BuLi. To obtain (*S*,*R*,*S*,*S*,*R*,*S*)-**3** in the highest yield of 14%, 1.2 equivalents of *sec*-BuLi with respect to the methyl group were required for mono- and dilithiation of the methyl groups of (*S*,*S*)-**1**. Optically active octaphosphine (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4** (29% yield) and dodecaphosphine (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5** (8% yield) were also prepared by the same method from (*S*,*R*,*R*,*S*)-**2** by using 5 equivalents of *sec*-BuLi (Scheme 3). In both cases, (−)-sparteine was used for the activation of BuLi, although the reactions did not involve an asymmetric reaction. Each reaction yielded the intramolecular coupling compound, that is, cyclic bisphosphine[11] from (*S*,*S*)-**1** and cyclic tetraphosphine[7a] from (*S*,*R*,*R*,*S*)-**2**. These optically active phosphines **2**–**5** were easily separated by SiO_2 column chromatography or recycling high-performance liquid chromatography (HPLC). All chiral oligophosphines were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as mass spectrometry. They were air- and moisture-stable owing to coordination of BH_3 to the phosphorus atoms, which prevented their oxidation.[12]

Abstract in Japanese:

不斉リン原子を２つ有する (*S*,*S*)-**1** を段階的に反応させていくことにより、不斉リン原子を複数個有する光学活性オリゴホスフィン (*S*,*R*,*R*,*S*)-**2**、(*S*,*R*,*S*,*S*,*R*,*S*)-**3**、(*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4**、(*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5** の合成、単離に成功した。(*S*,*S*)-**1**、(*S*,*R*,*R*,*S*)-**2** が低分子、(*S*,*R*,*S*,*S*,*R*,*S*)-**3** がアモルファス低分子、(*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4**、(*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5** がポリマーとしての性質を示すことを明らかにした。別途合成した光学不活性なオリゴホスフィン **1′**–**5′** と物性を比較し、光学純度と鎖長が固体状態に与える影響を検討した。

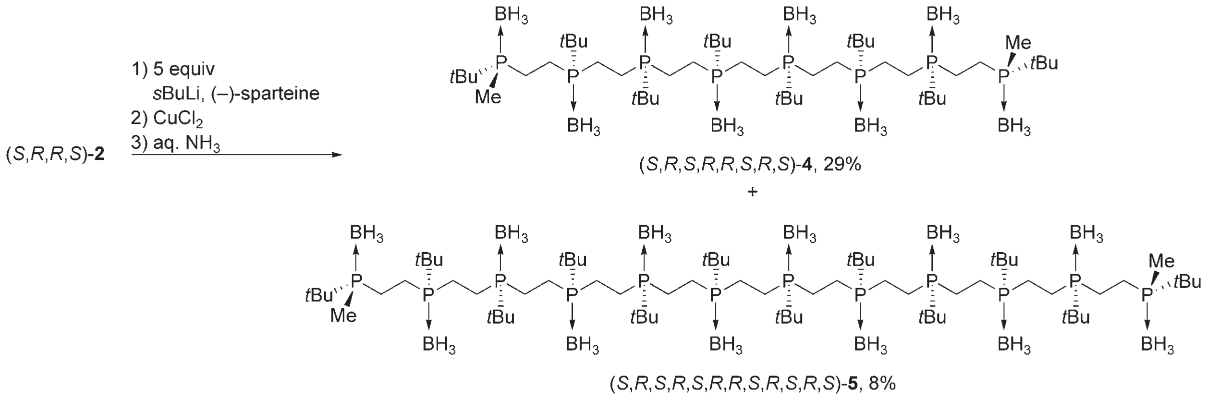


Scheme 2. Synthesis of optically active tetraphosphine (*S*,*R*,*R*,*S*)-**2** and hexaphosphine (*S*,*R*,*S*,*S*,*R*,*S*)-**3**.

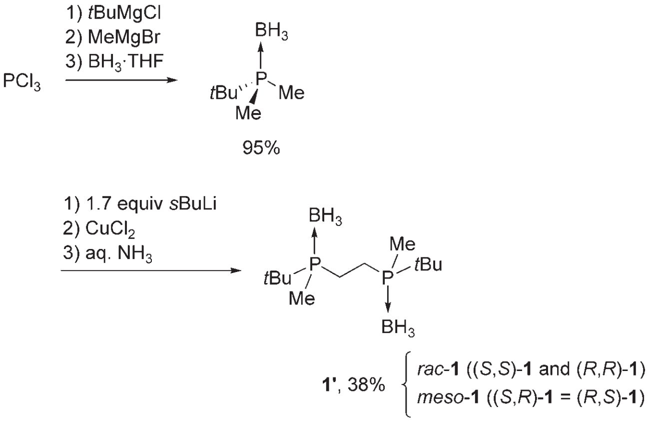
Synthesis of the Optically Inactive Oligophosphines

First, we synthesized optically inactive bisphosphine **1′** from *tert*-butyldimethylphosphineborane without (−)-sparteine, and **1′** was obtained in 38% yield as a mixture of *rac*-**1** ((*S*,*S*)-**1** and (*R*,*R*)-**1**) and *meso*-**1** ((*S*,*R*)-**1**=(*R*,*S*)-**1**) (Scheme 4). Optically inactive tetraphosphine **2′** and hexaphosphine **3′** were prepared from bisphosphine **1′** in 30 and 3% yield, respectively (Scheme 5).

