Synthesis of C_3 Symmetric, Optically Active Triamidoamine and Protetraazaphosphatrane

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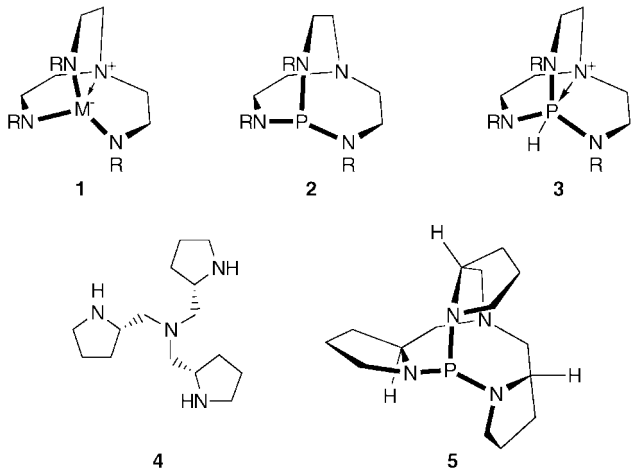
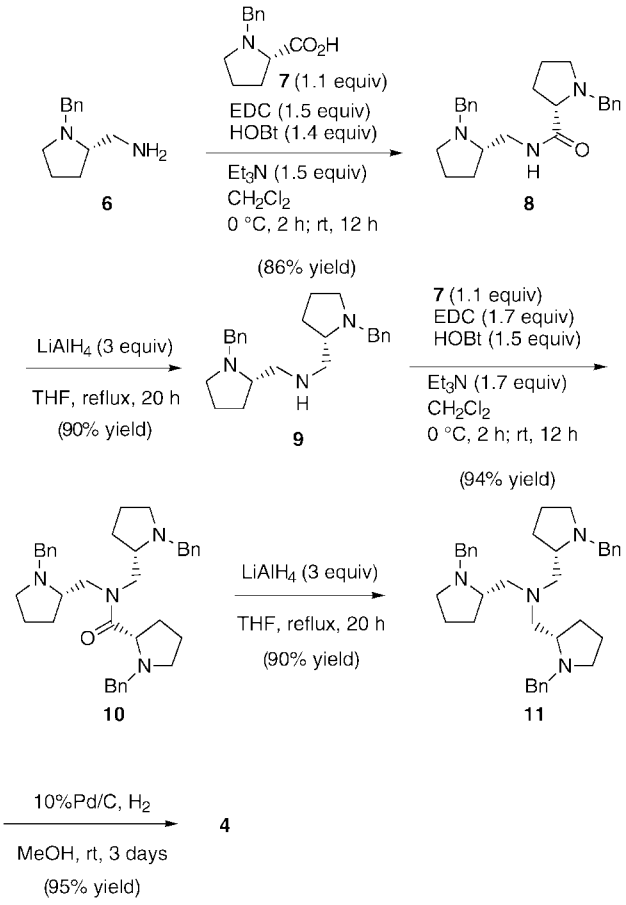
Triamidoamine ligands $[(RNCH_2CH_2)_3N]^{3-}$ can bind to a variety of transition metals and phosphorus in oxidation states 3+ or higher in a tetradentate manner like **1**.[1,2] Because of an interest in the C_3 symmetric structure of **1**, a number of novel transition tetraazametallatranes have been synthesized along with the study of their structural chemistry and chemical and redox reactivity.[1,3] Verkade and co-workers, pioneers of phosphatrane chemistry, have demonstrated that the bicyclic protetraazaphosphatrane **2** is a remarkably strong base, reacting with a proton to give the stable tetraazaphosphatrane **3**.[2,4] Cation **3** features a transannular P←N covalent bond that forms via inversion of the bridgehead nitrogen. Unusual basicity and reactivity of **2** can be explained by the delocalization of the bridgehead nitrogen lone pair into the three-center, four-electron bond systems along the molecular axes. Very recently, further important findings by the same group have shown that **2** is a nonionic superbase catalyst for the conversion of isocyanates to isocyanurates,[4b] acylation,[4d] and silylation of hindered alcohols,[4f,h] and dehydrohalogenation.[4g] This has stimulated interest in the asymmetric version of their reactions. Here, we report the first synthesis of chiral C_3 symmetric, optically active triamidoamine **4** and protetraazaphosphatrane **5**.



