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Journal of Organometallic Chemistry 691 (2006) 2213–2220
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis of enantiomerically pure Sb-chirogenic organoantimony compounds and their crystal structures

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Received 17 October 2005; accepted 24 October 2005
Available online 19 December 2005

Abstract

Sb-chirogenic organoantimony compounds (±)-**5a**–**c** bearing heteroatom moieties such as 4,4-dimethyl-2-oxazolinyl, methoxymethyl, and diphenylphosphanyl substituents on the *o*-position of an aryl group have been prepared by nucleophilic displacement of the ethynyl moiety on (1-naphthyl)(phenylethynyl)(*p*-tolyl)stibane (**3**) with aryllithium reagents (**2a**–**c**). The optical resolution of the racemic (±)-**5a**,**b** was attained via separation of a diastereomeric mixture of their palladium complexes (*S*)-**7** formed from the reactions of (±)-**5a**,**b** with di-μ-chlorobis[(*S*)-dimethyl(1-ethyl-α-naphthyl)aminato-C^2,*N*]dipalladium(II) (**6**). The enantiomerically pure Sb-chirogenic stibanes isolated here were optically stable, and no racemization on the chiral antimony center was observed even when they were allowed to stand at room temperature for over 72 h in chloroform. The structure of **5a**,**b** including the absolute configuration was determined by single crystal X-ray analyses of (+)-**5aB** and antimony–palladium complex (**7bB**), respectively. The analyses also revealed the presence of intramolecular interaction between the antimony and sp^2-nitrogen atoms in the molecule Sb(*S*)-(+)-**5aB**.

Keywords: Antimony; Nucleophilic substitution; Sb-chirogenic; Palladium complex; Optical resolution; X-ray analysis; Hypervalent coordination

1. Introduction

Optically active compounds bearing chirality on group 15 elements are currently a project of great interest in main group chemistry [1]. Among these, the most popular and actively investigated examples are P-chirogenic phosphine compounds which are important synthetic tools for ligand chemistry in asymmetric synthesis [2]. However, studies on Sb-chirogenic organoantimony(III) compounds (stibanes) have been very limited up to now. Synthesis of this kind of compounds was first demonstrated earlier by Campbell [3], who resolved optically active phenoxastibanes, stibafluorenes [4] and triarylstibanes [5] having a carboxyl or an amine group by complexation with resolving agents having these functional groups. However, this research field has not been investigated over a period of 50 years, because these compounds were reported to be not so stable and led to gradual racemization on the antimony center in solution. In view of this background, we are interested in the synthesis of Sb-chirogenic organoantimony compounds and their stereo-chemical properties. We have recently reported a versatile route for the synthesis of Sb-chirogenic organoantimony compounds through stepwise nucleophilic displacement of the ethynyl groups on diethynylstibanes with Grignard and/or organolithium reagents [6a], as well as their resolution into optically pure form via separation of a diastereomeric mixture of the palladium complex formed from the reaction of the Sb-chiral compounds and *ortho*-palladated benzylamine derivatives [6b,7]. As a further extension of this work, we report here the synthesis

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doi:10.1016/j.jorganchem.2005.10.042

of enantiomerically pure open-chain Sb-chirogenic organoantimony compounds having a heteroatom moiety at the *ortho*-position on an aryl group and the X-ray crystal structure of these molecules.

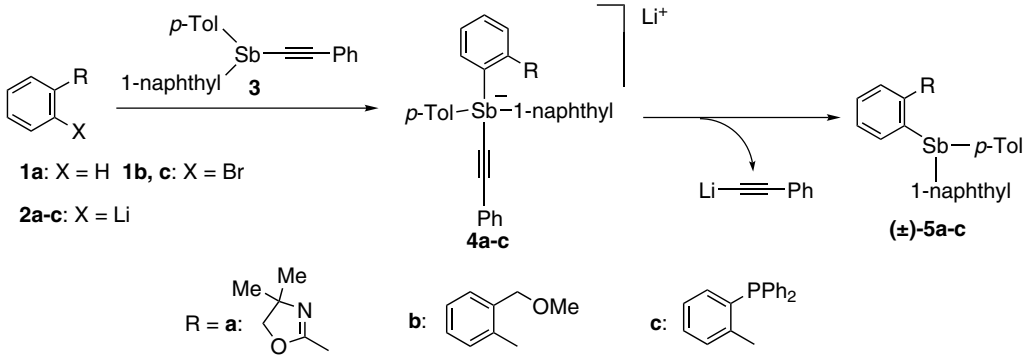
2. Results and discussion

2.1. Preparation of Sb-chirogenic stibanes

The Sb-chirogenic antimony compounds (**5a**–**c**) discussed in this paper were prepared according to the general route based on the modified method reported by us previously [6]. The synthetic route is shown in Scheme 1, and the results including the reaction conditions are listed in Table 1. Reaction of (1-naphthyl)(phenylethynyl)(*p*-tolyl)stibane (**3**) with excess (2–5 equiv.) of aryllithium reagents (**2a**–**c**) generated from **1a**–**c** and *n*-BuLi at low temperature brought about nucleophilic displacement of the phenylacetylene moiety on **3** into aryl groups to afford (±)-**5a**–**c** in good yields. We have recently reported that a thermodynamically more stable organolithium species is preferentially released in the ligand exchange reactions involving such intermediate as **4a**–**c**. In the present reaction, predominant elimination of the ethnyl group over the other three aryl groups occurred with the formation of phenylethnyllithium which is more stable than aryllithium.

