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New optically active organoantimony (BINASb) and bismuth (BINABi) compounds comprising a 1,1′-binaphthyl core: synthesis and their use in transition metal-catalyzed asymmetric hydrosilylation of ketones

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Abstract—Racemic 2,2′-bis[diarylstibano]-1,1′-binaphthyls [(±)-BINASbs] and 2,2′-bis[di(*p*-tolyl)bismuthano]-1,1′-binaphthyl [(±)-BINABi], which are the antimony and bismuth congeners of BINAP, have been prepared from 2,2′-dibromo-1,1′-binaphthyl (DBBN) via 2,2′-dilithio-1,1′-binaphthyl intermediate by treatment with the appropriate metal halides [$(p\text{-Tol})_2SbBr$, Ph_2SbBr and $(p\text{-Tol})_2BiCl$]. The optical resolution of the (±)-BINASbs could be achieved via the separation of a mixture of the diastereomeric Pd-complexes derived from the reaction of (±)-BINASbs with di-μ-chlorobis{(*S*)-2-[1-(dimethylamino)-ethyl]phenyl-C^1,*N*}dipalladium(II). Optically active (*R*)-BINASb and (*R*)-BINABi could be also obtained from optically active (*R*)-DBBN by the same procedure. The enantiopure BINASbs have been shown to be effective chiral ligands for the rhodium-catalyzed asymmetric hydrosilylation of ketones.

1. Introduction

During the last two decades, transition metal-catalyzed asymmetric reactions by use of enantiopure ligands have been a most interesting research field in synthetic chemistry and have recently been the focus of much attention.[1] Among these, optically pure ligands comprising a 1,1′-binaphthyl system have been most actively explored in synthetic chemistry, because the atropisomeric nature of the 1,1-binaphthyl core and its C_2-symmetry make a highly advantageous chiral environment in a variety of stoichiometric and catalytic asymmetric syntheses.[2] For example, the phosphorous derivatives of 1,1′-binaphthyl, 2,2′-bis(diphenylphosphano)-1,1′-binaphthyl (BINAP), deserve particular attention and enantioselective reactions by use of transition metal catalysts with BINAP provide an outstanding example of the efficiency of the ligand in asymmetric reactions.[3,4] Along with the remarkable development of asymmetric reactions by use of BINAP, a variety of 2,2-disubstituted-1,1′-binaphthyl derivatives having nitrogen,[5,6] oxygen,[7,8] and sulfur[9] moieties have been synthesized and their effectiveness for a wide range of asymmetric reactions were well demonstrated. Recently, it has also been reported that optically active arsenic analogues of BINAP such as 2,2′-bis(diphenylarsano)-1,1′-binaphthyl (BINAs)[10] and 2-diphenylarsano-2′-diphenylphosphano-1,1′-binaphthyl (BINAPAs),[11] are useful chiral ligands for enantioselective Heck reactions. Despite these remarkable developments, however, asymmetric reactions with optically active organoantimony ligands have not been reported so far due to the limited access to this class of compounds. In the course of our current studies on the synthesis of optically active organoantimony compounds and their applications for asymmetric reaction as chiral ligands, we have recently reported an efficient method for the resolution of racemic Sb-chiral organoantimony compounds via separation of a diastereomeric mixture of the palladium complexes formed from the reaction with di-μ-chlorobis{(*S*)-2-[1-(dimethylamino)-ethyl]phenyl-C^1,*N*}dipalladium(II) (*S*)-**5**.[12] We present here the synthesis of (±)-2,2′-bis(diarylstibano)-1,1′-binaphthyls (**1a**,**b**: BINASbs) and (±)-2,2′-bis[di(*p*-tolyl)bismuthano]-1,1′-binaphthyls

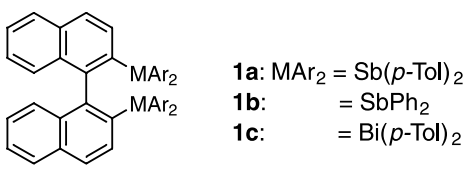

Figure 1.

Keywords: 2,2′-bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl; 2,2′-bis[di(*p*-tolyl)bismuthano]-1,1′-binaphthyl; optical resolution; asymmetric reaction; *C*2-symmetry.

