Supporting Information

Synthesis and coordination behaviors of P-stereogenic polymers

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General

$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on a JEOL EX 400 spectrometer, and samples were analyzed in CDCl$_3$ or DMF-$d_7$ using Me$_4$Si as an internal standard. $^{31}$P (161.9 MHz) NMR spectra were also recorded on a JEOL EX 400 spectrometer, and samples were analyzed in CDCl$_3$ or DMF-$d_7$ using H$_3$PO$_4$ as an external standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, m: multiplet, q: quartet, sep: septet, and br: broad. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Enantiomeric purity was confirmed by a HPLC (TOSOH UV-8020) equipped with a Daicel Chiralcel OD-H column (0.46 cm × 25 cm) using 2-propanol/hexane as an eluent. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL IV instrument using CHCl$_3$ as a solvent. Column chromatography was performed with Wakogel C-300 SiO$_2$. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials

THF was purchased and purified by passage through purification column under Ar pressure. Dehydrated grade solvents of toluene and CHCl$_3$ were purchased and used without further purification. N,N,N’,N'-Tetramethylethlenediamine (TMEDA), (−)-sparteine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased and distilled from KOH under Ar atmosphere. sec-BuLi (1.0 M in cyclohexane and n-hexane solution), BH$_3$-THF (1.0 M in THF), CuI, aqueous NH$_3$ (28%), NaH (60 wt% in mineral oil), triethyleneglycol bis(p-toluenesulfonate), PdCl$_2$(cod), and PtCl$_2$(cod) were purchased and used without purification. Compounds (S,S)-1-BH$_3$ and 4 were prepared by the procedure of the literature. All reactions were performed under Ar atmosphere using standard Schlenk techniques.
Synthesis of (S,S)-2-BH₃

A solution of (S,S)-1-BH₃ (1.09 g, 3.0 mmol) and PPh₃ (3.15 g, 12 mmol) in CH₂Cl₂ (30 mL) was cooled to −78 °C under Ar atmosphere. To the stirred solution, CBr₄ (3.58 g, 10.8 mmol) was added in one portion. After 15 minutes, the reaction mixture was allowed to gradually warm to room temperature. After stirring for additional 6 h at room temperature, the reaction mixture was evaporated. The residue was subjected to column chromatography on SiO₂ with hexane/EtOAc (v/v = 1:1). The solvent was removed in vacuo, and recrystallization from toluene and hexane gave (S,S)-2-BH₃ (1.18 g, 2.4 mmol, 80%) as a colorless solid.

Rₙ = 0.80 (hexane/EtOAc: v/v = 1:1); [α]²⁶D 48.4 (c 0.5 in CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 0.7 (br q, J_HB = 129.8 Hz, -BH₃, 6H), 1.85 (m, -PCH₂-, 2H), 2.17 (m, -PCH₂-, 2H), 2.50 (m, -PCH₂-, 4H), 3.19 (m, -CH₂Br, 2H), 3.50 (m, -CH₂Br, 2H), 7.40-7.51 and 7.54-7.61 (m, -C₆H₅, 10H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 19.0 (d, J_CP = 34.6 Hz, -PCH₂-), 24.3 (s, -CH₂Br), 30.2 (d, J_CP = 30.5 Hz, -PCH₂-), 125.1 (d, -C₆H₅, J_CP = 50.0 Hz), 129.3 (-C₆H₅), 131.9 (-C₆H₅), 132.3 (-C₆H₅) ppm; ³¹P{¹H} NMR (CDCl₃, 161.9 MHz) δ +18.1 ppm. HRMS (FAB) calcd. for C₁₈H₂₈Br₂P₂: [M⁺]⁺: 486.0219, found 486.0204. Anal. calcd. for C₁₈H₂₈Br₂P₂: C 44.32; H 5.79; found: C 44.10; H 5.79.
Synthesis of (S,S)-3-BH3