2.2. Resolution of Sb-chirogenic stibanes via separation of a diastereomeric mixture of their palladium complex

We have recently reported a useful route for resolution of racemic stibindoles via separation of a diastereomeric mixture of the antimony–palladium complex formed from the reaction of the stibindoles with an optically active *ortho*-palladated benzylamine derivative as a preliminary communication [7]. According to this finding, we performed the separation of these new open-chain Sb-chirogenic antimony compounds [(±)-**5a**–**c**] via antimony–palladium complexes. Treatment of (±)-**5a**–**c** with di-μ-dichloro-bis{(*S*)-2-[(dimethylamino)methyl]phenyl-C^1,*N*}dipalladium(II) resulted in coordination of the antimony to the palladium to form antimony–palladium complexes. However, all attempts to separate the diastereomeric mixture by fractional recrystallization from a variety of solvents or by column chromatography have been unsuccessful. Therefore, we altered the resolving reagent from the *ortho*-palladate benzylamine derivative to di-μ-chlorobis[(*S*)-dimethyl(1-ethyl-α-naphthyl)aminato-C^2,*N*]dipalladium(II) (**6**). The reaction of (±)-**5a**–**c** with **6** in dichloromethane at room temperature resulted in the coordination to give rise to a diastereomeric mixture of the palladium complexes (**7a**–**c**) in almost quantitative yields. In the case of **7a**, the TLC analysis on silica gel showed a large difference in R_f values between both diastereomers [$R_f = 0.43$ for **7aA** and 0.21 for **7aB** (dichloromethane:ether = 20:1)], and the mixture could be easily separated into diastereomerically pure **7aA** (less polar) and **7aB** (polar) by silica gel column chromatography using the same solvent system for TLC as an eluent. Similar chromatographic separation of **5b**–palladium complex (**7b**) afforded **7bA** (less polar) and **7bB** (polar) in good yield. Unfortunately, many attempts to separate the mixture of **5c**–palladium complex (**7c**) having a phosphorous moiety were unsuccessful so far. The diastereomerically pure palladium complexes **7aA** and **7aB** bearing an oxazoline ring were obtained as yellow foams, whereas those of **7bA** and



Scheme 1.

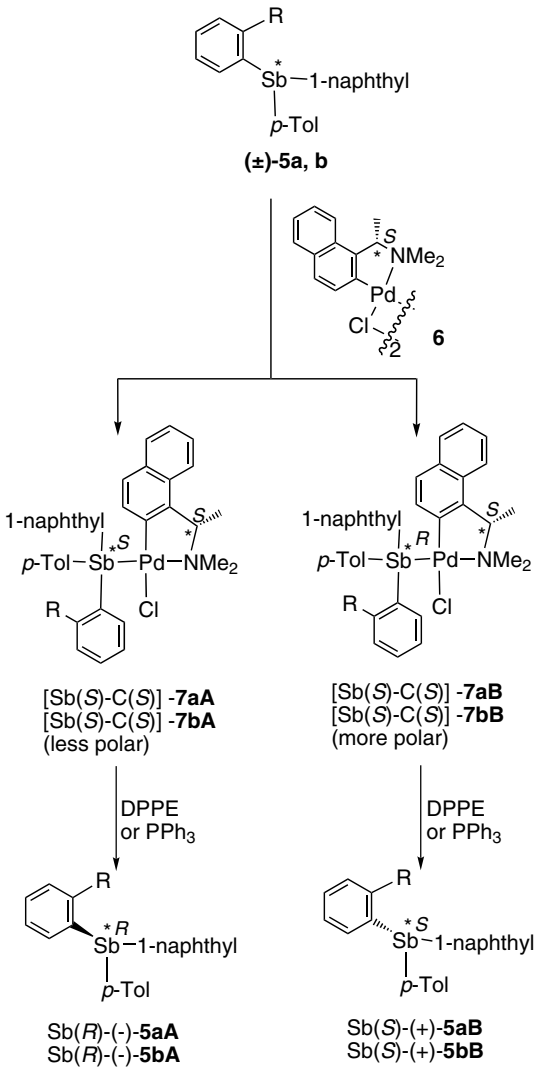
Table 1
Nucleophilic displacement reaction of (1-naphthyl)(phenylethynyl)(*p*-tolyl)stibane (**3**) with aryllithium reagents (**2**)

Aryllithium (equiv.)	Time (h)	Temp. (°C)	Product	Yield (%)	Appearance
2a (5.0)	4	0	(±)-**5a**	73	Mp. 148–150 °C
2b (2.0)	2	−20	(±)-**5b**	90	Mp. 93.5–95 °C
2c (3.0)	2	−80 to −20	(±)-**5c**	88	Colorless oil

7bB having a methoxymethyl group were isolated as yellow prisms (see Scheme 2).