To synthesize a chiral triamidoamine concisely, (*S*)-proline, a readily available and inexpensive material, was used as a chiral amine fragment. The route to chiral triamidoamine **4** based on (*S*)-proline is shown in Scheme 1. In the first step, (*S*)-*N*-benzyl-2-aminomethylpyrrolidine (**6**)[5] and *N*-benzyl-(*S*)-proline (**7**)[6] were condensed using 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) and *N*-hydroxybenzotriazole (HOBt) in the presence of triethylamine in anhydrous dichloromethane to give (*S*,*S*)-amide **8** in 86% yield. Subsequent reduction by lithium aluminum hydride gave (*S*,*S*)-bis(*N*′-benzyl-2-pyrrolidinylmethyl)amine (**9**) in 90% yield. The next step, introduction of the third proline fragment, was conducted in a similar manner. Thus, tris(*N*′-benzyl-

Scheme 1



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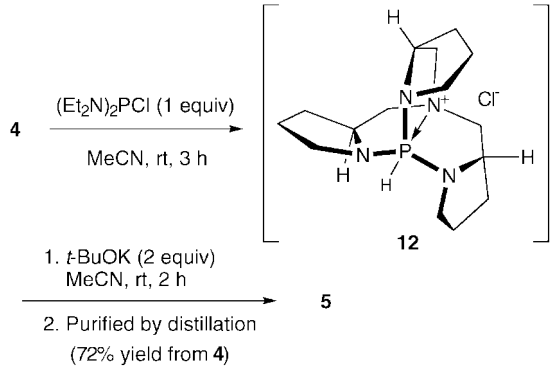
Scheme 2



2-pyrrolidinylmethyl)amine (**11**) was synthesized from **6** in 65% overall yield. Deprotection of *N*-benzylated triamidoamine **11** was easily achieved using Pd/C under a hydrogen atmosphere to give the desired optically pure triamidoamine **4** quantitatively. Judging from the fact that only one diastereomer has been observed for each of products **8**-**11**, little or no racemization has occurred in the amide-coupling and the subsequent reduction steps.

Chiral protetraazaphosphatrane **5** was synthesized in a one-pot two-step procedure according to the literature[4a] with a slight modification, as shown in Scheme 2. In the first step the reaction of one molar equiv of **4** and bis(diethylamino)chlorophosphane gave the stable cation **12** prepared as the chloride quantitatively. Subsequently, the treatment of **12** with potassium *tert*-butoxide gave **5** in 72% isolated yield.

Treatment of **12** with $AgBF_4$ in CH_2Cl_2 gave HBF_4 salt **13** in quantitative yield. The ^1H NMR chemical shift of 5.88 ppm for the H−P hydrogen in **13** is indicative of four- or five-coordinative phosphorus, as is its one-bond H−P coupling constant of 477 Hz.[7,8] The structure of **13** was confirmed by X-ray crystallography (Figure 1). Although the H−P hydrogen in **13** could not be located exactly, the high electron density of this hydrogen was certainly distributed in the direction of the H−P−N_{ax} angle (177.4°). Also, the sum of the NPN angles in the equatorial plane (357.9°), the nearly right-angle relationship of the N_{ax}−P bond with the N_{eq}−P linkages (average 85.2°), the detection of the $^1H-^{31}P$ coupling in solution, and the directionality of the N_{ax} lone pair toward the phosphorus are consistent with the H−P proton occupying the vacant axial position. The P−N_{ax} bond distance in **13** (2.039 Å) is similar to that in **3**−BF_4^- (R = Me, 1.967 Å) reported previously.[7] The considerably shorter P−N_{eq} distances (average 1.659 Å) compared with the P−N_{ax} bond distance in **13** may reflect a combination of the diminished σ bond order in the axial three-center four electron system[9] and the lack of N_{ax}−P π bonding.