A solution of (S,S)-2-BH3 (732 mg, 1.5 mmol) and NaN₃ (390 mg, 6.0 mmol) in DMF (5.0 mL) was stirred at room temperature under Ar atmosphere. After stirring overnight, the reaction mixture was treated with saturated NH₄Claq and extracted with EtOAc (30 mL × 3). The organic layer was dried over MgSO₄. MgSO₄ was removed by filtration, and the solvent was removed in vacuo. The residue was subjected to column chromatography on SiO₂ with hexane/EtOAc (v/v = 1:1). The solvent was removed in vacuo, the compound was purified by preparative HPLC (CHCl₃) and recrystallization from toluene and hexane to obtain (S,S)-3-BH₃ (276.0 mg, 0.67 mmol, 45%) as a colorless solid.

\[ R_f = 0.80 \text{ (hexane/EtOAc: v/v = 1:1); } [\alpha]^{26}_D = 42.9 \text{ (c 0.5 in CHCl}_3) \text{; } ^1H \text{ NMR (CDCl}_3, 400 MHz \delta 0.7 \text{ (br q, } J_{HB} = 122.5 \text{ Hz, -BH}_3, 6H), 1.87 \text{ (m, -PCH}_2-, 2H), 2.04-2.26 \text{ (m, -PCH}_2-, 6H), 3.31 \text{ (m, -CH}_2N_3, 2H), 3.57 \text{ (m, -CH}_2N_3, 2H), 7.46-7.51 \text{ (m, -C}_6H_5, 4H), 7.52-7.67 \text{ (m, -C}_6H_5, 6H) \text{ ppm; } ^13C \text{ NMR (CDCl}_3, 100 MHz) \delta 19.3 \text{ (d, } J_{CP} = 35.4 \text{ Hz, -PCH}_2), 25.8 \text{ (d, -PCH}_2- J_{CP} = 33.8 \text{ Hz, -PCH}_2), 45.7 \text{ (-CH}_2N_3), 125.7 \text{ (d, } J_{CP} = 55.2 \text{ Hz, -C}_6H_5), 129.3 \text{ (-C}_6H_5), 131.9 \text{ (-C}_6H_5), 132.3 \text{ (-C}_6H_5) \text{ ppm; } ^31P \{^1H\} \text{ NMR (CDCl}_3, 161.9 MHz) \delta +16.0 \text{ ppm. HRMS (FAB) calc. for } \text{C}_{18}H_{28}N_6P_2B_2 [M-H]\text{ 411.1959, found 411.1961. Anal. calcd. for } \text{C}_{18}H_{28}N_6P_2B_2: \text{ C 52.47; H 6.85; N 20.40, found: C 52.24; H 6.92; N 20.11.} \)
Synthesis of polymer 5-BH₃

A solution of (S,S)-3-BH₃ (61.8 mg, 0.15 mmol), 9,9-didodecyl-2,7-diehynylfluorene (4) (82.6 mg, 0.15 mmol), and Cu(MeCN)₄PF₆ (5.6 mg, 0.015 mmol) in DMF (1.5 mL) was stirred at 50 °C under Ar atmosphere. After stirring for 6 h, the reaction mixture was poured into 1% aqueous NH₃ and extracted with CHCl₃ (30 mL × 3). The organic layer was washed with 2 N HCl and brine, and then, it was dried over MgSO₄. MgSO₄ was removed by filtration, and the solvent was dried in vacuo. Reprecipitation from CHCl₃ and hexane gave polymer 5-BH₃ (85.4 mg, 0.089 mmol, 59%) as a pale yellow solid.