We next performed the decomplexation of the palladium complexes **7aA**, **7aB**, **7bA** and 7**bB** to obtain enantiomerically pure Sb-chirogenic stibanes (+)- and (−)-(**5a**,**b**). Thus, the oxazoline-substituted palladium complexes **7aA** and **7aB**, on treatment with 1,2-bis(diphenylphosphino)ethane in dichloromethane, brought about an easy ligand exchange reaction to afford enantiomerically pure Sb-chirogenic stibanes (−)-**5aA** {m.p. 139–142 °C, $[\alpha]_D^{24} = -14.8°$} and (+)-**5aB** {m.p. 139–141 °C, $[\alpha]_D^{24} = +14.3°$}, respectively, in excellent yields. The decomplexation of methoxymethyl group-substituted stibanes **7bA** and 7**bB** was also achieved by their reaction with triphenylphosphine giving rise to the corresponding palladium-free (−)-**5bA** {Colorless oil, $[\alpha]_D^{24} = -9.0°$} and **5bB** {Colorless oil, $[\alpha]_D^{24} = +8.7°$}, respectively.

The absolute configurations on the antimony center of these optically pure Sb-chirogenic stibanes could be determined to be *R* for (−)-**5aA** and *S* for (+)-**5aB** by the single crystal X-ray analysis of **5aB**, and those of (−)-**5bA** and (+)-**5bB** were inevitably assigned to be *R* for (−)-**5bA** and *S* for (+)-**5bB** on the basis of the result of the X-ray analysis of **7bB** noted in the following section.



Scheme 2.

2.3. X-ray crystal structures of Sb-chirogenic stibanes

In order to gain deeper insight into the stereochemistry of the palladium complexes (**7**) and optically pure stibanes (**5**), single crystal X-ray analyses of **7bB** and **5aB** were made, and the results are shown in Fig. 1 and Table 2 for **7bB**, and Fig. 2 and Table 3 for **5aB**.

In the molecular structure of **7bB**, only the antimony atom coordinates to the palladium on the *ortho*-palladated naphthylethylamine derivative with the bond length of Pd–Sb to be 2.5221(6) Å. Also apparent is that the antimony and the nitrogen on the palladacycle develop a *trans* relationship with the bond angles of N–Pd–Sb to be 178.54(12)°, and the palladium of **7bB** adopts square-planar geometry. Similar relationship was observed in the crystal structure of the palladium complex of 1-phenylstibindole [7]. It also appeared that the antimony atom in **7bB** has *R*-configuration. It is noteworthy that an intramolecular coordination between the antimony and oxygen atoms (Sb···O: 3.00 Å) is observed in the crystal structure of **7bB**, and the central antimony is in the *quasi*-tetrahedral (TH) geometry.

Single crystal X-ray analysis of **5aB** revealed its *S*-configuration at the Sb-chiral center and the presence of

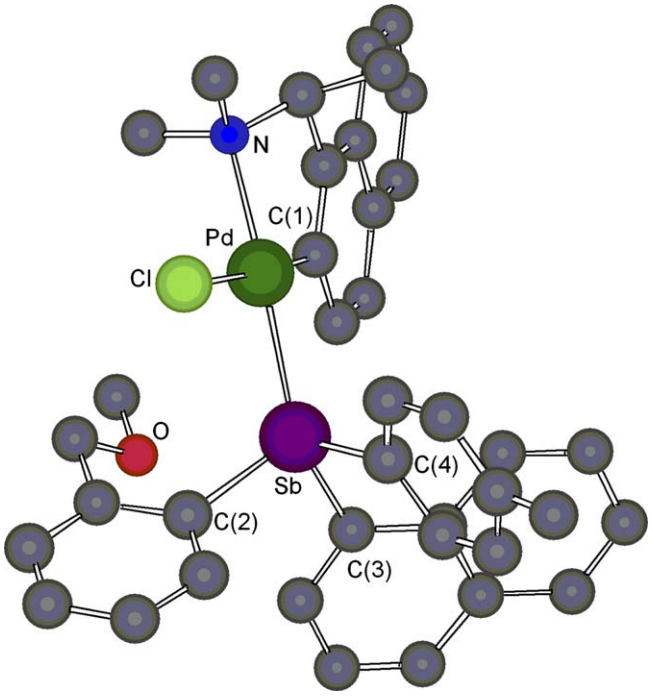


Fig. 1. Molecular structure of Sb(*S*),C(*S*)-**7bB**. All hydrogen atoms and benzene molecule in the crystal were omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for **7bB**

Bond lengths	
N–Pd	2.126(4)
Pd–C(1)	2.006(5)
Pd–Cl	2.3956 (11)
Pd–Sb	2.5221(6)
Sb–C(2)	2.133(5)
Sb–C(3)	2.132(5)
Sb–C(4)	2.137(5)
Sb–O	3.001(4)
Bond angles	
N–Pd–Cl	94.75(11)
N–Pd–C(1)	81.04(17)
Sb–Pd–Cl	84.21(3)
Sb–Pd–C(1)	99.94(13)
N–Pd–Sb	178.54(12)
C(1)–Pd–Cl	174.57(12)
Pd–Sb–C(2)	115.09(14)
Pd–Sb–C(3)	127.82(12)
Pd–Sb–C(4)	112.60(12)
C(2)–Sb–C(3)	100.99(18)
C(2)–Sb–C(4)	96.98(17)
C(3)–Sb–C(4)	98.08(17)