Protetraazaphosphatrane **5** was examined for silylation of benzyl alcohol (eq 1). As expected, **5** behaved as a base catalyst as strong as **2** (R = Me).[7] However, no asymmetric induction was observed in incomplete silylation

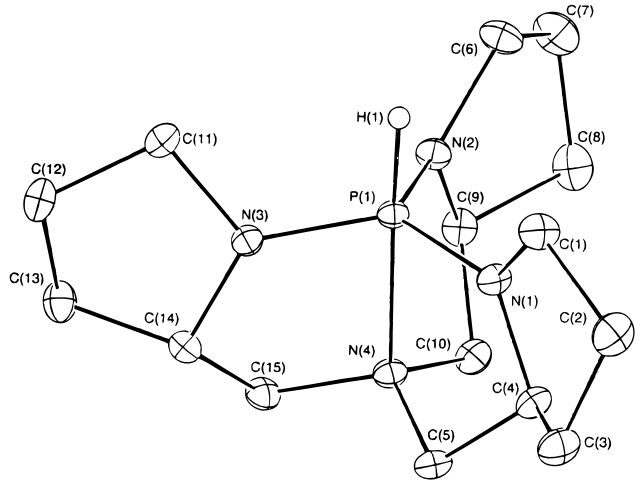
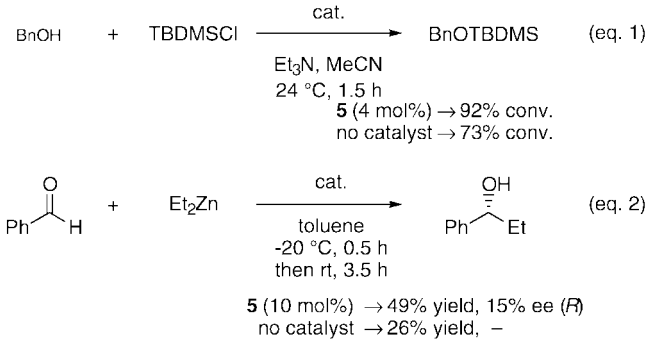


Figure 1. ORTEP drawing and atomic numbering scheme for **13**. (BF^{4-} is excluded from the figure. Although the H−P bond distance shown here is not positive, its direction could be detected.) Pertinent bond distances are P(1)−N(1), 1.652(1); P(1)−N(2), 1.660(1); P(1)−N(3),1.664(1); and P(1)−N(4), 2.039(1) Å; important bond angles are N(1)P(1)N(2), 120.3(1); N(2)P(1)N(3), 118.1(1); N(3)P(1)N(1), 119.5(1); N(1)P(1)N(4), 84.9(1); N(2)P(1)N(4), 85.5(1); N(3)P(1)N(4), 85.3(1); N(1)P(1)H(1), 94.6(5); N(2)P(1)H(1), 92.6(5); and N(3)P(1)H(1), 97.1(5)°.

of racemic 1-phenylethanol with sterically hindered trialkylsilyl chlorides such as *tert*-butyldimethylsilyl chloride, triisopropylsilyl chloride, and triphenylsilyl chloride. Next, **5** was examined as a chiral catalyst for ethylation of benzaldehyde with diethylzinc (eq 2). Certain catalytic activity and asymmetric induction were observed, although they were entirely insufficient.



In conclusion, the first chiral C_3 symmetric protetraazaphosphatrane **5** has been developed. Exploratory studies indicate that this area of research will produce other chiral protetraazaphosphatrane and tetraazametallatrane structures and various useful enantioselective reactions. Applications of **5** and its derivatives in asymmetric synthesis as a potent chiral ligand or catalyst are currently being investigated in our laboratories.

Experimental Section

General. All experiments were carried out under an atmosphere of dry argon. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF,$_{254}$ 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel E. Merck 9385. Microanalyses were accomplished at the School of Agriculture, Nagoya University. The high-resolution mass spectra (HRMS) were conducted at Daikin Industries, Ltd.

