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Synthesis of Sb-chiral organoantimony compounds having intramolecular Sb···N interaction and their separation into optically pure compounds via *ortho*-palladated benzylamine complexes

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Abstract

A diastereomeric mixture of Sb-chiral triarylstibanes having an amine moiety on an aryl group, Sb(*R*/*S*)-(aryl)[2-(*S*)-(1-dimethylaminoethyl)phenyl](*p*-tolyl)stibanes (**4a**–**c**), has been prepared by stepwise nucleophilic displacement of the ethynyl groups on bis(phenylethynyl)(*p*-tolyl)stibane (**1**) with Grignard reagents **2a**–**c** and 2-[(*S*)-(dimethylamino)ethyl]phenyllithium. Although direct separation of the diastereomeric mixtures of **4** was unsuccessful, they could be separated with ease via their palladium complexes **6** formed from the reactions of the stibanes **4** with di-μ-dichlorobis(2-dimethylaminobenzyl-C^1,*N*)dipalladium(II) (**5**). The diastereomerically pure Sb-chiral stibanes isolated here were optically stable, and no racemization on the chiral antimony center was observed even when they were heated at 110 °C over 24 h in toluene or pyridine. The single X-ray crystal analysis of Sb(*S*)–[2-(*S*)-(1-dimethylaminoethyl)phenyl](1-naphthyl)(*p*-tolyl)stibane (**4b-B**) revealed the presence of intramolecular interaction between the antimony and nitrogen atoms.

Keywords: Antimony; Nucleophilic substitution; Sb-Chiral compounds; Palladium complexes; Optical resolution

1. Introduction

Stibanes bearing three different ligands have a chiral antimony center and are of considerable interest as potential chiral sources for the inductive generation of optical activity. On the other hand, a variety of optically pure P-chiral phosphanes [1,2] and As-chiral arsanes [3] have been reported to be effective chiral ligands for a wide range of transition metal-catalyzed asymmetric reactions. However, no report on Sb-chiral organoantimony (III) compounds (stibanes) has been presented because information for the preparation of Sb-chiral stibanes was unavailable till quite recently. In the course of our studies on optically active stibanes, we have recently established a new general method for the preparation of Sb-chiral stibanes based on stepwise nucleophilic displacement of the phenylethynyl moieties in bisethynylstibane with Grignard and/or organolithium reagents [4]. We also demonstrated efficient and stereoselective resolution of racemic Sb-chiral stibindoles via separation of a diastereomeric mixture of palladium complexes by use of optically active *ortho*-palladated benzylamine derivatives as the resolving agent [5]. As a further extension of this work, we now report the synthesis and X-ray crystal structure of some Sb-chiral triarylstibanes having intramolecular interaction between the antimony and nitrogen of the (*S*)-*N*,*N*-dimethylaminnoethyl moiety on an aryl group [6,7]. In the present study, the introduction of a 2-[(*S*)-1-(*N*,*N*-dimethylamino)ethyl]phenyl group onto the chiral antimony center as an additional chiral source led to a mixture of two diastereomers of **4**, which could be easily separated via their palladium complexes **6** formed from the reactions of the stibanes **4** with *ortho*-palladated benzylamine derivative **5**, although direct separation of the two diastereomers of **4** was unsuccessful.

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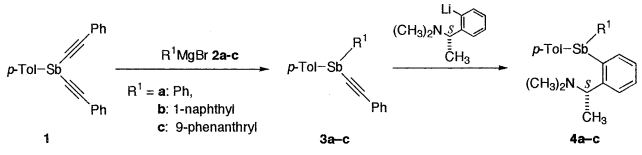
2. Results and discussion

According to our recent results [4] and knowing that *N*,*N*-dimethylbenzylamine forms a 2-lithio derivative by treatment with an alkyllithium reagent [8], diastereomerically pure Sb-chiral triarylstibanes having an amine moiety on an aryl group can be considered to arise from a stepwise nucleophilic displacement of the ethynyl moiety on bisethynylstibane **1** with Grignard and/or organolithium reagents, followed by separation of the resulting diastereomeric mixture.

The preparation of Sb-chiral triarylstibanes **4a**–**c** is shown in Scheme 1. Reaction of bis(phenylethynyl)(*p*-tolyl)stibane (**1**), prepared from dibromo(*p*-tolyl)stibane by treatment with 2 equiv. of phenylethynyllithium, with Grignard reagents (R^1MgBr; R^1 = **a**: phenyl, **b**: 1-naphthyl, and **c**: 9-phenanthryl) resulted in nucleophilic displacement of one ethynyl group on **1** to afford monoethynylstibanes **3a**–**c** in good yields. The reaction conditions and the results of these reactions are listed in Table 1. In these reactions, only one ethynyl group on **1** was displaced with the aryl group of the organomagnesium reagents, even when the reagents were used in excess (2 equiv.), except for the reaction with phenylmagnesium bromide (1.1 equiv.). When lithium reagents such as phenyllithium or 1-naphthyllithium were used instead of the magnesium reagents in the present reaction, both of the ethynyl groups on **1** were replaced to furnish diphenyl(*p*-tolyl)stibane and di(1-naphthyl)(*p*-tolyl)stibane, respectively. These results should be explained by the difference in reactivity between the organomagnesium and organolithium reagents, in that the nucleophilicity of magnesium reagents is weaker than that of lithium reagents. The absorptions at 2136–2139 cm^{-1} in the IR spectra for **3a**–**c** showed the presence of a carbon–carbon triple bond in their molecules.