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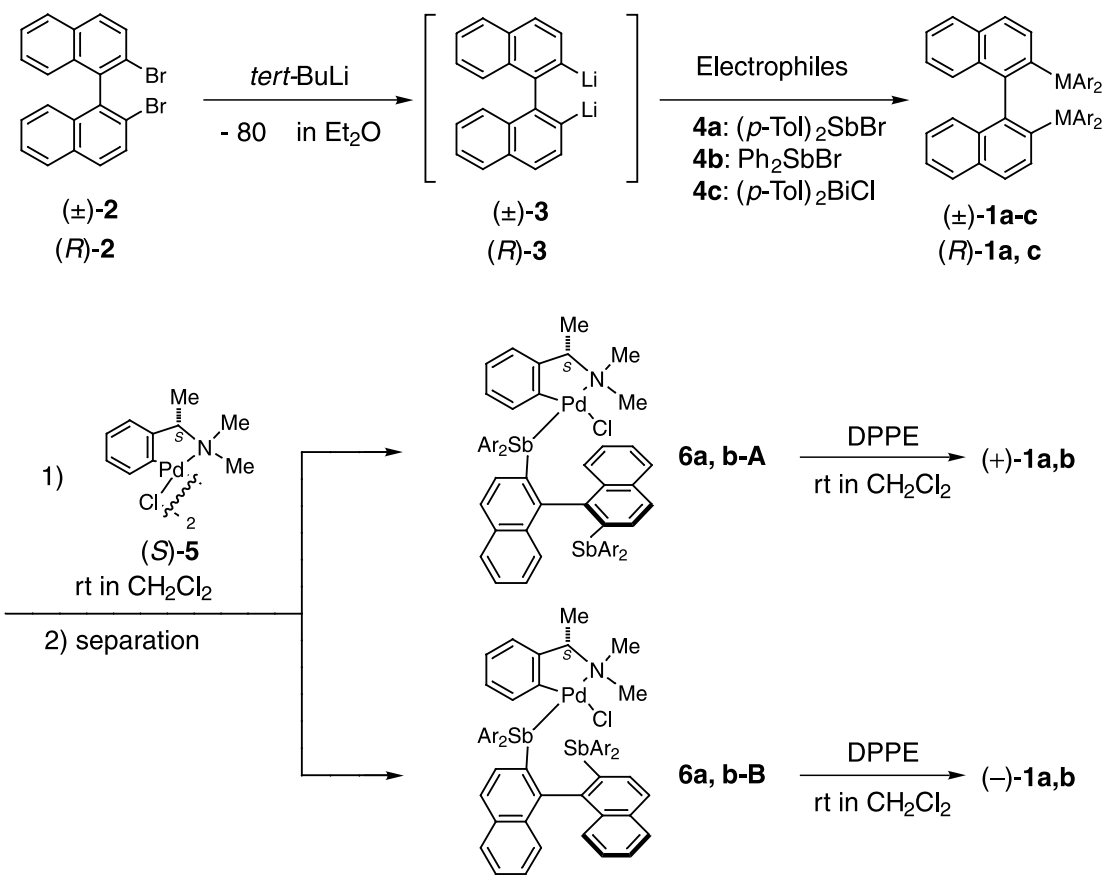
(**1c**: BINABi) from (±)-2,2′-dibromo-1,1′-binaphthyl (DBBN) **2** via a common 2,2′-dilithio-1,1′-binaphthyl intermediate **3**, and optical resolution of (±)-**1a**,**b** using an optically active *ortho*-palladated benzylamine derivative (*S*)-**5** as a resolving agent.[13] In the present study, optically active BINABi (*R*)-**1c** was directly prepared from optically active (*R*)-DBBN (*R*)-**2**, because (±)-**1c** could not be resolved by this procedure. It was also revealed that the optically pure BINASbs (+)-**1a**,**b** and (−)-**1a**,**b** obtained here can be used as effective chiral ligands for rhodium-catalyzed enantioselective hydrosilylation of ketones (Fig. 1).[14,15]

2. Results and discussion

2.1. Preparation of optically active BINASbs 1 via palladium complexes 6

The preparation of (±)-BINASbs **1a**,**b** and their resolution in optically pure compounds are outlined in Scheme 1. Treatment of racemic DBBN (±)-**2** with *tert*-butyllithium in ether at −80°C provided 2,2′-dilithio-1,1′-binaphthyl intermediate **3** which was allowed to couple with 2 equiv. of bromodiarylstibanes **4a**,**b** to afford the desired stibanes (±)-**1a**,**b** in moderate yields (65–49%). The resolution of (±)-**1** is based on the separation of a pair of internally diastereomeric palladium complexes derived from the reaction of (±)-**1a**,**b** and optically active palladium reagent (*S*)-**5** which have been reported to be a useful resolving agent for a wide range of racemic phosphorus,[16,17] arsenic,[18] and antimony compounds.[12,13]

The reaction of (±)-**1a** with 0.5 equiv. of dimeric palladium reagent (*S*)-**5** resulted in coordination of the antimony to the palladium atom to form a 1:1 mixture of the diastereomeric Pd-complexes **6a**-**A** and **6a**-**B**, quantitatively. Although many attempts to separate the diastereomeric mixture by fractional recrystallization from a variety of solvents were unsuccessful, they could be separated by silica gel column chromatography with dichloromethane–ethyl acetate (5:1) as an eluent. When the diastereomeric mixture was separated by the column chromatography, it furnished a 7:1 mixture of (+)-**1a** and (−)-**1a** in 50% yield, along with **6a**-**A** (9% yield) and **6a**-**B** (38% yield). This result indicates not only that chromatographic separation of the diastereomeric mixture on silica gel column chromatography underwent partial decomplexation of the Pd-complexes **6a** to form the palladium-free BINASbs **1a** but also that **6a**-**A** is much more susceptible to the decomposition than **6a**-**B**. Fractional recrystallization of the above 7:1 mixture of (+)-**1a** and (−)-**1a** with hexane–diethyl ether (8:1) afforded enantiopure (+)-**1a** in 34% yield [calculated from (±)-**1a** used]. The palladium atom in the complexes **6a**-**A** and **6a**-**B** is assumed to coordinate one of the two antimony atoms on the bases of the following chromatographic property. The R_f values on TLC (chloroform–ethyl acetate 3:1) for **6a**-**A** (0.41) and **6a**-**B** (0.35) are similar to those of mono-coordinated (+)- (0.49) and (−)-1-phenyl-2-trimethylsilyl-stibindol–(*S*)-**5** complexes (0.45),[12a] and are largely different from those of BINAP-(*S*)-**5** complexes (0.015 for



Scheme 1.