[α]²⁶°D 15.9 (c 0.5 in CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 0.24-1.32 (m, -BH₃ and dodecyl-H), 1.78 (br, -PCH₂⁻), 1.90-2.18 (br, -PCH₂⁻), 2.55 and 2.74 (br, -PCH₂⁻), 4.47 and 4.68 (br, -CH₂-triazole-), 7.30-7.82 (m, -Ar) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 14.1, 19.4 (d, JCP = 37.1 ppm, -PCH₂⁻), 22.6, 23.9, 26.8 (d, JCP = 35.5 Hz, -PCH₂⁻), 29.2-30.1, 31.8, 40.5, 44.7 (-CH₂-triazole-), 55.4 (fluorene), 119.9-120.2, 124.3-124.9, 129.0-129.2, 131.9-132.4, 140.8, 148.0, 151.6 ppm; ³¹P {¹H}NMR (CDCl₃, 161.9 MHz) δ +16.1 ppm.
Synthesis of polymer 5-Pt

A solution of polymer 5-BH₃ (48.1 mg, 0.05 mmol) and DABCO (56.1 mg, 0.50 mmol) in CHCl₃ (5.0 mL) was stirred at 50 °C under Ar atmosphere. After stirring for 6 h, the reaction mixture was poured into hexane under Ar atmosphere, and the solvent was removed with a syringe. The residue was solved in CHCl₃ (5.0 mL). To the CHCl₃ solution was added PtCl₂(cod) (18.7 mg, 0.05 mmol) under Ar atmosphere. After stirring for 12 h, the reaction mixture was poured into hexane to obtain polymer complex 5-Pt as a pale yellow solid (38.0 mg, 0.032 mmol, 63%).

[α]²⁵ 40.2 (c 0.5 in CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 0.64 (br -C₁₂H₂₅), 0.82 (br -C₁₂H₂₅), 0.94-1.26 (br -C₁₂H₂₅), 2.04 (br, -PCH₂-), 3.16 (br, -PCH₂-), 4.98 (br, -CH₂-triazole-), 7.37 (br, -Ar), 7.51-7.72 (br, -Ar), 7.78 (br, -Ar), 7.97 (br, -Ar) ppm; ³¹P [¹H]NMR (CDCl₃, 161.9 MHz) δ +42.2 (Jₚ-Pt = 3577 Hz) ppm.
Synthesis of polymer 5-Cu

![Diagram of polymer synthesis]

A solution of polymer 5-BH₃ (28.9 mg, 0.03 mmol), DABCO (33.6 mg, 0.30 mmol) in CHCl₃ (3.0 mL) was stirred at 50 °C. After stirring for 6 h, the reaction mixture was poured into hexane under Ar atmosphere, and the solvent was removed with a syringe. The residue was solved in DMF (3.0 mL), and Cu(MeCN)₄PF₆ was added to the DMF solution. After stirring for 12 h, the reaction mixture was poured into toluene to obtain polymer 5-Cu as a pale yellow solid (25.3 mg, 0.022 mmol, 73%).

[α]²⁵D 8.4 (c 0.5 in CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 0.60-1.45 (br, -C₁₂H₂₅), 1.93-2.48 (br, -PCH₂), 4.87 (br, -CH₂-triazole), 7.11-8.30 (br, -Ar), 8.94 (br, -Ar) ppm;

³¹P {¹H} NMR (CDCl₃, 161.9 MHz) δ –8.1, –145.7 (sep, Jₚ₂ = 710.7 Hz) ppm.
Synthesis of model compound (\(S,S\))-M1-BH\(_3\)

![Chemical Structure](image)

A solution of (\(S,S\))-3-BH\(_3\) (124.0 mg, 0.30 mmol), phenylacetylene (110 mL, 1.0 mmol), and Cu(MeCN)\(_4\)PF\(_6\) (11.2 mg, 0.03 mmol) in DMF (3.0 mL) was stirred at 50 °C under Ar atmosphere. After stirring for 6 h, the reaction mixture was poured into 1% NH\(_3\)aq and extracted with CHCl\(_3\) (30 mL × 3). The organic layer was washed with 2 N HCl and brine, and it was dried over MgSO\(_4\). MgSO\(_4\) was removed by filtration, and the solvent was dried in vacuo. The residue was purified by reprecipitation from CHCl\(_3\) and hexane, following recrystallization from toluene and hexane gave (\(S,S\))-M1-BH\(_3\) (135.1 mg, 0.22 mmol, 73%) as a colorless solid.