Both **2′** and **3′** are a mixture of *rac*- and *meso*-oligophosphines; however, simple SiO_2 column chromatography easily separated each oligophosphine (**2′**: $R_f = 0.67$ in CH_2Cl_2, 100%; **3′**: $R_f = 0.58$ in CH_2Cl_2, 100%). Optically inactive octaphosphine **4′** and dodecaphosphine **5′** were also synthe-

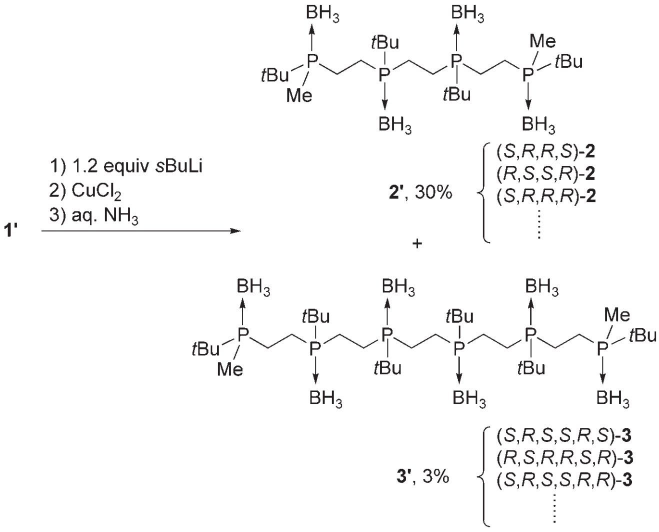


Scheme 3. Synthesis of optically active octaphosphine (*S,R,S,R,R,S,R,S*)-**4** and dodecaphosphine (*S,R,S,R,S,R,R,S,R,S,R,S*)-**5**.

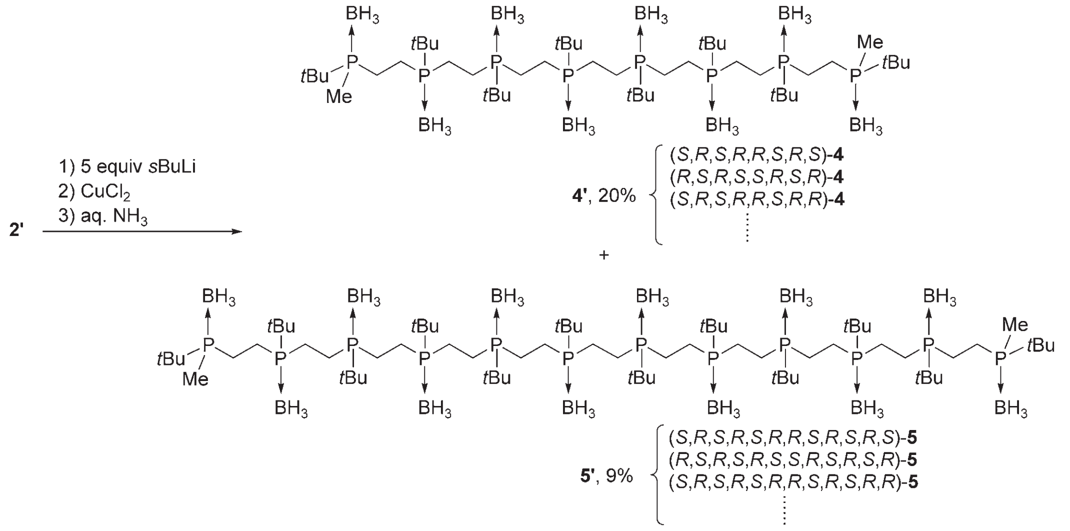


Scheme 4. Synthesis of optically inactive bisphosphine **1′**.

sized by the same procedure with 5 equivalents of *sec*-BuLi in 20 and 9% yield, respectively (Scheme 6).



Scheme 5. Synthesis of optically inactive tetraphosphine **2′** and hexaphosphine **3′**.



Scheme 6. Synthesis of optically inactive octaphosphine **4′** and dodecaphosphine **5′**.

DSC Analysis of the Optically Active and Inactive Oligophosphines

Differential scanning calorimetry (DSC) analysis of the oligophosphines revealed their behavior in the solid state under heating. Although we have already shown the DSC curves of optically active oligophosphines (*S*,*R*,*R*,*S*)-**2**, (*S*,*R*,*S*,*S*,*R*,*S*)-**3**, and (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4** in previous work,[7] we summarize and discuss again their DSC results along with optically active dodecaphosphine (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5** and the corresponding optically inactive oligophosphines **2′**–**5′**.

DSC thermograms are shown in Figure 1: Figure 1 A–D for optically active oligophosphines **2**–**5** and Figure 1 E–H for optically inactive oligophosphines **2′**–**5′**.[13]

As shown in Figure 1 A, optically active tetraphosphine (*S*,*R*,*R*,*S*)-**2** behaved as a simple small molecule with the only melting point (T_m) at 204–205 °C without a glass-transition temperature (T_g). Incidentally, it is reported that bisphosphine (*S*,*S*)-**1** has its only T_m at 169–171 °C.[9]

In Figure 1 B, hexaphosphine (*S*,*R*,*S*,*S*,*R*,*S*)-**3** exhibited two different solid states. In the first cycle, (*S*,*R*,*S*,*S*,*R*,*S*)-**3** had its only T_m at 194 °C. In the second cycle, it showed a T_g of 59 °C, a recrystallization point (T_c) of 154 °C, and a T_m of 192 °C. When the sample was allowed to cool to ambient temperature after recrystallization and before melting in the third cycle, (*S*,*R*,*S*,*S*,*R*,*S*)-**3** exhibited its only T_m at 191 °C again, without T_g and T_c in the fourth cycle. Optically active hexaphosphine (*S*,*R*,*S*,*S*,*R*,*S*)-**3** behaved as a crystalline solid; however, once melted, it behaved as an amorphous solid. This result indicates that (*S*,*R*,*S*,*S*,*R*,*S*)-**3** is an amorphous small molecule, a so-called molecular glass.[14] XRD analysis also supports this interpretation (see below).

