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Diphosphine Oxide−Brφnsted Acid Complexes as Novel Hydrogen-Bonded Self-Assembled Molecules

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Abstract: Novel hydrogen-bonded supramolecules based on interactions between an acid and a base have been prepared from (*R*,*R*)-1,2-bis(1-adamantylmethylphosphinyl)ethane (**1**) and tetrafluoroboric acid. Both linear and cyclic structures have been observed. Recrystallization from CH_2Cl_2−AcOEt gave the linear supramolecule **2**. The structure of **2** was confirmed by single-crystal X-ray analysis. On the other hand, cyclic dimer **3** was produced by recrystallization from $CHCl_3$−AcOEt. The structure of **3** was estimated by electron spray ionization mass spectrometry and single crystal X-ray analysis. Significantly different enantioselectivities were observed in asymmetric protonation reactions of these two supramolecules with silyl enolates.

Introduction

Supramolecular chemistry has evolved into a rapidly growing, prominent area in contemporary chemistry.[1,2] Hydrogen bonding is a very useful means of constructing molecular assemblies because it can fix molecules in a particular geometry by virtue of its directionality.[3] Indeed, hydrogen-bonding motifs, such as amide,[4] urea,[5] sulfamide,[6] carboxylic acid,[7] the cyanuric acid−melamine system,[8] pyridone dimers,[9] and 2-aminopyridine−carboxylic acid complexes[10] have been used for the design of various molecular aggregates. However, these approaches are often limited by the kinetic instability of the resulting constructs due to their weak hydrogen bonding. In an effort to surmount this difficulty, we designed a new hydrogen-bonded supramolecule system based on interaction between a Brφnsted acid and a base.[11] Figure 1 illustrates our idea. In this system, basic subunits are connected by the acidic proton with robust hydrogen bonding, enabling the construction of supramolecules. It is expected that this system is applicable to the synthesis of various types of hydrogen-bonded supramolecules. On the basis of this idea, diphosphine oxide was selected as the basic subunit, and a strong Brφnsted acid was employed as the source of an acidic proton.

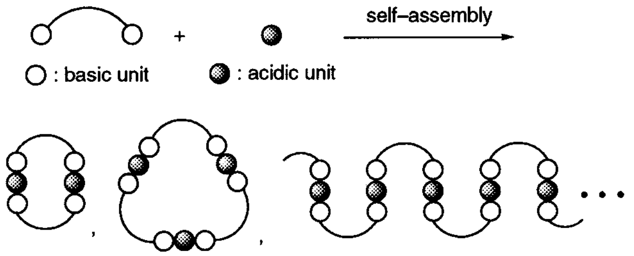

Figure 1. Concept of acid−base interacted supramolecules.

Results and Discussion

Our initial investigation was undertaken using (*R*,*R*)-1,2-bis(1-adamantylmethylphosphinyl)ethane (**1**)[12] and tetrafluoroboric acid to construct a chiral environment. Tetrafluoroboric acid−dimethyl ether complex was slowly added to a solution of **1** in

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[1] (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304−1319.

[2] For recent representative reports on this area, see: (a) Corbin, P. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 3779−3780. (b) Sharma, C. V. K.; Clearfield, A. *J. Am. Chem. Soc.* **2000**, *122*, 1558−1559. (c) Kim, J.; Jung, I.-S.; Kim, S.-Y.; Lee, E.; Kang, J.-K.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2000**, *122*, 540−541. (d) Cabezon, B.; Cao, J.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 148−151. (e) Prince, B. B.; Brunsveld, L.; Meijer, E. W.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 228−230. (f) Kobayashi, K.; Shirasaka, T.; Horn, E.; Furukawa, N.; Yamaguchi, K.; Sakamoto, S. *Chem. Commun.* **2000**, 41−42. (g) Choi, I.; Bowden, N.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3078−3081. (h) Schoonbeek, F. S.; van Esch, J. H.; Wegewijs, B.; Rep, D. B. A.; de Haas, M. P.; Klapwijk, T. M.; Kellogg, R. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1393−1397. (i) Olenyuk, B.; Whiteford, J. A.; Fechtenkötter, A.; Stang, P. J. *Nature* **1999**, *398*, 796−799. (j) Takeda, N.; Umemoto, K.; Yamaguchi, K.; Fujita, M. *Nature* **1999**, *398*, 794−796. (k) Gong, B.; Zheng, C.; Zeng, H.; Zhu, J. *J. Am. Chem. Soc.* **1999**, *121*, 9766−9767. (l) Renslo, A. R.; Rudkevich, D. M.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 7459−7460. (m) Prins, L. J.; Huskens, J.; de Jong, F.; Timmerman, P.; Reinhoudt, D. N. *Nature*, **1999**, *398*, 498−502. (n) Cardenas, D. J.; Collin, J.-P.; Pablo, G.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1999**, *121*, 5481−5488. (o) Tucci, F. C.; Rudkevich, D. M.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 4928−4929. (p) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52−55.