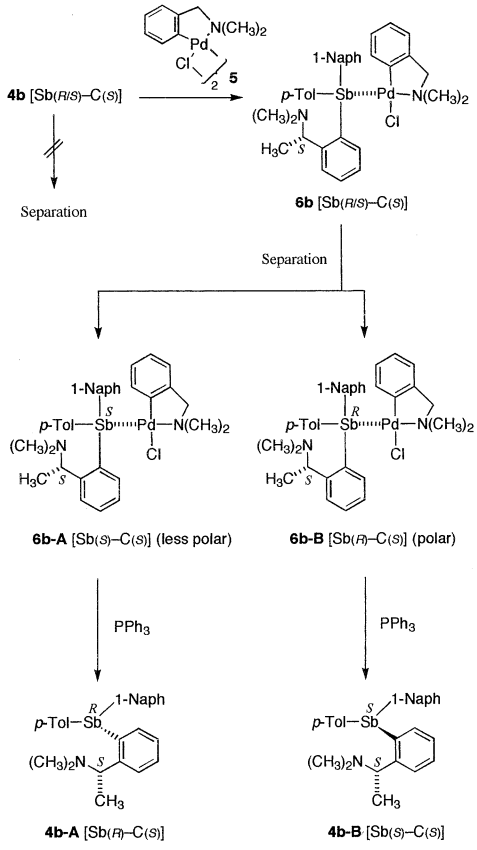
We have recently reported that the ethynyl group on monoethynylstibanes could be easily displaced by treatment with a variety of magnesium and/or lithium reagents and that, moreover, the latter reagents were superior to the former [4]. The displacement of the remaining ethynyl group on **3a**–**c** with a benzylamine moiety was carried out by use of a lithium reagent. The reaction of (*S*)-*N*,*N*-dimethyl-1-phenethylamine with *n*-butyllithium at room temperature over 24 h in dry ether resulted in the lithiation of the 2-position of the phenyl group to form a yellow solution of 2-[(*S*)-(dimethylamino)ethyl]phenyllithium. Subsequent treatment of the yellow solution with monoethynylstibanes **3a**–**c** gave the expected Sb-chiral stibanes **4a**–**c** in moderate yields. The ^{1}H-NMR spectrum of **4a**–**c** showed that all of the Sb-chiral triarylstibanes **4** obtained here consisted of an ca. 1:1 diastereomeric mixture. All attempts to separate the diastereomeric mixture of **4a**–**c** by column chromatography on silica gel or alumina by use of a variety of solvents as an eluent were unsuccessful. We have recently demonstrated a convenient resolution of racemic 2,2′-bis[di(*p*-tolyl)stibano]-1,1′-binaphthyl (BINASb) via a diastereomeric mixture of the antimony–palladium complex formed from the reaction of BINASb with optically active *ortho*-palladated benzylamine derivative and a large difference in R_f values on TLC was observed [9]. According to this finding, we next examined the separation of **4a**–**c** via antimony–palladium complexes. Reactions of the diastereomeric mixture of **4a**–**c** with di-μ-dichloro-bis{2-[(dimethylamino)methyl]phenyl-C^1,N}dipalladium(II) (**5**) in dichloromethane at room temperature resulted in coordination of the antimony to the palladium to give the palladium complexes **6a**–**c** as a yellow foam in almost quantitative yields. In spite of careful and elaborate attempts to separate the diastereomeric mixture of the palladium complexes **6a** on silica gel chromatography by use of various solvents (dichloromethane, hexane, benzene, ether, ethyl acetate, etc.) as eluents, the separation of it into each diastereomer was unsuccessful. But, in the case of **6b**, the TLC analysis on silica gel showed a large difference in R_f values between both diastereomers [R_f = 0.44 for **6b-A** and 0.27 for **6b-B** (hexane:dichloromethane:ether = 1:1:2)], and the diastereomeric mixture could be easily separated into diastereomerically pure **6b-A** (less polar) and **6b-B** (polar) by silica gel column chromatography with a 1:9 mixture of ether and dichloromethane as an eluent. Similar chromatographic separation of **6c** afforded **6c-A** (less polar) and **6c-B** (polar) in good yield. All of the diastereomerically pure palladium complexes **6b-A**, **6b-B**, **6c-A**, and **6c-B** were isolated as a yellow foam and their FABMS spectra showed the corresponding molecular ion peaks. We next performed the decomplexation of the palladium complexes **6** to obtain diastereomerically pure Sb-chiral stibanes **4**. Treatment of **6b-A** with 1.1 equiv. of triphenylphosphine in dichloromethane underwent ligand exchange reaction of the antimony moiety of the palladium complex with the phosphine to give the expected diastereomerically pure **4b-A** in almost quantitative yield. Similar reactions of the other palladium complexes **6b-B**, **6c-A**, and **6c-B** with the phosphine also afforded **4b-B**, **4c-A**, and **4c-B**, respectively. Although **4b-A** and **4c-B** were obtained as viscous oils, **4b-B** and **4c-A** were isolated as crystalline forms (Scheme 2).



Scheme 1.

Table 1
Arylation of the bis(phenylethynyl)(*p*-tolyl)stibane **1** with Grignard reagents; formation of the (aryl)(phenylethynyl)(*p*-tolyl)stibanes **3a**–**c**

Grignard reagent	Equivalent	Time (h) (temperature (°C))	Product	Yield (%)	Melting point (°C)
Phenyl–MgBr	1.1	6 (0)	**3a**	83	57–59
1-Naphthyl–MgBr	2.0	16 (r.t.)	**3b**	80	96–98
9-Phenanthryl–MgBr	2.0	12 (r.t.)	**3c**	91	153–155



Scheme 2.