\(\lbrack\alpha\rbrack_\text{D}^{26} +9.9\ (c\ 0.5\ \text{in\ CHCl}_3)\); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 0.75 (br q, \(J_{BH_3} = 98.6\ \text{Hz}\,\text{H},\ 6\)H), 1.61 (m, -PCH\(_2\)-, 2H), 2.00 (m, -PCH\(_2\)-, 2H), 2.52 (m, -PCH\(_2\)-, 2H), 2.69 (m, -PCH\(_2\)-, 2H), 4.43 (m, -CH\(_2\)-triazole, 2H), 4.63 (m, -CH\(_2\)-triazole, 2H), 7.3-7.5 (m, -Ar, 18H), 7.61 (s, triazole-\(H\), 2H), 7.68 (d, \(J = 7.2\ \text{Hz}\), -Ar, 2H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 19.2 (s, -PCH\(_2\)-), 26.7 (d, \(J_{CP} = 34.6\ \text{Hz}\), -PCH\(_2\)-), 44.7 (-CH\(_2\)-triazole-), 100.5, 120.3, 125.7, 128.2, 128.8, 129.2, 129.3, 130.2, 131.8, 132.4, 147.6 ppm; \(^{31}\)P\{\(^1\)H\} NMR (CDCl\(_3\), 161.9 MHz) \(\delta\) +16.1 ppm. HRMS (ESI) calc. for C\(_{34}\)H\(_{40}\)N\(_6\)P\(_2\)B\(_2\) [M+H]\(^+\) 617.3054, found 617.3049.
Synthesis of model compound (S,S)-M1-BH₃

A solution of (S,S)-M1-BH₃ (24.6 mg, 0.04 mmol), DABCO (44.8 mg, 0.40 mmol) in toluene (4.0 mL) was stirred at 50 °C. After stirring for 6 h, the reaction mixture was poured into hexane under Ar atmosphere, and the solvent was removed with a syringe. The residue was solved in CH₂Cl₂ (3.0 mL), and PtCl₂(cod) (15.0 mg, 0.04 mmol) was added to the CH₂Cl₂ solution. After stirring for 12 h, the reaction mixture was subjected to reprecipitation from CH₂Cl₂ and hexane to obtain polymer (S,S)-M1-Pt as a colorless solid (29.8 mg, 0.035 mmol, 87%).

[α]²⁶D 39.6 (c 0.5 in DMF); ¹H NMR (CDCl₃, 400 MHz) δ 2.2-2.5 (m, -PCH₂-), 3.16 (m, -PCH₂-, 4H), 4.89 (m, -CH₂-triazole, 4H), 7.35 (m, -Ar, 14H), 7.63 (m, -Ar, 2H), 7.75 (s, triazole-H, 2H), and 7.92 (m, -Ar, 4H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 25.8 (d, JCP = 34.5 Hz, -PCH₂-), 26.7 (d, JCP = 34.6 Hz, -PCH₂-), 45.7 (-CH₂-triazole-), 100.1, 124.7-125.8, 128.3-130.0, 128.2, 132.7-132.9, 147.9 ppm; ³¹P{¹H} NMR (CDCl₃, 161.9 MHz) δ +41.3 (JPPt = 3556) ppm. HRMS (ESI) calc. for C₃₄H₃₄N₆Cl₂P₂Pt [M+Na]^+ 876.1243, found 876.1230.
Synthesis of model compound (S,S)-M1-Cu

A solution of (S,S)-M1-BH₃ (43.1 mg, 0.07 mmol), DABCO (78.4 mg, 0.70 mmol) in toluene (3.0 mL) was stirred at 50 °C. After stirring for 6 h, the reaction mixture was poured into hexane under Ar atmosphere, and the solvent was removed with a syringe. The residue was solved in DMF (3.0 mL), and Cu(MeCN)₄PF₆ (26.1 mg, 0.07 mmol) was added to the DMF solution. After stirring for 12 h, the solvent was removed in vacuo. The residue was purified by reprecipitation from CHCl₃ and hexane to obtain polymer (S,S)-M1-Cu as a colorless solid (24.0 mg, 0.030 mmol, 43%).

