Enantioselective Catalysis, 101 [1] Synthesis and Coordination Properties of (3′S,4′S)-(+)-1,2-Bis(3′,4′-dimethoxyphospholano)benzene, a New Chiral Diphosphane

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Chiral Bisphosphanes, Expanded Phosphanes, Rhodium Complexes, Cyclic Sulfates

A new bisphospholane, BDPB, derived from 1,2-bisphosphanobenzene and tartaric acid as well as the complex [Rh(COD)(BDPB)]PF_6 were synthesized. The strong binding of BDPB to metals and the presence of four functional groups in the periphery of the molecule make this bisphospholane a good starting point for new expanded bisphosphanes.

Introduction

Chiral chelating bisphosphanes with two aryl groups on each phosphorus atom are excellent ligands for asymmetric catalysis [2, 3]. Though the chirality is usually located close to the phosphorus atoms, the group of Hayashi achieved high optical inductions in asymmetric allylations with phosphane ligands having the chiral groups at relatively large distances from the phosphorus atoms [4, 5]. Our group developed the concept of the expanded phosphanes, ligands designed to induce long range effects in enantioselective catalysis [6–8]. They consist of two phosphorus atoms bridged by a rigid backbone and surrounded by an assembly of chiral and nonchiral layers.

Phospholane derivatives of 1,2-bisphosphanobenzene proved to be very good ligands for enantioselective catalysis [9]. Our objective was to synthesize a chiral bisphospholane ligand with the possibility of future expansion. In the present work, we report on the synthesis of a new bisphospholane derived from 1,2-bisphosphanobenzene and tartaric acid, (3′S,4′S)-(+)-1,2-bis(3′,4′-dimethoxyphospholano)benzene (BDPB), as well as a rhodium(I) complex of this ligand. The related compound derived from 1,2-bisphosphanoethane is already reported in the literature but a different synthetic procedure was used for its preparation [10]. We carried out the synthesis of BDPB because of the greater rigidity of the 1,2-phenylene backbone as compared to the ethano bridge.

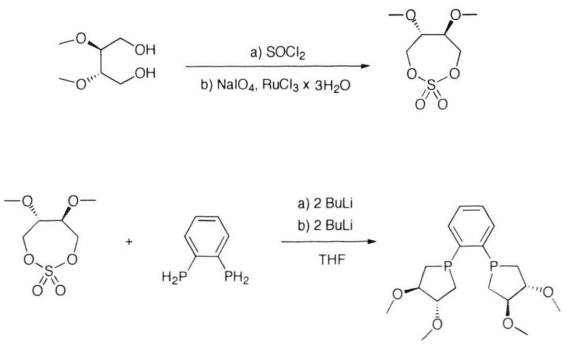
Results and Discussion

The first attempt to synthesize (3′S,4′S)-(+)-1,2-bis(3′,4′-dimethoxyphospholano)benzene (BDPB) was in analogy to the synthesis of DIOP [11]. However, the dilithium salt of 1,2-bisphosphanobenzene did not react with (2S,3S)-(+)-2,3-dimethoxytetramethylen-1,4-bis-*p*-toluenesulfonate in the desired manner.

The new bisphospholane BDPB could be finally obtained using the cyclic sulfate (5S,6S)-(+)-5,6-dimethoxy-1,3,2-dioxathiepane-2,2-dioxide. Cyclic sulfates have been shown to be convenient reagents for the synthesis of similar phosphanes [9]. In contrast to the bistosylates, the second nucleophilic attack in cyclic sulfates is much slower than the first one. This favors the desired intramolecular reaction with respect to an intermolecular attack leading to oligomerization.

The cyclic sulfate was obtained from the corresponding dialcohol according to the reactions in the Scheme. It is a crystalline, rather unstable, white compound, turning red within several hours on standing at room temperature. Its MS spectrum could not be obtained because of this thermal instability.