In order to gain deeper insight into the stereochemistry of the products, a single crystal X-ray analysis of **4b-B** was made, and the results are shown in Fig. 1Table 3. These results revealed that **4b-B** has *S*-configuration at the Sb-chiral center, and an intramolecular interaction was present between the antimony and nitrogen atoms; the distance between the antimony and nitrogen atoms is 2.886(5) Å which corresponds to 77% of the sum of the van der Waals radii of both elements [10]. It is also apparent that the central antimony atom was in quasi-trigonal bipyramid (TBP) structure, and that C(1″) on the tolyl group and the nitrogen atom lie approximately *trans* to each other; the bond angle of N–Sb–C(1″) is 161.2(2)°. The bond distance between the antimony and C(1″) [2.184(6) Å] which adopts an apical position is slightly longer than those of Sb–C(1) [2.172(6) Å] and Sb–C(1′) [2.163(7) Å]. It has been reported that not only some organoantimony compounds having intramolecular interaction [11] but also five-coordinated λ^5-stibanes [12] have the TBP structure, in which the apical bonds were longer than the equatorial bonds. The intramolecular interactions between heavier elements and nitrogen, oxygen, or sulfur have been observed in a large number of Group 14 (Si, Ge, Sn), Group 15 (P, As, Sb, Bi), and Group 16 (S, Se, Te) compounds [13]. It is also known that some Group 15 and 16 compounds having intramolecular interactions (hypervalent compounds) underwent intramolecular positional isomerization of the substituents on the heavier atoms [8b, 14]. However, the diastereomerically pure Sb-chiral stibanes **4b**, **c-A** and **4b**, **c-B** isolated here were stereochemically stable, and no racemization took place on the chiral antimony centers even when they were heated at 110 °C over 24 h in toluene or pyridine.

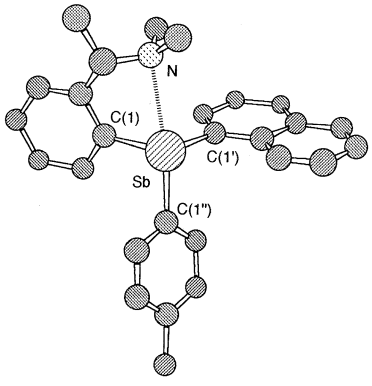


Fig. 1. Molecular structure of the triarylstibane **4b-B**. All hydrogen atoms were omitted for clarity.

3. Conclusion

To gain deeper insight into the stereochemical properties of Sb-chiral organoantimony compounds, we have studied the synthesis of triarylstibanes having an *N,N*-dimethylaminoethylphenyl group on the antimony atom and have shown that they could be obtained by stepwise displacement reaction of bisethynylstibane with organomagnesium and lithium reagents. We have also demonstrated that the resulted diastereomeric mixture of these compounds could be easily separated via their palladium complexes. This experimental technique for the separation of organoantimony compounds via a palladium

complex will be applicable to a wide range of the compounds that have ability to coordinate palladium or other transition metals. The diastereomerically pure Sb-chiral stibanes isolated here were stereochemically stable, and no racemization on the chiral antimony center took place even when they were heated at 110 °C over 24 h in solvents.

4. Experimental

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. Dibromo-*p*-tolylstibane (m.p. 83–85 °C) was prepared by a redistribution reaction of a 1:2 mixture of tri-*p*-tolylstibane and tribromostibane according to the literature method [15]. 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-GSX-400 (400 and 100 MHz) and JEOL JNM-ECP500 (500 and 125 MHz) spectrometers in $CDCl_3$ unless otherwise stated. IR spectra were recorded on a HORIBA FT-720 instrument. 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 JASCO 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}.

4.1. Preparation of bis(phenylethynyl)(p-tolyl)stibane (1)

All solvents used in this procedure (diethyl ether, hexane, water, benzene, and ethanol) were deaerated by stirring the solvents over 15 min under reduced pressure (20–100 mmHg) on cooling (−20 to 0 °C), and then by filling with argon at atmospheric pressure. This deaeration of the solvents was repeated three times before use.

To a stirred solution of phenylethynyllithium, generated from phenylacetylene (6.76 g, 66.3 mmol) and *n*-BuLi (1.60 M solution in hexane, 42 ml, 67.2 mmol) in anhydrous ether (200 ml), was added a solution of dibromo(*p*-tolyl)stibane (11.2 g, 30 mmol) in anhydrous ether (200 ml) dropwise over 1 h at −20 °C. After being stirred for an additional 1 h at the same temperature, the mixture was allowed to warm slowly at room temperature (r.t.), then the stirring was continued for an additional 16 h. Ether (200 ml) and water (100 ml) were added to the reaction mixture with stirring at 0 °C. The resulting organic layer was separated and the aqueous layer was extracted with hexane (200 ml × 2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The resulting solids were recrystallized from a mixture of benzene and ethanol (30–70 ml) to give **1** as white needles (11.1 g, 89% yield), m.p. 92–93 °C. ^{1}H-NMR (500 MHz) δ: 2.37 (3H, s), 7.25 (2H, d, $J = 7.8$ Hz), 7.82 (2H, d, $J = 7.8$ Hz), 7.25–7.35(6H, m), 7.45–7.55(4H, m). ^{13}C-NMR δ: 21.45 (q), 83.65 (s), 110.22 (s), 122.99 (s), 128.17 (d), 128.66 (d), 130.02 (d), 132.09 (d), 132.84 (s), 135.73 (d), 139.43 (s). IR (KBr) (cm^{-1}): 2140 ($\nu_{C\equiv C}$). EIMS (relative intensity) *m/z*: 414 [M$^+$, 17], 337 (15), 293 (65), 222 (base), 202 (52), 192 (42), 91 (26). EIHRMS *m/z*: 414.0378 (Calc. for $C_{23}H_{17}Sb$: 416.0368). Anal. Calc. for $C_{23}H_{17}Sb$: C, 66.54; H, 4.13. Found: C, 66.89; H, 4.02%.

The bisethynylstibane **1** obtained here is relatively susceptible to air and moisture, but can be stored in a refrigerator under argon atmosphere without any decomposition over 1 year.

