Organometallics 1992, 11, 2803-2811

Synthesis and Characterization of Chiral (–)-Menthyltin(IV) Compounds. X-ray Structure of *tert*-Butyl-8-(dimethylamino)naphthyl-(–)-menthyltin Hydride

Herbert Schumann,* Birgit C. Wassermann, and F. Ekkehardt Hahn

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin,
W-1000 Berlin 12, Germany

Received February 24, 1992

A series of optically active (–)-menthyltin(IV) derivatives with tin directly bound to a chiral carbon atom has been synthesized and characterized. The Grignard reagent derived from (–)-menthyl chloride stereospecifically reacts with trimethyltin chloride to afford (–)-menthyltrimethyltin (1). 1 is derivatized by selective bromodemetalation, alkylation, and hydrogenation, yielding (–)-menthyldimethyltin bromide (2), *tert*-butyl-(–)-menthyldimethyltin (3), *tert*-butyl-(–)-menthyltin dibromide (4), and each prochiral at the tin center as well as *tert*-butyl-8-(dimethylamino)naphthyl-(–)-menthyltin bromide (5) and hydride (6), in which an additional center of asymmetry has been created at the tin atom. By means of multinuclear NMR investigations, the conformation of the optically active ligand in 1–6 was determined, the coordination behavior of the potentially bidentate aminonaphthyl ligand in 5 and 6, resulting in a trigonal bipyramidal (5) or a distorted tetrahedral (6) structure in solution, was established, and for 5 and 6, the ratio of epimers differing in the absolute configuration at the tin center was determined to be 45:55 and 40:60, respectively. The single-crystal X-ray structural analysis of 6 revealed a pair of R_{Sn}/S_{Sn} epimers. 6 crystallizes monoclinically, space group $P2_1$, with $a = 17.786$ (8) Å, $b = 10.890$ (4) Å, $c = 13.700$ (8) Å, $\beta = 108.0$ (4)°, and $Z = 4$. The structure was solved from 4449 observed reflections with $I \geq 3\sigma(I)$ and refined to a final R factor of 0.028. The coordination geometry around tin for the two molecules in the asymmetric unit is that of a trigonal bipyramidal-like monocapped tetrahedron showing a very weak Sn–N interaction with a Sn–N distance of 2.931 (3) (molecule A) or 2.885 (3) Å (molecule B). The Sn–H bond lengths are 1.52 (5) and 1.63 (5) Å, respectively.

Introduction

Chiral organotin compounds have received considerable attention both from a stereochemical standpoint[1,2] and as reagents in asymmetric synthesis.[3] Tin compounds, mainly tetraorganotins, with the center of chirality located at the ligand site[4-8] and/or at the tin atom itself, have been investigated.[9-13] Contrary to tetraorganotins, triorganotin halides are configurationally instable.[14] Increased configurational stability was observed by introduction of sterically demanding ligands[15,16] like the neophyl group or by rendering the tin atom pentacoordinate[17-22] as in 2-[(dimethylamino)methyl]phenylmethylphenyltin bromide. Using an optically active chelating ligand, diastereomerically pure 2-[1-(*S*)-(dimethylamino)ethyl]phenylmethylphenyltin bromide could be isolated.[23] Optically active triorganotin hydrides RR′R″SnH are reported conditionally stable with regard to their configuration racemizing under radical or polar conditions.[24,25]

In order to control the metal configuration, we chose the optically active (–)-menthyl ligand for attachment at the tin. For the first time, we synthesized asymmetric triorganotin hydrides containing a chiral tin center linked to a chiral carbon of an optically active substituent.[26] Furthermore, for maximum assistance of this control, we used the bulky *tert*-butyl substituent as well as the potentially bidentate, rigid 8-(dimethylamino)naphthyl ligand. The synthesis of the corresponding "doubly chiral" organotin hydride, *tert*-butyl-8-(dimethylamino)naphthyl-(–)-menthyltin hydride (6), starting from (–)-menthyl chloride is described in this paper. All the novel (–)-menthyltin derivatives prepared on the route to 6 have been fully characterized, especially by means of multinuclear NMR investigations, the results of which are discussed. Finally, an X-ray crystal structure determination of 6 is presented.

