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ORIGINAL ARTICLE

Synthesis of unsymmetrical P-stereogenic oligophosphines and chemoselective cleavage of phosphine-borane coordinate bonds

Hiroaki Imoto, Ryosuke Kato, Yasuhiro Morisaki and Yoshiki Chujo

This paper describes the synthetic details and coordination abilities of optically active P-stereogenic tetraphosphine and hexaphosphine with different substituted groups on their phosphorus atoms. The polymers consist of two types of phosphine units, that is, *tert*-butyl- and phenylphosphines. The boranes on the phenylphosphine moieties were chemoselectively removed by organic base such as diazabicyclo[2.2.2]octane.
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INTRODUCTION

Phosphorus atom is a unique element in its ability to create chiral architectures because a trivalent phosphorus atom can adopt a conformationally stable tetrahedral structure arising from its high inversion energy.[1] In fact, several such P-stereogenic phosphines have been prepared, and in particular, P-stereogenic bisphosphines have been widely employed as chelate ligands for transition metal-catalyzed asymmetric reactions.[2–6] However, despite the widespread use of P-stereogenic phosphines, polymers containing chiral phosphorus atoms in their backbones have rarely been prepared.[7] Recently, we synthesized P-stereogenic optically active polymers[8–13] and oligomers[14–16] using P-stereogenic bisphosphines as chiral building blocks. These molecules formed higher-ordered chiral structures derived from P-stereogenic centers, and their conformations could be controlled through metal coordination with bisphosphine moieties.[11–13] On the other hand, well-defined oligophosphines could potentially be used as platforms for binding transition metals in an orderly fashion. Several types of optically active P-stereogenic oligophosphines have already been prepared (Figure 1). Wild and co-workers reported the syntheses and coordination behaviors of optically active P-stereogenic tetraphosphines and hexaphosphines, which were obtained by separating a mixture of stereoisomers by column chromatography and successive complexation with chiral palladium complexes.[17–23] Our group[14–16] and Imamoto's group[24–29] independently succeeded in synthesizing optically active P-stereogenic tetraphosphines (Figure 1) through different synthetic routes. Imamoto *et al.*[28] prepared their transition metal complexes, and the obtained complexes were used as chiral catalysts for transition metal-catalyzed asymmetric hydrogenations.

To the best of our knowledge, all of the previously synthesized oligophosphines possess only one type of substitution group on the phosphorus atoms. For example, P-stereogenic hexaphosphine synthesized by Wild and co-workers contains phenyl substituents whereas the P-stereogenic dodecaphosphine that we synthesized contains twelve *tert*-butyl substituents on the phosphorus atoms. The coordination ability of a phosphorus atom is significantly affected by the substituents, and therefore, oligophosphines possessing more than one type of substituent on the phosphorus atoms could be promising as ligands specific to heteromultimetallic complexes. Herein, we report the synthesis of unsymmetric P-stereogenic oligophosphines with phosphorus atoms that are bound to different substitution groups. Namely, the tetraphosphine and hexaphosphine obtained have two types of phosphorus atoms possessing *tert*-butyl and phenyl substituents (Figure 2), and these phosphorus atoms have different coordination abilities. The *tert*-butylphosphine unit has a stronger basicity than the phenylphosphine unit, leading to the different coordination sites within a single oligophosphine chain. The synthetic procedures and coordination behaviors with boranes were investigated in detail as the first step toward the successful use for heteromultimetallics.

EXPERIMENTAL PROCEDURES

General methods

^{1}H (399.2 MHz) and ^{13}C (100.3 MHz) NMR spectra were recorded on an EX 400 spectrometer (JEOL, Tokyo, Japan), and samples were analyzed in $CDCl_3$ using Me_4Si as an internal standard. ^{31}P (161.5 MHz) NMR spectra were also recorded on an EX 400 spectrometer (JEOL), and samples were analyzed in $CDCl_3$ using H_3PO_4 as an external standard. The following abbreviations are

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan
Correspondence: Dr Y Morisaki or Professor Y Chujo, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.
E-mail: ymo@chujo.synchem.kyoto-u.ac.jp or chujo@chujo.synchem.kyoto-u.ac.jp
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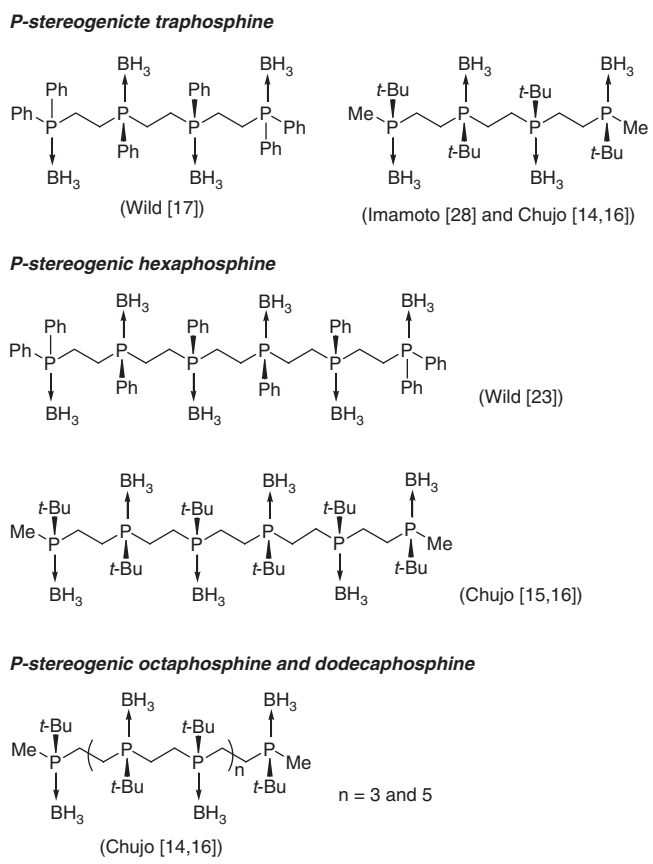


Figure 1 P-stereogenic oligophosphines reported thus far.