[3] Lawrence, D. S.; Jiang, T.; Levitt, M. *Chem. Rev.* **1995**, *95*, 2229−2260.

[4] Weinstein, S.; Leiserowitz, L.; Gil-Av, E. *J. Am. Chem. Soc.* **1980**, *102*, 2768−2772.

[5] (a) van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Tetrahedron Lett.* **1997**, *38*, 281−284. (b) Hanabusa, K.; Shimura, K.; Hirose, K.; Kimura, M.; Shirai, H. *Chem. Lett.* **1996**, 885−886.

[6] Gong, B.; Zheng, C.; Skrzypczak-Jankunn, E.; Yan, Y.; Zhang, J. *J. Am. Chem. Soc.* **1998**, *120*, 11194−11195.

[7] Zimmerman, S. C.; Zeng, F.; Reichert, D. E. C.; Kolotuchin, S. V. *Science* **1996**, *271*, 1095−1098.

[8] (a) Vreekamp, R. H.; van Duynhoven, J. P. M.; Hubert, M.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1215−1218. (b) Whitesides, G. M.; Simanek, E. E.; Methias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37−44.

[9] Boucher, E.; Simard, M.; Wuest, J. D. *J. Org. Chem.* **1995**, *60*, 1408−1412.

[10] Yang, J.; Fan, E.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 5314−5315.

[11] For theoretical studies on an acid−base hydrogen bonded system, see: (a) Zundel, G. *Adv. Chem. Phys.* **2000**, *111*, 1−217. (b) Roland, L.; Zundel, G. *J. Phys. Chem. A* **1998**, *102*, 6635−6642.

[12] (a) Matsukawa, S.; Sugama, H.; Imamoto, T. *Tetrahedron Lett.* **2000**, *41*, 6461−6465. (b) Imamoto, T.; Watanabe, J.; Wada, Y.; Masuda, H.; Yamada, H.; Tsuruta, H.; Matsukawa, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1635−1636.

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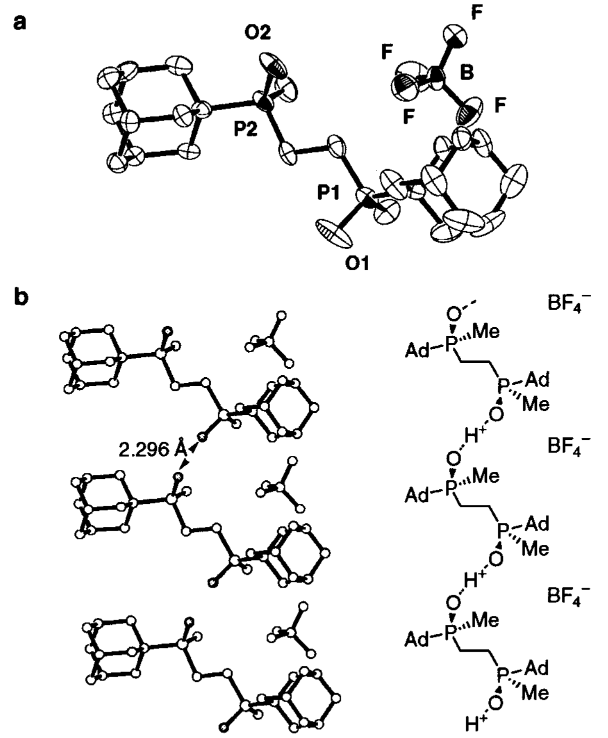

Figure 2. (a) ORTEP diagram of **2**, showing 30% probability ellipsoids. The solvent molecule (CH_2Cl_2) is omitted for clarity. Selected bond lengths (Å): P1−O1 = 1.558(7), P2−O2 = 1.529(6). (b) Packing diagram of complex **3** looking down the *c* axis. The distance between two intermolecular oxygen atoms is 2.296(9) Å.