Experimental Section

All reactions were carried out in an atmosphere of dry, oxygen-free argon. CHN analyses were performed on a Perkin-Elmer 240 C elemental analyzer; Sn contents were determined with a Perkin-Elmer 2380 atomic absorption spectrophotometer. Optical rotations were measured on a Polartronic-D (Schmidt + Haensch)

---

(1) Gielen, M.; Simon, S.; Tondeur, Y.; Van de Steen, M.; Hoogzand, C.; Van den Eynde, I. *Isr. J. Chem.* **1976/1977**, *15*, 74.

(2) Gielen, M. *Top. Curr. Chem.* **1982**, *104*, 57.

(3) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, Great Britain, 1987.

(4) Rahm, A.; Pereyre, M.; Petraud, M.; Barbe, B. *J. Organomet. Chem.* **1977**, *139*, 49.

(5) Young, D.; Jones, M.; Kitching, W. *Aust. J. Chem.* **1986**, *39*, 563.

(6) Krishnamurti, R.; Kuivila, H. G. *J. Org. Chem.* **1986**, *51*, 4947.

(7) Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1203.

(8) Krämer, T.; Schwark, J.-R.; Hoppe, D. *Tetrahedron Lett.* **1989**, *30*, 7037.

(9) Otera, J.; Yano, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 387.

(10) Otera, J.; Yoshinaga, Y.; Yamaji, T.; Yoshioka, T.; Kawasaki, Y. *Organometallics* **1985**, *4*, 1213.

(11) Gielen, M.; Barthels, M. R.; De Clercq, M.; Dehouck, C.; Mayence, G. *J. Organomet. Chem.* **1972**, *34*, 315.

(12) Lequan, R. M.; Lequan, M. *Tetrahedron Lett.* **1981**, *22*, 1323.

(13) Lequan, M.; Lequan, R. M.; Brienne, M. J.; Jacques, J. *J. Organomet. Chem.* **1982**, *238*, 335.

(14) Gielen, M.; Mokhtar-Jamai, H. *J. Organomet. Chem.* **1977**, *129*, 325.

(15) Gielen, M.; Mokhtar-Jamai, H. *Bull. Soc. Chim. Belg.* **1975**, *84*, 1037.

(16) Gielen, M.; Tondeur, Y. *Nouv. J. Chim.* **1978**, *2*, 117.

(17) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5393.

(18) van Koten, G.; Noltes, J. G.; Spek, A. L. *J. Organomet. Chem.* **1976**, *118*, 183.

(19) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Verhoeckx, G. J.; Spek, A. L.; Kroon, J. *J. Chem. Soc., Dalton Trans.* **1980**, 1352.

(20) Jastrzebski, J. T. B. H.; van Koten, G.; Knaap, C. T.; Schreurs, A. M. M.; Kroon, J.; Spek, A. L. *Organometallics* **1986**, *5*, 1551.

(21) Jastrzebski, J. T. B. H.; Wehman, E.; Boersma, J.; van Koten, G.; Goubitz, K.; Heijdenrijk, D. *J. Organomet. Chem.* **1991**, *409*, 157.

(22) Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1991**, *413*, 43.

(23) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021.

(24) Gielen, M.; Tondeur, Y. *J. Organomet. Chem.* **1979**, *169*, 265.

(25) Gielen, M. *Pure Appl. Chem.* **1980**, *52*, 657.

(26) Schumann, H.; Wassermann, B. C. *J. Organomet. Chem.* **1989**, *365*, C1.

