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Non-C_2-symmetrical antimony–phosphorus ligand, (*R*/*S*)-2-diphenylphosphano-2′-di(*p*-tolyl)stibano-1,1′-binaphthyl (BINAPSb): preparation and its use for asymmetric reactions as a chiral auxiliary

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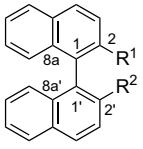
Abstract—A new non-C_2-symmetrical antimony–phosphorous ligand, (±)-2-diphenyl-phosphano-2′-di(*p*-tolyl)stibano-1,1′-binaphthyl (BINAPSb) **3**, has been prepared from 2-bromo-2′-diphenylphosphano-1,1′-naphthyl **4** via its borane complex **6**, and could be resolved by the separation of a mixture of the diastereomeric palladium complexes **8A** and **8B** derived from the reaction of (±)-**3** with optically active palladium reagent (*S*)-**7**. The enantiomerically pure BINAPSb **3** has proved to be highly effective in the palladium-catalyzed asymmetric hydrosilylation of styrene as a chiral auxiliary.

Catalytic asymmetric synthesis using transition metal complexes with chiral 2,2′-substituted-1,1′-binaphthyl ligands is a powerful and economically promising method for the synthesis of enantiomerically enriched compounds.[1] Among them, the most useful chiral ligand is phosphorus compounds such as 2,2′-bis(diphenylphosphano)-1,1′-binaphthyl (BINAP) **1**, which exhibit high enantioselectivity in various types of asymmetric reactions.[1,2] Taking advantage of the marked efficiency of the 1,1′-binaphthyl core as a chiral inducer, a variety of hetero-bidentate 1,1′-binaphthyls bearing one phosphorous and one other heteroatom group such as nitrogen,[3] arsenic,[4] oxygen[5] and sulfur[6] on the 2,2′-positions of the 1,1′-binaphthyl backbone have been developed and employed successfully in a wide range of enantioselective reactions, during the last two decades. Recently, a versatile synthesis of optically active 2′-substituted 2-phosphano-1,1′-binaphthyls containing group 14 (silicon, tin) and 17 (iodine) elements was attained, although



1: $R^1 = R^2 = PPh_2$
2: $R^1 = R^2 = Sb(p\text{-Tol})_2$
3: $R^1 = PPh_2$, $R^2 = Sb(p\text{-Tol})_2$

Figure 1.

these were derived from optically active BINAP.[7] In the course of our current studies on organoantimony compounds, we are interested in the synthesis and utilization of optically active organoantimony compounds for asymmetric reaction as a chiral auxiliary.[8] As a part of our research, we have recently reported the synthesis of an enantiomerically pure C_2-symmetrical antimony–antimony ligand, 2,2′-bis(diarylstibano)-1,1′-binaphthyl (BINASb) **2**, and its efficiency for palladium-catalyzed asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propen-1-yl acetate as a chiral inducer.[9] We present here the synthesis and resolution of a new non-C_2-symmetrical antimony–phosphorous ligand,

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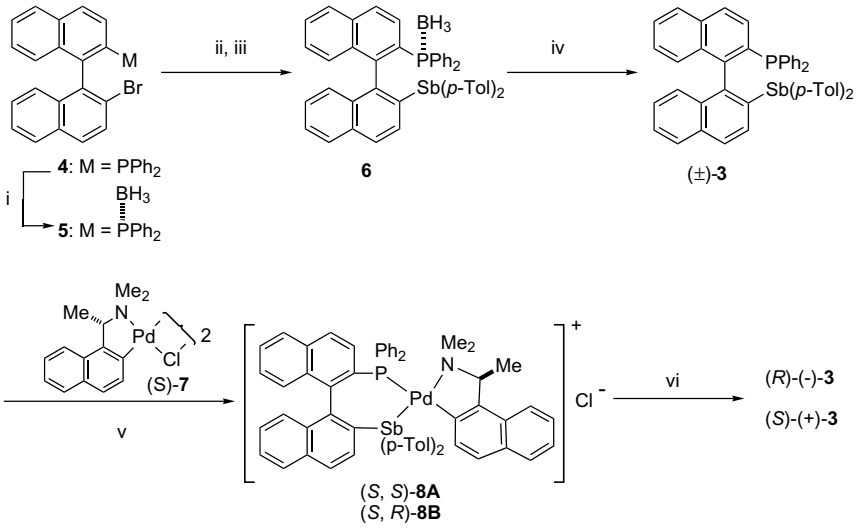