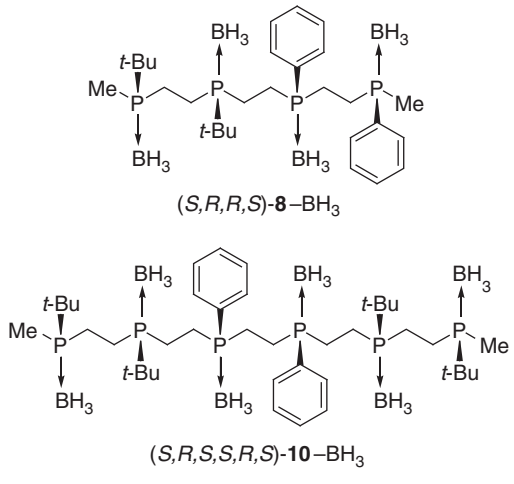


Figure 2 Unsymmetrical P-stereogenic oligophosphines (*S,R,R,S*)-**8**–BH_3 and (*S,R,S,S,R,S*)-**10**–BH_3.

used; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. High-resolution mass spectra (HRMS) were obtained on a JMS-SX102A spectrometer (JEOL). Optical rotations were measured on an AUTOPOL IV instrument (Rudolph Research Analytical, Hackettstown, USA) using $CHCl_3$ as a solvent. Analytical thin-layer chromatography was performed with silica gel 60 Merck F_{254} plates (Merck, Whitehouse, USA). Column chromatography was performed with Wako gel C-300 SiO_2 (Wako Pure Chemical Industries, Osaka, Japan).

Materials

Tetrahydrofuran (THF) was purchased and purified by passage through purification column under Ar pressure.[30] Dehydrated grade solvents of toluene and $CHCl_3$ were purchased and used without further purification. *N,N,N′,N′*-tetramethylethylenediamine was purchased and distilled from KOH under Ar atmosphere. *sec*-BuLi (1.0 M in cyclohexane and hexane), BuLi (1.6 M in hexane), $BH_3 \cdot THF$ (1.0 M in THF), $RuCl_3 \cdot nH_2O$, $K_2S_2O_8$, KOH, PPh_3, CBr_4, 1,4-diazabicyclo[2.2.2]octane (DABCO), morpholine, $CuCl_2$ and aqueous NH_3 (28%) were purchased and used without purification. Bisphosphines (*S,S*)-**1** $-BH_3$,[31] (*S,S*)-**4** $-BH_3$,[32] (*R,R*)-**9** $-BH_3$,[13] and (*S,S*)-**11** $-BH_3$[14–16] were prepared by the procedure of the literature. All reactions were performed under Ar atmosphere using standard Schlenk techniques.

(*S,S*)-2 $-BH_3$

A THF solution (30 ml) of (*S,S*)-**1** $-BH_3$ (786.0 mg, 3.0 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (0.58 ml, 3.9 mmol) was cooled to $-78\,^{\circ}C$ under Ar atmosphere. *sec*-BuLi (1.0 M in cyclohexane and hexane, 3.9 ml, 3.9 mmol) was added by a syringe. After stirring for 3 h, dry O_2 was bubbled into the reaction mixture. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of 2 N HCl (100 ml). The organic layer was extracted with ethyl acetate (100 ml × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2, with ethyl acetate and hexane ($v/v = 1/3$) as an eluent ($R_f = 0.20$, ethyl acetate/hexane $v/v = 1/2$). The solvent was evaporated to obtain (*S,S*)-**2** $-BH_3$ (349.0 mg, 1.26 mmol, 42%) as a colorless solid. $[\alpha]_D^{22} + 1.1$ (c 0.5 in $CHCl_3$); hydrogen nuclear magnetic resonance (^1H NMR) (399.2 MHz, $CDCl_3$) δ 0.38 (br, 6H, P-BH_3), 1.20 (m, 21H, P-*t*-Bu and P-Me), 1.70–2.07 (m, 5H, P-CH_2CH_2-P and OH), 4.06 (s, 2H, P-CH_2-O) p.p.m.; carbon nuclear magnetic resonance (^{13}C NMR) ($CDCl_3$, 100.3 MHz) δ 5.4 (d, $J_{C-P} = 34.7$ Hz), 11.9 (d, $J_{C-P} = 29.8$ Hz), 15.8 (d, $J_{C-P} = 31.4$ Hz), 25.1, 25.8, 27.4, 27.8, 28.2, 28.5, 56.1 (d, $J_{C-P} = 35.6$ Hz) p.p.m.; phosphorus nuclear magnetic resonance (^{31}P NMR) ($CDCl_3$, 161.5 MHz) δ +28.8 (m), +35.3 (m) p.p.m.; HRMS (electrospray ionization (ESI)) calcd. for $[M + Na]^+$ 301.2163, found 301.2163.

(*S,S*)-3 $-BH_3$

An H_2O solution (10 ml) of KOH (729.3 mg, 13.0 mmol) and $K_2S_2O_8$ (1.054 g, 3.9 mmol) was cooled to 0 °C. After addition of $RuCl_3 \cdot 3H_2O$ (34.0 mg, 0.13 mmol) to the H_2O solution, an acetone solution (5 ml) of (*S,S*)-**2** $-BH_3$ (361.4 mg, 1.3 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature. After stirring for 22 h, the reaction was quenched by addition of 2 N HCl (100 ml). The organic layer was extracted with ethyl acetate (100 ml × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2, with ethyl acetate and hexane ($v/v = 1/1$) as an eluent ($R_f = 0.50$, ethyl acetate/hexane $v/v = 1/2$). The solvent was evaporated to obtain (*S,S*)-**3** $-BH_3$ (234.0 mg, 0.94 mmol, 72%) as a colorless solid. $[\alpha]_D^{22}$ +30.8 (c 0.5 in $CHCl_3$); ^1H NMR (399.2 MHz, $CDCl_3$) δ 0.43 (br q, $J_{H-B} = 106.7$ Hz, 6H, P-BH_3), 1.21 (m, 21H, P-*t*-Bu and P-Me), 1.58–2.12 (m, 4H, P-CH_2CH_2-P), 4.36 (d, $J = 352.5$ Hz, 1H, P-H) p.p.m.; ^{13}C NMR ($CDCl_3$, 100.3 MHz) δ 5.8 (d, $J_{C-P} = 33.9$ Hz), 11.8 (d, $J_{C-P} = 30.6$ Hz), 16.9 (d, $J_{C-P} = 30.6$ Hz), 25.1, 26.8, 27.1, 27.5, 27.6, 27.9 p.p.m.; ^{31}P NMR ($CDCl_3$, 161.5 MHz) δ + 23.9 (m), +28.1 (m) p.p.m.; HRMS (ESI) calcd. for $[M + Na]^+$ 271.2058, found 271.2055.