0276-7333/92/2311-2803$03.00/0

polarimeter using a 200-mm cell. The IR spectrum was recorded on a Perkin-Elmer 457 grating infrared spectrophotometer. Mass spectra (70-eV electron impact ionization) were run on a Varian MAT 311 A instrument. ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained in 5-mm tubes on a Bruker WH 270 (WM 400) spectrometer at resonance frequencies of 270 (400) and 67.93 MHz; chemical shifts are referenced to $(CH_3)_4Si$, with positive shifts referring to lower field. ^{117}Sn{^{1}H inverse gated} NMR spectra were obtained in 10-mm tubes on a Bruker WP 80 SY spectrometer at a resonance frequency of 28.552 MHz; chemical shifts are referenced to $(CH_3)_4Sn$, with positive shifts referring to lower field.

(−)-Menthyltrimethyltin (1). A solution of 75.1 g (377 mmol) of trimethyltin chloride in 340 mL of diethyl ether was added dropwise over a period of 5 h at 0 °C to a vigorously stirred solution of the Grignard reagent[27] prepared from 130 g (744 mmol) of (−)-menthyl chloride[28] {$[\alpha]^{20}{}_D$ −44.6° (neat)} and 23.2 g (955 mmol) of magnesium in 475 mL of tetrahydrofuran. After stirring for 48 h at room temperature, the mixture was treated dropwise with 7.4 mL (411 mmol) of water at 0 °C, stirred for a further 60 min at room temperature, and dried over anhydrous sodium sulfate. Removal of the solvents in vacuo and fractionated distillation afforded 107 g (94%) of 1 as a colorless liquid; bp 75 °C/1.4 mbar. $[\alpha]^{20}{}_D$ −32.5° (*c* 2.12, benzene). MS (70 eV, 25 °C): *m/z* (%) 304 (5) $[M]^+$, 289 (22) $[M - CH_3]^+$, 261 (12) $[M - C_3H_7]^+$, 165 (100) $[Me_3Sn]^+$, 151 (54) $[Me_2SnH]^+$, 150 (21) $[Me_2Sn]^+$, 139 (17) $[C_{10}H_{19}]^+$, 138 (37) $[C_{10}H_{18}]^+$, 135 (16) $[MeSn]^+$, 120 (3) $[Sn]^+$, 97 (8) $[C_7H_{13}]^+$, 95 (12) $[C_7H_{11}]^+$, 83 (44) $[C_6H_{11}]^+$, 81 (17) $[C_6H_9]^+$, 69 (20) $[C_5H_9]^+$, 67 (7) $[C_5H_7]^+$, 57 (15) $[C_4H_9]^+$, 55 (35) $[C_4H_7]^+$, 43 (13) $[C_3H_7]^+$, 41 (21) $[C_3H_5]^+$. Anal. Calcd for $C_{13}H_{28}Sn$: C, 51.52; H, 9.31; Sn, 39.17. Found: C, 51.61; H, 9.40; Sn, 39.29.

(−)-Menthyldimethyltin Bromide (2). A vigorously stirred emulsion of 100 g (330 mmol) of 1 in 1200 mL of methanol was treated dropwise with 51.7 g (324 mmol) of bromine at 0 °C under exclusion of light. Stirring for 12 h at room temperature afforded an orange solution. Removal of the methanol in vacuo and fractionated distillation gave 114 g (96%) of 2 as a colorless liquid; bp 86 °C/0.15 mbar. $[\alpha]^{20}{}_D$ −31.6° (*c* 1.45, benzene). MS (70 eV, 60 °C): *m/z* (%) 368 (1) $[M]^+$, 353 (1) $[M - CH_3]^+$, 325 (8) $[M - C_3H_7]^+$, 289 (1) $[M - Br]^+$, 229 (16) $[M - C_{10}H_{19}]^+$, 151 (2) $[Me_2SnH]^+$, 139 (39) $[C_{10}H_{19}]^+$, 97 (15) $[C_7H_{13}]^+$, 95 (7) $[C_7H_{11}]^+$, 83 (100) $[C_6H_{11}]^+$, 81 (10) $[C_6H_9]^+$, 69 (31) $[C_5H_9]^+$, 67 (5) $[C_5H_7]^+$, 57 (28) $[C_4H_9]^+$, 55 (34) $[C_4H_7]^+$, 43 (11) $[C_3H_7]^+$, 41 (16) $[C_3H_5]^+$. Anal. Calcd for $C_{12}H_{25}BrSn$: C, 39.17; H, 6.85; Sn, 32.26. Found: C, 39.26; H, 6.75; Sn, 31.69.