$CHCl_3$. After 30 min, $CHCl_3$ was removed under reduced pressure, and the residual solid was recrystallized from CH_2Cl_2−AcOEt (ca. 1:1) for 2 days to afford linear supramolecule **2** as colorless prisms (74%). The structure of **2** was confirmed by X-ray crystallographic analysis (Figure 2a).[12] According to the X-ray data, the diphosphine oxide subunit has a cationic structure. The P−O bond lengths for P(1)−O(1) and P(2)−O(2) are 1.558 and 1.529 Å, respectively. These bonds are longer than usually observed P═O bond lengths (av 1.489 Å) in $R_3P{=}O$,[13] suggesting that an interaction exists between the oxygen atom and the proton. A packing diagram of **2** looking down the *c* axis is shown in Figure 2b. The distance between two oxygens from different subunits is 2.296 Å, suggesting the existence of a strong hydrogen bond between them.

Cyclic dimer **3** was obtained by recrystallization from $CHCl_3$−AcOEt (ca. 2:1) for 10 days (43%).[14] The electron spray ionization mass spectrum (ESI-MS)[15] obtained by using CH_2Cl_2 as eluent at 20 °C showed a peak at *m*/*z* 933.6 corresponding to the ion of cyclic dimer **3** ([**3**$-BF_4^-]^+$) together with a fragment ion of **3** ([**3**$-BF_4^- - HBF_4]^+$) (*m*/*z* 845.7) (Figure 3). On the other hand, the ESI-MS of **2** showed only one strong fragment peak (*m*/*z* 423.5) corresponding to the monomeric structure. Generally, hydrogen bonding easily cleaves during ionization. We consider that linear supramolecule **2** is dissociated under the ESI-MS conditions, whereas **3** is stable under the same conditions due to their cyclic structure.

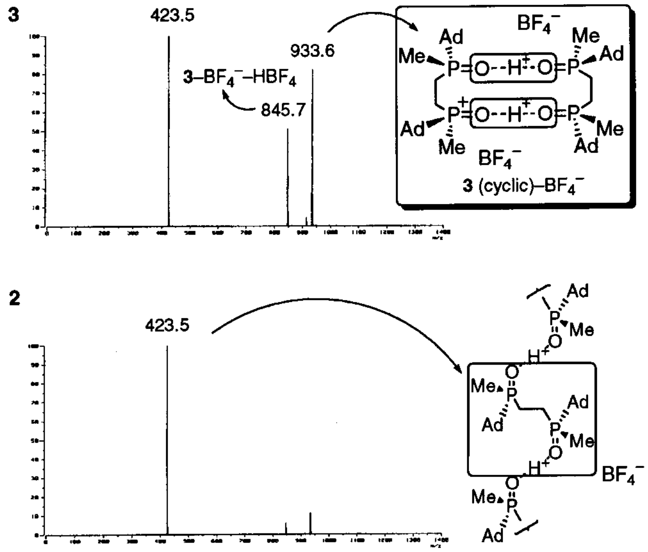

Figure 3. ESI-MS spectra of **3** and **2** using CH_2Cl_2 as eluent at 20 °C.