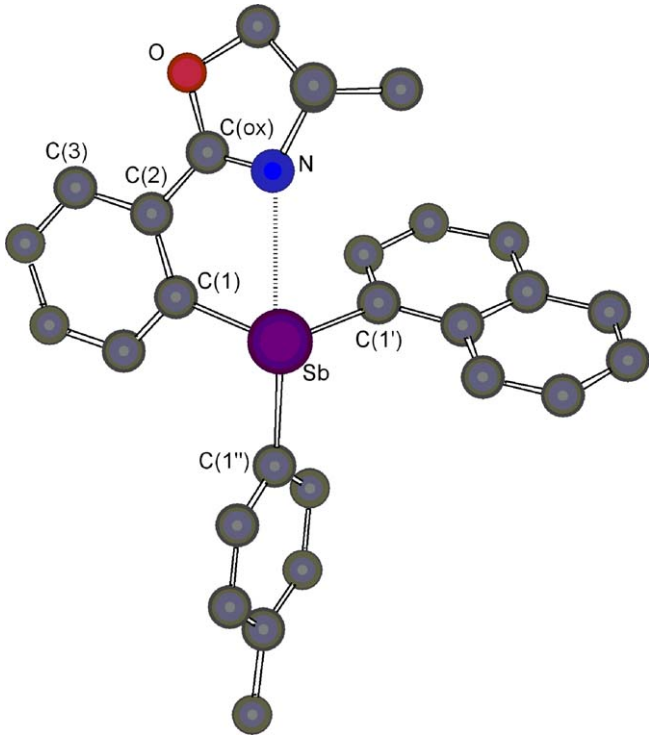


Fig. 2. Molecular structure of Sb(*S*)-(+)-**5aB**. All hydrogen atoms were omitted for clarity.

an intramolecular coordination between the antimony and nitrogen atoms; the distance between the antimony and nitrogen atoms is 2.813(4) Å, which corresponds to 75% of the sum of the van der Waals radii of both elements and accords with 133% of the covalent bond length (2.11 Å) [8]. The central antimony atom exhibits a

Table 3
Selected bond lengths (Å) and bond angles (°) for **5aB**

Bond lengths	
Sb–C(1)	2.177(5)
Sb–C(1′)	2.170(5)
Sb–C(1″)	2.183(5)
Sb–N	2.813(4)
Bond angles	
C(1)–Sb–C(1′)	100.3(2)
C(1)–Sb–C(1″)	94.5(2)
C(1′)–Sb–C(1″)	93.8(2)
C(1)–Sb–N	70.3(2)
C(1′)–Sb–N	76.9(2)
C(1″)–Sb–N	160.0(2)
Dihedral angles	
Sb–C(1)–C(2)–C(ox)	12.7(6)
C(1)–C(2)–C(ox)–N	7.7(8)
C(3)–C(2)–C(ox)–O	8.3(7)

pseudo-trigonal bipyramid (TBP) structure, and C(1″) on the tolyl group and the nitrogen on the oxazoline ring lie approximately *trans* to each other with the bond angle of N–Sb–C(1″) to be 160.0(2)°. These results showed that, in the structure of **5aB**, the 1-naphthyl and oxazoline-substituted aryl groups occupy an equatorial position with a pair of electrons on antimony, and the nitrogen on the oxazoline ring and the *p*-tolyl group adopt apical position. The bond distance between the antimony and C(1″) [2.183(5) Å] which hold apical positions is slightly longer than those of Sb–C(1) [2.177(5) Å] and Sb–C(1′) [2.170(5) Å]. These results are consistent with our previous reports for the TBP structure in organoantimony compounds having intramolecular interaction [9]. It is well known that a more electronegative substituent tends to prefer an apical position and the apical bond is longer than that of the equatorial bond in the TBP structure [10]. Taking these facts and our above finding into account, the *p*-tolyl group is considered to be more electronegative than the 1-naphthyl group, although their steric factor could not be accounted for. To the best of our knowledge, this is the first example for disclosing the existence of an intramolecular interaction between antimony and sp^2-nitrogen atoms, although trivalent organoantimony compounds bearing an aryl group with NMe_2 or CH_2NMe_2 substituent in the *ortho*-position have been widely reported to have the interaction between the antimony and sp^3-nitrogen atoms [9,11]. The small torsional angles of C(1)–C(2)–C(ox)–N [7.7(8)°] and C(3)–C(2)–C(ox)–O [8.3(7)°] indicate that the planes of the dimethyl-2-phenyl-2-oxazoline and its phenyl rings lie in nearly horizontal geometry.

Some group 15 and 16 compounds having intramolecular interactions (hypervalent compounds) underwent intramolecular positional isomerization of the substituents on the heavier atom [11]. However, the enantiomerically pure Sb-chirogenic stibanes **5aA**, **5bA**, **5bA**, and **5bB** isolated here were stereochemically stable, and no racemization took place on the chiral antimony centers even when they

were allowed to stand at room temperature for over 72 h in chloroform, which could be ascertained by measuring the change of their optical rotation.