(+)-BINAP-(*S*)-**5** and 0.02 for (−)-BINAP-(*S*)-**5**) in that the palladium atom coordinates to both of the phosphorous atoms and thus these BINAP-(*S*)-**5** complexes are salt structure.[17a] However, the ^{1}H and ^{13}C NMR spectra of these palladium complexes were complicated to a great extent and no plausible assignment of each signal could be made. Consequently, the structures of the Pd-complexes **6a**-**A** and **6a**-**B** were characterized mainly by their mass spectrometry and the following chemical transformation. The FAB mass spectra of both **6a**-**A** and **6a**-**B** showed a weak fragment ion peak at *m*/*z* 1114, attributed to a cation with $[\mathbf{6}-\mathrm{Cl}]^{+}$. It is noteworthy that their electrospray ionization (ESI) mass spectra showed a strong fragment ion peak at *m*/*z* 1114 and a moderate combination peak at *m*/*z* 1405 based on the a cation with $[\mathbf{1a}+\mathbf{5}-\mathrm{Cl}]^{+}$. These results indicate the presence of a 1:2 antimony–palladium complex between **1a** and **5** in the solution. Similarly, treatment of (±)-**1b** with (*S*)-**5** and subsequent chromatographic separation of the resulted diastereomeric mixture gave **6b**-**A** and **6b**-**B**, along with a 5:1 mixture of palladium-free compounds (+)-**1b** and (−)-**1b**.

We next performed the decomplexation of the separated Pd-complexes **6a**,**b** with ligand exchange reaction to obtain optically active BINASbs. Optically active BINASbs (+)-**1a**, (−)-**1a**, (+)-**1b** and (−)-**1b** were obtained from the separated complexes **6a**-**A**, **6a**-**B**, **6b**-**A** and **6b**-**B** by treatment with a phosphorous reagent, 1,2-bis(diphenylphosphano)ethane (DPPE), in dichloromethane at ambient temperature, followed by passing through a short silica gel column for purification, respectively. The pair of free ligands, **1a** and **1b**, thus obtained had optical activity of $[\alpha]_{D}^{21}=15.2-15.3$ (*c* 2.0, benzene) and $[\alpha]_{D}^{28}=4.0-4.1$ (*c* 2.0, benzene) with opposite signs, respectively. These optically pure BINASbs **1a**,**b** showed no noticeable decomposition and change in optical rotation neither when they were heated at 80°C over 24 h in benzene nor when they were permitted to stand in an acidic (5% AcOH–benzene) or a basic (pyridine) condition for 48 h at rt. These results indicate that the optically active BINASbs should be stable under the usual reaction conditions employed in a wide range of asymmetric reactions.

2.2. Preparation of optically active (*R*)-BINABi (*R*)-1c from (*R*)-DBBN (*R*)-2

The synthetic approach to racemic BINABi (±)-**1c** is similar to that employed for the synthesis of BINASbs **1a**,**b** noted earlier. The reaction of (±)-**3** with chlorodi(*p*-tolyl)bismuthane **4c** in ether at −80°C afforded (±)-**1c** in 54% yield as a colorless solid. As is distinct from the reaction of BINASbs **1a**,**b** with the palladium reagent (*S*)-**5**, however, the reaction of the (±)-**1c** with (*S*)-**5** did not give the expected palladium complex, and all of (±)-**1c** was recovered unchanged. This result led us to examine the preparation of optically active BINABi from optically active DBBN (*R*)-**2**.[19a] When (*R*)-**2** (>98% ee) was used as the starting compound in the present synthesis, optically active (*R*)-(+)-**1c** ($[\alpha]_{D}^{25}=+14.3$) was obtained in 29% yield. Similar reaction of (*R*)-**2** with antimony reagent (*p*-Tol)$_2$SbBr **4a** afforded optically active (*R*)-(−)-**1a** in 64% yield; however, the optical purity of the product was relatively low (56% ee; calculated by comparison with the $[\alpha]_{D}$ value of the optically pure (*R*)-(−)-**1a**). These results indicate that a partial recemization of 2,2′-dilithio-1,1′-binaphthyl intermediate (*R*)-**3** should take place under this reaction condition, and the former route starting from easily accessible racemic (±)-**2** is superior to the latter route starting from optically active (*R*)-**2** for the preparation of optically pure BINASbs from the standpoint of low cost. Similar racemization has been observed in the synthesis of 2,2′-silyl-substituted 1,1′-binaphthyl derivatives in that (*R*)-DBBN was treated with 2.2 equiv. of BuLi at −60°C.[19] In fact, recrystallization of the partially recemized product of **1c** obtained here gave less optically active (*R*)-**1c** ($[\alpha]_{D}^{25}=+13.0$) as solids and more active (*R*)-**1c** ($[\alpha]_{D}^{27}=+19.7$) as a pale yellow oil.

2.3. X-Ray crystal structure of BINABi 1c

The structure of novel binaphthyl derivatives **1a**-**c** obtained here was elucidated by ^{1}H NMR, mass spectral and elemental combustion analyses. To gain deeper insight into the stereo-structure of these binaphthyl derivatives, single crystal X-ray analysis of the BINABi **1c** was made and the results were compared with those of the BINASb (*R*)-(−)-**1a** reported by us.[13] The ORTEP drawing of BINABi **1c** is illustrated in Figure 2. The selected data of the molecular structure for **1c** is also summarized in Table 1 with that for (*R*)-(−)-**1a**. These results revealed that the two naphthyl groups in **1c** are adopted almost perpendicular to each other; the dihedral angles of C(10)–C(1)–C(1′)–C(10′) is 96(1)° which is comparable to that for (*R*)-(−)-**1a** [90(1)°]. In both compounds, the C–C distances of the aromatic binaphthyl system are in the typical range of 1.35–1.44 Å; the corresponding angles are 117–122°. There are several differences in the bond angles around the metal atoms and in the bond length of the central σ-bond connecting both of the naphthyl groups between **1c** and (*R*)-(−)-**1a**. The bond angles around the bismuth atom for **1c** (92–94°) are smaller than those around the antimony atom for (*R*)-(−)-**1a** (95–99°), and the central C(1)–C(1′)