(*S,S*)-6 $-BH_3$

A THF solution (40 ml) of (*S,S*)-**4** $-BH_3$ (1.208 g, 4.0 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (0.66 ml, 4.4 mmol) was cooled to $-78\,^{\circ}C$ under Ar atmosphere. *sec*-BuLi (1.0 M in cyclohexane and hexane, 4.4 ml, 4.4 mmol) was added by a syringe. After stirring for 3 h, dry CO_2 was bubbled into the reaction mixture. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After the addition of 2 N HCl (100 ml) to the reaction mixture, the organic layer was extracted with ethyl acetate (100 ml × 3). The combined organic layers were washed with brine and dried

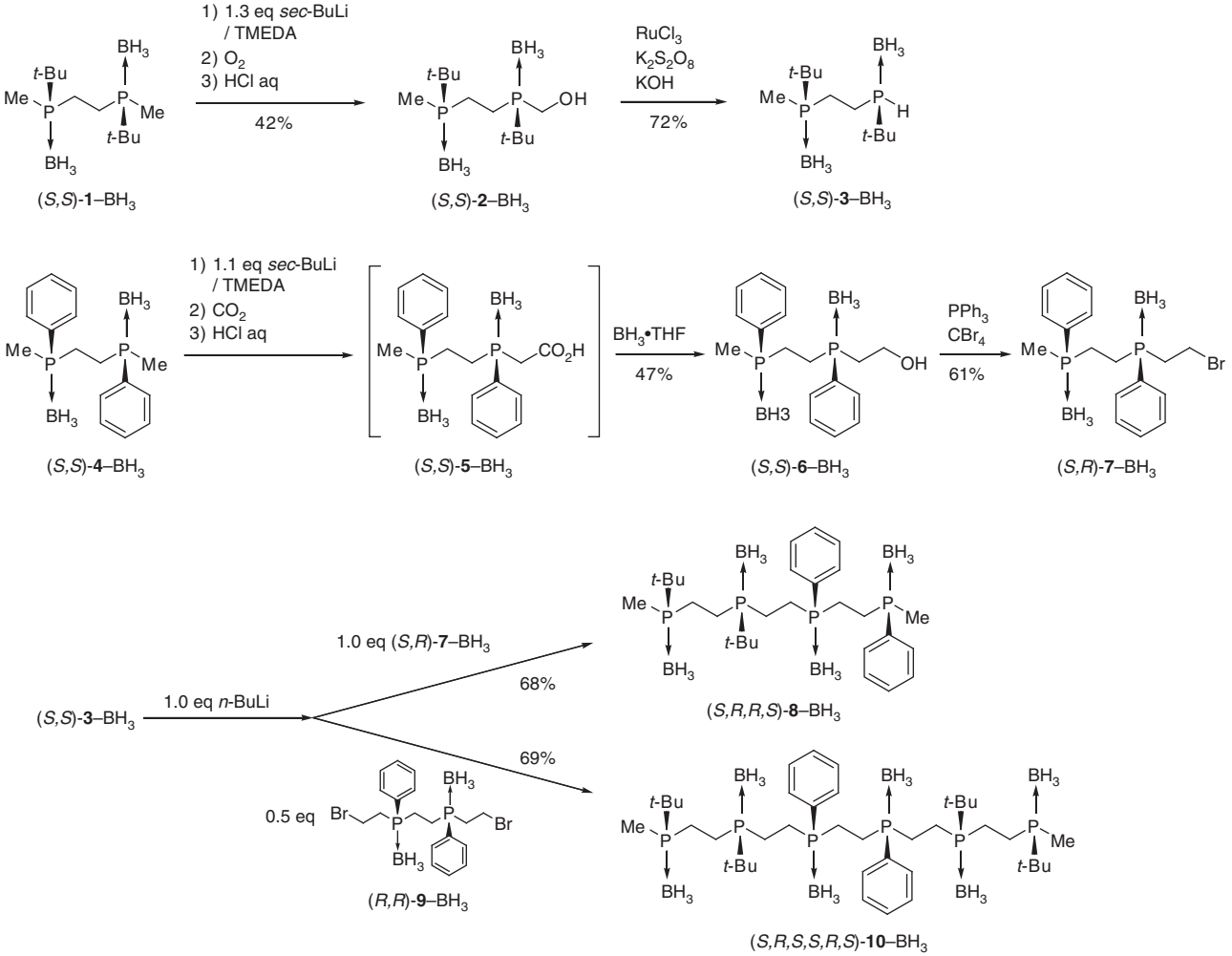
over $MgSO_4$. After filtration, the solvent was removed in vacuo to yield crude (*S,S*)-**5** $-BH_3$. Without purification, $BH_3 \cdot THF$ (1.0 M in THF solution, 10.0 ml, 10.0 mmol) was added to the residue at 0 °C. After stirring for 15 h at room temperature, 2 N HCl (100 ml) was slowly added. The organic layer was extracted with ethyl acetate (100 ml × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2, with ethyl acetate and hexane ($v/v = 1/2$) as an eluent ($R_f = 0.40$, ethyl acetate/hexane $v/v = 1/1$). The solvent was evaporated to obtain (*S,S*)-**6** $-BH_3$ (629.0 mg, 1.89 mmol, 47%) as a colorless solid. $[\alpha]_D^{22}$ +22.7 (c 0.5 in $CHCl_3$); ^1H NMR (399.2 MHz, $CDCl_3$) δ 0.70 (br q, $J_{H-B} = 112.3$ Hz, 6H, P-BH_3), 1.55 (d, $J = 10.2$ Hz, 3H, P-Me), 1.66–2.24 (m, 7H, P-CH_2CH_2-P, P-CH_2-, and -OH), 3.82 (m, 2H, CH_2-O), 7.40–7.65 (m, 10H, P-Ph) p.p.m.; ^{13}C NMR ($CDCl_3$, 100.3 MHz) δ 11.0 (d, $J_{C-P} = 38.9$ Hz), 19.6 (d, $J_{C-P} = 35.5$ Hz), 20.7 (d, $J_{C-P} = 35.5$ Hz), 29.3 (d, $J_{C-P} = 34.7$ Hz), 57.4, 126.6 (d, $J_{C-P} = 52.9$ Hz), 128.2 (d, $J_{C-P} = 53.7$ Hz), 129.0 (m), 131.7 (m) p.p.m.; ^{31}P NMR ($CDCl_3$, 161.5 MHz) δ +11.4 (m), +14.7 (m) p.p.m.; HRMS (ESI) calcd. for $[M+Na]^+$ 355.1694, found 355.1697.