3. Conclusion

We have presented here a versatile synthetic route of enantiomerically pure open-chain Sb-chirogenic organoantimony compounds having a heteroatom moiety on an aryl group. The racemic stibanes synthesized by nucleophilic displacement of the ethynyl moiety on (α-naphthyl)(phenylethynyl)(*p*-tolyl)stibane with appropriate aryllithium reagents could be easily separated via their palladium complexes. The enantiomerically pure Sb-chirogenic stibanes isolated here were stereochemically stable and no racemization took place even if the stibanes bear the fourth ligand with intramolecular coordination. Along with these findings, the structures of the antimony–palladium complex of **7bB** and Sb-chirogenic stibane Sb(*S*)-(+)-**5aB** were made clear by their single crystal X-ray analyses. These analyses also revealed the presence of intramolecular coordination between the antimony and the oxygen in the palladium complex **7bB**, and that of antimony···sp^2-nitrogen coordination in the palladium-free Sb(*S*)-(+)-**5aB** in the crystal state.

4. Experimental

4.1. General

Reactions requiring anhydrous conditions were performed with the usual precaution for rigorous exclusion of air and moisture 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. ^{1}H 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 JEOL JNM-EX-90 (90 MHz) and JEOL JNM-ECP500 (500 and 125 MHz) spectrometers in $CDCl_3$ unless otherwise stated. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 μA). Optical rotations were measured on a JUSCO DIP-370 digital polarimeter. All chromatographic separations were accomplished with Silica Gel 60 N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey-Nagel Pre-coated TLC plates Sil G25 UV_{254}. 1-Bromo-2-methoxymethylbenzene (**1b**) [12], (2-bromophenyl)diphenylphosphane (**1c**) [13], (phenylethynyl)(1-naphthyl)(*p*-tolyl)stibane (**3**) [6b] and (+)-di-μ-chlorobis{(*S*)-2-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}dipalladium(II) (**6**) [14] were prepared according to the reported procedures. 4,4-Dimethyl-2-phenyl-2-oxazoline (**1a**) was purchased from the Sigma–Aldrich Japan. *n*-Butyl lithium (*n*-BuLi: 1.51–1.60 M solution in hexane) was obtained from Kanto Chemical Co., Inc. Japan.

4.2. Nucleophilic displacement of (1-naphthyl)-(phenylethynyl)(p-tolyl)stibane (3) with aryllithiums (2a–c)

4.2.1. (±)-4,4-Dimethyl-2-{2-[(1-naphthyl)(4-tolyl)-stibano]phenyl}-1,3-oxazoline (5a)

To a stirring solution of aryllithium (**2a**) [15], generated from 4,4-dimethyl-2-phenyl-2-oxazoline (**1a**: 3.50 g, 20 mmol) and *n*-BuLi (1.57 M solution in hexane, 14 mL, 22 mmol) in anhydrous ether (60 mL), solids of (1-naphthyl)(phenylethynyl)(*p*-tolyl)stibane (**3**: 1.76 g, 4 mmol) was added in small portions over 40 min at 0 °C. After stirring for 6 h at the same temperature, the reaction mixture was diluted with ether (50 mL) and water (50 mL). The organic layer was separated and the aqueous layer was extracted with ether (50 mL). The combined organic solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was subjected to column chromatography on silica gel with a mixture of hexane–dichloromethane (4:1) to give (±)-**5a** as colorless prisms (1.50 g, 73%), m.p. 148–150 °C (from ethanol–dichloromethane). ^{1}H NMR (500 MHz) δppm: 0.75 (3H, s), 1.07 (3H, s), 2.31 (3H, s), 3.91 (2H, s), 7.07 (2H, d, $J = 8.3$ Hz), 7.21–7.46 (9H, m), 7.78 (1H, d, $J = 7.8$ Hz), 7.83–7.85 (1H, m), 7.92 (1H, d, $J = 7.8$ Hz), 8.34–8.37 (1H, m). ^{13}C NMR (125 MHz) δppm: 21.37 (q), 27.82 (q), 28.16 (q), 79.31 (t), 125.37 (d), 125.65 (d), 126.23 (d), 128.12 (s), 128.20 (d), 138.55 (d), 128.70 (d), 129.34 (d), 129.42 (s), 130.89 (d), 132.52 (s), 133.59 (s), 134.86 (d), 136.54 (d), 137.24 (d), 137.49 (d), 137.97 (d), 139.16 (s), 142.70 (s), 144.01 (s), 162.49 (s). EI-MS (relative intensity) *m/z*: 513 (M^+, 0.6), 422 (85), 386 (100), 349 (42), 314 (52), 247 (13). Anal. Calc. for $C_{28}H_{26}NOSb$: C, 65.40; H, 5.10; N, 2.72. Found: C, 65.40; H, 5.20; N, 2.72%.