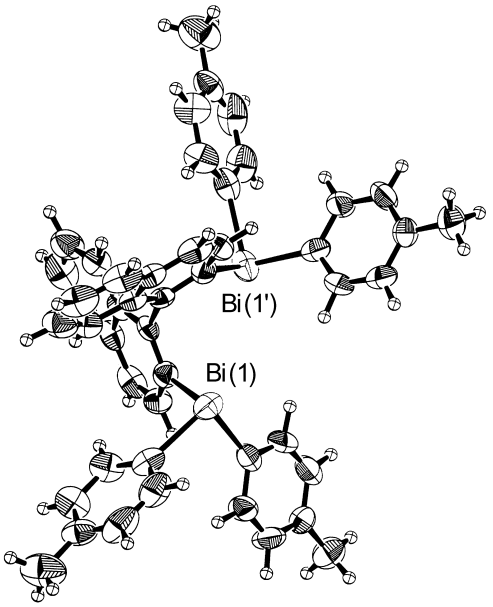
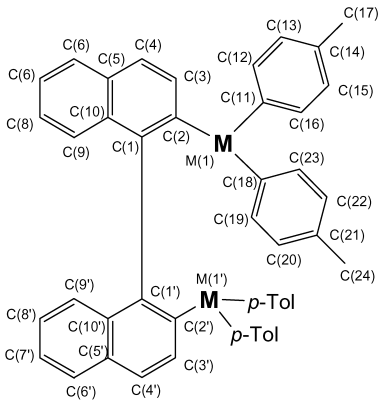


Figure 2. ORTEP drawing of BINABi **1c**.

Table 1. Comparison of selected bond distances and bond angles in crystal structure for BINASb (*R*)-(−)-**1a** and BINABi **1c**



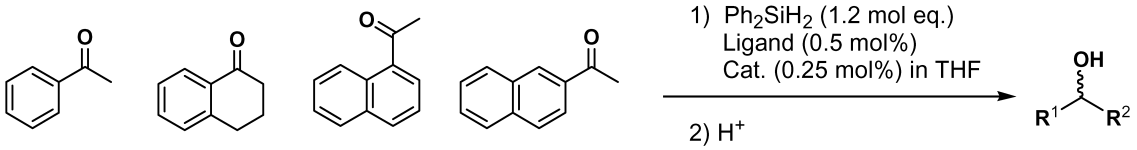
	BINASb (−)-**1a**	BINABi **1c**
Bond distance (Å)		
C(1)–C(1′)	1.49(2)	1.47(2)
M(1)–C(2)	2.164(10)	2.281(10)
M(1)–C(11)	2.15(1)	2.21(1)
M(1)–C(18)	2.16(1)	2.29(1)
Bond angle (°)		
C(2)–M(1)–C(11)	97.4(4)	92.7(3)
C(2)–M(1)–C(18)	94.8(4)	94.4(3)
C(11)–M(1)–C(18)	98.5(4)	94.2(3)
C(2)–C(1)–C(1′)–C(2′)	86(1)	86(1)
C(10)–C(1)–C(1′)–C(10′)	90(1)	96(1)
C(1)–C(10)–C(5)–C(6)	177.4(10)	179.7(8)

bond for **1c** [1.47(2) Å] is shorter than that for (*R*)-(−)-**1a** [1.49(2) Å]. These results imply that steric repulsion between two *p*-tolyl groups and the naphthyl group on the metal atoms and intramolecular interaction between two naphthyl groups become smaller when the metal atoms (Sb and Bi) set in heavier. These variations should be correlated to the difference in the covalent bond radii between the Sb and Bi atoms. Similar disposition can be observed in the molecular structure between 2,2′-bis(trimethylgermyl)- and 2,2′-bis(trimethylstannyl)-1,1′-binaphthyls.[20]

2.4. Enantioselective hydrosilylation of ketones 7a-d with enantiopure BINASbs 1a,b

Finally, the enantiopure ligands **1a**,**b** obtained in the present synthesis were tested as chiral inducer in the asymmetric reduction of ketones with transition metal catalysts, $[RhCl_2(COD)]_2$[21] and $[PhRuCl_2]_2$,[22] and the results are summarized in Table 2. Treatment of acetophenone **7a** with diphenylsilane and the rhodium catalyst in the presence of (−)-**1a** as a chiral inducer resulted in enantioselective hydrosilylation to give (*R*)-1-phenylethanol (*R*)-**8a** (32% ee; determined by HPLC) in 78% isolated yield (entry 2). Also apparent were that addition of excess ligand (entries 3 and 4), the reactions at lower temperature (entries 5 and 6), and the presence of $AgBF_4$ in the reaction mixture (entry 7) did not affect the results of the reaction in terms of catalytic activity and enantioselectivity. Furthermore, the ruthenium catalyst showed unsatisfactory catalytic activity for this type of reaction (entries 8 and 9). (*S*)-1-Phenylethanol (*S*)-**8a** having the opposite sign and almost equal optical purity was obtained, when (+)-**1a** was used as a chiral ligand instead of

Table 2. Transition metal-catalyzed asymmetric hydrosilylation of ketones **7a-d** with enantiopure organoantimony ligands **1a**,**b**