4.2. Preparation of (aryl)(phenylethynyl)(p-tolyl)stibane (3)

4.2.1. (Phenyl)(phenylethynyl)(p-tolyl)stibane (3a)

To a stirred solution of **1** (2.08 g, 5 mmol) in ether (50 ml) was added a solution of phenylmagnesium bromide (**2a**, 1 M in THF, 5.5 ml, 5.5 mmol) over 10 min at 0 °C. After stirring for 6 h at the same temperature, the reaction mixture was diluted with hexane (100 ml) and water (50 ml). The resulting organic layer was separated and the aqueous layer was extracted with hexane (100 ml). The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel with a mixture of hexane and benzene (10:1) to furnish diphenyl(*p*-tolyl)stibane (63 mg, 3% yield) and **3a**, successively. Diphenyl(*p*-tolyl)stibane: colorless prisms (ethanol), m.p. 38–40 °C. ^{1}H-NMR (500 MHz) δ: 2.37 (3H, s), 7.14 (2H, d, $J = 8.2$ Hz), 7.29–7.32(6H, m), 7.33(2H, d, $J = 8.2$ Hz), 7.42–7.45 (4H, m). ^{13}C-NMR δ: 21.4 (q), 128.5 (d), 128.8 (d), 129.7 (d), 134.5 (s), 136.18 (d), 136.24 (d), 138.48 (s), 138.53 (s). EIMS (relative intensity) *m/z*: 366 [M$^+$, 18], 289 (15), 212 (29), 198 (base), 168 (54), 154 (20), 91 (24), 77 (15). EIHRMS *m/z*: 366.0373 (Calc. for $C_{19}H_{17}Sb$: 366.0368). Anal. Calc. for $C_{19}H_{17}Sb$: C, 62.16; H, 4.67. Found: C, 62.01; H, 4.76%. Compound **3a**: colorless prisms (ethanol). ^{1}H-NMR (500 MHz) δ: 2.33 (3H, s), 7.17 (2H, d, $J = 7.8$ Hz), 7.29–7.35 (6H, m), 7.50–7.52 (2H, m), 7.62 (2H, d, $J = 7.8$ Hz), 7.72 (2H, dd, $J = 7.8$ and 1.8 Hz). ^{13}C-NMR δ: 21.4 (q), 85.9 (s), 111.1 (s), 123.3 (s), 128.2 (d), 128.5 (d), 128.8 (d), 128.9 (d), 129.8 (d), 132.0 (d), 134.3 (s), 135.5 (d), 135.6 (d), 138.3 (s), 138.8 (s). IR (KBr) (cm^{-1}): 2136 ($\nu_{C\equiv C}$). EIMS (relative intensity) *m/z*: 390 [M$^+$, 77], 269 (65), 222 (43), 212 (56), 198 (73),

192 (base), 178 (71), 91 (27), 77 (20). EIHRMS *m/z*: 390.0366 (Calc. for $C_{21}H_{17}Sb$: 390.0368). Anal. Calc. for $C_{21}H_{17}Sb$: C, 64.49; H, 4.38. Found: C, 64.35; H, 4.52%.

4.2.2. (Phenylethynyl)(1-naphthyl)(*p*-tolyl)stibane (**3b**)

1-Naphthylmagnesium bromide (**2b**) was prepared from 1-bromonaphthalene (2.08 g, 10 mmol) and magnesium turnings (0.25 g, 10.5 mmol) in dry ether (80 ml) by the usual procedure. To this solution was added a solution of **1** (2.07 g, 5 mmol) in ether (20 ml) dropwise over 30 min at 0 °C, and the mixture was stirred for 16 h at r.t. After cooling, the reaction mixture was diluted with benzene (100 ml) and water (50 ml). The resulting organic layer was separated and the aqueous layer was extracted with benzene (100 ml). The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel with a mixture of hexane and benzene (10:1) to give (phenylethynyl)(1-naphthyl)(*p*-tolyl)stibane **3b**, colorless prisms (hexane–benzene 10:1). ^{1}H-NMR (500 MHz) δ: 2.30 (3H, s), 7.13 (2H, d, $J = 7.8$ Hz), 7.29–7.30 (3H, m), 7.43–7.51 (5H, m), 7.63 (2H, d, $J = 7.8$ Hz), 7.84 (2H, d, $J = 8.2$ Hz), 8.15 (2H, d, $J = 6.9$ Hz). ^{13}C-NMR δ: 21.4 (q), 85.0 (s), 112.1 (s), 123.4 (s), 125.8 (d), 126.2 (d), 126.5 (d), 128.2 (d), 128.3 (d), 128.5 (d), 129.0 (d), 129.5 (d), 129.9 (d), 132.0 (d), 133.3 (d), 133.9 (d), 135.5 (d), 135.9 (d), 137.1 (s), 137.8 (s), 138.8 (s). IR (KBr) (cm^{-1}): 2139 ($\nu_{C\equiv C}$). EIMS (relative intensity) *m/z*: 440 [M$^+$, 85], 319 (98), 248 (90), 228 (base), 212 (88), 192 (39), 127 (23), 91 (27). EIHRMS *m/z*: 440.0521 (Calc. for $C_{25}H_{19}Sb$: 440.0525). Anal. Calc. for $C_{25}H_{19}Sb$: C, 68.06; H, 4.34. Found: C, 68.04; H, 4.51%.

4.2.3. (9-Phenanthryl)(phenylethynyl)(*p*-tolyl)stibane (**3c**)