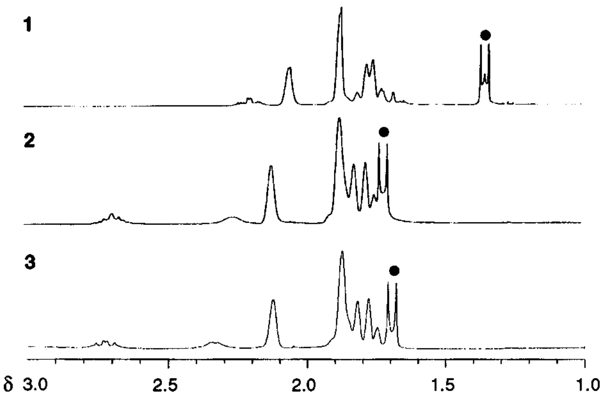

Figure 4. ^{1}H NMR spectra of diphosphine oxide **1**, linear supramolecule **2**, and cyclic supramolecule **3**. The point solid circle shows the methyl group on the phosphrous atom.

^{1}H NMR spectra of **1**, **2**, and **3** are shown in Figure 4. The simple ^{1}H NMR spectrum patterns indicate that both molecules **2** and **3** are symmetric. ^{31}P NMR also exhibited a single peak in each case at 73.7 ppm for **2** and 74.7 ppm for **3**. These peaks are observed at the lower field as compared to that of diphosphine precursor **1** (52.2 ppm). Both molecules **2** and **3** are comparatively stable in the solution. Indeed, no significant changes of these signals were observed after 1 day in $CDCl_3$. We found that compound **2** was very slowly converted into **3** in $CDCl_3$ over 2 weeks, indicating that cyclic dimer **3** is thermodynamically more stable than linear supramolecular **2**.

Interestingly, the $[\alpha]_D$ values of **2** and **3** were significantly different, i.e. −18.1 (*c* 0.3) in $CHCl_3$ at 25 °C for **2** and only −0.5 for **3** under the same conditions. These results led us to examine the enantioselectivity of these supramolecules in asymmetric protonation reactions of silyl enolates.[16] Silyl

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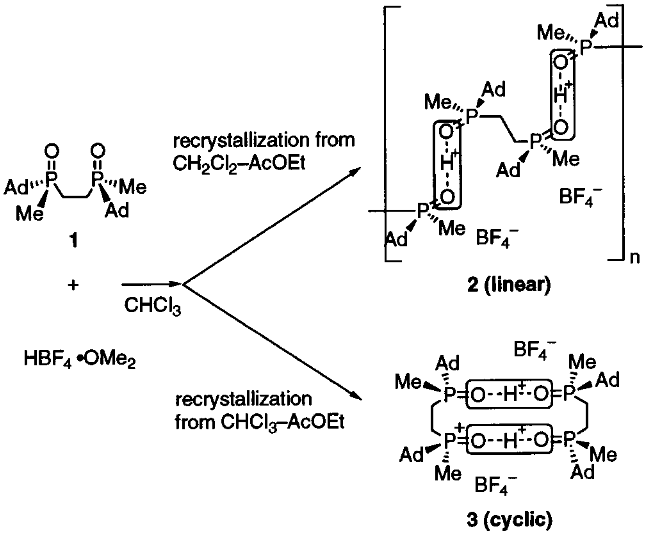
(13) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(14) Single-crystal X-ray structural analysis of **3** was examined. A cyclic structure was observed, but detailed structure could not be discussed due to the limited quality of the crystallographic data. A ball and stick plot of cyclic dimer **3** is given in the Supporting Information.

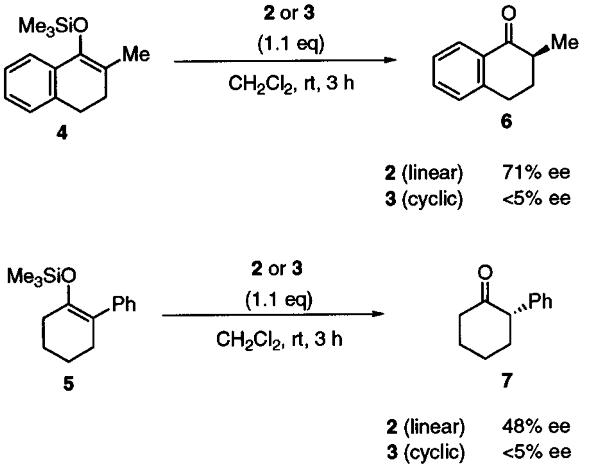
(15) ESI-MS is often used for the structure analysis of self-assembled molecules. For recent reports, see: (a) Sakamoto, S.; Fujita, M.; Kim. K.; Yamaguchi, K. *Tetrahedron* **2000**, 955−964. (b) Schalley, C. A.; Rivera, J. M.; Martín, T.; Santamaría, J.; Siuzdak, G.; Rebek, J., Jr. *Eur. J. Org. Chem.* **1999**, 1325−1331. (c) Scherer, M.; Sessler, J. L.; Moini, M.; Gebauer, A.; Lynch, V. *Chem. Eur. J.* **1998**, *4*, 152−158.