***tert*-Butyl-(−)-menthyldimethyltin (3).** A 1.7 M solution of *tert*-butyllithium (217 mL, 369 mmol) in pentane was slowly added to a stirred solution of 100 g (272 mmol) of 2 in 700 mL of pentane at 0 °C. The reaction mixture was stirred for 12 h at room temperature, treated dropwise at 0 °C with 6.6 mL (369 mmol) of water, and stirred for 1 h again at room temperature. After the mixture was dried over anhydrous sodium sulfate, solvent was removed in vacuo, and the residue was fractionally distilled, 75.3 g (80%) of 3 was obtained as a colorless liquid; bp 72 °C/0.02 mbar. $[\alpha]^{20}{}_D$ −30.5° (*c* 1.54, benzene). MS (70 eV, 30 °C): *m/z* (%) 346 (1) $[M]^+$, 331 (2) $[M - CH_3]^+$, 289 (42) $[M - C_4H_9]^+$, 207 (5) $[M - C_{10}H_{19}]^+$, 151 (100) $[Me_2SnH]^+$, 150 (31) $[Me_2Sn]^+$, 139 (7) $[C_{10}H_{19}]^+$, 135 (15) $[MeSn]^+$, 120 (3) $[Sn]^+$, 97 (3) $[C_7H_{13}]^+$, 95 (5) $[C_7H_{11}]^+$, 83 (19) $[C_6H_{11}]^+$, 81 (13) $[C_6H_9]^+$, 69 (11) $[C_5H_9]^+$, 67 (3) $[C_5H_7]^+$, 57 (32) $[C_4H_9]^+$, 55 (24) $[C_4H_7]^+$, 43 (10) $[C_3H_7]^+$, 41 (21) $[C_3H_5]^+$. Anal. Calcd for $C_{16}H_{34}Sn$: C, 55.68; H, 9.93; Sn, 34.39. Found: C, 55.47; H, 10.00; Sn, 33.98.

***tert*-Butyl-(−)-menthyltin Dibromide (4).** 3 (69.0 g, 200 mmol) in 750 mL of methanol was treated with 70.3 g (440 mmol) of bromine as described for the preparation of 2. After a reaction time of 4 days, the solvent was removed in vacuo and the reddish brown residue distilled to give the crude product as a yellowish liquid contaminated by a white solid. Filtration and renewed fractionated distillation yielded 55.2 g (58%) of 4 as a colorless liquid; bp 92 °C/0.01 mbar. $[\alpha]^{20}{}_D$ −26.7° (*c* 1.87, benzene). MS (70 eV, 80 °C): *m/z* (%) 476 (1) $[M]^+$, 338 (3) $[SnC_{10}H_{19}Br]^+$, 199 (2) $[SnBr]^+$, 139 (38) $[C_{10}H_{19}]^+$, 97 (10) $[C_7H_{13}]^+$, 95 (5) $[C_7H_{11}]^+$, 83 (63) $[C_6H_{11}]^+$, 81 (9) $[C_6H_9]^+$, 69 (16) $[C_5H_9]^+$, 67 (4) $[C_5H_7]^+$, 57 (100) $[C_4H_9]^+$, 55 (26) $[C_4H_7]^+$. Anal. Calcd for $C_{14}H_{28}Br_2Sn$: C, 35.41; H, 5.94; Sn, 25.00. Found: C, 35.81; H, 6.17; Sn, 25.15.

