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Synthesis and resolution of 2,2′-bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl (BINASb); the first example of an optically active organoantimony ligand for asymmetric synthesis

Shuji Yasuike,[a] Satoru Okajima,[a] Kentaro Yamaguchi,[b] Hiroko Seki[b] and Jyoji Kurita[a,*]

[a]*Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa 920-1181, Japan*
[b]*Chemical Analysis Center, Chiba University, 1-33, Yayoicho, Inage-ku, Chiba 263-8322, Japan*

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Abstract

Racemic 2,2′-bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl (BINASb) (±)-**2** has been prepared from 2,2′-dibromo-1,1′-binaphthyl **1** via 2,2′-dilithio-1,1′-binaphthyl intermediate, and has been resolved via the separation of a mixture of the diastereomeric Pd complexes **4A** and **4B**, derived from the reaction of (±)-**2** with di-μ-chlorobis{(*S*)-2-[1-(dimethylamino)ethyl]phenyl-*C*,*N*}dipalladium(II) **3**. The optically active BINASbs (*S*)-(+)-**2** and (*R*)-(−)-**2** have been shown to be effective chiral ligands for the rhodium-catalyzed asymmetric hydrosilylation of ketones.

The atropisomeric 1,1′-dinaphthyl core is the parent framework of a steadily increasing family of C_2-symmetric chiral auxiliaries of high efficiency.[1] Among these, phosphorus derivatives (BINAP) deserve particular attention, and enantioselective reactions by use of transition-metal catalysts with BINAP provide an outstanding example of the efficiency of these ligands in asymmetric catalysis.[2] Recently, it has also been demonstrated that optically active arsenic analogues of BINAP, 2,2′-bis(diphenylarsano)-1,1′-binaphthyl (BINAs)[3] and 2-diphenylarsano-2′-diphenylphosphano-1,1′-binaphthyl (BINAPAs),[4] are effective chiral ligands for enantioselective Heck reactions. However, asymmetric reactions with optically active organoantimony compounds have not been reported so far. Therefore, we are interested in the synthesis and utilization of optically active organoantimony compounds for asymmetric synthesis and have recently reported an efficient and stereoselective resolution of racemic Sb-chiral stibindoles.[5] We present here the synthesis and resolution of 2,2′-bis(di-*p*-tolylstibano)-1,1′-binaphthyls (BINASb) (*S*)-(+)-**2** and (*R*)-(−)-**2**, using an optically active *ortho*-palladated benzylamine

* Corresponding author. Tel: +00 81 76 229 1165; fax: +00 81 76 229 2781; e-mail: j-kurita@hokuriku-u.ac.jp

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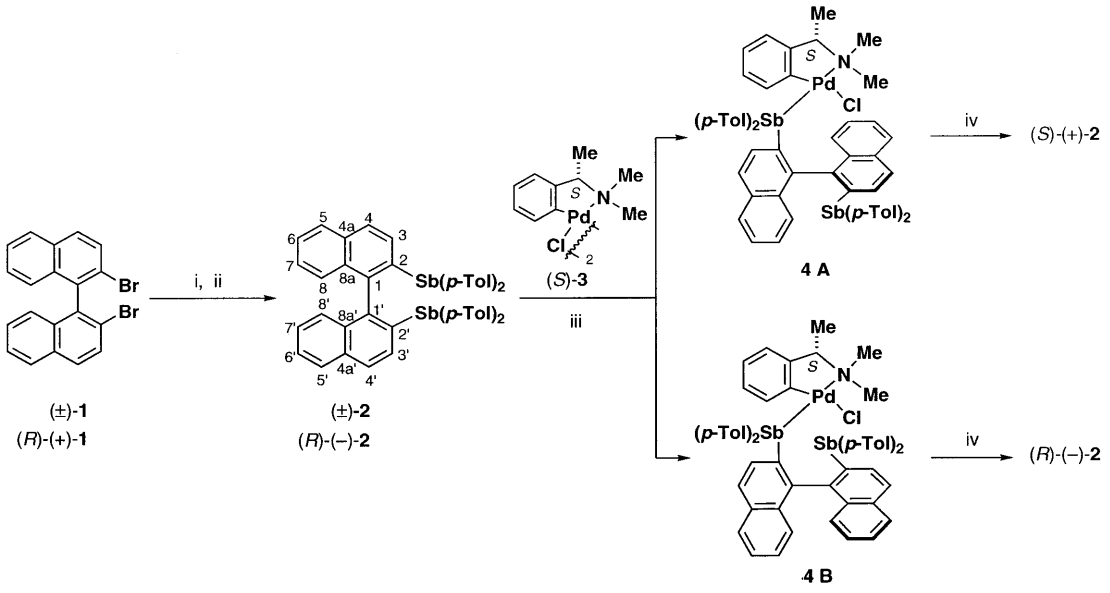
derivatives as a resolving agent, via the separation of the diastereomeric palladium complexes of the racemic **2** prepared from (±)-2,2′-dibromo-1,1′-binaphthyl (DBBN) **1**,[6] and also propose that the optically active BINASb (*S*)-(+)-**2** and (*R*)-(−)-**2** can be used as effective chiral ligands for the rhodium-catalyzed enantioselective hydrosilylation of ketones (Scheme 1).