7a **7b** **7c** **7d** **8a-d**

Entry	Ketone **7**	Ligand	Catalyst	Additive	Temperature (°C)	Time (h)	Yield (%)[a]	ee (%)[b]	Recovery of **7** (%)
1	**7a**	(*R*)-BINAP	$[Rh(COD)Cl]_2$	–	0	12	42	0.6(*R*)	36
2	(*R*)-(−)-**1a**	(*R*)-(−)-**1a**	$[Rh(COD)Cl]_2$	–	0	3	78	32(*R*)	13
3[c]	**7a**			–	0	2	74	28(*R*)	15
4[d]	**7a**			–	0	2	76	31(*R*)	17
5	**7a**			–	−20	10	57	24(*R*)	29
6	**7a**			–	−80	24	51	34(*R*)	36
7	**7a**			$AgBF_4$[e]	0	3	71	28(*R*)	0
8	**7a**		$[PhRuCl_2]_2$		rt	24	–	–	84
9	**7a**		$[PhRuCl_2]_2$	AgOTf[f]	0	20	2	24(*S*)	83
10	(*S*)-(+)-**1a**	(*S*)-(+)-**1a**	$[Rh(COD)Cl]_2$	–	0	3	71	28(*S*)	21
11	(−)-**1b**	(−)-**1b**		–	0	3	72	26(*R*)	22
12	**7a**	Sb(*S*)-Stibindole[g]		–	0	3	70	5(*R*)	14
13	**7a**	C(*S*)-AMSb[g]		–	0	3	22	–	46
14	(−)-**1a**	(−)-**1a**	$[Rh(COD)Cl]_2$	–	0	3	64	7(*R*)	30
15	**7c**			–	0	7.5	86	12(*R*)	12
16	**7d**			–	0	3.5	91	26(*R*)	9

[a] Isolated yield after chromatigraphic separation.
[b] Determined by HPLC (Daicel Chiralpak OB).
[c] Rh cat.:ligand=1:2.
[d] Rh cat.:ligand=1:4.
[e] 1 mol%.
[f] 2 mol%.
[g] Lit.[15]

(−)-**1a**. The same reaction with the ligand (−)-**1b** gave almost similar catalytic activity and enantioselectivity. These results were comparable to those of the reactions with Sb- and C-chiral optically active organoantimony ligands such as (*S*)-stibindole and (*S*)-[α-methyl-2-di(*p*-tolyl)stibanobenzyl]dimethylamine (AMSb) as chiral inducer[15] (entries 12 and 13). When optically active (*R*)-(+)-BINAP was used instead of these optically pure organoantimony ligands in the present reaction, neither noticeable catalytic activity nor perceptible enantioselectivity was observed {0°C, 12 h, 42% yield (recovery, 36%), 0.6% ee} (entry 1). In order to clarify the ability of these ligands for enantioselective hydrosilylation, we attempted the reaction of the other ketones **7b-d**. The ketones were subjected to the standard conditions employed for entry 2 in Table 2. The results indicate that the ligands (−)-**1a** could be applicable for this type of enantioselective reduction of ketones into the corresponding alcohols **8b-d** with the same configurational selectivity. These results show that the optically active BINASbs **1a**,**b** display both catalytic activity and enantioselectivity in the rhodium-catalyzed asymmetric hydrosilylation of prochiral ketones, although the enantioselectivity was relatively low.

3. Conclusion

For new development of optically pure ligands used for asymmetric reactions, we have demonstrated the synthesis of optically active BINASbs and BINABi which are the first examples of antimony and bismuth analogues of BINAP. In the present study, resolution of racemic BINASbs was accomplished via a separation of their diastereomeric mixture of Pd-complexes formed from the reaction of BINASbs and *ortho*-palladated benzylamine derivative. The enantiopure organoantimony ligands obtained here were tested as a chiral inducer, and BINASbs were proved to be effective chiral ligands for rhodium-catalyzed asymmetric reduction of prochiral ketones into secondary alcohols, although enantioselectivity of the reaction was relatively low. The results imply that these new, optically active organoantimony ligands comprising a 1,1′-binaphthyl core should be a useful chiral inducer for other types of asymmetric reactions.

4. Experimental

4.1. General

All reactions were carried out in pre-dried glassware under an argon atmosphere. Ether was distilled from its $LiAlH_4$ suspension and dried over sodium wire. Melting points were taken on a Yanagimoto micro melting point hot-stage apparatus and are not corrected. ^1H NMR (TMS: δ: 0.00 as an internal standard) and ^{13}C NMR ($CDCl_3$: δ: 77.00 as an internal standard) spectra were recorded on a JEOL JNM-GSX-400 (400 MHz and 100 MHz) spectrometer in $CDCl_3$ unless otherwise stated. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a JEOL JMP-DX300 instrument. Optical rotations were measured on a JUSCO DIP-370 digital polarimeter. All chromatographic separations were accomplished with either Kieselgel 60 (Merck) or Silica Gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey–Nagel Pre-coated TLC plates Sil G25 UV_{254}. Bromodi(*p*-tolyl)stibane and bromodiphenylstibane were prepared by a redistribution reaction of a 1:2 mixture of triarylstibane and tribromostibane according to the literature method.[23] Chlorodi(*p*-tolyl)bismuthane was generated in a stirred solution of tri(*p*-tolyl)bismuthane and trichlorobismuth (2:1) in ether at room temperature.[24] All electrophiles (*p*-Tol_2SbBr, Ph_2SbBr, *p*-Tol_2BiCl) were made up fresh each time before use.