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N-Benzyl-(*S*)-proline derivatives **6**[5] and **7**[6] were prepared according to the literature procedures. Silylation of alcohols catalyzed by **5** was carried out according to the reported procedures.[4f,h]

(*S,S*)-*N*-Benzyl-2-[*N*-(*N*′-benzylprolyl)aminomethyl]pyrrolidine (8). To a solution of EDC (21.3 g, 111.0 mmol) and HOBt (14.0 g, 103.6 mmol) in dichloromethane (200 mL) was added a solution of **7** (16.7 g, 81.4 mmol) and **6** (14.1 g, 74.0 mmol) in dichloromethane (200 mL) at 0 °C. To the mixture was added dropwise triethylamine (15.5 mL, 111.0 mmol) at the same temperature. After being stirred for 2 h, the reaction mixture was allowed to warm to ambient temperature. The reaction was left to stir at room temperature overnight (ca. 12 h). Subsequently, water was added to the reaction mixture and the resulting aqueous solution was extracted with dichloromethane. The combined organic extracts were washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. Filtration followed by solvent evaporation afforded a crude product. The residue was purified using flash chromatography on silica gel [hexane/ethyl acetate mixtures (1:1→1:0) as eluents] to give **8** (24.0 g, 63.6 mmol, 86%) as a colorless oil: TLC (ethyl acetate) $R_f = 0.77$; $[\alpha]^{24.5}_D = -131.1$ ($c = 2.1$, $CHCl_3$); IR (film) 2967, 2801, 1674, 1500, 1455, 1372, 1129, 741, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.40−1.52 (m, 1H), 1.52−1.65 (m, 2H), 1.65−1.82 (m, 2H), 1.82−1.96 (m, 2H), 2.12−2.34 (m, 3H), 2.68−2.75 (m, 1H), 2.92−3.02 (m, 2H), 3.17−3.28 (m, 2H), 3.25 (d, $J = 12.7$ Hz, 1H), 3.38 (d, $J = 12.8$ Hz, 1H), 3.67 (ddd, $J = 2.0$, 8.4, 13.9 Hz, 1H), 4.03 (d, $J = 12.8$ Hz, 1H), 4.04 (d, $J = 12.9$ Hz, 1H), 7.10−7.20 (m, 3H), 7.20−7.32 (m, 3H), 7.32−7.37 (m, 4H), 8.17 (d, $J = 6.0$ Hz, 1H); HREIMS calcd for $C_{24}H_{31}N_3O$ [M^+] 377.2467, found 377.2460.

(*S,S*)-Bis(*N*′-benzyl-2-pyrrolidinylmethyl)amine (9). A solution of **8** (24.2 g, 64.0 mmol) in THF (100 mL) was added, under an argon atmosphere, to a suspension of lithium aluminum hydride (7.29 g, 192 mmol) in THF (100 mL). This mixture was heated under reflux for 20 h and subsequently cooled to 0 °C. Next 10% aqueous potassium hydroxide (11 mL) was carefully added and the resulting mixture was heated under reflux for 1 h until the salts were white. After cooling to room temperature the salts were removed by filtration. These salts were again heated under reflux for 1 h with THF (100 mL) and water (2 mL). After removal of the salts by filtration, the THF layers were combined and dried over Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash chromatography on silica gel [CH_2Cl_2/methanol mixtures (20:1→10:1→7:1) as eluents] to give **9** (20.9 g, 57.6 mmol, 90%) as a colorless oil: TLC (CH_2Cl_2/methanol = 8:1) $R_f = 0.32$; $[\alpha]^{24.9}_D = -96.4$ ($c = 1.4$, $CHCl_3$); IR (film) 2961, 2874, 2789, 1495, 1453, 1372, 1352, 1210, 1119, 1075, 1028, 787, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.62−1.76 (m, 7H), 1.86−2.02 (m, 2H), 2.20 (q, $J = 8.5$ Hz, 2H), 2.55−2.76 (m, 6H), 2.88−2.96 (m, 2H), 3.32 (d, $J = 13.1$ Hz, 2H), 4.03 (d, $J = 13.1$ Hz, 2H), 7.18−7.36 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.0 (3C), 29.2 (3C), 54.1 (3C), 54.4 (3C), 59.7 (3C), 63.6 (3C), 126.6 (3C), 128.0 (6C), 128.7 (6C), 139.9 (3C); HREIMS calcd for $C_{24}H_{33}N_3$ [M^+] 363.2666, found 363.2675.