In Figure 1 C, optically active octaphosphine (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4** exhibited a typical T_g at 53 °C and T_c at 138 °C in the first scan, and it showed a T_g at 76 °C in the second scan. The rise in T_g seems to be attributed to a decrease in mobility of (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4** due to local crystallization.

In Figure 1 D, dodecaphosphine (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5** also exhibited its T_g at 78 °C and T_c at 146 °C in the first scan; after that, a T_g at the higher temperature of 105 °C was observed. Optically active oligophosphines **4** and **5** behaved like polymers. However, we cannot conclude that oligophosphines **4** and **5** are polymers on the basis of Figure 1 C and D. On the other hand, the distinct changes in

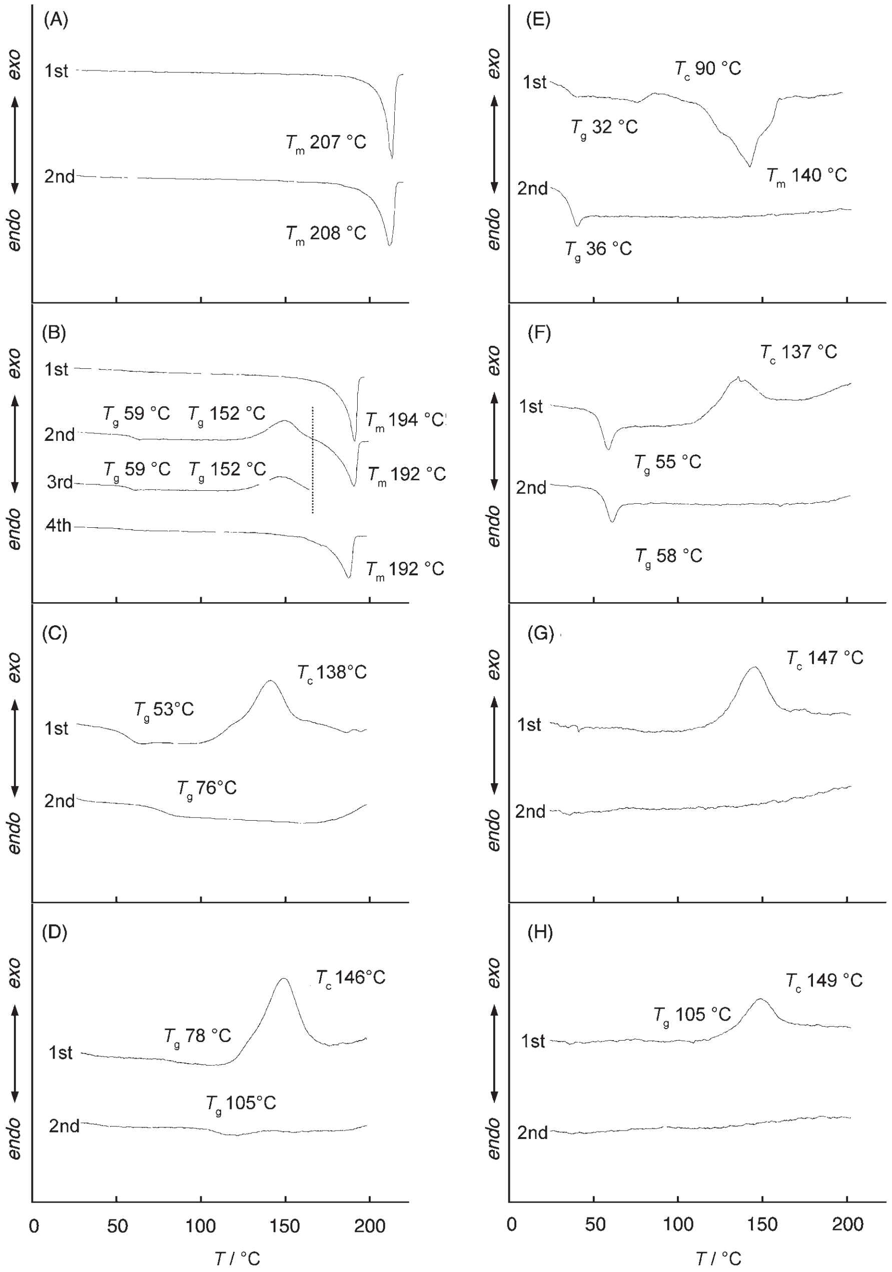


Figure 1. DSC thermograms of optically active phosphines A) (*S*,*R*,*R*,*S*)-**2**, B) (*S*,*R*,*S*,*S*,*R*,*S*)-**3**, C) (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4**, and D) (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5**, and optically inactive phophines E) **2′**, F) **3′**, G) **4′**, and H) **5′**.

crystallinity on elongating the oligomer main chain suggest that optically active oligophosphines **4** and **5** have become polymer-like.