4.1.1. General procedure for the synthesis of (±)-2,2′-bis(diarylmetalano)-1,1′-binaphthyl 1a-c. To a stirred solution of *t*-BuLi (1.6 M solution in pentane, 7.5–37.5 mL, 6 mol equiv.) in anhydrous ether (30–60 mL) was added a solution of (±)-DBBN **2** (824 mg–4.12 g, 2–10 mmol) in anhydrous ether (40–200 mL) dropwise over 15–45 min at −80°C and the solution was stirred for 30 min at the same temperature. A solution of an antimony reagent [*p*-Tol_2SbBr **4a** or Ph_2SbBr **4b** (6 mol equiv.) in ether (40–80 mL)] or a suspension of a bismuth reagent [*p*-Tol_2BiCl **4c** (6 mol equiv.) in ether (50 mL)] was added dropwise with stirring for 15–30 min period to the above reaction mixture at −80°C. After stirring for an additional 30 min, the mixture was allowed to warm slowly to 0°C. The reaction mixture was quenched with water (50–200 mL) and diluted with benzene (100–300 mL). The resulting organic layer was separated and the aqueous layer was extracted with benzene (50–100 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was subjected to silica gel chromatography with hexane–benzene (4:1) to give (±)-BINASbs **1a**,**b** or (±)-BINABi **1c**.

4.1.2. (±)-2,2′-Bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl (±)-1a. Colorless prisms (65% yield), mp 240–242°C (benzene–ether 1:1), ^1H NMR ($CDCl_3$, 400 MHz) δ 2.27 (6H, s), 2.29 (6H, s), 6.95 (4H, d, J=7.7 Hz), 6.9 (2H, t, J=8.1 Hz), 7.01 (2H, d, J=8.1 Hz), 7.03 (4H, d, J=7.7 Hz), 7.05 (4H, d, J=8.1 Hz), 7.14 (4H, d, J=8.1 Hz), 7.35 (2H, t, J=8.1 Hz), 7.57 (2H, d, J=8.4 Hz), 7.83 (2H, d, J=8.1 Hz), 7.84 (2H, d, J=8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.32 (q), 126.10 (d), 126.20 (d), 126.99 (d), 127.85 (d), 128.35 (d), 129.30 (d), 129.53 (d), 132.27 (d), 133.31 (s), 133.35 (s), 135.15 (s), 135.59 (s), 136.01 (d), 136.32 (d), 137.78 (s), 137.98 (s), 140.42 (s), 147.54 (s); FAB MS *m*/*z* 860 $[M]^+$. Anal. calcd for $C_{48}H_{40}Sb_2$: C, 67.01; H, 4.69. Found: C, 67.18; H, 4.83.

4.1.3. (±)-2,2′-Bis(diphenylstibano)-1,1′-binaphthyl (±)-1b. Colorless prisms (49% yield), mp 217–219°C (benzene–hexane 1:2); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.95 (2H, t, J=8.0 Hz), 7.01 (2H, d, J=8.0 Hz), 7.12–7.35 (22H, m), 7.56 (2H, d, J=8.4 Hz), 7.84 (2H, d, J=8.8 Hz), 7.86 (2H, d, J=8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 126.20 (d), 126.39 (d), 126.95 (d), 127.88 (d), 128.16 (d), 128.33 (d), 128.49 (d), 128.76 (d), 132.27 (d), 133.28 (s), 133.38 (s), 136.05 (d), 136.34 (d), 138.90 (s), 139.25 (s), 140.21 (s), 147.64 (s); FAB MS *m*/*z* 804 $[M]^+$. Anal. calcd for $C_{44}H_{32}Sb_2$: C, 65.71; H, 4.01. Found: C, 65.88; H, 4.23.

4.1.4. (±)-2,2′-Bis[di(*p*-tolyl)bismuthano]-1,1′-binaphthyl (±)-1c. Colorless prisms (54% yield), mp 231.5–234°C (ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27 (12H, s), 7.05 (2H, t, J=7.3 Hz), 7.06 (4H, d, J=7.3 Hz), 7.11 (4H, d, J=7.3 Hz), 7.13 (2H, d, J=8.1 Hz), 7.35 (4H, d, J=7.7 Hz), 7.36 (2H, t, J=7.3 Hz), 7.37 (4H, d, J=7.7 Hz), 7.86 (2H, d, J=8.1 Hz), 7.91 (2H, d, J=8.4 Hz), 8.04 (2H, d, J=8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.42 (q), 125.92 (d), 126.30 (d), 126.93 (d), 128.05 (d), 130.48 (d), 131.02 (d), 131.24 (d), 133.12 (s), 133.88 (s), 134.98 (d), 136.88 (s), 137.25 (d), 137.67 (d), 147.95 (s), 152.92 (s), 153.36 (s), 157.36 (s); FAB MS m/z 1034 $[M]^+$. Anal. calcd for $C_{48}H_{40}Bi_2$: C, 55.71; H, 3.90. Found: C, 55.72; H, 4.02.

4.2. Typical procedure for the preparation of 2,2′-bis(diarylstibano)-1,1′-binaphthyl-palladium complexes 6a-A, 6a-B, 6b-A and 6b-B

To a stirred solution of (±)-BINASbs **1a**,**b** (1.2–4.0 g, 1.5–4.65 mmol) in dichloromethane (20–50 mL) was added solids of di-μ-chlorobis{(*S*)-2-[1-(dimethylamino)-ethyl]-phenyl*C*,*N*}-dipalladium(II) (*S*)-**6** (423 mg–1.35 g, 0.5 mol equiv.) in small portions at room temperature and the mixture was stirred for 10–15 min. The reaction mixture was concentrated in vacuo and the resulting residue was subjected to column chromatography on silica gel using the solvents shown below as eluents to give 2,2′-bis(diarylstibano)-1,1′-binaphthyl-palladium complexes **6a**-**A**, **6a**-**B**, **6b**-**A** and **6b**-**B**.