(*S,R*)-7 $-BH_3$

A CH_2Cl_2 solution (10 ml) of (*S,S*)-**6** $-BH_3$ (498.0 mg, 1.5 mmol) and PPh_3 (524.6 mg, 2.0 mmol) was cooled to 0 °C. To this solution, CBr_4 (663.2 mg, 2.0 mmol) was added in one portion. After 5 min, the reaction mixture was allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was evaporated. The residue was subjected to column chromatography on SiO_2, with ethyl acetate and hexane ($v/v = 1/2$) as an eluent ($R_f = 0.50$, ethyl acetate/hexane $v/v = 1/2$). The solvent was evaporated to obtain (*S,R*)-**7** $-BH_3$ (363.8 mg, 0.92 mmol, 61%) as a colorless solid. $[\alpha]_D^{22}$ +39.1 (c 0.5 in $CHCl_3$); ^1H NMR (399.2 MHz, $CDCl_3$) δ 0.68 (br q, $J_{H-B} = 111.7$ Hz, 6H, P-BH_3), 1.56 (d, $J = 10.3$ Hz, 3H, P-Me), 1.68–2.18 (m, 4H, P-CH_2CH_2-P), 2.47 (m, $J = 9.0$ Hz, 2H, P-CH_2-), 3.16–3.56 (m, 2H, -CH_2-Br), 7.42–7.64 (m, 10H, P-Ph) p.p.m.; ^{13}C NMR ($CDCl_3$, 100.3 MHz) δ 11.1 (d, $J_{C-P} = 38.3$ Hz), 19.3 (d, $J_{C-P} = 34.7$ Hz), 20.7 (d, $J_{C-P} = 34.7$ Hz), 24.3, 30.5 (d, $J_{C-P} = 29.8$ Hz), 125.4 (d, $J_{C-P} = 51.2$ Hz), 128.1 (d, $J_{C-P} = 53.7$ Hz), 129.1 (d, $J_{C-P} = 9.9$ Hz), 129.3 (d, $J_{C-P} = 9.9$ Hz), 131.5 (d, $J_{C-P} = 9.1$ Hz), 131.8, 132.0 (d, $J_{C-P} = 9.1$ Hz), 132.3 p.p.m.; ^{31}P NMR ($CDCl_3$, 161.5 MHz) δ +11.6 (m), +17.9 (m) p.p.m.; HRMS (ESI) calcd. for $[M+Na]^+$ 417.0850, found 417.0847.

(*S,R,R,S*)-8 $-BH_3$

A THF solution (15 ml) of (*S,S*)-**3** $-BH_3$ (198.3 mg, 0.80 mmol) was cooled to −78 °C. BuLi (1.6 M in hexane, 0.50 ml, 0.80 mmol) was added by a syringe. After stirring for 2 h, a THF solution (10 ml) of (*S,R*)-**7** $-BH_3$ (315.9 mg, 0.80 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature. After stirring for 21 h, the reaction was quenched by addition of 2 N HCl (100 ml). The organic layer was extracted with ethyl acetate (100 ml × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2, with ethyl acetate and hexane ($v/v = 1/4$) as an eluent ($R_f = 0.35$, ethyl acetate/hexane $v/v = 1/2$). The



Scheme 1 Synthesis of unsymmetrical P-stereogenic oligophosphines (*S,R,R,S*)-**8**–BH_3 and (*S,R,S,S,R,S*)-**10**–BH_3.

solvent was evaporated to obtain (*S,R,R,S*)-**8** $-BH_3$ (310.9 mg, 0.55 mmol, 69%) as a colorless solid. $[\alpha]_D^{22}$ +8.1 (c 0.5 in $CHCl_3$); ^1H NMR (399.2 MHz, $CDCl_3$) δ 0.51 (br, 12H, P-BH_3), 1.06 (d, J = 13.7 Hz, 9H, P-*t*-Bu), 1.18 (d, J = 13.9 Hz, 9H, P-*t*-Bu), 1.24 (d, J = 9.5 Hz, 3H, P-Me), 1.30–2.25 (br, 12H, P-CH_2CH_2-P), 1.48 (d, J = 10.2 Hz, 3H, P-Me), 7.40–7.67 (m, 10H, P-Ph) p.p.m.; ^{13}C NMR ($CDCl_3$, 100.3 MHz) δ 5.3 (d, J_{C-P} = 33.9 Hz), 11.1 (d, J_{C-P} = 38.0 Hz), 13.9 (d, J_{C-P} = 28.9 Hz), 14.7 (d, J_{C-P} = 28.9 Hz), 16.0 (d, J_{C-P} = 30.6 Hz), 19.5 (d, J_{C-P} = 34.7 Hz), 20.1 (d, J_{C-P} = 33.9 Hz), 20.8 (d, J_{C-P} = 34.7 Hz), 25.1, 25.4, 27.6 (d, J_{C-P} = 33.0 Hz), 29.0 (d, J_{C-P} = 31.4 Hz), 125.3 (d, J_{C-P} = 50.4 Hz), 128.1 (d, J_{C-P} = 53.7 Hz), 129.1 (d, J_{C-P} = 9.9 Hz), 129.3 (d, J_{C-P} = 9.9 Hz), 131.5 (d, J_{C-P} = 9.1 Hz), 131.8, 132.2 (d, J_{C-P} = 9.1 Hz), 132.3 p.p.m.; ^{31}P NMR ($CDCl_3$, 161.5 MHz) δ +11.6 (m), +21.6 (m), +29.0 (m), +36.9 (m) p.p.m.; HRMS (ESI) calcd. for $[M+NH_4]^+$ 580.4199, found 580.4208.