***tert*-Butyl-8-(dimethylamino)naphthyl-(−)-menthyltin Bromide (5).** A suspension of 19.3 g (76.9 mmol) of 8-(dimethylamino)naphthyllithium etherate[29] in 420 mL of diethyl ether was added dropwise over a period of 4 h to a stirred solution of 36.5 g (76.9 mmol) of 4 in 200 mL of diethyl ether at 10 °C. The resulting solution was stirred for 50 h at room temperature. After removal of the solvent in vacuo, the residue was extracted with hot benzene. Concentration of the benzene filtrate afforded a yellow oil, which was crystallized from a toluene/pentane mixture (10/90 v/v) at −30 °C. Recrystallization from pentane yielded 26.0 g (60%) of 5 as colorless crystals; mp 125 °C. $[\alpha]^{20}{}_D$ −34.3° (*c* 1.23, benzene). MS (70 eV, 150 °C): *m/z* (%) 508 (93) $[M - C_4H_9]^+$, 486 (17) $[M - Br]^+$, 426 (22) $[M - C_{10}H_{19}]^+$, 370 (23) $[MH - C_4H_9 - C_{10}H_{19}]^+$, 369 (12) $[M - C_4H_9 - C_{10}H_{19}]^+$, 290 (100) $[SnC_{10}H_6NMe_2]^+$, 275 (38) $[SnC_{10}H_6NMe]^+$, 170 (57) $[C_{10}H_6NMe_2]^+$, 154 (25) $[C_{11}H_8N]^+$, 139 (4) $[C_{10}H_{19}]^+$, 127 (14) $[C_{10}H_7]^+$, 120 (2) $[Sn]^+$, 97 (7) $[C_7H_{13}]^+$, 95 (4) $[C_7H_{11}]^+$, 84 (3) $[C_5H_{10}N]^+$, 83 (35) $[C_6H_{11}]^+$, 81 (5) $[C_6H_9]^+$, 77 (3) $[C_6H_5]^+$, 69 (18) $[C_5H_9]^+$, 67 (4) $[C_5H_7]^+$, 57 (39) $[C_4H_9]^+$, 56 (3) $[C_3H_6N]^+$, 55 (40) $[C_4H_7]^+$, 43 (17) $[C_3H_7]^+$, 42 (44) $[C_2H_4N]^+$, 41 (36) $[C_3H_5]^+$. Anal. Calcd for $C_{26}H_{40}BrNSn$: C, 55.25; H, 7.13; N, 2.48; Sn, 21.00. Found: C, 55.53; H, 7.10; N, 2.81; Sn, 21.37.

***tert*-Butyl-8-(dimethylamino)naphthyl-(−)-menthyltin Hydride (6).** A solution of 5.0 g (8.8 mmol) of 5 in 25 mL of diethyl ether was slowly added to a stirred suspension of 0.34 g (8.8 mol) of lithium aluminum hydride in 15 mL of diethyl ether at room temperature. After the mixture was stirred for 12 h and subsequently refluxed for 50 h, 0.64 mL (35.4 mmol) of water in 2.3 mL of dioxane was added dropwise at 0 °C. After the reaction mixture was stirred for another 30 min at room temperature, the solution was filtered off and the residue washed with diethyl ether. The combined yellow filtrate was dried over anhydrous sodium sulfate, and the solvents were removed in vacuo. Extraction of the residue with pentane gave a solution which upon cooling to −30 °C afforded 4.0 g (93%) of 6 as colorless crystals; mp 80 °C. $[\alpha]^{20}{}_D$ −11.0° (*c* 0.68, benzene). IR: ν(Sn–H) 1781 (s) cm^{-1}. MS (70 eV, 80 °C): *m/z* (%) 486 (1) $[M - H]^+$, 430 (22) $[M - C_4H_9]^+$, 348 (8) $[M - C_{10}H_{19}]^+$, 290 (47) $[SnC_{10}H_6NMe_2]^+$, 275 (25) $[SnC_{10}H_6NMe]^+$, 170 (53) $[C_{10}H_6NMe_2]^+$, 154 (23) $[C_{11}H_8N]^+$, 139 (3) $[C_{10}H_{19}]^+$, 127 (15) $[C_{10}H_7]^+$, 120 (8) $[Sn]^+$, 115 (48) $[C_9H_7]^+$, 97 (16) $[C_7H_{13}]^+$, 95 (13) $[C_7H_{11}]^+$, 91 (5) $[C_7H_7]^+$, 86 (100) $[C_5H_{12}N]^+$, 84 (46) $[C_5H_{10}N]^+$, 83 (15) $[C_6H_{11}]^+$, 81 (21) $[C_6H_9]^+$, 77 (11) $[C_6H_5]^+$, 69 (17) $[C_5H_9]^+$, 67 (14) $[C_5H_7]^+$, 58 (39) $[C_3H_8N]^+$, 57 (44) $[C_4H_9]^+$, 56 (22) $[C_3H_6N]^+$, 55 (39) $[C_4H_7]^+$, 44 (69) $[C_2H_6N]^+$, 43 (40) $[C_3H_7]^+$, 42 (68) $[C_2H_4N]^+$, 41 (34) $[C_3H_5]^+$. Anal. Calcd for $C_{26}H_{41}NSn$: C, 64.21; H, 8.50; N, 2.88; Sn, 24.41. Found: C, 64.00; H, 8.56; N, 3.27; Sn, 24.23.