4.2.1. C_2(*R*/*S*)-2,2′-Bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl-palladium complexes 6a-A and 6a-B. Chromatographic separation of the reaction mixture obtained from the reaction of (±)-**1a** (4.0 g, 4.65 mmol) with (*S*)-**5** (1.35 g, 2.33 mmol) on silica gel using a mixture of dichloromethane–ethyl acetate (5:1) as an eluent afforded a 7:1 mixture of (+)-**1a** and (−)-**1a** (2.00 g, 50%), diastereomerically pure **6a**-**A** (0.56 g, 9% yield) and **6a**-**B** (2.04 g, 38% yield), successively. Fractional recrystallization of the mixture of (+)-**1a** and (−)-**1a** obtained above from hexane–diethyl ether (ca. 8:1) afforded optically pure (+)-**1a** (1.35 g, 34% yield).

Compound **6a**-**A**. Yellow powder, mp 149–151°C (ethyl acetate); R_f=0.41 (chloroform–ethyl acetate=3:1); $[\alpha]_D^{20}$=+42.4 (*c* 1, benzene); FAB MS m/z: 1114 $[M-Cl]^+$; ESI MS m/z: 1114.3 {$[M-Cl]^+$, 100%}, 1405.3 {$[\mathbf{1a}+\mathbf{5}-Cl]^+$, 31%}. Anal. calcd for $C_{58}H_{54}ClNPdSb_2$: C, 60.55; H, 4.73; N, 1.22. Found: C, 61.14; H, 4.94; N, 1.33.

Compound **6a**-**B**. Yellow powder, mp 169.5–173°C decomp. (ethyl acetate–isopropyl ether=1:1); R_f=0.35 (chloroform–ethyl acetate=3:1); $[\alpha]_D^{20}$=−17.4 (*c* 1, benzene); FAB MS m/z: 1114 $[M-Cl]^+$; ESI MS m/z: 1114.3 {$[M-Cl]^+$, 100%}, 1405.4 {$[\mathbf{1a}+\mathbf{5}-Cl]^+$, 18%}. Anal. calcd for $C_{58}H_{54}ClNPdSb_2$: C, 60.55; H, 4.73; N, 1.22. Found: C, 60.21; H, 5.02; N, 1.24.

4.2.2. C_2(*R*/*S*)-2,2′-Bis(diphenylstibano)-1,1′-binaphthyl-palladium complexes 6b-A and 6b-B. Chromatographic separation of the reaction mixture obtained from the reaction of **1b** (1.2 g, 1.5 mmol) with (*S*)-**5** (423 mg, 0.75 mmol) on silica gel using a mixture of dichloromethane–ethyl acetate (5:1) as an eluent afforded a 5:1 mixture of (+)-**1b** and (−)-**1b** (550 mg, 46%), diastereomerically pure **6b**-**A** (80 mg, 5% yield) and **6b**-**B** (780 mg, 48% yield), successively.

Compound **6b**-**A**. Yellow foam, R_f=0.36 (chloroform–ethyl acetate=3:1); $[\alpha]_D^{27}$=+33.5 (*c* 2, benzene); FAB MS m/z:1058 $[M-Cl]^+$; FAB-HRMS m/z: 1059.0841 (calcd for $C_{54}H_{46}NPdSb_2$: 1059.0840).

Compound **6b**-**B**. Yellow foam, R_f=0.30 (chloroform–ethyl acetate=3:1); $[\alpha]_D^{28}$=−5.7 (*c* 2, benzene); FAB MS m/z: 1058 $[M-Cl]^+$. FAB-HRMS m/z: 1059.0842 (calcd for $C_{54}H_{47}NPdSb_2$: 1059.0840).

4.3. General procedure for the preparation of optically pure C_2(*R*)- and C_2(*S*)-2,2′-bis(diarylstibano)-1,1′-binaphthyl (+)-1a, (−)-1a, (+)-1b and (−)-1b from the palladium complexes 6a-A, 6a-B, 6b-A and 6b-B

To a stirred solution of the diastereomerically pure palladium complexes **6a**-**A**, **6a**-**B**, **6b**-**A** and **6b**-**B** (0.5–1 mmol) in dichloromethane (10–20 mL) were added solids of 1,2-bis(diphenylphosphino)ethane (1.1 mol equiv.) in small portions at room temperature and the mixture was stirred for 10 min. The reaction mixture was concentrated in vacuo and the resulting residue was subjected to column chromatography on silica gel using a mixture of hexane–dichloromethane (10:1–5:1) as an eluent to give the corresponding optically pure BINASbs (+)-**1a**, (−)-**1a**, (+)-**1b** and (−)-**1b**, respectively.

4.3.1. (*S*)-2,2′-Bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl (+)-1a. Colorless prisms (93% yield), mp 183–185°C (hexane–ether); $[\alpha]_D^{21}$=+15.3 (*c* 2.0, benzene). The ^{1}H NMR spectrum of (+)-**1a** was superimposable to that of (±)-**1a**.

4.3.2. (*R*)-2,2′-Bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl (−)-1a. Colorless prisms (95% yield), mp 183–185°C (hexane–ether); $[\alpha]_D^{21}$=−15.2 (*c* 2.0, benzene). The ^{1}H NMR spectrum of (−)-**1a** was superimposable to that of (±)-**1a**.

4.3.3. (+)-2,2′-Bis(diphenylstibano)-1,1′-binaphthyl (+)-1b. Colorless oil (92% yield); $[\alpha]_D^{28}$=+4.0 (*c* 2.0, benzene). The ^{1}H NMR spectrum of (+)-**1b** was superimposable to that of (±)-**1b**.