(*S,S*)-*N*-(*N*′-Benzylprolyl)-bis(*N*′-benzyl-2-pyrrolidinylmethyl)amine (10). To a solution of EDC (20.9 g, 109 mmol) and HOBt (13.0 g, 96.0 mmol) in dichloromethane (125 mL) was added a solution of **7** (15.4 g, 70.4 mmol) and **9** (23.3 g, 64.0 mmol) in dichloromethane (125 mL) at 0 °C. To the mixture was added dropwise triethylamine (15.2 mL, 109 mmol) at the same temperature. After being stirred for 2 h, the reaction mixture was allowed to warm to ambient temperature. The reaction was left to stir at room temperature overnight (ca. 12 h). Subsequently, water was added to the reaction mixture and the resulting aqueous solution was extracted with dichloromethane. The combined organic extracts were washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. Filtration followed by solvent evaporation afforded a crude product. The residue was purified using flash chromatography on silica gel [CH_2Cl_2/methanol mixtures (60:1→30:1→15:1→10:1) as eluents] to give **10** (33.1 g, 60.2 mmol, 94%) as a coloress oil: TLC (CH_2Cl_2/methanol = 8:1) $R_f = 0.50$; IR (film) 2965, 2793, 1646, 1455, 1215, 1121, 749, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58−2.07 (m, 12H), 2.14 (q, $J = 6.9$ Hz, 1H), 2.24 (q, $J = 8.4$ Hz, 1H), 2.38−2.56 (m, 2H), 2.76−2.85 (m, 1H), 2.85−2.98 (m, 2H), 3.03−3.14 (m, 2H), 3.18 (t, $J = 6.9$ Hz, 1H), 3.31 (d, $J = 13.4$ Hz, 1H), 3.33 (d, $J = 13.4$ Hz, 1H), 3.38−3.53 (m, 3H), 3.78 (d, $J = 12.9$ Hz, 1H), 3.98 (d, $J = 12.9$ Hz, 2H), 4.16 (d, $J = 13.5$ Hz, 1H), 7.20−7.40 (m, 15H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.4, 22.5, 22.6, 29.0 (3C), 50.4, 52.2, 52.4, 53.6, 54.2, 57.2, 59.0, 59.6, 61.9, 62.0, 62.8, 126.3, 126.5, 126.6, 127.7 (4C), 127.9 (2C), 128.2 (2C), 128.3 (2C), 128.8 (2C), 138.8, 139.1, 139.5, 173.4; HREIMS calcd for $C_{36}H_{46}N_4O$ [M^+] 550.3657, found 550.3672.

(*S,S,S*)-Tris(*N*′-benzyl-2-pyrrolidinylmethyl)amine (11). A solution of **10** (34.1 g, 62.0 mmol) in THF (125 mL) was added, under an argon atmosphere, to a suspension of lithium aluminum hydride (7.06 g, 186 mmol) in THF (125 mL). This mixture was heated under reflux for 20 h and subsequently cooled to 0 °C. Next 10% aqueous pottasium hydroxide (11 mL) was carefully added and the resulting mixture was heated under reflux for 1 h until the salts were white. After cooling to room temperature the salts were removed by filtration. These salts were again heated under reflux for 1 h with THF (100 mL) and water (2 mL). After removal of the salts by filtration, the THF layers were combined and dried over Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash chromatography on silica gel [hexane/CH_2Cl_2 mixtures (1:1→1:2) as eluents] to give **11** (30.0 g, 55.8 mmol, 90%) as a coloress oil: TLC (CH_2Cl_2/MeOH = 8:1) $R_f = 0.43$; $[\alpha]^{28}_D = -212.8$ ($c = 1.40$, $CHCl_3$); IR (film) 2975, 2797, 1495, 1453, 1370, 1117, 1075, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58−1.80 (m, 9H), 1.93−2.05 (m, 3H), 2.11−2.21 (m, 3H), 2.34 (dd, $J = 10.2$, 12.3 Hz, 3H), 2.45 (dd, $J = 3.2$, 12.3 Hz, 3H), 2.53−2.65 (m, 3H), 2.89−2.97 (m, 3H), 3.25 (d, $J = 12.8$ Hz, 3H), 4.02 (d, $J = 12.8$ Hz, 3H), 7.20−7.40 (m, 15H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.2, 31.0, 55.4, 60.3, 61.2, 62.6, 127.3, 128.7 (2C), 129.5 (2C), 140.2. Anal. Calcd for $C_{36}H_{48}N_4$: C, 80.51; H, 9.01; N, 10.43. Found: C, 80.26; H, 9.20; N, 10.59.