The reaction was carried out essentially the same as in the preparation of **3b** noted above, except for the use of 9-phenanthrylmagnesium bromide (**2c**) instead of **2b** as Grignard reagent. The reaction mixture resulted from the reaction of 9-bromophenanthrene (2.58 g, 10 mmol), magnesium turning (0.25 g, 10 mmol) and **1** (2.09 g, 5.0 mmol) in dry ether (total 150 ml) was separated by column chromatography on silica gel with a mixture of hexane and benzene (10:1) to give (9-phenanthryl)(phenylethynyl)(*p*-tolyl)stibane **3c**, white needles (hexane–benzene 10:1). ^{1}H-NMR (500 MHz) δ: 2.28 (3H, s), 7.12 (2H, d, $J = 7.3$ Hz), 7.27–7.32 (3H, m), 7.51–7.64 (6H, m), 7.66 (2H, d, $J = 7.3$ Hz), 7.83 (1H, d, $J = 7.8$ Hz), 8.15 (1H, d, $J = 7.8$ Hz), 8.47 (1H, brs), 8.63 (1H, d, $J = 8.2$ Hz), 8.69 (1H, d, $J = 8.2$ Hz). ^{13}C-NMR δ: 21.37 (q), 85.33 (s), 112.38 (s), 122.54 (d), 123.29 (d), 123.37 (s), 126.45 (d), 126.68 (d), 126.71 (d), 127.13 (d), 128.27 (d), 128.58 (d), 128.79 (d), 129.08 (d), 129.88 (d), 130.51 (s), 130.86 (s), 131.97 (d), 132.12 (s), 133.15 (s), 135.02 (s), 135.94 (d), 136.34 (s), 137.36 (d), 138.90 (s). IR (KBr) (cm^{-1}): 3139 ($\nu_{C\equiv C}$). EIMS (relative intensity) *m/z*: 490 [M$^+$, 41], 369 (30), 298 (41), 278 (base), 268 (16), 212 (33), 176 (17), 91 (8). EIHRMS *m/z*: 490.0681 (Calc. for $C_{29}H_{21}Sb$: 490.0681). Anal. Calc. for $C_{29}H_{21}Sb$: C, 70.90; H, 4.31. Found: C, 71.09; H, 4.59%.

4.3. General procedure for the preparation of (aryl)[2-(*S*)-(1-dimethylaminoethyl)phenyl](*p*-tolyl)stibanes (**4a–c**)

A mixture of (*S*)-*N*,*N*-dimethyl-1-phenylethylamine (9 mmol) and *n*-butyl lithium (1.56 M in hexane, 8.5 mmol) in ether (70 ml) was stirred for 24 h at r.t. To the resulting yellow solution which contained 2-[(*S*)-(1-dimethylamino)ethyl]phenyllithium, solids of **3a–c** (3 mmol) was added in small portions over 10 min at 0 °C. After stirring for 3 h at r.t., the reaction mixture was diluted with ether (100 ml) and water (25 ml). The resulting organic layer was separated and the aqueous layer was extracted with ether (50 ml). The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was subjected to column chromatography on silica gel with dichloromethane as an eluent to give **4a–c** as ca. 1:1 diastereomeric mixtures. Although these diastereomeric mixtures were not separated by column chromatography on silica gel or alumina using various solvents as eluent, they could be separated via their palladium complexes **6** shown below, except for **4a**. The results are listed in Table 2 and the spectral data for **4a** are shown below.

4.3.1. Sb(*R*/*S*)-[2-(*S*)-(1-dimethylaminoethyl)-phenyl](phenyl)(*p*-tolyl)stibane (**4a**)

^{1}H-NMR (500 MHz) δ: 1.36 (3H, d, $J = 6.9$ Hz), 1.812 (6H of one diastereomer, s), 1.814 (6H of the other diastereomer, s), 2.33 (3H, s), 3.78 (1H, q, $J = 6.9$ Hz), 7.10 (2H, d, $J = 7.6$ Hz), 7.14 (1H, br-t, $J = 7.6$ Hz), 7.23–7.35 (8H, m), 7.39–7.42 (1H, m), 7.44–7.46 (1H, m). EIMS (relative intensity) *m/z*: 437 [M$^+$, 4], 360 (base), 346 (63), 289 (3), 91 (10), 77 (5). EIHRMS *m/z*: 437.1108 (Calc. for $C_{23}H_{26}NSb$: 437.1103).

4.4. Typical procedure for the preparation of diastereomerically pure Sb(*R*)- and Sb(*S*)-(aryl)[2-(*S*)-(1-dimethylaminoethy)phenyl](*p*-tolyl)stibane–palladium complexes (**6**)

To a stirred solution of a diastereomeric mixture of **4a–c** (3 mmol) in dichloromethane (30 ml) was added solids of di-μ-dichlorobis(2-dimethylaminobenzyl-C^1,*N*)dipalladium(II) (**5**) (1.5 mmol) in small portions at r.t. 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 the solvents shown below as

Table 2
Arylation of the (aryl)(phenylethynyl)(*p*-tolyl)stibanes **3a**–**c**; formation of the Sb(*R*/*S*)-(aryl)[2-(*S*)-(1-dimethylaminoethyl)phenyl](*p*-tolyl)stibanes **4a**–**c**

3 (R^1)	Product	Yield (%)	Melting point (°C)	$[\alpha]_D$ (c 2, benzene) (temprature (°C))
3a (Phenyl-)	Sb(*R*/*S*)-**4a**	47	oil	+9.6°(26)
3b (1-naphthyl-)	Sb(*R*/*S*)-**4b**	69	113–115	−2.5°(24)
3c (9-phenanthryl-)	Sb(*R*/*S*)-**4c**	57	175.5–177	+29.7°(25)

eluents to give (aryl)[2-(*S*)-(1-dimethylaminoethyl)phenyl](*p*-tolyl)stibane–palladium complexes **6a**–**c**.

4.4.1. Sb(*R*/*S*)-[2-(*S*)-(1-dimethylaminoethyl)-phenyl](phenyl)(*p*-tolyl)stibane–palladium complex (**6a**)

Chromatographic separation of the reaction mixture obtained from the reaction of **4a** with **5** on silica gel using a mixture of ether and dichloromethane (1:9) as an eluent afforded **6a** (2.10 g, 98% yield) as a 1:1 diastereomeric mixture. Many attempts to separate this diastereomeric mixture by column chromatography on silica gel and alumina using a variety of solvents as an eluent were unsuccessful. Compound **6a**: Yellow foam, ^{1}H-NMR (500 MHz) δ: 1.19 (3H, d, $J = 5.5$ Hz), 1.96 (6H, s), 2.30 (3H of one diastereomer, s), 2.34 (3H of the other diastereomer, s), 2.86 (6H, s), 4.05 (2H, br-s), 4.19 (1H, m), 6.42 (1H, m), 6.86 (2H, m), 7.01 (1H, d, $J = 6.9$ Hz), 7.07 (1H, d, $J = 7.3$ Hz), 7.14 (1H, d, $J = 7.3$ Hz), 7.21–7.42 (7H, m), 7.60 (1H, m), 7.74 (2H, d, $J = 6.0$ Hz), 7.85 (1H, d, $J = 5.0$ Hz). FABMS (relative intensity) *m*/*z*: 715 ($[M+1]^+$, 4), 679 (5), 438 (8), 436 (8), 360 (73), 346 (40), 154 (MNBA, base), 148 (73), 91 (22). FABHRMS *m*/*z*: 715.0880 (Calc. for $C_{32}H_{39}ClN_2PdSb$: 715.0881).