Scheme 1. Reagents and conditions: (i) BH_3–THF, THF, 0 °C, 1 h, 98%; (ii) *n*-butyllithium, THF, −80 °C, 1 h; (iii) $(p\text{-Tol})_2SbBr$, THF, −80 °C to 0 °C, 2 h, 58%; (iv) diethylamine, THF, 40 °C, 1 h, 91%; (v) dichloromethane, room temperature, 30 min, 94%; (vi) triphenylphosphine, dichloromethane, room temperature, 30 min, 85–91%.

2-diphenylphosphano-2′-di(*p*-tolyl)-stibano-1,1′-binaphthyl (BINAPSb) **3**, as well as its usefulness for palladium-catalyzed asymmetric hydrosilylation of styrene as a chiral auxiliary.

First, introduction of a di(*p*-tolyl)antimony group at the 2′-position on the 2-diphenylphosphano-1,1′-binaphthyl core was performed by a straightforward procedure including lithiation of 2-bromo-2′-diphenylphosphano-1,1′-binaphthyl **4**[10] with *n*-butyllithium and subsequent trapping with bromodi(*p*-tolyl)stibane [$(p\text{-Tol})_2SbBr$] at low temperature (−80 °C). However, this direct metal insertion reaction on **4** produced the expected BINAPSb **3** in low yield (<8%), probably due to the instability of the lithio intermediate and/or carbon–phosphorus bond cleavage with *n*-butyllithium. This result led us to attempt a modern metallation pathway including a phosphorous-borane complex developed by Hayashi and co-workers.[7] The borane complex **5** was readily prepared from **4** by treatment with borane in THF.[11] The transformation of **5** into BINAPSb-borane complex **6** could be achieved by lithiation with *n*-butyllithium at −80 °C followed by reaction with $(p\text{-Tol})_2SbBr$ in 58% yield, presumably via a stable 2′-lithio binaphthyl intermediate. The borane complex **6** underwent ligand exchange reaction upon treatment with diethylamine to yield (±)-BINAPSb **3** in 90% yield. According to this procedure, (±)-**3** was obtained in more than 50% overall yield from **4** (Scheme 1).

Next, we attempted the resolution of (±)-**3** via their diastereomeric complexes using optically active palladium reagent, di-μ-chlorobis[(*S*)-dimethyl(1-ethyl-α-naphthyl)aminato-C^2,*N*]dipalladium(II) (*S*)-**7**, which have been reported to be a useful resolving agent for antimony compounds.[8a,b,d] The reaction of (±)-**3** with (*S*)-**7** afforded an equimolar amount of a diastereomeric mixture of **8A** and **8B**, which could be separated by silica gel column chromatography by use of a mixture of ethyl acetate/dichloromethane/ethanol (8:4:1) as an eluent. Thus, the palladium complexes (–)-**8A** and (+)-**8B** were obtained in 84% and 99% yields, respectively. The structures of **8A** and **8B** were elucidated mainly by their MS(FAB), NMR spectral and elemental analyses. The palladium complexes **8A** and **8B** are presumed to be a cationic salt structure by the following evidence. The R_f values on TLC ($AcOEt/CH_2Cl_2/EtOH$ = 8:4:1) for **8A** (0.49) and **8B** (0.17) are similar to those for BINAP-(*S*)-**7** complexes [0.10 for (+)-BINAP-(*S*)-**7** and 0.09 for (–)-BINAP-(*S*)-**7**], and are largely different from those of BINASb-(*S*)-**7** complexes [0.95 for (+)-BINASb-(*S*)-**7** and 0.91 for (–)-BINASb-(*S*)-**7**] which have been known to be a nonsalt structure. Diastereomeric