(16) Reviews: (a) Yanagisawa, A.; Ishihara, K.; Yamamoto, H. *Synlett* **1997**, 411−420. (b) Fehr, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2566−2587. For recent reports, see: (c) Yamashita, Y.; Emura, Y.; Odashima, K.; Koga, K. *Tetrahedron Lett.* **2000**, *41*, 209−213. (d) Fujihara, H.; Tomioka, K. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2377−2381. (e) Takeuchi, S.; Nakamura, Y.; Ohgo, Y.; Curran, D. P. T*etrahedron Lett.* **1998**, *39*, 8691−8694. (f) Vedejs, E.; Krüger, A. W. *J. Org. Chem.* **1998**, *63*, 2792−2793. (g) Sugiura, M.; Nakai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2366−2368.

Scheme 1



Scheme 2



enolates **4** and **5** were chosen as the model substrates, and the reactions were carried out in CH_2Cl_2 at room temperature. The results are shown in Scheme 2. It is noted that the reaction with **2** afforded α-substituted ketones with moderate to high enantiomeric excesses, i.e. 71% ee for **4** and 48% ee for **5**. In contrast, cyclic dimer **3** provided the corresponding products with less than 5% ee. These results suggest that although their basic subunits of **2** and **3** are the same, their enentioselectivities are significantly different due to the different nature of the assembled structure.

In summary, we have prepared novel hydrogen-bonded supramolecules based on interaction between a P-chirogenic diphosphine oxide and a Brϕnsted acid. Both linear and cyclic structures have been observed. Furthermore, their properties are significantly different depending on the nature of the assembled structure, linear or cyclic. We believe that the present system will provide an effective strategy for constructing hydrogen-bonded molecular assemblies.

Experimental Section

General. All reactions were performed under argon atmosphere. Chloroform, dichloromethane, and ethyl acetate were purchased as a dehydrated grade from Wako Pure Chemical Industries Co. Optical rotations were measured with a JASCO DIP-370 polarimeter. NMR spectra were obtained on a JEOL GSX-400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) or a JEOL LA-400 (^{1}H at 400 MHz, ^{13}C at 100 MHz, ^{31}P at 162 MHz) spectrometer with chemical shifts reported in ppm (δ) relative to tetramethylsilane (TMS) (^{1}H and ^{13}C) and phosphoric acid (^{31}P). IR spectra were obtained on a Hitachi-IR 215 spectrophotometer. HPLC analyses were performed on a Simadzu LC-10A Dvp liquid chromatograph with a SPD-10Avp UV−Vis detector and CTO-10ACvp column oven with an appropriate chiral column. ESI-MS were obtained on a JEOL JMS-700T spectrometer. Measurement conditions of ESI-MS are as follows: acceleration voltage, 5.0 kV; needle voltage, 2.6 kV; orifice voltage, 187 V; resolution, 5000; sample flow, 10 μL/min; spray temperature, −20 °C; and ion source temperature, 20 °C.