Starting from this cyclic sulfate, the desired bisphospholane could be obtained in a two step one pot reaction (see Scheme). The nucleophilic attack of the phosphide at the second α-carbon atom of the sulfate takes several hours, a slower process



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than similar reactions described in the literature [9]. The new phosphane BDPB is a white, crystalline, strongly smelling, air sensitive compound.

Since our aim was to design ligands for enantioselective catalysis, and hydrogenation is the most extensively studied reaction in this field, we synthesized the rhodium complex $[Rh(COD)(BDPB)]PF_6$. The cation was easily formed and isolated as its hexafluorophosphate salt by reaction of an equimolar mixture of $[Rh(\mu\text{-}Cl)(COD)]_2$ and $AgPF_6$ with BDPB at −78 °C. When the reaction was performed at higher temperature, mixtures of complexes were obtained. Attempts to synthesize this complex using other starting materials and counterions always led to mixtures containing the cation $[Rh(COD)(BDPB)]^+$ besides other components. Similar problems to obtain this type of complex were also encountered for other dialkylphosphanes derived from 1,2-bisphosphanobenzene [8].

Experimental Section

All reactions and manipulations were performed under nitrogen by using standard Schlenk techniques. Solvents were purified and dried by standard procedures. 1,2-Bisphosphanobenzene [12], (2S,3S)-(+)-2,3-dimethoxy-1,4-butanediol [13] and $[Rh(\mu\text{-}Cl)(COD)]_2$ [14] were prepared as described in the literature.

^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded in deuterated chloroform on a Bruker ARX 400 or on a Bruker AC 250 instrument (21 °C) using TMS as internal standard (^1H and ^{13}C) or H_3PO_4 as external standard (^{31}P). Mass spectra (EI, LR) were obtained on a Finnigan Mat 112 S spectrometer. Optical rotations were measured at 24 °C on a Perkin-Elmer 241 polarimeter.

Synthesis of (5S,6S)-(+)-dimethoxy-1,3,2-dioxathiepane-2,2-dioxide

The preparation of the cyclic sulfate is based upon the method used by Burk *et al.* to prepare similar compounds [9]. The mixture which resulted by addition of 6.06 ml (9.90 g, 83.2 mmol) of thionyl chloride to a solution of 10.0 g (66.6 mmol) of (2S,3S)-(+)-2,3-dimethoxy-1,4-butanediol in 60 ml of CCl_4 was stirred under reflux for 1.5 h. After cooling, the solvent was evaporated to dryness in a rotary evaporator. The cyclic sulfite, obtained as a brown oil, was dissolved in 60 ml of CCl_4, 60 ml of CH_3CN and 90 ml of H_2O. After cooling to 0 °C, 100 mg (0.38 mmol) of $RuCl_3$-trihydrate and 28.3 g (132.5 mmol) of $NaIO_4$ were added with stirring. Two yellow layers formed which gradually became black. Later, a yellow precipitate appeared and the solution became yellow again. After stirring for 1 h, 400 ml of water and 200 ml of ether were added. The two layers were separated and the aqueous phase was extracted with 3 x 200 ml of ether. The combined organic extracts were washed with 2 x 100 ml of a saturated aqueous solution of NaCl and dried over Na_2SO_4. The resulting organic solution was filtered through silica gel and reduced in volume to 20 ml. Colorless needles formed (11.6 g). After recrystallization from ether, 10.0 g of the pure cyclic sulfate were obtained (70.8% yield) which were stored below 0 °C.

Melting point: 100–101 °C. $[\alpha]_D^{25} = +85.1°$ (c = 1.0, CH_2Cl_2).

Elemental analysis for $C_6H_{12}O_6S$

Calcd	C 33.96	H 5.70%,
Found	C 33.98	H 5.79%.

^1H NMR (250 MHz, $CDCl_3$, ppm): 4.59 (2H, d, J = 13.0 Hz, CH_2); 4.38 (2H, dm, J = 13.0 Hz, CH_2); 3.49 (2H, m, C**H**OMe); 3.47 (6H, s, OMe). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): 77.1 (**C**HOMe); 66.8 (CH_2); 57.3 (OCH_3).