X-ray Structure Analysis of 6. Crystals of 6 were obtained at −30 °C from a pentane solution. The crystals are slightly air sensitive. A suitable specimen was quickly selected in air, glued on top of a glass fiber, and transferred directly into the cold stream (−100 (5) °C) of an Enraf-Nonius CAD-4 diffractometer. Important crystal and data collection details are listed in Table I. Data were collected at −100 (5) °C and reduced to structure factors (and their esd's) by correcting for scan speed, Lorentz, and polarization effects.[30] No decay correction was necessary (maximum fluctuation in intensity standards was 0.5%). The data were corrected for absorption by means of five ψ scans. The structure was solved by standard Patterson methods, and all non-hydrogen atoms were refined with anisotropic thermal parameters by full matrix least squares using the programs of the SDP package.[30] The asymmetric unit contains two molecules of 6. Hydrogens, with the exception of the Sn-bound hydrogens H1A and H1B, were added to the structure model on calculated positions [d(C–H) = 0.95 Å].[31] The positional parameters of H1A and H1B were identified from a difference Fourier map and were refined in the least-squares procedure with a fixed isotropic temperature factor $B_{iso,H}$ = 4.0 Å^2. The isotropic temperature factors for all other

---

[27] Tanaka, M.; Ogata, I. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1049.

[28] Smith, J. G.; Wright, G. F. *J. Org. Chem.* **1952**, *17*, 1116.

[29] Jastrzebski, J. T. B. H.; Knaap, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287.

[30] *Structure Determination Package Users Guide, 1982*; B. A. Frenz and Associates: College Station, TX 77840.

[31] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

Table I. Crystal and Data Collection Parameters for 6[a]

formula	$C_{26}H_{41}NSn$
fw	486.31
cryst size, mm	0.61 × 0.62 × 0.45
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
Z	4
a, Å	17.786 (8)
b, Å	10.890 (4)
c, Å	13.700 (8)
β, deg	108.0 (4)
V, Å^3	2524 (4)
d_c, g/cm^3	1.280
d_o, g/cm^3	1.29
radiation, λ, Å	Mo Kα, 0.71073
μ_c, cm^{-1}	10.25
2θ range, deg	$2 \leq 2\theta \leq 50$
hkl range	$0 \leq h \leq 21$ $0 \leq k \leq 12$ $-15 \leq l \leq 15$
scan type	θ–2θ
scan speed, θ, deg/min	min 1.8, max 6.7
no. of unique data	4685
no. of obsd data	4449 $I \geq 3\sigma(I)$
R, %	2.77
R_w, %	3.91
w	$[\sigma(F_o)^2]^{-1}$
no. of variables	510
max shift/error	0.01
res electr dens	1.02 (near SnA)
abspn correction	empirical, 5ψ scans