Figure 1 E–H shows the DSC thermograms of optically inactive oligophosphines **2′**–**5′**. The thermograms display the same trend as those of the optically active phosphines **2**–**5**. Furthermore, each optically inactive oligophosphine exhibited a more amorphous property compared to the corresponding optically active oligophosphine with the same oligomer chain length. For example, whereas (*S*,*R*,*R*,*S*)-**2** exhibited only a T_m without a T_g (Figure 1 A), optically inactive tetraphosphine **2′** displayed a T_g (Figure 1 E). In the second cycles of **4′** and **5′**, the small T_g peaks were observed at around 80 and 100 °C, respectively (Figure 1 G and H). Each optically inactive oligophosphine is a mixture of enantiomers and diastereomers dissimilar to the optically pure oligophosphine. Therefore, the crystallinity of the optically active oligophosphine seems to be better than that of the optically inactive counterpart. The properties of the oligophosphines in the solid state are affected by the enantiomeric purity as well as the oligomer chain length.

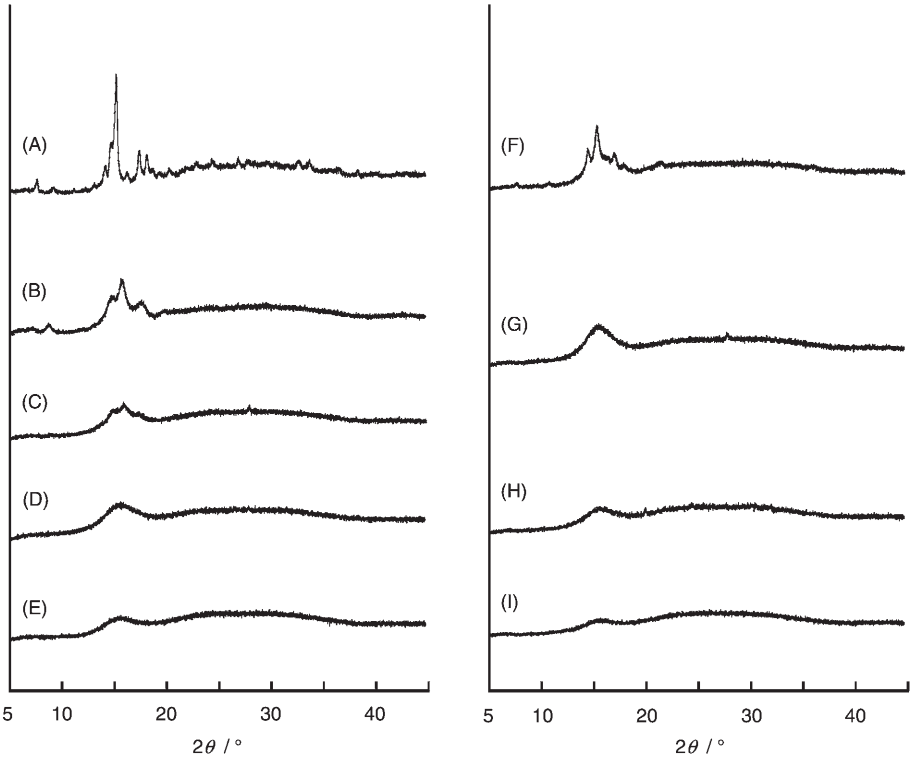


Figure 2. XRD profiles of optically active phosphines A) (*S*,*R*,*R*,*S*)-**2**, B) (*S*,*R*,*S*,*S*,*R*,*S*)-**3** (pristine), C) (*S*,*R*,*S*,*S*,*R*,*S*)-**3** (after solidification of melt), D) (*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4**, and E) (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5**, and optically inactive phosphines F) **2′**, G) **3′**, H) **4′**, and I) **5′**.

XRD analysis of the Optically Active and Inactive Oligophosphines

Changes in the solid state of optically active oligophosphines **2**–**5** and optically inactive oligophosphines **2′**–**5′** can be seen by the XRD patterns in Figure 2 A and B, respectively. The longer the chain length of the oligophosphines, the lower their crystallinity, which is consistent with the results of the DSC analysis. The XRD pattern of each optically inactive oligophosphine is broader (Figure 2 B) than that of the corresponding optically active oligophosphine (Figure 2 A), thus indicating that optically inactive oligophosphines **2′**–**5′** are more amorphous than optically active oligophosphines **2**–**5**.

On the other hand, the XRD pattern of optically active hexaphosphine (*S*,*R*,*S*,*S*,*R*,*S*)-**3** depends on its solid state (Figure 2 A). The pristine sample of (*S*,*R*,*S*,*S*,*R*,*S*)-**3** produced a relatively high-resolution diffraction pattern, whereas the sample after solidification of the melt showed a gave peak. DSC and XRD analyses of (*S*,*R*,*S*,*S*,*R*,*S*)-**3** thus suggest that it is intermediate between a small molecule and a polymer.[15,16]

Measurement of Optical Rotation

To investigate the behavior of the optically active oligophosphines **2**–**5** in solution, measurement of their optical rotations was carried out, and the results are shown in Table 1. It was previously reported that the specific rotation $[\alpha]_D^{27}$ ($c=1.0\,\text{M}$ in $CHCl_3$) of optically active bisphosphine (*S*,*S*)-**1** was −9.1 (run 1).[9] The specific rotations $[\alpha]_D^{25}$ ($c=1.0\,\text{M}$ in $CHCl_3$) of (*S*,*R*,*R*,*S*)-**2** and $[\alpha]_D^{25}$ ($c=0.5\,\text{M}$ in $CHCl_3$) of (*S*,*R*,*S*,*S*,*R*,*S*)-**3** were −3.4 and −1.8 (runs 2 and 3), respectively. In our system, the specific rotation $[\alpha]_D$ of the oligophosphine should reach zero as the number of chiral phosphorus atoms increases, because long oligophosphines seem like syndiotactic polymers. However, the specific rotations

Table 1. Specific rotations of optically active oligophosphines **1**–**5**.