(*S,R,S,S,R,S*)-10 $-BH_3$

A THF solution (15 ml) of (*S,S*)-**3** $-BH_3$(247.9 mg, 1.0 mmol) was cooled to −78 °C. BuLi (1.6 M in hexane, 0.61 ml, 1.0 mmol) was added by a syringe. After stirring for 2 h, a THF solution (10 ml) of (*R,R*)-**9** $-BH_3$ (243.9 mg, 0.50 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature. After stirring for 21 h, the reaction was quenched by addition of 2 N HCl (100 ml). The organic layer was extracted with ethyl acetate (100 ml × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2, with ethyl acetate as an eluent (R_f = 0.30, ethyl acetate/hexane v/v = 1/2). The solvent was evaporated to obtain (*S,R,S,S,R,S*)-**10** $-BH_3$ (280.2 mg, 0.34 mmol, 68%) as a colorless solid. ^1H NMR (399.2 MHz, $CDCl_3$) δ 0.52 (br, 18H, P-BH_3), 1.06 (d, J = 13.6 Hz, 18H, P-*t*-Bu), 1.18 (d, J = 13.6 Hz, 18H, P-*t*-Bu), 1.25 (d, J = 9.7 Hz, 6H, P-Me), 1.36–2.22 (m, 20H, P-CH_2CH_2-P), 7.44–7.61 (m, 10H, P-Ph) p.p.m.; ^{13}C NMR ($CDCl_3$, 100.3 MHz) δ 5.4 (d, J_{C-P} = 34.7 Hz), 13.9 (d, J_{C-P} = 28.9 Hz), 14.6 (d, J_{C-P} = 28.9 Hz), 16.0 (d, J_{C-P} = 30.6 Hz), 19.4 (d, J_{C-P} = 34.7 Hz), 20.0 (d, J_{C-P} = 34.7 Hz), 25.1, 25.4, 27.7 (d, J_{C-P} = 33.1 Hz), 29.0 (d, J_{C-P} = 31.4 Hz), 128.6 (d, J_{C-P} = 81.0 Hz), 129.4 (t, J_{C-P} = 5.0 Hz), 132.2 (t, J_{C-P} = 4.5 Hz), 132.4 p.p.m.; ^{31}P NMR ($CDCl_3$, 161.5 MHz) δ +21.7 (s), +29.2 (m), +37.0 (s) p.p.m.; HRMS (FAB) calcd. for $C_{40}H_{90}B_6P_6$ 822.6027, found 822.6041.

(*S,R,R,S*)-12 $-BH_3$

A THF solution (40 ml) of (*S,S*)-**4** $-BH_3$ and *N,N,N′,N′*-tetramethylethylenediamine (0.72 ml, 4.8 mmol) was cooled to −78 °C under Ar atmosphere. *sec*-BuLi (1.0 M in cyclohexane and hexane, 4.8 ml, 4.8 mmol) was added slowly by a syringe. After stirring for 3 h, $CuCl_2$ (807.0 mg, 6.0 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by 28% aqueous NH_3. The organic layer was extracted with ethyl acetate (100 ml × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO_2, with hexane and dichloromethane (v/v = 2/3 to 0/10) as an eluent (R_f = 0.30, ethyl acetate/hexane v/v = 1/2). The solvent was evaporated to obtain (*S,R,R,S*)-**12** $-BH_3$(455.5 mg, 0.76 mmol, 63%) as a colorless solid. ^1H NMR (399.2 MHz, $CDCl_3$) δ 0.65 (br d, J_{H-B} = 107.7 Hz, 12H, P-BH_3), 1.54 (d, J = 10.2 Hz, 6H, P-Me), 1.63–1.85 (m, 6H, P-CH_2CH_2-P), 1.93–2.06 (m, 6H, P-CH_2CH_2-P), 7.37–7.62 (m, 20H, P-Ph) p.p.m.; ^{13}C NMR ($CDCl_3$, 100.3 MHz) δ 11.1 (d, J_{C-P} = 38.0 Hz), 18.8, 19.0, 19.1, 19.4, 20.7 (d, J_{C-P} = 34.7 Hz), 125.2 (d, J_{C-P} = 51.3 Hz), 128.0 (d, J_{C-P} = 53.7 Hz), 129.0, 129.1, 129.2, 131.5, 131.5, 131.8, 132.0, 132.2 p.p.m.; ^{31}P NMR ($CDCl_3$, 161.5 MHz) δ 11.5, 21.1 p.p.m. HRMS (ESI) calcd. for $[M+NH_4]^+$ 620.3573, found 620.3553.

^1H, ^{13}C, and ^{31}P NMR spectra of all new compounds are shown in Supplementary Figures S1–S21 in Supplementary Information.

Deboranation by morpholine

Tetraphosphine (*S,R,R,S*)-**8** $-BH_3$ (5.6 mg, 0.01 mmol) was dissolved in degassed morpholine (1.0 ml). After stirring for 48 h at 50 °C, morpholine was removed in vacuo. The residue was dissolved in $CDCl_3$ and subjected to NMR spectroscopy.

Deboranation by DABCO

Oligophosphine (*S,R,R,S*)-**8** $-BH_3$ (5.6 mg, 0.01 mmol) or (*S,R,S,S,R,S*)-**10** $-BH_3$ (8.2 mg, 0.01 mmol) was dissolved in $CDCl_3$, together with DABCO. After stirring for 18 h at 55 °C, the ^{31}P NMR spectrum was measured.

RESULTS AND DISCUSSION

The synthetic routes for the production of enantiomerically pure unsymmetrical P-stereogenic tetraphosphine (*S,R,R,S*)-**8** $-BH_3$ and hexaphosphine (*S,R,S,S,R,S*)-**10** $-BH_3$ are shown in Scheme 1. Bisphosphine precursors (*S,S*)-**1** $-BH_3$[31] and (*S,S*)-**4** $-BH_3$[32] were synthesized as described previously. Bisphosphine (*S,S*)-**1** $-BH_3$ was lithiated with 1.3 equivalent *sec*-butyllithium, and after O_2 babbling, (*S,S*)-**2** $-BH_3$ was obtained in 42% yield.[33] The ruthenium-catalyzed oxidation and base-promoted decarboxylation[26] of (*S,S*)-**2** $-BH_3$ provided (*S,S*)-**3** $-BH_3$ in 72% yield. The treatment of bisphosphine (*S,S*)-**4** $-BH_3$ with 1.1 equivalent *sec*-butyllithium and CO_2 gas gave (*S,S*)-**5** $-BH_3$.[34,35] Without purification of (*S,S*)-**5** $-BH_3$, its reduction with $BH_3 \cdot THF$ was carried out to obtain (*S,S*)-**6** $-BH_3$ in 47% yield, which was followed by the Appel reaction[36] of (*S,S*)-**6** $-BH_3$ to afford (*S,R*)-**7** $-BH_3$ in 61% yield. After the lithiation of (*S,S*)-**3** $-BH_3$, the addition of 1.0 equivalent (*S,R*)-**7** $-BH_3$ provided the target tetraphosphine (*S,R,R,S*)-**8** $-BH_3$ in 68% yield, whereas the addition of 0.5 equivalent (*R,R*)-**9** $-BH_3$[13] gave hexaphosphine (*S,R,S,S,R,S*)-**10** $-BH_3$ in 69% yield.