[α]D²⁵ 39.6 (c 0.5 in CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 2.16 (br, -PC₆H₂-), 4.85 (m, -CH₂-triazole), 5.06 (m, -CH₂-triazole), 7.3–7.5, 7.75, 7.82, 8.84 (s, triazole-H) ppm; ³¹P{¹H} NMR (CDCl₃, 161.9 MHz) δ –9.2, –145.8 (sep, JPF = 710.7 Hz) ppm. HRMS (ESI) calc. for C₃₄H₃₄N₆P₃F₆Cu [M-PF₆]⁺ 651.1611, found 651.1601.
Figure S1. \(^1\)H NMR spectrum (400 MHz) of \((S,S)-2\)-BH\(_3\) in CDCl\(_3\).

Figure S2. \(^{13}\)C NMR spectrum (100 MHz) of \((S,S)-2\)-BH\(_3\) in CDCl\(_3\).
Figure S3. $^{31}$P NMR spectrum (161.9 MHz) of (S,S)-2-BH$_3$ in CDCl$_3$. 
Figure S4. $^1$H NMR spectrum (400 MHz) of (S,S)-3-BH$_3$ in CDCl$_3$.

Figure S5. $^{13}$C NMR spectrum (100 MHz) of (S,S)-3-BH$_3$ in CDCl$_3$. 
Figure S6. $^{31}$P NMR spectrum (161.9 MHz) of (S,S)-3-BH$_3$ in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum (400 MHz) of 5-BH$_3$ in CDCl$_3$.

Figure S8. $^{13}$C NMR spectrum (100 MHz) of 5-BH$_3$ in CDCl$_3$. 
Figure S9. $^{31}\text{P}$ NMR spectrum (161.9 MHz) of 5-BH$_3$ in CDCl$_3$. 
Figure S10. $^1$H NMR spectrum (400 MHz) of 5-Pt in CDCl$_3$.

Figure S11. $^{31}$P NMR spectrum (161.9 MHz) of 5-Pt in CDCl$_3$. 
Figure S12. $^1$H NMR spectrum (400 MHz) of 5-Cu in DMF-$d_7$.

Figure S13. $^{31}$P NMR spectrum (161.9 MHz) of 5-Cu in DMF-$d_7$. 
Figure S14. $^1$H NMR spectrum (400 MHz) of (S,S)-M1-BH$_3$ in CDCl$_3$.

Figure S15. $^{13}$C NMR spectrum (100 MHz) of (S,S)-M1-BH$_3$ in CDCl$_3$. 
Figure S16.  $^{31}$P NMR spectrum (161.9 MHz) of (S,S)-M1-BH$_3$ in CDCl$_3$. 
Figure S17. $^1$H NMR spectrum (400 MHz) of (S,S)-M1-Pt in CDCl$_3$.

Figure S18. $^{13}$C NMR spectrum (100 MHz) of (S,S)-M1-Pt in CDCl$_3$. 
Figure S19. $^{31}$P NMR spectrum (161.9 MHz) of (S,S)-M1-Pt in CDCl$_3$. 
Figure S20. $^1$H NMR spectrum (400 MHz) of (S,S)-M1-Cu in DMF-$d_7$.

Figure S21. $^{31}$P NMR spectrum (161.9 MHz) of (S,S)-M1-Cu in DMF-$d_7$. 
Figure S22. (a) $^{31}$P and (b) $^1$H NMR spectra of (S,S)-M1-BH$_3$ (in CDCl$_3$), (S,S)-M1-Pt (in CDCl$_3$), and (S,S)-M1-Cu (in DMF-$d_7$).

Figure S23. (a) $^{31}$P and (b) $^1$H NMR spectra of 5-BH$_3$ (in CDCl$_3$), 5-Pt (in CDCl$_3$), and 5-Cu (in DMF-$d_7$). This is the same figure as “Fig.1” in the manuscript.
References