Run	Oligophosphine	$[\alpha]_D^{25}$ ($CHCl_3$)
1	(*S*,*S*)-**1**	−9.1[a] ($c=1.0\,\text{M}$)
2	(*S*,*R*,*R*,*S*)-**2**	−3.4 ($c=1.0\,\text{M}$)
3	(*S*,*R*,*S*,*S*,*R*,*S*)-**3**	−1.8 ($c=0.5\,\text{M}$)
4	(*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*)-**4**	+5.2 ($c=1.0\,\text{M}$)
5	(*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5**	+4.7 ($c=0.5\,\text{M}$)

[a] $[\alpha]_D^{27}$.[9]

of (*S,R,S,R,R,S,R,S*)-**4** and (*S,R,S,R,S,R,R,S,R,S,R,S*)-**5** exhibited positive values (runs 4 and 5). This result indicates that chiral phosphorus atoms rotate the plane of polarized light counterclockwise, whereas the higher-ordered structure in the present system rotates it clockwise. Furthermore, it also suggests that optically active oligophophines (*S,R,S,R,R,S,R,S*)-**4** and (*S,R,S,R,S,R,R,S,R,S,R,S*)-**5** show the features of a polymer in solution as well as in the solid state (see above).

Conclusions

Optically active and inactive oligophosphines were successfully synthesized by a step-by-step oxidative coupling reaction. According to DSC and XRD measurements, we found that these oligophosphines changed gradually from crystalline to amorphous as the oligomer chain length increased. Optically active bisphosphine (*S,S*)-**1** and tetraphosphine (*S,R,R,S*)-**2** behaved like a small molecule, hexaphosphine (*S,R,S,S,R,S*)-**3** acted as an amorphous small molecule, and octaphosphine (*S,R,S,R,R,S,R,S*)-**4** and dodecaphosphine (*S,R,S,R,S,R,R,S,R,S,R,S*)-**5** behaved like a polymer. Comparison of the optically active oligophosphine with the corresponding optically inactive oligophosphine revealed that the latter exhibits more amorphous behavior because of the mixture of racemates and diastereomers. It is considered that the properties of oligophosphines depend on the enantiomeric purity as well as the oligomer chain length.

Experimental Section

General

^{1}H (270 or 400 MHz) and ^{13}C (67.5 or 100 MHz) NMR spectra were recorded on a JEOL EX270 or EX400 spectrometer, and samples were analyzed in $CDCl_3$ with Me_4Si as an internal standard. ^{31}P (109.3 or 161.9 MHz) NMR spectra were also recorded on a JEOL EX270 or EX400 spectrometer, and samples were analyzed in $CDCl_3$ with H_3PO_4 as an external standard. The following abbreviations are used: s = singlet, d = doublet, q = quartet, br = broad. DSC thermograms were recorded on a Seiko DSC200 instrument with approximately 10-mg samples at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The sample was preheated to 110°C and allowed to cool to 0°C. The midpoint of the T_g peak in the thermogram was adopted as the value of the glass-transition temperature. XRD data were obtained on a Rigaku MiniFlex diffractometer with $Cu_{K\alpha}$ radiation in the range $3 \leq 2\theta \leq 45°$ at intervals of 0.01° at a scanning rate of 0.25° min^{-1}. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL IV instrument with $CHCl_3$ as a solvent. Low- and high-resolution mass spectra were obtained on a JEOL JMS-SX102A spectrometer. MALDI-TOF mass spectra were obtained on a PerSeptive Biosystems Voyager DE-STR spectrometer. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F_{254} plates. Column chromatography was performed with Wakogel C-300 silica gel. Recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model 918R) was performed with JAIGEL-1H and 2H columns (GPC) and $CHCl_3$ as an eluent. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials

THF was distilled from sodium benzophenone ketyl under nitrogen. (−)-Sparteine was distilled from KOH under nitrogen. *tert*-Butyl(dimethyl)phosphineborane and (*S,S*)-**1** were prepared as described in the literature.[9] Optically active oligophosphines (*S,R,R,S*)-**2**,[7a] (*S,R,S,S,R,S*)-**3**,[7b] and (*S,R,S,R,R,S,R,S*)-**4**[7a] and optically inactive oligophosphines **1′**, **2′**, and **3′** were synthesized as described in our previous report;[7b] however, we summarize again their synthetic procedures herein. The other materials were purchased and used without further purification. All reactions were performed under nitrogen atmosphere with standard Schlenk techniques.