The ^{31}P NMR spectrum of tetraphosphine (*S,R,R,S*)-**8** $-BH_3$ showed four signals at +11.6, +21.6, +29.0 and +36.9 p.p.m., as expected. It is known that bisphosphines (*S,S*)-**1** $-BH_3$[31] and (*S,S*)-**4** $-BH_3$,[32] consisting of *tert*-butyl- and phenylphosphines exhibit ^{31}P NMR signals at +28.2 and +11.1 p.p.m., respectively. In addition, the signals of tetraphosphine (*S,R,R,S*)-**11** $-BH_3$[14–16,28] with *tert*-butyl substituents appear at +31.5 and +39.9 p.p.m.; these signals are

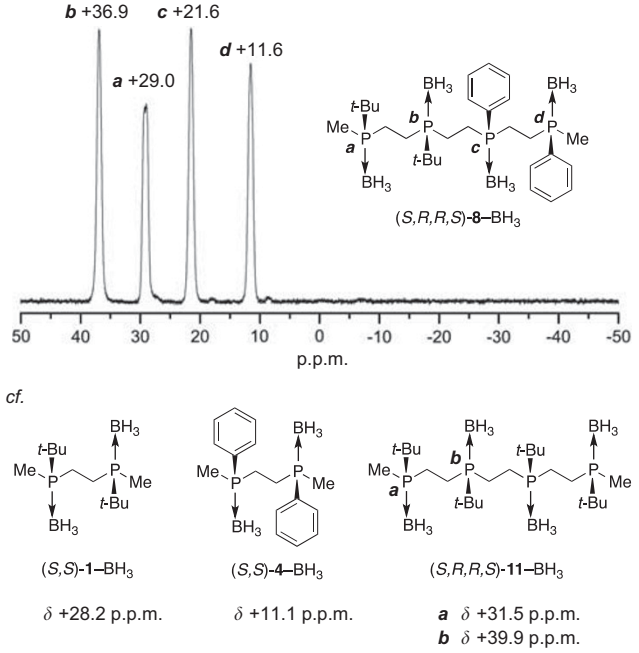


Figure 3 ^{31}P NMR spectrum of (*S,R,R,S*)-**8**–BH_3 and comparison of chemical shifts.

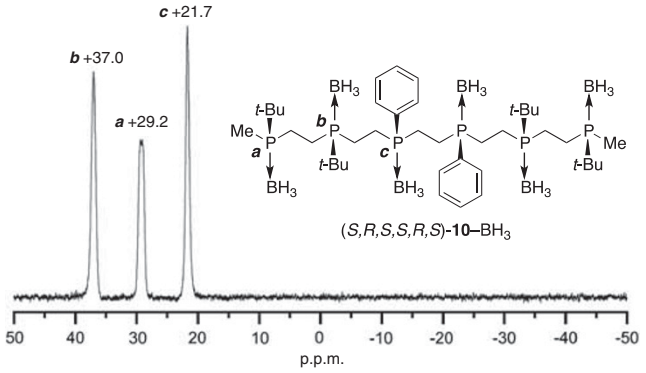


Figure 4 ^{31}P NMR spectrum of (*S,R,S,S,R,S*)-**10**–BH_3.

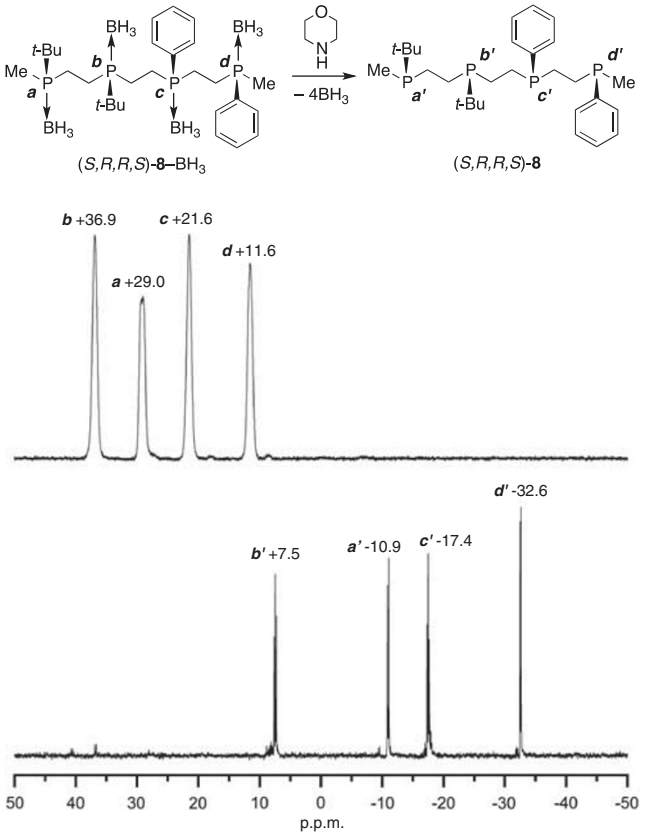


Figure 5 Removal of BH_3 from (*S,R,R,S*)-**8**–BH_3 with morpholine, and ^{31}P NMR spectra.

assigned to outer and inner phosphorus atoms, respectively. Thus, the peaks representing the outer *tert*-butylphosphines are observed at around 30 p.p.m., and representing the inner *tert*-butylphosphines appear at magnetic fields ~8 p.p.m. below those of the outer ones. These results lead to an assignment of the tetraphosphine (*S,R,R,S*)-**8** $-BH_3$ signals, as summarized in Figure 3.