4.4.2. Sb(*S*)-(**6b-A**) and Sb(*R*)-[2-(*S*)-(1-dimethylaminoethyl)phenyl](1-naphthyl)(*p*-tolyl)stibane–palladium complexes (**6b-B**)

Chromatographic separation of the reaction mixture obtained from the reaction of **4b** with **5** on silica gel using a mixture of ether and dichloromethane (1:9) as an eluent afforded diastereomerically pure **6b-A** (1.30 g, 53% yield) and **6b-B** (0.98 g, 43% yield), successively. Compound **6b-A**: Yellow foam, $R_f = 0.44$ (hexane:dichloromethane:ether = 1:1:2). ^{1}H-NMR (400 MHz) δ: 1.27 (3H, d, $J = 5.9$ Hz), 1.77 (6H, br-s), 2.29 (3H, s), 2.54 (3H, s), 2.99 (3H, s), 3.48 (1H, d, $J = 13.2$ Hz), 4.56 (1H, d, $J = 13.2$ Hz), 5.33 (1H, q, $J = 5.9$ Hz), 6.48 (1H, t, $J = 7.4$ Hz), 6.86 (1H, t, $J = 7.0$ Hz), 6.93–7.01 (4H, m), 7.12 (1H, d, $J = 7.3$ Hz), 7.20–7.48 (8H, m), 7.60 (1H, d, $J = 6.6$ Hz), 7.85 (1H, d, $J = 7.0$ Hz), 7.90 (1H, d, $J = 8.4$ Hz), 8.97 (1H, d, $J = 8.1$ Hz). $[\alpha]_D^{27}$ +58.2 (c 2, benzene). FABMS (relative intensity) *m*/*z*: 765 ($[M+1]^+$, 3), 729 (4), 486 (11), 396 (29), 360 (base), 148 (73), 134 (53), 91 (16). FABHRMS *m*/*z*: 765.1035 (Calc. for $C_{36}H_{41}ClN_2PdSb$: 765.1039). **6b-B**: Yellow foam, $R_f = 0.27$ (hexane:dichloromethane:ether = 1:1:2). ^{1}H-NMR (400 MHz) δ: 1.30 (3H, d, $J = 5.9$ Hz), 1.73 and 1.97 (2H and 4H, each br-s), 2.29 (3H, s), 2.86 (6H, br-s), 4.02 (1H, d, $J = 13.2$ Hz), 4.14 (1H, d, $J = 13.2$ Hz), 4.65 (1H, br.q), 6.15 (1H, br-t), 6.73 (2H, m), 6.86–7.38 (10H, m), 7.53 (1H, d, $J = 6.6$ Hz), 7.35–7.89 (4H, m), 8.17 (1H, br-d, $J = 7.3$ Hz). $[\alpha]_D^{27}$ +48.2 (c 2, benzene). FABMS (relative intensity) *m*/*z*: 765 ($[M+1]^+$, 3), 729 (4), 486 (9), 396 (37), 360 (base), 148 (62), 134 (53), 91 (17). FABHRMS *m*/*z*: 765.1036 (Calc. for $C_{36}H_{41}ClN_2PdSb$: 765.1039).

4.4.3. Sb(*R*/*S*)-[2-(*S*)-(1-dimethylaminoethyl)-phenyl](9-phenanthryl)(*p*-tolyl)stibane–palladium complexes (**6c-A** and **6c-B**)

Chromatographic separation of the reaction mixture obtained from the reaction of **4c** with **5** on silica gel using a mixture of ethyl acetate and dichloromethane (1:9) as an eluent afforded diastereomerically pure **6c-A** (1.12g, 46% yield) and **6c-B** (1.21 g, 50% yield), successively. **6c-A**: Yellow foam, $R_f = 0.40$ (ethyl acetate:dichloromethane = 1:4). ^{1}H-NMR (500 MHz) δ: 1.29 (3H, d, $J = 5.5$ Hz), 1.78 (6H, br-s), 2.24 (3H, s), 2.55 (3H, s), 3.00 (3H, s), 3.50 (1H, d, $J = 12.8$ Hz), 4.57 (1H, d, $J = 12.8$ Hz), 5.36 (1H, br-s), 6.45 (1H, t, $J = 7.3$ Hz), 6.83–7.39 (4H, m), 7.54–7.71 (4H, m), 7.88 (1H, s), 8.72 (2H, t, $J = 8.2$ Hz), 9.06 (1H, d, $J = 7.3$ Hz). FABMS (relative intensity) *m*/*z*: 815 ($[M+1]^+$, 2), 779 (2), 538 (6), 446 (11), 360 (35), 307 (20), 289 (13), 154 (MNBA, base), 148 (25), 91 (17). $[\alpha]_D^{26}$ +38.1 (c 2, benzene). FABHRMS *m*/*z*: 815.1212 (Calc. for $C_{40}H_{43}ClN_2PdSb$: 815.1197). **6c-B**: Yellow foam, $R_f = 0.25$ (ethyl acetate:dichloromethane = 1:4). ^{1}H-NMR (500 MHz) δ: 1.30 (3H, d, $J = 5.9$ Hz), 1.73 and 1.97 (2H and 4H, each br-s), 2.29 (3H, s), 2.86 (6H, br-s), 4.02 (1H, d, $J = 13.2$ Hz), 4.14 (1H, d, $J = 13.2$ Hz), 4.65 (1H, br.q), 6.15 (1H, br-t), 6.73 (2H, m), 6.86–7.38 (10H, m), 7.53 (1H, d, $J = 6.6$ Hz), 7.35–7.89 (4H, m), 8.17 (1H, br-d, $J = 7.3$ Hz). $[\alpha]_D^{27}$ +77.9 (c 2, benzene). FABMS (relative intensity) *m*/*z*: 815 ($[M+1]^+$, 2), 779 (1), 538 (1), 446 (5), 360 (18), 154 (MNBA, base), 148 (10), 91 (18). FABHRMS *m*/*z*: 815.1191 (Calc. for $C_{40}H_{43}ClN_2PdSb$: 815.1197).

