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2,2′-Bis(diarylstibano)-1,1′-binaphthyls (BINASbs); a useful chiral ligand for palladium-catalyzed asymmetric allylic alkylation, and the structure of a BINASb–$PdCl_2$ complex

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

[a]*Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181, Japan*
[b]*Chemical Analysis Center, Chiba University, 1-33 Yayoicho, Inage-ku, Chiba 263-8522, Japan*

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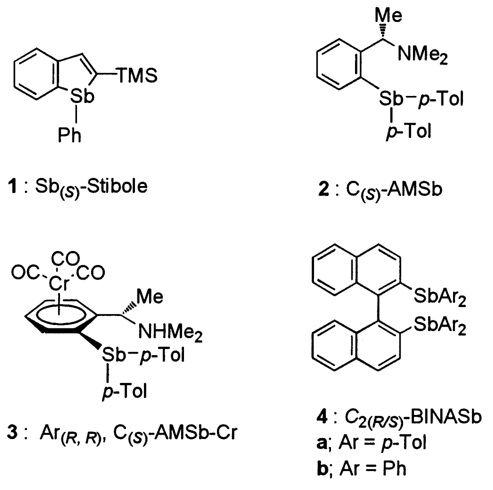
Abstract—The first attempt to use enantiopure antimony ligands **1**–**4** as a chiral auxiliary was successfully accomplished in a palladium-catalyzed asymmetric alkylation of 1,3-diphenylprop-2-ene-1-yl acetate with dimethyl malonate. Under the optimized conditions, the allylation product can be obtained with up to 96% ee in 84% chemical yield by use of enantiopure C_2-symmetric 2,2′-bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl [BINASb(*p*-Tol)] **4a** as a chiral ligand with O-bis(trimethylsilyl)acetamide (BSA) and potassium acetate. The structure of the intermediary BINASb–$PdCl_2$ complex was elucidated by single crystal X-ray analysis, implying that the BINASb should work as a bidentate chiral ligand in the reaction.

Palladium-catalyzed asymmetric allylic substitutions with chiral ligands are known to be one of the most effective methods for the enantioselective construction of carbon–carbon and/or carbon–heteroatom bonds, and have recently been the subject of much attention.[1,2] In order to achieve high enantioselectivity in these reactions, a growing number of ligands containing group 15 (N, P) and 16 (S, Se) elements have been examined. The ligands used in the recent studies can be classified into four categories: (1) chiral mono-[3,4] or di-phosphine ligands,[5,6] (2) chiral dinitrogen ligands,[7] (3) chiral P,N-chelate ligands[8,9] and (4) chiral ligands with mixed donor atoms such as sulfur[2d,10] and selenium. However, transition metal-catalyzed asymmetric allylic substitutions with optically active organoantimony compounds have not been reported so far due to the limited availability of enantiopure organoantimony compounds. In the course of our current studies on optically active organoantimony compounds as a chiral auxiliary, we have recently reported the synthesis of enantiopure organoantimony compounds such as stibindole **1**,[11] α-methyl-[2(α-naphthyl)(*p*-tolyl)stibano]-benzyldimethylamine,[12] α-methyl-[2-di(*p*-tolyl)stibano]-benzyldimethylamine (AMSb) **2**,[13] tricarbonyl(η^6-{α-methyl-[2-di(*p*-tolyl)stibano]benzyldimethylamine})-chromium (AMSb-Cr) **3**[12] and 2,2′-bis(diarylstibano)-1,1′-binaphthyls (BINASbs) **4a**,**b**,[14] some of which were proved to be useful ligands for rhodium-catalyzed asymmetric reduction of unsymmetrical ketones (Fig. 1).[13,14] Herein, we describe the first application of the antimony ligands for palladium-catalyzed asymmetric allylic alkylation. In the present studies, good results in terms of chemical yield and enantioselectivity were



1 : $Sb_{(S)}$-Stibole

2 : $C_{(S)}$-AMSb

3 : $Ar_{(R,R)}$, $C_{(S)}$-AMSb-Cr

4 : $C_{2(R/S)}$-BINASb
a; Ar = *p*-Tol
b; Ar = Ph

Figure 1.

Keywords: antimony and compounds; asymmetric reactions; asymmetric allylic alkylations; 2,2′-bis(diarylstibano)-1,1′-binaphthyl (BINASb); X-ray crystal structures.

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

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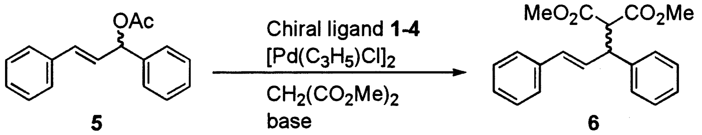
obtained in the allylic alkylation of 1,3-diphenylprop-2-ene-1-yl acetate with dimethyl malonate when BINASb was employed as a chiral ligand with O-bis(trimethylsilyl)acetamide (BSA) and potassium acetate (AcOK).