(*R*,*R*)-1,2-Bis(1-adamantylmethylphosphinyl)ethane (1). To a solution of (*S*,*S*)-1,2-bis[1-adamantyl(boranato)methylphosphino]ethane (2.09 g, 5 mmol)[12b] in $CHCl_3$ (60 mL) was added *m*-CPBA (8.90 g, 45 mmol) at 0 °C. After being stirred at 0 °C for 1 h, a solution of Na_2SO_3 (7.90 g, 50 mmol) in water (100 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ twice. The combined extracts were washed with $NaHCO_3$, water, and brine, and then dried over Na_2SO_4. The solvent was removed on an evaporator to leave white residue, which was recrystallized from hot EtOAc to give pure **1** as colorless needles (1.58 g, 75%). Mp 278−279 °C; $[\alpha]^{25}_D$ +16.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, $^2J_{HP}$ = 11.4 Hz, 6H), 1.61−1.95 (m, 26H), 2.01−2.10 (br s, 6H), 2.13−2.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.2 (dd, J_{CP} = 64.1 Hz, $^4J_{CP}$ = 17.6 Hz), 16.6 (dd, J_{CP} = 56.9 Hz, $^4J_{CP}$ = 21.7 Hz), 27.3, 35.0, 35.4 (dd, J_{CP} = 36.2 Hz, $^4J_{CP}$ = 15.5 Hz), 36.5; ^{31}P NMR (160 MHz, $CDCl_3$) δ 52.2; IR (KBr) 2910, 1340, 1300, 1160, 860 cm^{-1}; HRMS calcd for $C_{24}H_{41}O_2P_2$ ($M^+ + H$) 423.2582, found 423.2582.

(*R*,*R*)-1,2-Bis(1-adamantylmethylphosphinyl)ethane−Tetrafluoroboric Acid Complex, Linear Supramolecule (2). Tetrafluoroboric acid−dimethyl ether complex (122 μL, 1 mmol) was slowly added to a solution of (*R*,*R*)-1,2-bis(1-adamantylmethylphosphinyl)ethane (**1**) (422 mg, 1 mmol) in $CHCl_3$ (10 mL). After 30 min, $CHCl_3$ was removed under reduced pressure. The residual solid was dissolved in CH_2Cl_2 (10 mL), and then AcOEt (10 mL) was carefully added to the solution. After 2 days, linear supramolecule **2** was obtained as colorless prisms (377 mg, 74%). Mp 228−229 °C; $[\alpha]^{25}_D$ −18.1 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (d, $^2J_{HP}$ = 11.9 Hz, 6H), 1.74−1.95 (m, 26H), 2.11 (br s, 6H), 2.28 (br s, 6H), 2.57 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.0 (d, J_{CP} = 72.0 Hz), 14.2 (d, J_{CP} = 67.5 Hz), 26.8, 34.2, 34.4 (d, J_{CP} = 61.2 Hz), 36.2; ^{31}P NMR (160 MHz, $CDCl_3$) δ 73.7; IR (KBr) 2910, 1350, 1200, 1060, 840 cm^{-1}; ESI-MS (10 mM, CH_2Cl_2) (rel intensity) 423.4 ($[M - BF_4^-]^+$, 100), 845.7 ($[2M - HBF_4 - BF_4^-]^+$, 6), 933.6 ($[2M - BF_4^-]^+$, 11).

(*R*,*R*)-1,2-Bis(1-adamantylmethylphosphinyl)ethane−Tetrafluoroboric Acid Complex, Cyclic Supramolecule (3). Tetrafluoroboric acid−dimethyl ether complex (122 μL, 1 mmol) was slowly added to a solution of (*R*,*R*)-1,2-bis(1-adamantylmethylphosphinyl)ethane (**1**) (422 mg, 1 mmol) in $CHCl_3$ (10 mL). After 30 min, $CHCl_3$ was removed under reduced pressure. The residual solid was dissolved in $CHCl_3$ (20 mL), and then AcOEt (10 mL) was carefully covered to the solution. After 10 days, cyclic supramolecule **3** was obtained as colorless needles (219 mg, 43%). Mp 225−226 °C; $[\alpha]^{25}_D$ −0.5 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (d, $^2J_{HP}$ = 11.9 Hz, 6H), 1.74−1.92 (m, 26H), 2.11 (br s, 6H), 2.35 (br s, 6H), 2.63(br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.8 (d, J_{CP} = 73.0 Hz), 13.9 (d, J_{CP} = 54.5 Hz), 26.8, 34.0, 34.2 (d, J_{CP} = 53.5 Hz), 36.0; ^{31}P NMR (160 MHz, $CDCl_3$) δ 74.7; IR (KBr) 2910, 1340, 1200, 1060, 860 cm^{-1}; ESI-MS (10 mM, CH_2Cl_2) (rel intensity) 423.4 ($[M - BF_4^-]^+$, 100), 845.7 ($[2M - HBF_4 - BF_4^-]^+$, 51), 933.6 ($[2M - BF_4^-]^+$, 81).