Scheme 1. *Reagents and conditions*: (i) *tert*-butyllithium, ether, −80°C, 1 h; (ii) (*p*-Tol)$_2$SbBr, ether, −80 to 0°C, 4 h, 65%; (iii) dichloromethane, room temp., 5 min, quantitative; (iv) 1,2-bis(diphenylphosphano)ethane, dichloromethane, room temp., 10 min, 94–96%

The preparation of the desired BINASb (±)-**2**[7] could be readily accomplished by the reaction of 2,2′-dilithio-1,1′-binaphthyl intermediate, generated from racemic DBBN **1** by treatment with *tert*-butyllithium in ether at −80°C, with bromodi(*p*-tolyl)stibane[8] in 65% yield. We next attempted the resolution of (±)-**2** via their diastereomeric complexes using optically active di-μ-chlorobis{(*S*)-2-[1-(dimethylamino)ethyl]phenyl-*C*,*N*}dipalladium(II) (*S*)-**3**, which has been reported to be a useful resolving agent for a wide range of chiral phosphorus,[9,10] arsenic,[11] and antimony[5] compounds. Treatment of (±)-**2** with 0.5 mol equiv. of dimeric palladium reagent (*S*)-**3** resulted in coordination of antimony to palladium to form a 1:1 mixture of the diastereomeric palladium complexes **4A** and **4B** quantitatively. Although many attempts to separate the diastereomers **4A** and **4B** by fractional recrystallization from a variety of solvents were unsuccessful, they could be separated by column chromatography. When the diastereomeric mixture of **4A** and **4B** was separated by silica gel column chromatography by use of dichloromethane/ethyl acetate (5:1) as an eluent, it furnished a 7:1 mixture of (+)-**2** and (−)-**2** in 46% yield, along with **4A** (9.5% yield) and **4B** (41% yield).[12] This result indicates not only that a partial decomplexation of the complexes **4** occurred during chromatographic separation but that **4A** is much more susceptible to decomplexation than **4B**. Fractional recrystallization of the above mixture with (+)-**2** and (−)-**2** from a hexane/diethyl ether (8:1) mixture afforded enantiomerically pure (+)-**2** in 32% yield (calculated from (±)-**2** used). The structures of **4A** and **4B** were elucidated mainly by their MS (FAB), ^{1}H NMR spectral and elemental analyses. In the Pd complexes **4A** and **4B**, the palladium atom is assumed to coordinate one of the two antimony