4.2.2. (±)-(2-Methoxymethylphenyl)(1-naphthyl)-(p-tolyl)stibane (5b)

To a stirring solution of aryllithium (**2b**) [16], generated from 1-bromo-2-methoxymethylbenzene (**1b**) (3.02 g, 15 mmol) and *n*-BuLi (1.57 M solution in hexane, 9.3 mL, 14.6 mmol) in anhydrous ether (40 mL), solids of **3** (3.31 g, 7.5 mmol) was added in small portions over 50 min at −20 °C. After stirring for 2 h at the same temperature, the reaction mixture was allowed to stand for 1 h at r.t. The mixture was diluted with ether (150 mL) and water (100 mL). The resulting organic layer was separated and the aqueous layer was extracted with ether (50 mL). The combined organic solution was washed with brine, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel with a mixture of hexane–dichloromethane (4:1) to give (±)-**5b** as colorless prisms (3.10 g, 90%), m.p. 93.5–95 °C (from hexane–benzene). ^{1}H NMR (500 MHz) δppm: 2.33 (3H, s), 3.11 (3H, s), 4.56 (2H, s), 7.08–7.12 (6H, m), 7.19 (1H, d, $J = 6.4$ Hz), 7.24–7.36 (6H, m), 7.41–7.48 (2H, m), 7.82 (1H, d,

$J = 7.8$ Hz), 7.85 (1H, d, $J = 7.8$ Hz), 8.18 (1H, d, $J = 8.2$ Hz). ^{13}C NMR (125 MHz) δppm: 21.39 (q), 57.50 (q), 76.31 (t), 125.66 (d), 126.00 (d), 126.20 (d), 128.25 (d), 128.38 (d), 138.47 (d), 128.79 (d), 128.90 (d), 129.20 (d), 129.64 (d), 133.68 (s), 134.31 (s), 135.50 (d), 136.69 (d), 137.17 (d), 137.85 (s), 138.20 (s), 138.54 (s), 139.47 (s), 143.62 (s). EI-MS (relative intensity) *m/z*: 460 (M^+, 53), 369 (26), 333 (100), 342 (42), 212 (21). Anal. Calc. for $C_{25}H_{23}OSb$: C, 65.11; H, 5.03. Found: C, 65.15; H, 5.14%.

4.2.3. (±)-(2-Diphenylphosphinophenyl)(1-naphthyl)-(p-tolyl)stibane (**5c**)

To a stirring solution of aryllithium (**2c**) [13b], generated from (2-bromophenyl)diphenylphosphane (**1c**) (1.02 g, 3 mmol) and *t*-BuLi (1.41 M solution in hexane, 4.25 mL, 6 mmol) in anhydrous ether (30 mL), solids of **3** (440 mg, 1.0 mmol) was added in small portions over 25 min at −80 °C. After stirring for an additional 30 min, the reaction mixture was allowed to warm slowly to −20 °C. The mixture was diluted with benzene (50 mL) and water (30 mL). The organic layer was separated and the aqueous layer was extracted with benzene (30 mL). The combined organic solution was washed with brine, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel with a mixture of hexane–benzene (5:1) to give (±)-**5c** as colorless oil (528 mg, 88%). ^{1}H NMR (500 MHz) δppm: 2.31 (3H, s), 7.08 (2H, d, $J = 6.4$ Hz), 7.12–7.27 (17H, m), 7.32 (1H, d, $J = 6.4$ Hz), 7.38 (1H, t, $J = 7.6$ Hz), 7.44 (1H, t, $J = 7.6$ Hz), 7.77 (1H, d, $J = 8.2$ Hz), 7.82 (1H, d, $J = 8.2$ Hz), 8.04 (1H, d, $J = 8.2$ Hz). ^{13}C NMR (125 MHz) δ ppm: 21.36 (q), 125.07 (d), 125.62 (d), 125.94 (d), 126.13 (d), 128.22 (d, $J_{C,P}$), 128.46 (d), 128.71 (d), 128.87 (d), 129.01 (d), 129.64 (d), 129.76 (d), 130.13 (d), 133.51 (d, $J_{C,P}$), 133.62 (d, $J_{C,P}$), 134.14 (s), 135.85 (d), 136.52 (s), 136.91 (d), 137.73 (s), 138.14 (s), 141.75 (d). EI-MS (relative intensity) *m/z*: 600 (M^+, 100), 523 (63), 473 (88), 382 (19), 183 (64). EI-HRMS *m/z*: 600.0963 (Calc. for $C_{35}H_{28}PSb$: 600.0967).

4.3. Preparation and separation of diastereomerically pure Sb(R)- and Sb(S)-(aryl)(1-naphthyl)(p-tolyl)stibane–palladium complexes (7)

4.3.1. Sb(R)- and Sb(S)-4,4-dimethyl-2-{2-[(1-naphthyl)-(4-tolyl)stibano]phenyl}-1,3-oxazoline–palladium complexes (**7aA**, **7aB**)