Syntheses

(*S,R,R,S*)-**2** and (*S,R,S,S,R,S*)-**3**: A solution of (−)-sparteine (0.67 mL, 2.9 mmol) in THF (15 mL) was cooled to −78°C under N_2 atmosphere. *sec*-BuLi (1.0 M in cyclohexane/*n*-hexane = 95:5, 2.9 mL, 2.9 mmol) was added to this solution with stirring by a syringe. After 15 min, a solution of (*S,S*)-**1** (0.64 g, 2.4 mmol) in THF (5.0 mL) was added dropwise, and the mixture was stirred at −78°C for 3 h. Dry $CuCl_2$ (0.49 g, 3.7 mmol) was added in one portion with vigorous stirring, and the reaction mixture was allowed to warm slowly to room temperature. After 15 h, the reaction mixture was quenched by the addition of 28% aqueous NH_3 (5.0 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with aqueous NH_3 (5%), HCl (2 M), and brine. The organic layer was dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (3:1–0:10 *v*/*v*) to give (*S,R,R,S*)-**2** (0.16 g, 0.31 mmol, 26%) and (*S,R,S,S,R,S*)-**3** (87 mg, 0.11 mmol, 14%) as colorless solids. (*S,R,R,S*)-**2**: $R_f = 0.67$ (CH_2Cl_2, 100%); m.p.: 207–208°C (DSC); $[\alpha]_D^{25} = -3.4$ ($c = 1.0$ M, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.40 (br q, $J_{H,B} = 98.8$ Hz, 12 H, BH_3), 1.17 (d, $J_{H,P} = 13.6$ Hz, 18 H, $PC(CH_3)_3$), 1.20 (d, $J_{H,P} = 13.6$ Hz, 18 H, $PC(CH_3)_3$), 1.24 (d, $J_{H,P} = 10$ Hz, 6 H, PCH_3), 1.57–1.83 (m, 6 H, PCH_2), 1.83–2.11 ppm (m, 6 H, PCH_2); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 5.4 (d, $J_{C,P} = 35.2$ Hz, PCH_3), 14.7 (d, $J_{C,P} = 29.2$ Hz, PCH_2), 14.8 (d, $J_{C,P} = 29.1$ Hz, PCH_2), 16.0 (d, $J_{C,P} = 30.4$ Hz, tBuCH$_3$P*C*H$_2$), 25.0 ((CH$_3$)$_3$CCH$_3$P), 25.7 (CH$_2$PC(CH$_3$)$_3$CH$_2$), 27.6 (d, $J_{C,P} = 32.8$ Hz, (CH$_3$)$_3$$CCH_3$P), 29.0 ppm (d, $J_{C,P} = 31.5$ Hz, CH$_2$PC(CH$_3$)$_3$CH$_2$); ^{31}P{^{1}H} NMR (109.3 MHz, $CDCl_3$): δ = 31.5, 39.9 ppm; HRMS (FAB): *m*/*z* calcd for $C_{24}H_{65}P_4B_4$: 521.4409 $[M-H]^+$; found: 521.4392; elemental analysis: calcd (%) for $C_{24}H_{66}P_4B_4$: C 55.23, H 12.74; found: C 55.38, H 12.10. (*S,R,S,S,R,S*)-**3**: $R_f = 0.58$ (CH_2Cl_2, 100%); m.p.: 191–194°C; $[\alpha]_D^{25} = -1.8$ ($c = 0.5$ M, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00–0.87 (m, 18 H, BH_3), 1.17 (d, $J_{H,P} = 13.6$ Hz, 18 H, $PC(CH_3)_3$), 1.19 (d, $J_{H,P} = 13.6$ Hz, 18 H, $PC(CH_3)_3$), 1.20 (d, $J_{H,P} = 13.2$ Hz, 18 H, $PC(CH_3)_3$), 1.25 (d, $J_{H,P} = 9.6$ Hz, 6 H, PCH_3), 1.68–2.18 ppm (m, 20 H, PCH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.45 (d, $J_{C,P} = 33.9$ Hz, PCH_3) 14.6 (d, $J_{C,P} = 29.0$ Hz, PCH_2), 14.7 (d, $J_{C,P} = 29.8$ Hz, PCH_2), 14.8 (d, $J_{C,P} = 28.1$ Hz, PCH_2), 14.9 (d, $J_{C,P} = 29.8$ Hz, PCH_2), 15.9 (d, $J_{C,P} = 30.6$ Hz, tBuCH$_3$P*C*H$_2$), 25.2 ((CH$_3$)$_3$CCH$_3$P), 25.6 (CH$_2$PC(CH$_3$)$_3$CH$_2$), 25.7 (CH$_2$PC(CH$_3$)$_3$CH$_2$), 27.7 (d, $J_{C,P} = 33.1$ Hz, (CH$_3$)$_3$$CCH_3$P), 29.0 (d, $J_{C,P} = 31.5$ Hz, CH$_2$PC(CH$_3$)$_3$CH$_2$), 29.1 ppm (d, $J_{C,P} = 30.6$ Hz, CH$_2$PC(CH$_3$)$_3$CH$_2$); ^{31}P{^{1}H} NMR (109.3 MHz, $CDCl_3$): δ = 30.4, 39.2, 40.3 ppm; HRMS (FAB): *m*/*z* calcd for $C_{36}H_{97}B_6P_6$: 781.6574 $[M-H]^+$; found: 781.6560.