The palladium-catalyzed asymmetric allylic alkylation of racemic 1,3-diphenyl-2-propen-1-yl acetate (±)-**5** with dimethyl malonate, which has been known to be a typical representative in allylic chemistry, was taken as a model reaction. The effects of the base, counter anion, solvent, and the metal/ligand ratio on the reaction were investigated, and the results are summarized in Table 1. At first, the reaction of the 1,3-diphenyl-2-propen-1-yl acetate (±)-**5** with dimethyl sodium malonate (1.2 mol equiv.) generated in situ from dimethyl malonate and sodium hydride was performed in the presence of 2 mol% of $[Pd(C_3H_5)Cl]_2$ and 4 mol% of the chiral ligand at 50°C in tetrahydrofuran (THF) (entries 1,3,5,7). The results showed that the chromium complex **3** and the C_2-symmetric BINASb (*R*)-**4a** were proved to be effective for this type of reaction, and (*R*)-**4a** displayed better results in terms of chemical yield and enantioselectivity. It should be noted that, as are distinct from the ligands **3** and (*R*)-**4a**, the Sb-chiral **1** and the C-chiral ligands **2** were ineffective for the reaction. We next investigated the influence of the base, counter anion, solvent, and the metal/ligand ratio on this reaction employing the ligand (*R*)-**4a**. The reaction of (±)-**5** with dimethyl malonate by use of BSA (3 mol equiv.) and a catalytic amount of AcOK as a base instead of NaH in dichloromethane at room temperature afforded the allylation product **6** with up to 90% ee in 70% yield (entry 8). Although the use of diethylzinc as a base is known to give high ee of the product **6** when optically active BINAP is utilized as a chiral ligand,[15] it gave an unexpected result when (*R*)-**4a** was employed in this reaction (entry 9). It was also apparent that the use of cesium carbonate as a counter ion was superior in effectiveness to sodium, but inferior to BSA–AcOK system, the use of THF or acetonitrile as solvent afforded poorer results, excessive addition of the ligand did not affect the efficiency of the reaction, and BINASbs **4a**,**b** proved to be a more powerful ligands than BINAP under the same conditions. Consequently, the best result was obtained when (±)-**5** was treated with dimethyl malonate, BSA, and AcOK by use of $[Pd(C_3H_5)Cl]_2$ as a metal catalysis and (*R*)-**4a** as a ligand in 0.5:1 ratio in CH_2Cl_2 over 72 h at 0°C (entry 14).

In order to gain deeper insight into the structure of the intermediary palladium complex which participated in the above reaction and to determine the absolute configuration of the oily ligand (–)-**4b**, we attempted the synthesis of optically active BINASb–$PdCl_2$ complex **7**. Treatment of (–)-**4b** with an equimolar amount

Table 1. Asymmetric allylic alkylation of (±)-**5** using antimony ligands **1**–**4**[a]



Entry	Ligand	Base	Additive[b]	Solvent	Temp.	hr	Yield (%)[c]	Ee (%)[d]
1	**1**[e]	NaH	–	THF	50°C	30	–	–
2	**1**[e]	BSA	AcOK	CH_2Cl_2	rt	24	12	25 (*S*)
3	**2**	NaH	–	THF	50°C	30	–	–
4	**2**	BSA	AcOK	CH_2Cl_2	rt	24	13	3 (*S*)
5	**3**	NaH	–	THF	50°C	48	20	20 (*S*)
6	**3**	BSA	AcOK	CH_2Cl_2	rt	24	–	–
7	(*R*)-**4a**	NaH	–	THF	50°C	30	56	74 (*S*)
8	(*R*)-**4a**	BSA	AcOK	CH_2Cl_2	rt	24	70	90 (*S*)
9	(*R*)-**4a**	Et_2Zn	–	THF	rt	24	–	–
10	(*R*)-**4a**	Cs_2CO_3	–	CH_2Cl_2	rt	24	64	80 (*S*)
11	(*R*)-**4a**	BSA	AcOK	THF	rt	24	37	85 (*S*)
12	(*R*)-**4a**	BSA	AcOK	CH_3CN	rt	24	33	84 (*S*)
13	(*R*)-**4a**[e]	BSA	AcOK	CH_2Cl_2	rt	24	68	81 (*S*)
14	(*R*)-**4a**	BSA	AcOK	CH_2Cl_2	0°C	72	84	96 (*S*)
15	(*S*)-**4a**	BSA	AcOK	CH_2Cl_2	rt	24	73	93 (*R*)
16	(–)-**4b**	BSA	AcOK	CH_2Cl_2	rt	24	73	84 (*S*)
17	(*R*)-BINAP	BSA	AcOK	CH_2Cl_2	rt	24	48	49 (*S*)

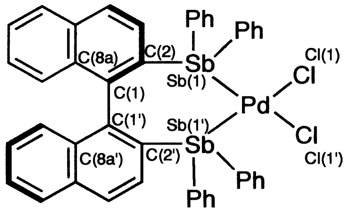
[a] The ratio of the reagents in entries 2, 4, 6, and 8–16 was allyl acetate:dimethyl malonate:base:ligand: $[Pd(C_3H_5)Cl]_2 = 1:3:3:0.04:0.02$, and that of other entries was allyl acetate:diinethyl rnalonate:base:ligand: $[Pd(C_3H_5)Cl]_2 := 1:1.5:1.2:0.04:0.02$.