To a stirring solution of (±)-**5a** (1.0 g, 2 mmol) in dichloromethane (5 mL), solids of (+)-di-μ-chlorobis{(*S*)-2-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}dipalladium(II) (**6**: 677 mg, 1 mmol) was added 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 separated by silica gel column chromatograph with dichloromethane–ether (20:1) to give a mixture of (+)- and (−)-**5a** (160 mg, 16%, colorless oil, $R_f = 0.90$), Sb(*S*),C(*S*)-**7aA** (512 mg, 30%), and Sb(*S*), C(*S*)–**7aB** (836 mg, 49%). The palladium-free (+)- and (−)-**5a** {$[\alpha]_D^{24} = -13.1°$ (c 1.0, chloroform), 88.5 %ee} were formed by the decomplexation of **7aA** and **7aB** during chromatographic separation, indicating **7aA** was more susceptible to depalladation than **7aB** under these separation conditions. **7aA**: yellow oil, $R_f = 0.43$ (dichloromethane:ether = 20:1), $[\alpha]_D^{24} = +63.5°$ (c 1.0, chloroform). ^{1}H NMR (90 MHz) δ ppm: 1.00 (6H, br-s), 1.99 (3H, d, $J = 5.1$ Hz), 2.32 (3H, s), 2.79 (6H, s), 3.91 (2H, s), 4.15–4.40 (1H, m), 6.97–8.80 (21H, m). FAB-MS (relative intensity) *m/z*: 855 ($M + 1^+$, 0.9), 819 (9), 422 (35), 386 (96), 295 (12), 198 (100). FAB-HRMS *m/z*: 855.1141 (Calc. for $C_{42}H_{42}ClN_2OPdSb$: 855.1147). **7aB**: yellow oil, $R_f = 0.21$ (dichloromethane:ether = 20:1), $[\alpha]_D^{24} = +3.63°$ (c 1.0, chloroform). ^{1}H NMR (90 MHz) δ ppm: 0.98 (6H, br-s), 1.85 (3H, d, $J = 5.9$ Hz), 2.32 (3H, s), 2.88 (3H, br-s), 2.89 (3H, br-s), 3.91–4.31 (3H, m), 6.81–8.48 (21H, m). FAB-MS (relative intensity) *m/z*: 855 ($M + 1^+$, 0.4), 819 (11), 422 (32), 386 (100), 295 (12), 198 (98). FAB-HRMS *m/z*: 855.1147 (Calc. for $C_{42}H_{42}ClN_2OPdSb$: 855.1147).

4.3.2. Sb(R)- and Sb(S)-(2-methoxymethylphenyl)-(1-naphthyl)(p-tolyl)stibane–palladium complexes (**7bA**, **7bB**)

The palladium complexes **7bA** and **7bB** were prepared according to the procedure described above from (±)-**5b** (1.84 g, 4.0 mmol) and **6** (1.36 g, 2.0 mmol). The crude product was separated by column chromatograph on silica gel using a mixture of dichloromethane–hexane (10:1) as an eluent to give diastereomerically pure **7bA** (1.53 g, 48%) and **7bB** (1.44 g, 45%). **7bA**: yellow prisms, m.p. 187–190 °C (from benzene–ether), $R_f = 0.48$ (dichloromethane:hexane = 10:1), $[\alpha]_D^{24} = +143.8°$ (c 1.0, chloroform). ^{1}H NMR (500 MHz) δppm: 1.93–2.01 (3H, m), 2.34 (3H, s), 2.86 (3H, s), 2.96 (3H, s), 3.05 (3H, s), 4.40–4.56 (3H, m), 6.88 (1H, d, $J = 8.4$ Hz), 7.09–7.92 (19H, m). FAB-MS (relative intensity) *m/z*: 766 ($M - Cl^+$, 12), 445 (2), 333 (9), 301 (7), 198 (100). FAB-HRMS *m/z*: 766.1110 (Calc. for $C_{42}H_{42}N_2OPdSb$: 766.1220). Anal. Calc. for $C_{39}H_{39}ClONPdSb$: C, 58.45; H, 4.91; N, 1.75. Found: C, 58.48; H, 5.30; N, 2.24%. **7bB**: yellow prisms m.p. 107–110 °C (from benzene–ether), $R_f = 0.34$ (dichloromethane:hexane = 10:1), $[\alpha]_D^{24} = +74.2°$ (c 1.0, chloroform). ^{1}H NMR (500 MHz) δ ppm: 1.91–2.03 (3H, m), 2.28 (3H, s), 2.77 (3H, s), 2.99 (3H, s), 3.29 (3H, s), 4.33 (1H, m), 5.02 (2H, br-s), 6.63 (1H, d, $J = 8.7$ Hz), 6.92 (1H, d, $J = 8.3$ Hz), 7.03–7.55 (15H, m), 7.65 (1H, d, $J = 8.7$ Hz), 7.82 (1H, d, $J = 7.8$ Hz). FAB-MS (relative intensity) *m/z*: 766 ($M - Cl^+$, 12), 445 (2), 333 (11), 301 (8), 198 (100). FAB-HRMS *m/z*: 766.1104 (Calc. for $C_{42}H_{42}N_2OPdSb$: 766.1220). Anal. Calc. for $C_{39}H_{39}ClONPdSb{+}C_6H_6$: C, 61.56; H, 5.17; N, 1.60. Found: C, 61.39; H, 5.15; N, 1.64%.

4.4. Preparation of enantiomerically pure Sb(R)- and Sb(S)-(aryl) (1-naphthyl)(p-tolyl)stibane (**5a,b**)

4.4.1. Sb(R)-(−)-4,4-dimethyl-2-{2-[(1-naphthyl)-(4-tolyl)stibano]phenyl}-1,3-oxazoline (**5aA**)

To a solution of diastereomerically pure palladium complex **7aA** (423 mg, 0.50 mmol) in benzene (10 mL), solids of 1,2-bis(dimethylphosphino)ethane (100 mg, 0.47 mmol, 0.94 equiv.) was added 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 chromatograph on silica gel using a mixture of hexane–dichloromethane (10:1) as an eluent to give (−)-**5aA**. Colorless prisms (174 mg, 72%), m.p. 139–142 °C (from ethanol–dichloromethane), $[\alpha]_D^{24} = -14.8^\circ$ (c 1.0, chloroform). The ^{1}H NMR spectrum of (−)-**5aA** was superimposable to that of (±)-**5a**.