(*S,R,S,R,R,S,R,S*)-**4** and (*S,R,S,R,S,R,R,S,R,S,R,S*)-**5**: A solution of (−)-sparteine (0.46 mL, 2.0 mmol) in THF (15 mL) was cooled to −78°C under nitrogen atmosphere. *sec*-BuLi (0.97 M in cyclohexane/*n*-hexane = 95:5, 2.1 mL, 2.0 mmol) was added to this solution with stirring by a syringe. After 15 min, a solution of (*S,R,R,S*)-**2** (0.21 g. 0.40 mmol) in THF (5.0 mL) was added dropwise, and the mixture was stirred at −78°C for 3 h. Dry $CuCl_2$ (0.16 g, 1.2 mmol) was added in one portion with vigorous stirring, and the reaction mixture was allowed to warm slowly to room temperature. After 15 h, the reaction was quenched by the addition of aqueous ammonia (28%, 5.0 mL), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with aqueous NH_3 (5%), HCl (2 M), and brine. The organic layer was dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by HPLC with $CHCl_3$ as an eluent to give 12-phosphacrown-4 tetraborane (21 mg, 0.060 mmol, 15%), (*S,R,S,R,R,S,R,S*)-**4** (59 mg, 0.12 mmol, 29%), and (*S,R,S,R,S,R,R,S,R,S,R,S*)-**5** (17 mg, 0.011 mmol, 8%) as colorless solids. (*S,R,S,R,R,S,R,S*)-**4**: $[\alpha]_D^{25} = +5.2$ ($c = 1.0$ M, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.01–0.90 (m, 24 H, BH_3), 1.10–1.34 (m, 72 H, $PC(CH_3)_3$), 1.25 (s, 6 H, PCH_3), 1.55–2.30 ppm (m, 28 H, PCH_2); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta=11.3$ (PCH_3), 14.0–15.7 (PCH_2), 25.6 ($PC(\mathit{C}H_3)_3$), 29.7 ppm ($P\mathit{C}(CH_3)_3$); $^{31}P\{^1H\}$ NMR (109.3 MHz, $CDCl_3$): $\delta=30.1$, 34.9, 39.2 ppm; LRMS (ESI): *m*/*z* calcd for $C_{48}H_{130}P_8B_8$: 1041.8 $[M-CH_3-H]^+$; found: 1025.8; MS (MALDI-TOF; dithranol as a matrix and sodium trifluoroacetate as a cationizing agent): *m*/*z* calcd for $C_{48}H_{130}P_8B_8$: 1041.8 $[M+Na]^+$; found: 1063.0. (*S*,*R*,*S*,*R*,*S*,*R*,*R*,*S*,*R*,*S*,*R*,*S*)-**5**: $[\alpha]_D^{25}=+4.7$ ($c=0.5$ м, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): $\delta=0.05$–0.90 (m, 36 H, BH_3), 1.04–1.32 (m, 108 H, PCH_3 and $PC(CH_3)_3$), 1.50–2.35 ppm (m, 44 H, PCH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=5.1$ (PCH_3), 14.6 (PCH_2), 25.6 ($PC(\mathit{C}H_3)_3$), 28.9 ppm ($P\mathit{C}(CH_3)_3$); ^{31}P NMR ($CDCl_3$, 161.9 MHz): $\delta=29.3$, 34.2, 35.6, 39.6 ppm; LRMS (ESI): *m*/*z* calcd for $C_{72}H_{194}P_{12}B_{12}$: 1561 $[M-H]^+$; found: 1560.

1′: A portion of Et_2O (28 mL) was cooled to −78 °C under N_2 atmosphere. *sec*-BuLi (1.0 м in cyclohexane/*n*-hexane = 95:5, 19.0 mL, 19.0 mmol) was then added with stirring by a syringe. After 15 min, a solution of *tert*-butyldimethylphosphine (1.5 g, 11.2 mmol) in Et_2O (11 mL) was added dropwise, and the mixture was stirred at −78 °C for 3 h. Dry $CuCl_2$ (2.3 g, 17 mmol) was added in one portion with vigorous stirring, and the mixture was allowed to warm slowly to room temperature. After 15 h, the reaction was quenched by the addition of aqueous NH_3 (28 %, 15 mL), and the mixture was extracted with CH_2Cl_2 (3 × 40 mL). The combined extracts were washed with aqueous ammonia (5 %), HCl (2 м), and brine, and then dried over $MgSO_{4.}$ After evaporation of solvent, the residue was purified by column chromatography on silica gel (hexane/$CH_2Cl_2=1:1$ *v*/*v*) to give **1′** (560 mg, 2.1 mmol, 38 %) as a colorless solid. $R_f=0.78$ (CH_2Cl_2, 100 %); ^1H NMR (400 MHz, $CDCl_3$): $\delta=0.39$ (q, $J_{H,B}=94.7$ Hz, 6 H, BH_3), 1.16 (d, $J_{H,P}=13.7$ Hz, 9 H, $PC(CH_3)_3$), 1.18 (d, $J_{H,P}=14.0$ Hz, 9 H, $PC(C\mathit{H}_3)_3$), 1.23 (d, $J_{H,P}=9.8$ Hz, 6 H, PCH_3), 1.52–1.70 (m, PCH_2, 2 H), 1.85–1.21 ppm (m, PCH_2, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=4.78$ (d, $J_{C,P}=33.9$ Hz, PCH_3), 5.79 (d, $J_{C,P}=34.8$ Hz, PCH_3) 14.9 (d, $J_{C,P}=29.8$ Hz, PCH_2), 16.1 (d, $J_{C,P}=30.6$ Hz, PCH_2), 25.1 ($PC(\mathit{C}H_3)_3$), 25.2 ($PC(\mathit{C}H_3)_3$), 27.6 (d, $J_{C,P}=34.0$ Hz, $P\mathit{C}(CH_3)_3$), 27.8 ppm (d, $J_{C,P}=34.0$ Hz, $P\mathit{C}(CH_3)_3$); $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): $\delta=$ 29.9 ppm.