[b] Additive 0.02 mol equiv.

[c] Isolated yield.

[d] Determined by HPLC (Daicel Chiralpak AD-H), the absolute configuration of the product was assigned by comparison of the chiroptical value with that of the literature.[7a]

[e] Ligand:Pd cat. = 4:1.



(*R*)-(+)-7

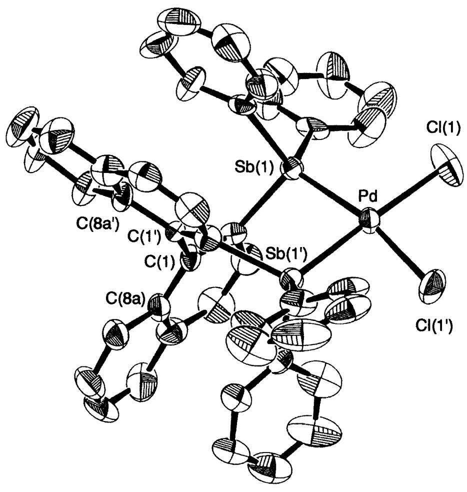


Figure 2. ORTEP drawing of (*R*)-(+)-**7**; selected bond lengths (Å) and angles (°): Sb(1)–Pd 2.5169(9), Sb(1′)–Pd 2.4949(9), C(2)–Sb(1) 2.139(9), C(2′)–Sb(1′) 2.138(9); Sb(1)–Pd–Sb(1′) 89.43(3), Sb(1)–Pd–Cl(1) 82.73(9), Sb(1′)–Pd–Cl(1′) 94.4(1), Cl(1)–Pd–Cl(1′) 93.9(1); C(8a)–C(1)–C(1′)–C(8a′) 75(1).

of $PdCl_2$(COD) resulted in coordination of the palladium to both of the antimony atoms to give the expected BINASb–$PdCl_2$ complex **7** as solids which could be recystallized from a mixture of diethyl ether and CH_2Cl_2 to furnish red prisms suitable for single crystal X-ray analysis.[16] The ORTEP drawing of the X-ray crystal structure for **7** is illustrated in Figure 2, along with selected data.[17] The absolute configuration of the C_2-symmetric center of **7** was determined to be *R*. The seven-membered ring formed by coordination of palladium to both of the antimony atoms on BINASb (−)-**4b** is highly skewed as well as the BINAP–$PdCl_2$ complex.[18] The dihedral angle of the two naphthalene rings [C(8a)–C(1)–C(1′)–C(8a′) = 75°] is smaller than that of the unchelated BINASb (*R*)-**4a** (90°C) itself.[14a] Around the palladium atom, the complex has a distorted-square-planar geometry; the sum of four angles involving Sb(1), Sb(1′), Cl(1) and Cl(1′) being 360.4°, and the bond angles of Sb(1)–Pd–Cl(1′) and Sb(1′)–Pd–Cl(1) being 175.0° and 168.3°, respectively. The bite angle of Sb(1)–Pd–Sb(1′) (89.4°) is slightly narrower than that of the BINAP–$PdCl_2$ complex (92.7°C).[18] Structural studies of the 1,3-diphenylallyl palladium complex with (*S*)-BINAP have been made and the dissimilarity of the two allylic phenyl groups on the π-allyl moiety is assumed to be the origin of enantioselectivity.[1,19] We considered that the asymmetric induction with BINASbs in the present reaction should be analogous with that with BINAP. In practice, the same reaction of (±)-**5** with NaH–dimethyl malonate in the presence of the BINASb–$PdCl_2$ complex **7** instead of BINASb with $[Pd(C_3H_5)Cl]_2$ resulted in asymmetric alkylation to afford (*S*)-**6** in similar chemical yield (58%) and enantioselectivity (66% ee). The result implies that BINASb **4** should serve as a bidentate chiral ligand in these reactions. Further application of BINASb itself and isolable BINASb–$PdCl_2$ complex **7** for other types of asymmetric reactions as well as the structural modification of BINASb with a variety of substituents on the antimony atoms are in progress.

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17. Crystal data for (*R*)-**7**: $C_{44}H_{32}Cl_2PdSb_2$, $M = 981.54$, orthorhombic, $a = 13.243(3)$, $b = 21.919(5)$, $c = 13.027(2)$ Å, $V = 3781(1)$ Å^3, $T = 298$ K, space group $P2_12_12_1$ (no. 19), $Z = 4$, μ(Cu Kα) = 165.37 cm^{-1}, 7760 reflections measured, 6853 reflections [$I > 1.50\sigma(I)$] were used in all calculations, $R = 0.053$, $R_w = 0.068$. The structure was solved by heavy-atom Patterson methods (PATTY) and the non-hydrogen atoms were refined anisotropically. Full details of the crystallographic results have been deposited with the Cambridge Crystallographic Data Center [no. CCDC 214297].
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