4.4.2. Sb(S)-(+)-4,4-dimethyl-2-{2-[(1-naphthyl)-(4-tolyl)stibano]phenyl}-1,3-oxazoline (**5aB**)

Prepared according to the procedure described above from palladium complex **7aB** (713 mg, 0.83 mmol) and 1,2-bis(dimethylphosphino)ethane (283 mg, 0.71 mmol, 0.86 equiv.). The crude product was purified by column chromatograph on silica gel using a mixture of hexane–dichloromethane (10:1) as an eluent to give (+)-**5aB**. Colorless prisms (327 mg, 90%), m.p. 139–141 °C (from ethanol–dichloromethane), $[\alpha]_D^{24} = +14.3^\circ$ (c 1.0, chloroform). The ^{1}H NMR spectrum of (+)-**5aB** was superimposable to that of (±)-**5a**.

4.4.3. Sb(R)-(−)-(2-methoxymethylphenyl)(1-naphthyl)-(p-tolyl)stibane (**5bA**)

To a solution of the diastereomerically pure palladium complex **7bA** (799 mg, 1.0 mmol) in dichloromethane (10 mL), solids of triphenylphosphine (288 mg, 1.1 mmol, 1.1 equiv.) was added 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 chromatograph on silica gel using a mixture of hexane–dichloromethane (4:1) as an eluent to give (−)-**5bA**. Colorless oil (427 mg, 93%), $[\alpha]_D^{24} = -9.0^\circ$ (c 2.48, chloroform). The ^{1}H NMR spectrum of (−)-**5bA** was superimposable to that of (±)-**5b**.

4.4.4. Sb(S)-(+)-(2-methoxymethylphenyl)-(1-naphthyl)(p-tolyl)stibane (**5bB**)

Prepared according to the procedure described above from palladium complex **7bB** (799 mg, 1.0 mmol) and triphenylphosphine (288 mg, 1.1 mmol, 1.1 equiv.). The crude product was purified by column chromatograph on silica gel using a mixture of hexane–dichloromethane (4:1) as an eluent to give (+)-**5bB**. Colorless oil (437 mg, 95%), $[\alpha]_D^{24} = +8.7^\circ$ (c 2.5, chloroform). The ^{1}H NMR spectrum of (+)-**5bB** was superimposable to that of (±)-**5b**.

4.5. Crystallography

4.5.1. Crystal date for Sb(S)-(+)-**5aB**

Crystal dimensions $0.50 \times 0.40 \times 0.20$ mm; $C_{28}H_{26}NOSb$, $M_r = 514.27$; orthorhombic space group $P2_12_12_1$ (#19), $a = 8.1695(17)$, $b = 16.261(4)$, $c = 17.989(4)$ Å, $V = 2389.8(9)$ Å^3, $Z = 4$, $D_{calc} = 1.429$ g cm^{-3}, $T = -100$ °C, 14071 reflections measured, refinement based on 2709 reflections, $F_{000} = 1040$, goodness-of-fit = 1.120, number of parameters = 282, $R = 0.0210$ [$I > 2.00\sigma(I)$, $2\theta < 56.78$], $R_w = 0.0587$. Data were collected on a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods (SIR 97) [17] and expanded using Fourier techniques (DIRDIF-94) [18]. The structure was refined by the full-matrix least-squares refinement. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation [19]. Selected bond distances and angles are given in Table 1.

4.5.2. Crystal date for Sb(R),C(S)-**7bB**

Crystal dimensions $0.38 \times 0.12 \times 0.10$ mm; $C_{39}H_{39}ClNOPdSb \cdot C_6H_6$, $M_r = 879.42$; orthorhombic space group $P2_12_12_1$, $a = 14.080(3)$, $b = 16.036(3)$, $c = 18.171(4)$ Å, $V = 4103.0(15)$ Å^3, $Z = 4$, $D_{calc} = 1.424$ g cm^{-3}, $T = -173$ °C, 29045 reflections measured, refinement based on 9272 reflections, $F_{000} = 1776$, goodness-of-fit = 0.999, number of parameters = 7659, $R = 0.039$ [$I > 2.00\sigma(I)$], $R_w = 0.086$. The data were measured using a Bruker Smart CCD diffractometer, using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using the program SHELXS-97 [20]. The refinement and all further calculations were carried out using SHELXL-97 [20]. The hydrogen atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-square. Selected bond distances and angles are given in Table 2.

5. Supplementary material

Crystallographic data for the structural analysis of **5aB** and **7bB** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 291152 for Sb(*S*)-(+)-**5aB** and No. 291153 for Sb(*S*),C(*S*)-**7bB**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1233 336 033; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgments

Partial financial support for this work was provided by a Grant-in Aid for Scientific Research (C) (J.K.) and Grant-in Aid for Encouragement of Young Scientists from the Japan Society for the Promotion Science (JSPS), and Takeda

Scientific Foundation (S.Y.). This work supported was also provided by the "Academic Frontier" Project for Private Universities from the Ministry of Education, Culture, Sports, Science and Technology of Japan, 2005–2009 (S.Y.). Financial support was also provided by the Special Research Fund from Hokuriku University.

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