4.5. General procedure for the preparation of diastereomerically pure Sb(R)- and Sb(S)-(aryl)[2-(S)-(1-dimethylaminoethyl)phenyl](p-tolyl)stibanes (**4b, c**) from the palladium complexes (**6b, c**)

To a stirred solution of the diastereomerically pure palladium complexes (**6b-A**, **6b-B**, **6c-A**, and **6c-B**; 1 mmol) in dichloromethane (30 ml) were added solids of triphenylphosphine (288 mg, 1.1 mmol) in small portions at r.t. 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 ether and dichloromethane (1:10) as an eluent to give the corresponding diastereomerically pure (aryl)[2-(*S*)-(1-dimethylaminoethyl)phenyl](*p*-tolyl)stibanes **4b-A**, **4b-B**, **4c-A**, and **4c-B**, respectively.

4.5.1. Sb(R)-[2-(S)-(1-dimethylaminoethyl)-phenyl](1-naphthyl)(p-tolyl)stibane (**4b-A**)

Colorless oil, 98% yield. ^{1}H-NMR (500 MHz) δ: 1.37 (3H, d, $J = 6.9$ Hz), 1.74 (6H, s), 2.31 (3H, s), 3.84 (1H, q, $J = 6.9$ Hz), 7.04 (1H, t, $J = 6.9$ Hz), 7.08 (2H, d, $J = 7.3$ Hz), 7.24–7.43 (9H, m), 7.77 (1H, d, $J = 8.2$ Hz), 7.82 (1H, d, $J = 7.8$ Hz), 8.19 (1H, d, $J = 8.2$ Hz). ^{13}C-NMR (125 MHz) δ: 11.58 (q), 21.36 (q), 39.84 (q), 63.49 (d), 125.35 (d), 125.49 (d), 125.98 (d), 126.14 (d), 127.30 (d), 128.10 (d), 128.17 (d), 128.68 (d), 129.18 (d), 129.47 (d), 133.63 (s), 135.43 (d), 136.42 (d), 137.37 (s), 137.752 (s), 137.756 (s), 138.11 (s), 139.57 (s), 143.00 (s), 149.14 (s). $[\alpha]_D^{24}$: −63.3° (c 2, benzene). EIMS (relative intensity) *m/z*: 487 [M$^+$, 4], 396 (41), 360 (base), 217 (8), 148 (5), 128 (5), 91 (7). EIHRMS *m/z*: 487.1258 (Calc. for $C_{27}H_{28}NSb$: 487.1260).

4.5.2. Sb(S)-[2-(S)-(1-dimethylaminoethyl)phenyl](1-naphthyl)(p-tolyl)stibane (**4b-B**)

Colorless prisms (hexane) m.p. 137–138.5 °C, 98% yield. ^{1}H-NMR (500 MHz) δ: 1.38 (3H, d, $J = 6.9$ Hz), 1.73 (6H, s), 2.31 (3H, s), 3.80 (1H, q, $J = 6.9$ Hz), 7.06 (1H, t, $J = 7.3$ Hz), 7.09 (2H, d, $J = 7.3$ Hz), 7.23–7.47 (9H, m), 7.77 (1H, d, $J = 8.2$ Hz), 7.84 (1H, d, $J = 7.3$ Hz), 8.34 (1H, d, $J = 7.8$ Hz). ^{13}C-NMR δ: 12.02 (q), 21.35 (q), 40.10 (q), 63.65 (d), 125.38 (d), 125.60 (d), 126.00 (d), 126.17 (d), 127.35 (d), 128.07 (d), 128.11 (d), 128.68 (d), 129.25 (d), 129.65 (d), 133.62 (s), 135.21 (d), 136.52 (d), 137.35 (s), 137.94 (s, 2C), 137.94 (s), 139.75 (s), 142.71 (s), 149.48 (s). $[\alpha]_D^{25}$: +53.8 ° (c 2, benzene). EIMS (relative intensity) *m/z*: 487 [M$^+$, 3], 396 (34), 360 (base), 217 (7), 148 (5), 128 (5), 91 (6). EIHRMS *m/z*: 487.1257 (Calc. for $C_{27}H_{28}NSb$: 487.1260). Anal. Calc. for $C_{27}H_{28}NSb$: C, 66.41; H, 5.78; N, 2.87. Found: C, 66.61; H, 5.86; N, 3.02%.