2′ and **3′**: A portion of THF (12 mL) was cooled to −78 °C under N_2 atmosphere. *sec*-BuLi (0.99 м in cyclohexane/*n*-hexane = 95:5, 2.6 mL, 2.6 mmol) was then added with stirring by a syringe. After 15 min, a solution of **1′** (0.56 g, 2.1 mmol) in THF (3 mL) was added dropwise, and the mixture was stirred at −78 °C for 3 h. Dry $CuCl_2$ (0.43 g, 3.2 mmol) was added in one portion with vigorous stirring, and the mixture was allowed to warm slowly to room temperature. After 15 h, the reaction was quenched by the addition of aqueous NH_3 (28 %, 3.0 mL), and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with aqueous NH_3 (5 %), HCl (2 м), and brine, and then dried over $MgSO_{4.}$ After evaporation of solvent, the residue was purified by column chromatography on silica gel (hexane/$CH_2Cl_2=3:1$–$1:2$ *v*/*v*) to give **2′** (166 mg, 0.32 mmol, 30 %) and **3′** (15 mg, 0.020 mmol, 3 %) as colorless solids. **2′**: $R_f=0.67$ (CH_2Cl_2, 100 %); m.p.: 145 °C (DSC); ^1H NMR (400 MHz, $CDCl_3$): $\delta=-0.15$–0.89 (m, 12 H, BH_3), 1.14 (d, $J_{H,P}=14.0$ Hz, 18 H, $PC(CH_3)_3$), 1.17 (d, $J_{H,P}=12.4$ Hz, 18 H, $PC(CH_3)_3$), 1.21 (d, $J_{H,P}=$ 9.7 Hz, 6 H, PCH_3), 1.55–2.08 ppm (m, 12 H, PCH_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=4.6$–5.8 (m, PCH_3), 13.8–16.4 (m, PCH_2), 25.1–25.2 (m, $PC(\mathit{C}H_3)_3$), 25.5–25.7 (m, $PC(\mathit{C}H_3)_3$), 27.4–27.8 (m, $P\mathit{C}(CH_3)_3$), 28.8–29.2 ppm (m, $P\mathit{C}(CH_3)_3$); $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): $\delta=30.4$, 39.0 ppm. **3′**: $R_f=0.58$ (CH_2Cl_2, 100 %); ^1H NMR (400 MHz, $CDCl_3$): $\delta=$ 0.00–0.90 (m, 18 H, BH_3), 1.17 (d, $J_{H,P}=13.2$ Hz, 27 H, $PC(CH_3)_3$), 1.20 (d, $J_{H,P}=12.8$ Hz, 27 H, $PC(CH_3)_3$), 1.24 (d, $J_{H,P}=9.2$ Hz, 6 H, PCH_3), 1.55–2.14 ppm (m, 20 H, PCH_2); ^{13}C NMR ($CDCl_3$): $\delta=4.7$–5.6 (m, PCH_3), 13.7–15.8 (m, PCH_2), 25.0–25.2 (m, $PC(\mathit{C}H_3)_3$), 25.4–25.6 (m, $PC(\mathit{C}H_3)_3$), 27.4–27.8 (m, $P\mathit{C}(CH_3)_3$), 28.6–29.2 ppm (m, $P\mathit{C}(CH_3)_3$); $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): $\delta=30.8$, 39.4 ppm.

4′ and **5′**: A portion of THF (12 mL) was cooled to −78 °C under nitrogen atmosphere. *sec*-BuLi (1.01 м in cyclohexane/*n*-hexane = 95:5, 0.55 mL, 0.55 mmol) was then added with stirring by a syringe. After 15 min, a solution of **2′** (0.058 g. 0.11 mmol) in THF (3 mL) was added dropwise, and the mixture was stirred at −78 °C for 3 h. Dry $CuCl_2$ (0.09 g, 0.67 mmol) was added in one portion with vigorous stirring, and the mixture was allowed to warm slowly to room temperature. After 15 h, the reaction was quenched by the addition of aqueous ammonia (28 %, 3.0 mL), and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with aqueous ammonia (5 %), HCl (2 м), and brine, and then dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by HPLC with $CHCl_3$ as an eluent to give **4′** (12 mg, 0.011 mmol, 20 %) and **5′** (5 mg, 3.0 µmol, 9 %) as colorless solids. **4′**: ^1H NMR ($CDCl_3$): $\delta=-0.05$–0.90 (m, 24 H, BH_3), 1.10–1.42 (m, 78H, PCH_3 and $PC(CH_3)_3$), 1.58–2.30 ppm (m, PCH_2, 28 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=4.6$–5.8 (m, PCH_3), 14.1–15.0 (m, PCH_2), 24.8–26.1 (m, $PC(\mathit{C}H_3)_3$), 28.7–29.2 ppm (m, $P\mathit{C}(CH_3)_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=30.6$, 34.8, 39.7, 42.3 ppm. **5′**: ^1H NMR ($CDCl_3$): $\delta=-0.10$–0.80 (m, 36 H, BH_3), 1.02–1.35 (m, 114 H, PCH_3 and $C(CH_3)_3$), 1.53–2.25 ppm (m, PCH_2, 44 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=4.6$–5.8 (m, PCH_3), 14.2–14.9 (m, PCH_2), 24.6–26.0 (m, $PC(\mathit{C}H_3)_3$), 28.8–29.1 ppm (m, $P\mathit{C}(CH_3)_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta=30.3$, 35.0, 39.8 ppm.

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