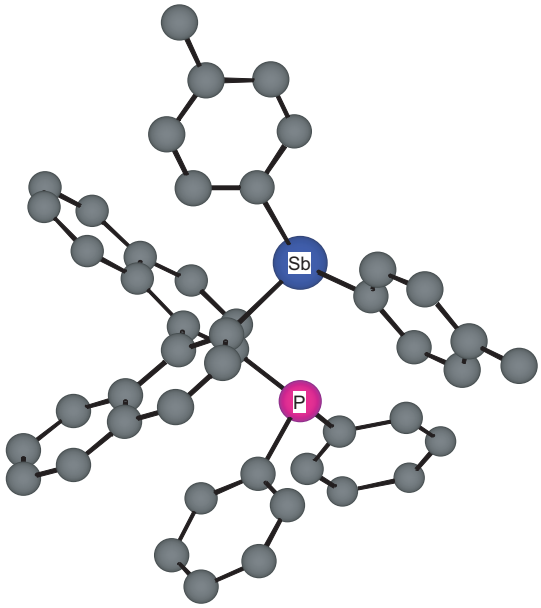
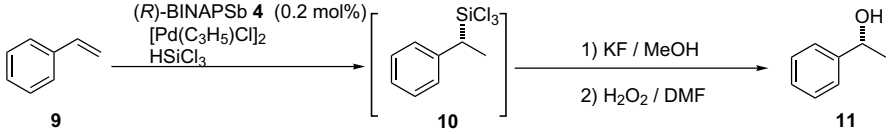


Figure 2. Molecular structure of (*S*)-(–)-**3**. Selected bond distances (Å) and angles (°): C(1)–C(1′) 1.500(8), C(2)–P 1.841(6), C(2′)–Sb 2.148(6), C(2)–C(1)–C(1′)–C(2′) 69.9(8), C(8a)–C(1)–C(1′)–C(8a′) 72.3(7).



Scheme 2.

purity of **8A** and **8B** was determined by the ^{31}P NMR spectra in that each ^{31}P signal appeared at 47.8 ppm for **8A** and 46.3 ppm for **8B**. Treatment of **8A** and **8B** with triphenylphosphine brought about ligand exchange reaction to afford optically pure (+)-**3** and (–)-**3**, respectively, in excellent yields.[12] Single-crystal X-ray analysis of (–)-**3** revealed that (–)-**3** is *S*-configuration (Fig. 1),[13] and the dihedral angle of the two naphthalene rings [C(8a)–C(1)–C(1′)–C(8a′) = 72.3°] is smaller than that of (*R*)-BINASb (90°) (Fig. 2).[8b]

We examined the ability of optically active BINAPSb **3** as a ligand in palladium-catalyzed asymmetric allylic alkylation[14] and asymmetric hydrosilylation.[15] The reaction of (±)-1,3-diphenyl-2-propen-1-yl acetate with dimethyl malonate by use of BSA, $[Pd(C_3H_5)Cl]_2$, (*R*)-BINAPSb **3A** and AcOK (acetate:malonate:BSA:Pd cat.:ligand:AcOK = 1:3:3:0.02:0.04:0.02) in dichloromethane over 24 h at room temperature afforded (*S*)-dimethyl(1,3-diphenylprop-2-en-1-yl)malonate in 30% yield with 45% ee. The result shows that the reaction rate and enantioselectivity with BINAPSb **3** were both lower compared to those with BINASb **2** (68%, 81% ee) (Scheme 2).[9]

The asymmetric hydrosilylation of styrene[15] with trichorosilane was carried out at 0 °C without a solvent in the presence of 0.2 mol% of the palladium catalyst generated in situ by mixing $[Pd(C_3H_5)Cl]_2$ with 2 equiv (to Pd) of the (*R*)-BINAPSb **3A**: (styrene:trichorosilane:[Pd-$(C_3H_5)Cl]_2$:ligand = 1000:1200:1:2). The hydrosilylation product, 1-trichlorosilyl-1-phenyl-ethane **10**, initially formed was oxidized to optically active 1-phenylethanol **11** by hydrogen peroxide in the presence of potassium fluoride.[16] Thus, (*R*)-**11** was obtained in good yield (78% yield) with high enantioselectivity (95% ee), when the reaction was carried out at 0 °C for 10 h with (*R*)-BINAPSb **3**.[17] Neither noticeable catalytic activity nor perceptible enantioselectivity was observed when (*R*)-BINASb **2** was employed instead of (*R*)-BINAPSb **3A** in the present reaction (0 °C, 24 h, 10% yield, 12% ee). These results suggest that BINAPSb **3** has similar ability to H-MOP and was proved to be a more powerful ligand than other 2′-heteroatom substituted 2-phosphano-1,1′-binaphthyls.[6b,15]