Typical Procedure for the Asymmetric Protonation Reaction of Silyl Enolate. To a solution of supramolecule **2** (280 mg, 0.55 mmol) in CH_2Cl_2 (10 mL) was added 2-methyl-1-[(trimethylsilyl)oxy]-3,4-dihydronaphthalene (**4**) (138 mg, 0.5 mmol) at room temperature. After 3 h, water was added and the resultant mixture was filtered. The organic layer was separated and the aqueous layer was extracted with Et_2O twice. The combined extracts were washed with $NaHCO_3$, water, and brine, and then dried over Na_2SO_4. The solvent was removed on an evaporator to leave white residue, which was purified by preparative TLC on silica gel (AcOEt:hexane = 1:5) to give (*S*)-methyl-3,4-dihydro-1(2*H*)-naphthalenone (**6**) as white solid. $[\alpha]^{25}_D$ −32.3 (*c* 1.0, 1,4-

dioxane) [71% ee (*S*)];[17] HPLC analysis (Daicel CHIRALCEL OD-H column, hexane:2-propanol = 200:1, flow rate = 1.0 mL/min, detection 254-nm light). $t_R = 10.7$ min for the (*R*)-isomer and 12.7 min for the (*S*)-isomer.

In a similar manner, compound **5** was allowed to react with **2** to give (*S*)-2-phenylcyclohexanone (**7**): $[\alpha]^{25}_D$ −41.3 (*c* 1.1, $CHCl_3$) [48% ee (*S*)];[18] HPLC analysis (Daicel CHIRALCEL OD-H column, hexane:2-propanol = 50:1, flow rate = 0.7 mL/min, detection 240-nm light). $t_R = 16.5$ min for the (*S*)-isomer and 18.8 min for the (*R*)-isomer.

X-ray Crystallographic Analysis of 2. The crystal was mounted on a glass fiber. Data collections were performed on a R-AXISII diffractometer with graphite-monochromated Mo Kα radiation. A laser-stimulated fluorescence image plate was used as a two-dimensional area detector. Because of the instability of the crystals, rapid analysis was required. The distance between the crystal and the detector was 80 mm. Thus, 27 frames were recorded at intervals of 6° and each exposure lasted for 5 min (ca. 135 min for the total data collection). The molecular structure of complex **2** was solved by direct method using the programs SIR 97.[19] Full-matrix least-squares refinements were carried out by minimizing the function $\sum\omega(|F_o| - |F_c|)^2$ where F_o and F_c were observed and calculated structure factors. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The residual electron densities were of no chemical significance. Crystal data for **2**: $C_{25}H_{43}BCl_2F_4O_2P_2$, $M = 595.27$, colorless prism, monoclinic, space group $P2_1$ (no. 4), $a = 13.75(1)$ Å, $b = 6.891(5)$ Å, $c = 16.07(2)$ Å, $\beta = 105.08(5)$ °, $V = 1469(2)$ Å^3, $\rho_{calcd} = 1.345$ g/cm^3, $Z = 2$, $F_{000} = 628.00$, μ(Mo Kα) = 3.76 cm^{-1}, λ(Mo Kα) = 0.71070 Å; temperature of data collection 100 K; 2936 reflections measured, 2695 observed ($I > 2.00\sigma$); number of variables 325; $R_1 = 0.086$, $R_w = 0.117$, GOF = 2.32.

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Supporting Information Available: Tables of X-ray data collection/refinement parameters, atomic position parameters, and anistropic displacement parameters for **2**; ball-and-stick plot for **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Jaousen, G.; Meyer, A. I. *J. Am. Chem. Soc.* **1975**, *97*, 4667−4672.

(18) Berti, G.; Macchia, B.; Macchia, F.; Menti, L. *J. Chem. Soc. C* **1971**, 3371−3375.

(19) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, 115−119.