Synthesis of (3'S,4'S)-(+)-1,2-bis(3',4'-dimethoxyphospholano)benzene (BDPB)

13 ml (20.0 mmol) of 1.6 N *n*-BuLi in hexane was added dropwise to a solution of 1.48 g (10.0 mmol) of 1,2-bisphosphanobenzene in 100 ml of THF. The pale yellow mixture was stirred for 1 h at 20 °C. After cooling to 0 °C, the cyclic sulfate (4.24 g, 20.0 mmol) was added and the colorless suspension was stirred for 2 h. Then, 2.2 equivalents of *n*-BuLi (14.3 ml) were added dropwise at 0 °C, and the orange suspension was stirred overnight. After 18 h, 60 ml of water was added to the pale yellow suspension, and the THF was evaporated. The mixture was extracted with 5 x 50 ml of ether. The ether solution was dried over Na_2SO_4 and the solvent was evaporated. The product was obtained as an oil which crystallized overnight. Yield: 2.61 g (68%). $[\alpha]_D^{25} = +51.9°$ (c = 0.7, CH_2Cl_2). MS (EI, LR): m/z = 370.0 ($M^{+\cdot}$).

Elemental analysis for $C_{18}H_{28}O_4P_2$

Calcd	C 58.37	H 7.62%,
Found	C 58.88	H 7.88%.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): -33.8 (s). $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$, ppm): 7.59 (2H, m, H_{arom}); 7.29 (2H, m, H_{arom}); 3.92 (2H, m, C**H**OMe); 3.86 (2H, m, C**H**OMe); 3.35 (6H, s,

OMe); 3.33 (6H, s, OMe); 2.43 (2H, dd, J_1 = 14.5 Hz, J_2 = 6.5 Hz, CH_2); 2.25 (2H, dd, J_1 = 14.1 Hz, J_2 = 5.3 Hz, CH_2); 2.06 (2H, dd, J_1 = 14.1 Hz, J_2 = 6.3 Hz, CH_2); 1.90 (2H, dd, J_1 = 14.5 Hz, J_2 = 5.2 Hz, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) [15]: 146.7 (m1, N = 5.8 Hz, C_{arom}–P); 131.3 (m2, N' = 5.6 Hz, CH_{arom}); 129.4 (s, CH_{arom}); 86.9 (**C**H-OMe); 86.7 (**C**H-OMe); 57.4 (OMe); 57.3 (OMe); 28.8 (m, CH_2).

Synthesis of [Rh(BDPB)(COD)]PF_6

372.4 mg (1.48 mmol) of $AgPF_6$ was added to a solution of 363.2 mg (0.74 mmol) of $[Rh(\mu\text{-}Cl)(COD)]_2$ in 10 ml of THF. A solution of 545.6 mg (1.48 mmol) of BDPB was added dropwise at -78 °C. After 1 h, the reaction mixture was allowed to warm to room temperature. The deep red solution was separated from the AgCl by filtration and the filtrate was evaporated. Crystallization of the residue from CH_2Cl_2 / pentane gave 838 mg of the red product (78% yield).

Elemental analysis for $C_{26}H_{40}F_6O_4P_3Rh$

Calcd	C 42.99	H 5.55%,
Found	C 43.15	H 5.59%.

$^{31}P\{^1H\}$NMR (162 MHz, $CDCl_3$, ppm): 55.1 (d, J = 151.3 Hz); -143.7 (sept, J = 713.3 Hz).

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[15] Second order AA′XX′ spectrum. m1 and m2 are multiplets which appear as 1:1:1:1 (m1) and 1:2:1 (m2) signals as if they were first order dd oder t, respectively. The signals were analysed according to a) H.M. McConnel, A.D. McLean, C.A. Reilly; J. Chem. Phys. 23, 1152 (1955) and b) R.J. Abraham, H.J. Bernstein, Can. J. Chem. 39, 216 (1961). N is $^1J_{PC} + {}^4J_{PC}$ and N′ is $^1J_{PC} + {}^2J_{PC}$.