(*S,S,S*)-Tris(2-pyrrolidinylmethyl)amine (4). *N*-Benzylated amine **11** (24.2 g, 45.0 mmol) and 10% palladium on activated carbon (3 g) were mixed in dry methanol (100 mL) and stirred at room temperature under atmospheric pressure of H_2 for 3 days. The catalyst was removed by filtration through a Celite pad under an argon atmosphere, and the filtrate was concentrated. The crude product was purified by distillation with a Kugelrohr aparatus (0.02 Torr, 110−120 °C) to give **4** (11.4 g, 42.7 mmol, 95%) as a colorless liquid: $[\alpha]^{28}_D = 55.1$ ($c = 1.23$, $CHCl_3$); IR (film) 3300 (br, NH), 2955, 1541, 1453, 1404, 1069, 814, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20−1.38 (m, 3H), 1.66−1.90 (m, 9H), 2.1−3.6 (br, 3H), 2.25−2.48 (m, 6H), 2.77−3.05 (m, 6H), 3.12−3.27 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.9 (3C), 29.4 (3C), 45.8 (3C), 56.2 (3C), 60.5 (3C). Anal. Calcd for $C_{15}H_{30}N_4$: C, 67.62; H, 11.35; N, 21.03. Found: C, 67.61; H, 11.13; N, 21.11.

(*S,S,S*)-Protetraazaphosphatrane (5). To a solution of triamidoamine **4** (2.18 g, 8.16 mmol) in dry acetonitrile (30 mL) was added bis(diethylamino)chlorophosphane (1.72 mL, 8.16 mmol) via a syringe over 5 min. After stirring of the reaction mixture at room temperature for 2 h, the solution was transferred by syringe or cannula to a flask containing *t*-BuOK (1.83 g, 16.3 mmol) in dry acetonitrile (6 mL). After stirring of the reaction mixture for 1 h at room temperature, the solvent was removed under vacuum and the residue was extracted overnight while being stirred with dry pentane (150 mL) which was transferred in by cannula. The extract was transferred by cannula to another flask and evaporated in vauo to give a white solid which was purified by vacuum sublimation (170 °C at 0.02 Torr), giving pure proazaphosphatrane **5** (1.73 g, 5.87 mmol, 72% yield): IR (Nujol) 1457, 1443, 1379, 1360, 1065 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) δ 1.10−1.22 (m, 3H), 1.52−1.68 (m, 6H), 1.68−1.80 (m, 3H), 2.32 (dd, $J = 11.4$, 13.8 Hz, 3H), 2.88−3.02 (m, 6H), 3.38−3.52 (m, 3H); ^{13}C NMR (CD_3CN) δ 27.8 (d, $J = 9.5$ Hz, 3C), 30.4 (3C), 50.2 (d, $J = 42.5$ Hz, 3C), 57.6 (d, $J = 6.3$ Hz, 3C), 60.3 (3C); HREIMS calcd for $C_{15}H_{27}N_4P$ [M^+] 294.1973, found 294.1969.