The ^{31}P NMR signals of hexaphosphine (*S,R,S,S,R,S*)-**10** $-BH_3$ were assigned, as shown in Figure 4. The signals were confirmed in the same manner as those of (*S,R,R,S*)-**8** $-BH_3$. The spectrum exhibited two peaks of the *tert*-butylphosphine units at $+29.2$ and

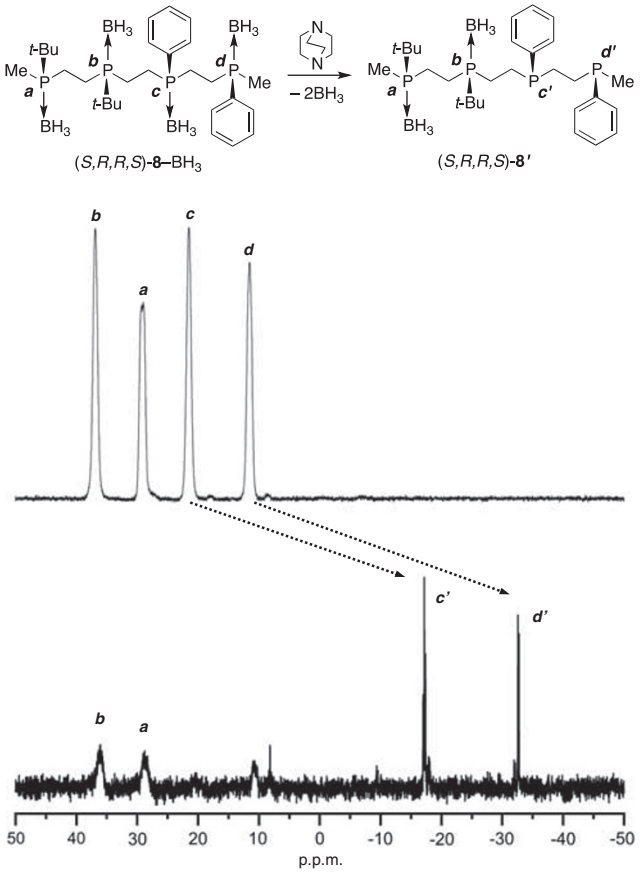


Figure 6 Chemoselective removal of BH_3 from (*S,R,R,S*)-**8**–BH_3 with diazabicyclo[2.2.2]octane (DABCO), and ^{31}P NMR spectra.

$+37.0$ p.p.m., and one peak representing the phenylphosphine units at $+21.7$ p.p.m.

We attempted to remove the boranes coordinated with the phosphorus atoms in tetraphosphine (*S,R,R,S*)-**8** $-BH_3$ by using organic bases such as morpholine[23] (For deboranation with morpholine; for example, see: Jarroux N, Keller P, Mingotaud A-F, Mingotaud C, & Skyes C. Shape-tunable Polymer nodules Grown from Liposomes via Ring-opening Metathesis Polymerisation J. Am. Soc. 126, 15958–15959 (2004)) and DABCO. (For deboranation with DABCO, for example, see: Morisaki *et al.*[11–13]). When (*S,R,R,S*)-**8** $-BH_3$ was stirred in morpholine for 48 h, all the boranes were readily removed. As shown in Figure 5 (^{31}P NMR spectra of (*S,S*)-**1** and (*S,S*)-**4** after deboranation appeared at -10.0 and -32.0 p.p.m., respectively), the ^{31}P NMR spectrum of (*S,R,R,S*)-**8** exhibited four signals at -32.6, -17.4, -10.9 and $+7.5$ p.p.m., which were observed at higher magnetic fields than the signals of (*S,R,R,S*)-**8** $-BH_3$ because the electron densities of phosphorus atoms had increased after deboranation.

On the other hand, we found that DABCO removed boranes selectively from the phenylphosphine moieties; in other words, the boranes on the *tert*-butylphosphine units remained. The coordinate bond between borane and *tert*-butylphosphine is stronger than that between borane and phenylphosphine, which allowed for the chemoselective removal of boranes from (*S,R,R,S*)-**8** $-BH_3$. The molar ratio of DABCO to phosphine was varied, and the ^{31}P NMR measurement for 6.0 equivalent DABCO is shown in Figure 6. (The trace of ^{31}P NMR spectra of (*S,R,R,S*)-**8** $-BH_3$ with DABCO is shown

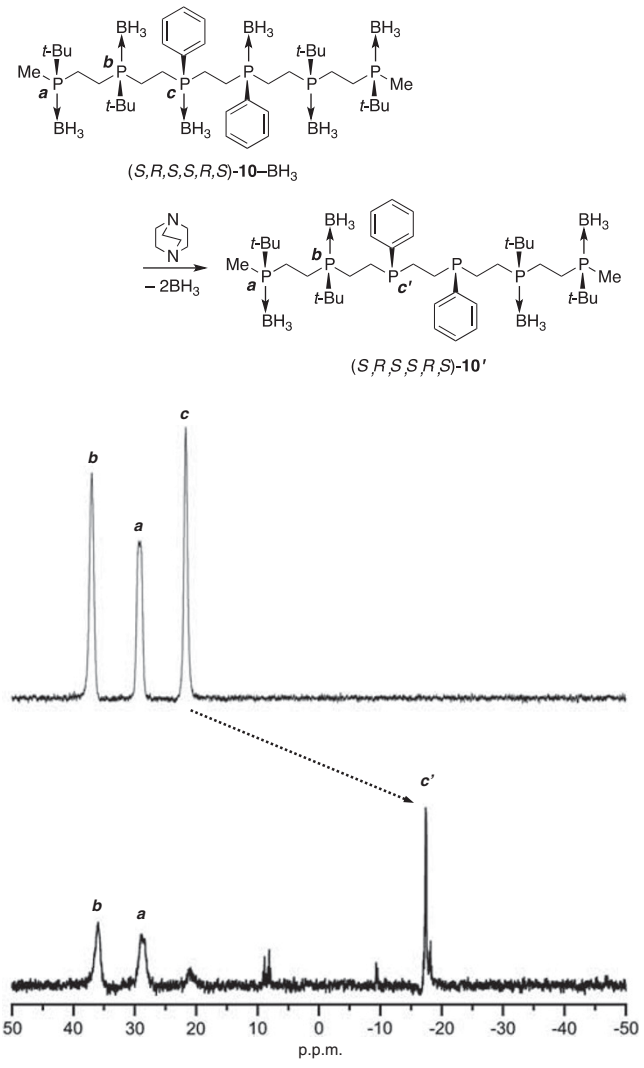
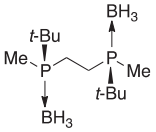
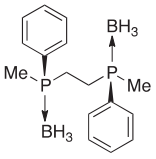
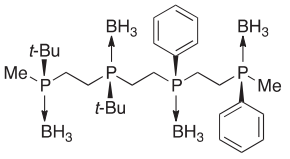
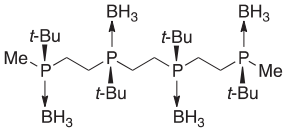
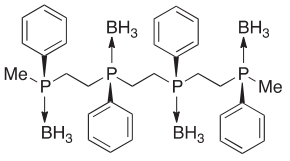