4.5.3. Sb(R or S)-[2-(S)-(1-dimethylaminoethyl)-phenyl](9-phenanthryl)(p-tolyl)stibanes (**4c-A**)

Colorless prisms (ethanol–benzene 10:1), m.p. 153–155 °C, 99% yield. ^{1}H-NMR (500 MHz) δ: 1.37 (3H, d, $J = 6.9$ Hz), 1.77 (6H, s), 2.33 (3H, s), 3.90 (1H, q, $J = 6.9$ Hz), 7.03 (1H, t, $J = 6.9$ Hz), 7.10 (2H, d, $J = 7.8$ Hz), 7.26 (1H, t, $J = 6.4$ Hz), 7.27 (1H, t, $J = 7.4$ Hz), 7.34 (1H, d, $J = 7.3$ Hz), 7.39 (2H, d, $J = 7.8$ Hz), 7.47 (1H, t, $J = 6.9$ Hz), 7.49 (1H, t, $J = 7.8$ Hz), 7.58 (1H, t, $J = 7.3$ Hz), 7.59 (2H, d, $J = 7.8$ Hz), 7.63 (1H, s), 8.23 (1H, d, $J = 6.9$ Hz), 8.66 (1H, d, $J = 8.2$ Hz), 8.71 (1H, d, $J = 7.8$ Hz). ^{13}C-NMR (125 MHz) δ: 11.10 (q), 21.41 (q), 39.71 (q), 63.25 (d), 122.42 (d), 122.95 (d), 126.01 (d), 126.08 (d), 126.27 (d), 126.36 (d), 127.35 (d), 128.14 (d), 128.45 (d), 129.24 (d), 130.02 (s), 130.17 (d), 130.46 (s), 132.07 (d), 136.45 (s, 2C), 136.97 (d), 137.44 (s), 137.48 (s), 137.758 (s), 137.761 (d), 139.60 (s), 141.88 (s), 149.00 (s). $[\alpha]_D^{25}$: +38.3° (c 2, benzene). EIMS (relative intensity) *m/z*: 537 [M$^+$, 4], 446 (37), 360 (base), 267 (8), 178 (16), 91 (7). EIHRMS *m/z*: 537.1414 (Calc. for $C_{31}H_{30}NSb$: 537.1416). Anal. Calc. for $C_{31}H_{30}NSb$: C, 69.16; H, 5.62; N, 2.60. Found: C, 69.14; H, 5.69; N, 2.73%.

4.5.4. Sb(R or S)-[2-(S)-(1-dimethylaminoethyl)-phenyl](9-phenanthryl)(p-tolyl)stibanes (**4c-B**)

Colorless oil, 99% yield. ^{1}H-NMR (500 MHz) δ: 1.41 (3H, d, $J = 6.9$ Hz), 1.77 (6H, s), 2.32 (3H, s), 3.80 (1H, q, $J = 7.8$ Hz), 7.07 (2H, d, $J = 7.8$ Hz), 7.09 (1H, t, $J = 7.3$ Hz), 7.26 (1H, t, $J = 7.8$ Hz), 7.29 (1H, t, $J = 7.3$ Hz), 7.33 (2H, d, $J = 7.8$ Hz), 7.36 (1H, d, $J = 8.2$ Hz), 7.48 (1H, t, $J = 7.8$ Hz), 7.53 (1H, t, $J = 7.8$ Hz), 7.56 (1H, d, $J = 7.3$ Hz), 7.59 (1H, d, $J = 8.8$ Hz), 7.61 (1H, s), 7.62 (1H, t, $J = 8.8$ Hz), 8.38 (1H, d, $J = 8.2$ Hz), 8.67 (1H, d, $J = 8.2$ Hz), 8.73 (1H, d, $J = 7.8$ Hz). ^{13}C-NMR (125 MHz) δ: 12.55 (q), 21.33 (q), 40.32 (q), 63.92 (d), 122.39 (d), 122.96 (d), 126.04 (d), 126.26 (d), 126.36 (d), 127.41 (d), 128.20 (d), 128.40 (d), 129.28 (d), 130.01 (s), 130.27 (d), 130.35 (s), 132.01 (s), 136.33 (s,), 136.56 (d, 2C), 136.78 (d), 137.44 (s), 137.60 (s), 138.02 (d), 139.60 (s), 141.47 (s), 149.58 (s). $[\alpha]_D^{26}$: +17.9 ° (c 2, benzene). EIMS (relative intensity) *m/z*: 537 [M$^+$, 3], 446 (30), 360 (base), 267 (8), 178 (12), 91 (6). EIHRMS *m/z*: 537.1415 (Calc. for $C_{31}H_{30}NSb$: 537.1416).

4.6. Crystallography

4.6.1. Data collection and refinement

Data were collected on a CCD area detector (Bruker Smart 1000, Bruker AXS, Madison, WI, USA) with graphite monochromated Mo–K_α radiation (λ = 0.71070 Å). The structure was solved by direct methods (SIR-92) [16] and expanded using Fourier techniques (DIRDIF-94) [17]. The structure was refined by the full-matrix least-squares procedures. The non-hydrogen atoms were refined using anisotropic displacement

Table 3
Selected bond lengths (Å) and bond angles (°) for **4b-B**

Bond lengths	
Sb–C(1)	2.172(6)
Sb–C(1′)	2.163(7)
Sb–C(1″)	2.184(6)
Sb–N	2.886(5)
Bond angles	
C(1)–Sb–C(1′)	101.2(2)
C(1)–Sb–C(1″)	94.6(2)
C(1′)–Sb–C(1″)	93.4(2)
C(1)–Sb–N	68.6(2)
C(1′)–Sb–N	81.0(2)
C(1″)–Sb–N	161.2(2)

parameters. Hydrogen atoms were included but not refined. All calculations were performed using TEXAN crystallographic software package of Molecular Structure Corporation (TEXAN for WINDOWS 1997) [18]. Crystal data for **4b-B**: crystal dimensions $0.35 \times 0.35 \times 0.30$ mm; $C_{27}H_{28}NSb$, $M_r = 488.27$; monoclinic space group $P2_1$ (#4), $a = 7.9910(7)$, $b = 9.6145(8)$, $c = 14.973(1)$ Å, $\beta = 94.647(1)^\circ$, $V = 1146.6(1)$ Å^3, $Z = 2$, $D_{calc} = 1.414$ g cm^{-3}, $T = -150$ °C, 6497 reflections measured, refinement based on 2530 reflections, $F(000) = 496$, goodness-of-fit = 1.09, number of parameters = 261, $R = 0.031$ [$I > 1.00\sigma(I)$], $R_w = 0.041$. Selected bond distances and angles are given in Table 3.

5. Supplementary material

Cryatallographic data for the structural analysis of **4b-B** have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 188456. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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