(*S,S,S*)-Tetraazaphosphatrane Tetrafluoroborate (13). To a solution of **5** (118 mg, 0.4 mmol) in acetonitrile (5 mL) was added 1 M HCl in ether (1 mL, 1 mmol) at room temperature. After 10 min, the solvents were pumped off. The residual solid was dissolved in dichloromethane (5 mL) and then silver tetrafluoroborate (78 mg, 0.4 mmol) was added. Silver chloride precipitated was filtered off and the filtrate was concentrated

in vacuo. The residual solid was recrystallized with acetonitrile (ca. 2 mL): IR (KBr) 2930, 2972, 1460, 1088, 1084, 575, 532 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.54−1.65 (m, 3H), 1.88−2.06 (m, 6H), 2.06−2.19 (m, 3H), 3.06−3.31 (m, 6H), 3.38−3.49 (m, 3H), 3.52−3.65 (m, 3H), 5.88 (d, J_{PH} = 477 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.3 (d, J = 8.4 Hz, 3C), 30.7 (d, J = 3.3 Hz, 3C), 46.8 (d, J = 9.0 Hz, 3C), 51.6 (d, J = 2.9 Hz, 3C), 54.6 (d, J = 10.8 Hz, 3C); Anal. Calcd for $C_{15}H_{28}N_4PBF_4$: C, 47.14; H, 7.38; N, 14.66. Found: C, 47.21; H, 7.39; N, 14.52.

Crystal Data for 13. X-ray diffraction analysis on **13** was carried out on a DIP2030−NW CEF diffractometer (MacScience) at 298 K. All diagrams and calculations were performed using maXus (MacScience). The structure of **13** ($C_{15}H_{28}N_4PBF_4$, M_w 382.19 amu) was determined from an orthorhombic crystal of dimensions 0.35 × 0.2 × 0.15 mm^3 (space group $P2_12_12_1$), with unit cell a = 8.3890 (3) Å, b = 9.2860 (4) Å, c = 24.2570 (8) Å, V = 1889.5(4) $Å^3$. It has four molecules per cell, d_{calcd} = 1.530 g/cm^3, μ = 1.894 cm^{-1}. Mo Kα radiation (λ = 0.71073 Å) was used, and 2473 unique reflections for $1 < \theta < 28°$ were collected 2368 being observed ($I > 3\sigma(I)$). The occupancies of the two orientations of the BF_4^- ion refined to 50% for one orientation. Refinement of 365 parameters converged with agreement factors of the following: R = 0.052 and R_w = 0.060.

Enantioselective Ethylation of Benzaldehyde with Diethylzinc Catalyzed by (*S*,*S*,*S*)-5. To a mixture of benzaldehyde (51 μL, 0.50 mmol) and a 0.1 M solution of (*S*,*S*,*S*)-**5** in toluene (0.5 mL, 0.05 mmol) in toluene (2 mL) was added a 1.0 M solution of diethylzinc in hexane (1.0 mL, 1.0 mmol) at −20 °C. After being stirred for 0.5 h at −20 °C, the reaction mixture was warmed to room temperature. After 3.5 h, 1 N aqueous HCl was added to the reaction mixture and the resulting aqueous solution was extracted with diethyl ether. The combined organic extracts were dried over $MgSO_4$. Filtration followed by solvent evaporation afforded a crude product. The residue was purified using flash chromatography on silica gel [hexane/ethyl acetate mixtures (5:1) as eluents] to give (*R*)-1-phenylpropanol (33.4 mg, 0.25 mmol, 49%) in 15% ee. The ee was determined by HPLC analysis [OD-H column, hexane−*i*-PrOH = 20:1, flow rate = 0.5 mL/min; t_R = 15.8 min for (*R*)-enantiomer, t_R = 17.6 min for (*S*)-enantiomer]. The absolute configuration was determined by comparison of optical rotation values with data in the literature.[10]

Supporting Information Available: ^1H NMR spectra for compounds **5**, **8**, **9**, and **10** and tables of crystal data, positional and anisotropic thermal parameters, and bond lengths and bond angles (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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