atoms on the basis of the following facts. The R_f values on TLC (chloroform/ethyl acetate 3:1) for **4A** (0.41) and **4B** (0.35) are similar to those of mono-coordinated (+)- (0.49) and (−)-1-phenyl-2-trimethylsilylstibindole–(*S*)-**3** complexes (0.45),[5] and are largely different from those of BINAP–(*S*)-**3** complexes (0.015 for (+)-BINAP–(*S*)-**3** and 0.02 for (−)-BINAP–(*S*)-**3**) in which the palladium atom coordinates to both of the two phosphorus atoms and thus these BINAP–(*S*)-**3** complexes are salt structures.[10a,13] In addition, the ^{35}Cl NMR spectroscopic analysis with a broad band, which has been reported to be useful for the detection of a chloride ion,[14] showed that both palladium complexes **4A** and **4B** have no chloride ion (Cl^-) in their molecules. The electrospray ionization mass spectra (ESI) of **4A** and **4B** (dissolved in acetonitrile) also showed *m*/*e* 1405 ion peaks {assigned to be [**2**+(2)×**3**−Cl]$^+$}, indicating the presence of a 1:2 antimony–palladium complex between **2** and **3** in the solution.

Treatment of isolated **4A** and **4B** with 1,2-bis(diphenylphosphano)ethane (DPPE) underwent ligand exchange reaction to afford optically pure (+)-**2** and (−)-**2** {mp 183–185°C, $[\alpha]_D^{22}=\pm15.3$ (*c* 2 benzene)}, respectively, in excellent yields. The X-ray crystal structure of (−)-**2**, including absolute configuration, is shown in Fig. 1,[15] which reveals that (−)-**2** has *R*-configuration, and two naphthalene rings are oriented perpendicular to each other with an accurately C_2-symmetric conformation; the dihedral angle of C(8a)–C(1)–C(1′)–C(8a′) is 90°. When optically active DBBN (*R*)-**1**[16] (> 98% ee) was used instead of racemic **1** as the starting compound in the present synthesis, optically active (*R*)-(−)-**2** ($[\alpha]_D^{23}=-9.5$) was formed in 59% yield; however, the enantiomeric purity of the product was relatively low (62% ee). Consequently, the former route starting from easily accessible racemic **1** is superior to the latter route starting from optically active **1** for the preparation of enantiomerically pure **2**, from the standpoint of low cost.