4.3.4. (−)-2,2′-Bis(diphenylstibano)-1,1′-binaphthyl (−)-1b. Colorless oil (95% yield); $[\alpha]_D^{28}$=−4.1 (*c* 2.0, benzene). The ^{1}H NMR spectrum of (−)-**1b** was superimposable to that of (±)-**1b**.

4.4. Synthesis of optically active (*R*)-2,2′-bis[di(*p*-tolyl)-stibano]- (*R*)-1a and (*R*)-2,2′-bis[di(*p*-tolyl)busmutho]-1,1′-binaphthyl (*R*)-1c from (*R*)-DBBN (*R*)-2

The reaction was carried out essentially the same as in the reaction with antimony and bismuth reagents described earlier, except for the use of optically active (*R*)-(+)-DBBN (*R*)-**2** instead of the racemic (±)-**2**.

4.4.1. (*R*)-2,2′-Bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl (*R*)-(−)-1a. The reaction mixture obtained from the reaction of (*R*)-(+)-**2** {$[\alpha]_D^{23}$=+32.6, 412 mg, 1 mmol} with *t*-BuLi (1.45 M, 4.1 mL, 6 mmol) and bromodi(*p*-tolyl)stibane (2.29 g, 6 mmol) was separated by column chromatography on silica gel with a mixture of hexane–benzene (4:1) to give (*R*)-(−)-**1a** {$[\alpha]_D^{21}$=−8.5, 292 mg, 34%}. The optical purity of this product was calculated to be 56% ee based on the $[\alpha]_D$ value of the optically pure (*R*)-(−)-**1a**.

4.4.2. (*R*)-2,2′-Bis[di(*p*-tolyl)bismuthano]-1,1′-binaphthyl (*R*)-(+)-1c. The reaction mixture obtained from the reaction of (*R*)-(+)-**2** {$[\alpha]_D^{23}$=+32.6, 300 mg, 0.73 mmol} with *t*-BuLi (1.56 M, 2.8 mL, 4.4 mmol) and chlorodi(*p*-tolyl)bisumuthane (1.86 g, 4.4 mmol) was separated by column chromatography on silica gel with a mixture of hexane–benzene (4:1) to give (*R*)-(+)-**1c** {$[\alpha]_D^{25}$=+14.3, 142 mg, 19%}. Recrystallization of the mixture (64 mg) from hexane–ether gave crystals {18 mg, $[\alpha]_D^{25}$=+13.0} and a more optically active product {37 mg, $[\alpha]_D^{27}$=+19.7 (*c* 2, benzene)} as an oil. The optical purity of this product is not known at present, because no methods to determine it have been found.

4.5. General procedure for hydrosilylation of ketones with diphenylsilane in the presence of transition metal catalyst

A solution of the metal catalysis {$[Rh(COD)Cl]_2$;12.5 mg, 0.025 mmol or $[PhRuCl_2]_2$; 13 mg, 0.025 mmol} and the BINASbs (0.05 mmol) in THF (2 mL) was stirred at room temperature under an argon atmosphere for 1 h. To the catalyst solution on ice-bath was added ketones **7a-d** (5 mmol) and diphenylsilane (1.10 g, 6 mmol) in THF (2 mL) and the mixture was stirred for 3–7.5 h at 0°C. For the work-up, methanol (12 mL) and hydrochloric acid (10%, 10 mL) were added to the reaction mixture at 0°C. After stirring for 1.5 h at 0°C, the mixture was extracted with ether (50 mL×1.30 mL×1). The combined extracts were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography with a mixture of diethyl ether–hexane (1:9) to give alcohols **8a-d**. The optical purity of **8a-d** was determined by the HPLC [Daicel Chiralcel OB column; eluent, *n*-hexane:*i*-PrOH=9:1; flow rate 0.5 mL/min; detection, UV 254 nm; retention times, **8a** (t_R=10.4 min, t_S=13.4 min), **8b** (t_R=9.4 min, t_S=12.9 min), **8c** (t_R=15.4 min, t_S=17.2 min), **8d** (t_R=14.2 min, t_S=17.8 min)].

4.6. Crystal structure determination of BINASb (*R*)-(−)-1a and BINABi 1c

4.6.1. BINASb (*R*)-(−)-1a. The short comments and selected crystal data for (*R*)-(−)-**1a** has been already reported in the preliminary communication.[13] Full details of the crystallographic results have been deposited with the Cambridge Crystallographic Data Center [no. CCDC 211421].

4.6.2. BINABi 1c. $C_{48}H_{40}Bi_2$, M=1034.80, monoclinic space group *C*2/*c* (#15), a=27.896(7) Å, b=8.948(2) Å, c=18.484(4) Å, β=121.760(3)°, V=3923(1) Å^3, T=299 K, space group *C*2/*c* (#15), Z=4, D_{calc}=1.752 g cm^{-3}. Crystal dimension 0.50×0.25×0.20 mm^3, μ(Mo Kα)=89.75 cm^{-1}. Data collection and processing: Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo Kα (λ=0.71069 Å) radiation, 11840 reflections measured, giving 2574 with $I>1.00\sigma(I)$, $2\theta<57.11$. Absorption correction was not applied. The structure was solved by direct methods using SIR97[25] and was refined by full-matrix least-squares techniques using DIRDIF94.[26] The non-hydrogen atoms were refined anisotropically. The final residuals for reflections with $I>1.00\sigma(I)$ were R=0.047, Rw=0.041. Full details of the crystallographic results have been deposited with the Cambridge Crystallographic Data Center [no. CCDC 211422].

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