Consequently, we have accomplished the synthesis of optically active 2′-antimony substituted 2-phosphano-1,1′-binaphthyl derivative BINAPSb, and demonstrated that this non-C_2-symmetrical antimony–phosphorous binaphthyl system should be useful for the enantioselective hydrosilylation of styrene with trichorosilane. Details of this reaction as well as further application of the optically active BINAPSb to other asymmetric reactions are now in progress.

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12. *Selected physical and spectral data* for (*S*)-(–)-**3**: mp 170–174 °C, $[\alpha]_D^{24}$ −23.8° (*c* 1.0, benzene), ^{1}H NMR (500 MHz, *J* Hz, $CDCl_3$): δ 2.27 (3H, s), 2.30 (3H, s), 6.85 (1H, d, *J* 8.2), 6.92–7.25 (21H, m) 7.30 (1H, t, *J* 6.9), 7.37 (1H, t, *J* 6.9), 7.42 (1H, dd, *J* 3.2, 8.7), 7.58 (1H, d, *J* 8.7), 7.79 (1H, d, *J* 7.8), 7.80 (1H, d, *J* 8.2), 7.84 (1H, d, *J* 8.2), 7.91 (1H, d, *J* 8.7); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ −15.2; *m*/*z* (FAB) 741 $[M + H]^+$. For (*R*)-(+)-**3**: mp 173–176 °C, $[\alpha]_D^{24}$ +24° (*c* 1.03, benzene). The ^{1}H and ^{31}P NMR spectra of (*R*)-**3** were superimposable to those of (*S*)-**3**; *m*/*z* (FAB) 741 $[M + H]^+$.
13. *Crystal data* for (*S*)-**3**: $C_{46}H_{36}PSb$, *M* = 741.51, tetragonal, *a* = 9.468(1), *c* = 39.759(7) Å, *V* = 3563.8(9) Å^3, *T* = 100 K, space group $P4_1$ (no.76), *Z* = 4, $\mu(MoK\alpha)$ = 8.5 cm^{-1}, 21632 reflections measured, 5894 reflections [$I > 2.00\sigma(I)$, $2\theta < 57.33°$] were used in all calculation, $R = 0.070$, $R_w = 0.091$. The structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Full details of the crystallographic results have been deposited with the Cambridge Crystallographic Data Centre [No. CCDC 252378].
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17. *Typical experiment*: To a mixture of $[Pd(C_3H_5)Cl]_2$ (3.66 mg, 0.01 mmol), (*R*)-BINAPSb **3A** (14.8 mg, 0.02 mmol) and styrene (1.1 ml, 10 mmol) was added trichlorosilane (1.2 ml, 12 mmol) at 0 °C, and the reaction mixture was stirred for 10 h at room temperature. The reaction mixture was carefully poured into a suspension of KF (10 g) in methanol (80 ml) and stirred for 30 min. After removal of the solvent in vacuo, the resulting solid was suspended in DMF (100 ml) and H_2O_2 (10 ml, 30% H_2O solution), and then the mixture was heated for 1 h at 65 °C. The mixture was diluted with CH_2Cl_2 (100 ml) and water (100 ml). The organic layers were separated and the aqueous layer was extracted with CH_2Cl_2 (50 ml × 2). The combined organic layer was washed with water (100 ml × 5), dried, and evaporated in vacuo. The residue was separated by column chromatography on silica gel with CH_2Cl_2/AcOEt (10:1) to give (*R*)-1-phenylethanol **11** (0.91 g, 78% yield). The absolute configuration (*R*) and the enantiomeric excess (95% ee) of the product obtained here were determined by chiral HPLC using commercially available (*R*)- and (*S*)-1-phenylethanols as an authentic sample [Daicel Chiral OD-H column; eluent, *n*-heptane: *i*-PrOH = 95:5; retention times, t_R = 13.6 min, t_S = 15.4 min].