Figure 7 Chemoselective removal of BH_3 from (*S,R,S,S,R,S*)-**10**–BH_3 with diazabicyclo[2.2.2]octane (DABCO), and ^{31}P NMR spectra.

Table 1 Specific rotation and melting point values of P-stereogenic oligophosphines

Run	*Oligophosphine*	$[\alpha]^T_D$	T_m/°C
1[a]	 (*S,S*)-**1**–BH_3	−9.1 T = 27 °C c 1.0 ($CHCl_3$)	176
2[b]	 (*S,S*)-**4**–BH_3	33.6 T = 23 °C c 0.98 (CH_2Cl_2)	145
3	 (*S,R,R,S*)-**8**–BH_3	8.1 T = 22 °C c 0.5 ($CHCl_3$)	180[d]
4	 (*S,R,R,S*)-**11**–BH_3	−3.4 T = 25 °C c 1.0 ($CHCl_3$)	208[d]
5	 (*S,R,R,S*)-**12**–BH_3	ND[c]	227[d,e]

[a]Taken from Imamoto *et al.*[31]
[b]Taken from reference Muci *et al.*[32]
[c]Not detected because of its low solubility.
[d]Measured with differential scanning calorimetry (Figures S24–26 in Supplementary Information).
[e]Glass transition temperature (T_g = 62 °C) and crystallization temperature (T_c = 215 °C) were observed simultaneously (Figure S26 in Supplementary Information).

in Figure S22 in Supplementary Information). This spectrum suggests that the borane on the inner phenylphosphine unit (before deboranation: δ + 21.6 p.p.m., after deboranation: δ −17.4 p.p.m.) was more easily removed. The deboranation of the external phenylphosphine unit (before deboranation: δ + 11.6 p.p.m., after deboranation: δ −32.6 p.p.m.) competed with that of the inner *tert*-butylphosphine unit (before deboranation: δ + 29.0 p.p.m., after deboranation: δ −10.9 p.p.m.). The excess amount of DABCO removed boranes on *tert*-butylphosphine units, and small peaks derived from the bare *tert*-butylphosphine appeared at around δ + 8 and −10 p.p.m. Thus, the addition of 4–6 equivalent DABCO was the optimized condition for the removal of boranes from (*S,R,R,S*)-**8** −BH_3. (The trace of ^{31}P NMR spectra of (*S,R,R,S*)-**8** −BH_3 with DABCO is shown in Figure S22 in Supplementary Information.)

We also studied the chemoselective deboranation of (*S,R,S,S,R,S*)-**10** −BH_3, and these results are shown in Figure 7. The signal that appeared at around −17 p.p.m. was assigned to the bare phosphorus atom of the phenylphosphine moiety. The use of 4–6 equivalent DABCO allowed for the most efficient chemoselective removal of boranes from (*S,R,S,S,R,S*)-**10** −BH_3 (The trace of ^{31}P NMR spectra of (*S,R,S,S,R,S*)-**10** −BH_3 with DABCO is shown in Figure S23 in Supplementary Information), similar to the result obtained for (*S,R,R,S*)-**8** −BH_3. This chemoselectivity arises from the different coordination affinities of the phosphorus atoms to boranes. Accordingly, various transition metals could potentially be added to these molecules to produce a desired sequence by utilizing unsymmetrical oligophosphines.

The specific optical rotations and melting points of the oligophosphines were also examined, and the results are summarized in Table 1. The specific rotation of (*S,R,R,S*)-**8** −BH_3 was + 8.1 (c 0.5 in $CHCl_3$), whereas that of (*S,R,R,S*)-**11** −BH_3 was −3.4 (c 1.0 in $CHCl_3$). The specific optical rotations of (*S,S*)-**1** −BH_3 and (*S,S*)-**4** −BH_3 were −9.1 (c 1.0 in $CHCl_3$) and + 33.6 (c 0.98 in CH_2Cl_2), respectively. The value of (*S,R,R,S*)-**11** −BH_3 was lower than that of (*S,S*)-**1** −BH_3 because the oligophosphine containing a unified substitution group resembles also-called isotactic oligomer from the

structural viewpoint. Melting points (T_m) were measured using differential scanning calorimetry. The T_m of (*S,R,R,S*)-**8** $-BH_3$was found to be 180 °C, which was lower than those of (*S,R,R,S*)-**11** $-BH_3$ (208 °C) and (*S,R,R,S*)-**12** $-BH_3$ (227 °C), owing to the lower crystallinity that results from its unsymmetrical structure. (DSC thermograms are shown in Figures S24–S26 in Supplementary Information.)

CONCLUSION

In conclusion, optically active P-stereogenic oligophosphines with different substituted groups on their phosphorus atoms were synthesized from P-stereogenic bisphosphines. Chemoselective deboranation was performed by selecting an adequate reaction condition; the boranes on the phenylphosphine unit were chemoselectively removed by DABCO. The coordination ability could thus be controlled by the substitution groups on the phosphorus atoms in a single oligomer chain. Therefore, heteromultimetallic complexes, in which transition metals are sequentially aligned, are possible to obtain. The synthesis of enantiomerically pure P-stereogenic polymers containing both phenyl and *tert*-butyl substituents is currently underway. Studies on the coordination behaviors and conformational changes of these P-stereogenic oligophosphines and polymers will form the next step toward the sequential alignment of metals on a single polymer chain.

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