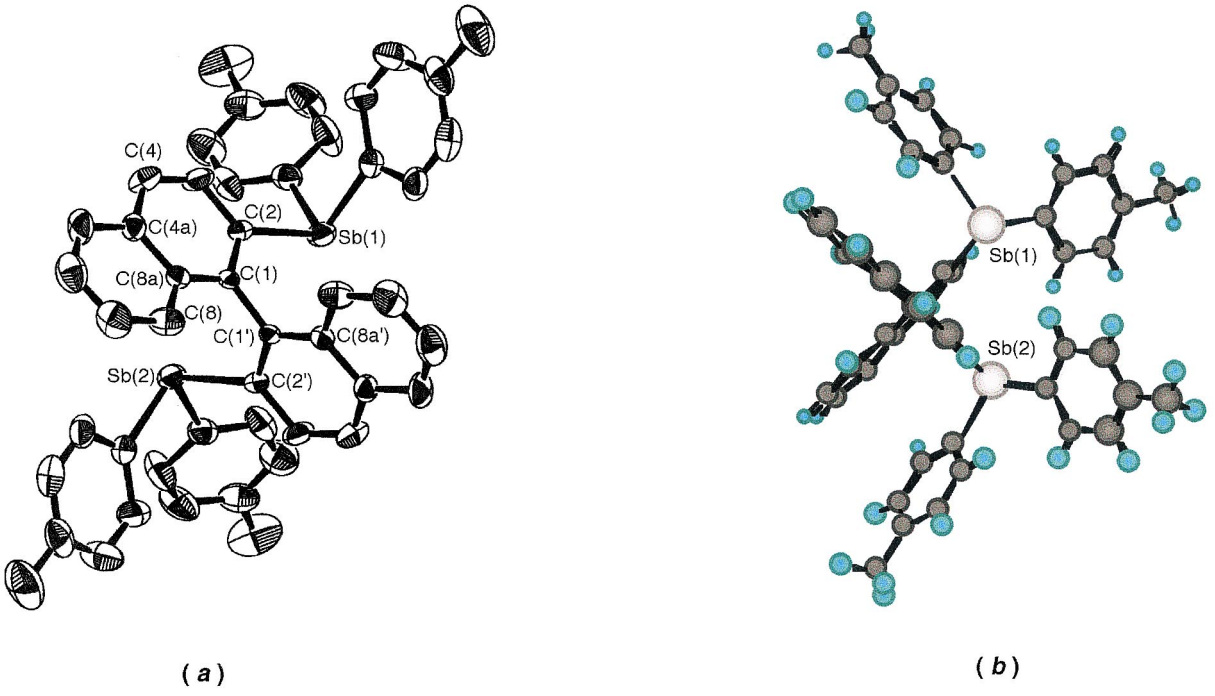


Figure 1. Molecular structure of (*R*)-(−)-**2**. (a) All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): C(1)–C(1′) 1.49(2), C(2)–Sb(1) 2.164(10), C(2)–(1)–(1′)–C(2′) 86(1), C(8a)–C(1)–C(1′)–C(8a′) 90(1), C(1)–C(8a)–C(4a)–C(5) 177.4(10), C(4)–C(4a)–C(8a)–C(8) 177(1). (b) Side view

Finally, the optically active ligand **2** was tested as a chiral inducer in the asymmetric reduction of ketones with $[RhCl_2(COD)]_2$ catalyst.[17] Treatment of acetophenone with diphenylsilane in the presence of rhodium catalyst with (−)-**2** (Ph_2SiH_2:acetophenone:(−)-**2**:Rh = 720:600:2:1; THF, 3 h, 0°C) resulted in enantioselective hydrosilylation to give (*R*)-1-phenylethanol (25% ee; determined by comparison with the $[\alpha]_D$ value of an authentic sample) in 78% isolated yield. (*S*)-1-Phenylethanol having the opposite sign and almost equal $[\alpha]_D$ value of the specific rotation was obtained when (+)-**2** was used as a chiral auxiliary. When optically active (*R*)-(+)-BINAP was used instead of the optically active BINASb **2** in the above reaction, neither noticeable catalytic activity nor perceptible enantioselectivity were observed (0°C, 12 h, 42% yield (recovery, 26%), 0.3% ee). This preliminary result shows that the optically active BINASb **2** displays both catalytic activity and enantioselectivity in the transition-metal catalyzed asymmetric hydrosilylation of ketones.

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12. *Experimental procedures* for **4A** and **4B**: A mixture of (±)-**2** (4.0 g, 4.65 mol) and dimeric (*S*)-**3** (1.35 g: 2.33 mol) in dichloromethane (50 ml) was stirred for 5 min at room temperature. After removal of the solvent in vacuo, the

resulting residue was separated by chromatography on silica gel (dichloromethane/ethyl acetate 4:1) to give a 1:7 mixture of (+)-**2** and (−)-**2** (1.85 g, 46% yield), **4A** (0.51 g, 9.5% yield) and **4B** (2.2 g, 41% yield), successively. Fractional recrystallization of the mixture of (+)-**2** and (−)-**2** obtained above from hexane/diethyl ether (ca. 8:1) afforded optically pure (+)-**2** (1.35 g, 34% yield). *Selected data* for **4A**: yellow needles (ethyl acetate), mp 149–151°C; $[\alpha]_D^{21}=+42.4$ (*c* 1, benzene); *m*/*e* (FAB) 1114 $[M-Cl]^+$. For **4B**: yellow powder, $[\alpha]_D^{21}=-17.4$ (*c* 1, benzene); *m*/*e* (FAB) 1114 $[M-Cl]^+$. Unambiguous assignments of the molecular structure are difficult to make from ^1H NMR spectra of **4A** and **4B** due to the complexities of the signals.

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