[a] Estimated standard deviations are given in parentheses in this and all subsequent tables.

hydrogens on calculated positions were fixed to be 1.3 times the B_{eq} of the parent carbon atom. The correct enantiomer in the polar space group $P2_1$ was determined by inversion of the positional parameters and selection of the set of coordinates giving the better residuals (difference in residuals was 2.4%). In addition, the correct stereochemistry of carbon atoms C18 and C24 of the menthyl ligand was known and could not have changed during the reaction. Thus, the correct stereoisomers were unequivocally determined. ORTEP[32] was used for all molecular drawings. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table II.

Results and Discussion

Synthesis. Starting from optically active (−)-menthyl chloride [(1*R*,2*S*,5*R*)-1-chloro-5-methyl-2-isopropylcyclohexane], the corresponding Grignard reagent[27] reacts with trimethyltin chloride stereospecifically to give **1**. No (+)-neomenthyltrimethyltin is formed; i.e., no inversion at the asymmetric menthyl C_1 atom takes place during the C–Sn bond formation. **1** can be isolated as a colorless, distillable liquid in excellent yield.

Table II. Fractional Coordinates and B_{eq} Values for 6

atom	x	y	z	B_{eq},[a] Å^2
SnA	0.45181 (1)	0.103	0.74414 (1)	2.334 (5)
SnB	−0.05175 (1)	0.22504 (3)	0.74731 (2)	2.729 (5)
NA	0.5284 (1)	0.0088 (3)	0.9514 (2)	2.41 (5)
NB	0.0277 (2)	0.2762 (3)	0.9610 (2)	2.63 (6)
C1A	0.4182 (2)	0.2225 (4)	0.6067 (3)	3.46 (8)
C1B	−0.0929 (2)	0.1328 (4)	0.5962 (3)	4.06 (9)
C2A	0.4793 (2)	0.3253 (4)	0.6204 (3)	4.4 (1)
C2B	−0.0386 (3)	0.0217 (5)	0.5999 (4)	5.4 (1)
C3A	0.4099 (2)	0.1516 (5)	0.5087 (3)	4.17 (9)
C3B	−0.0969 (3)	0.2121 (6)	0.5026 (3)	5.5 (1)
C4A	0.3389 (2)	0.2778 (5)	0.6032 (3)	4.9 (1)
C4B	−0.1754 (2)	0.0860 (6)	0.5864 (4)	5.7 (1)
C5A	0.5666 (2)	0.0232 (4)	0.7624 (2)	2.59 (7)
C5B	0.0655 (2)	0.2962 (4)	0.7725 (2)	2.92 (7)
C6A	0.5972 (2)	0.0388 (4)	0.6832 (2)	2.90 (7)
C6B	0.0961 (2)	0.2974 (4)	0.6908 (3)	3.51 (8)
C7A	0.6611 (2)	−0.0321 (5)	0.6739 (3)	3.71 (8)
C7B	0.1617 (2)	0.3645 (6)	0.6911 (3)	4.6 (1)
C8A	0.6928 (2)	−0.1196 (4)	0.7426 (3)	3.63 (8)
C8B	0.1976 (2)	0.4375 (5)	0.7731 (3)	4.40 (9)
C9A	0.6642 (2)	−0.1403 (4)	0.8271 (3)	2.91 (7)
C9B	0.1709 (2)	0.4432 (4)	0.8590 (3)	3.45 (8)
C10A	0.6037 (2)	−0.0650 (3)	0.8405 (2)	2.41 (6)
C10B	0.1060 (2)	0.3664 (4)	0.8610 (3)	2.70 (7)
C11A	0.5817 (2)	−0.0810 (3)	0.9324 (2)	2.48 (6)
C11B	0.0840 (2)	0.3663 (3)	0.9530 (2)	2.64 (7)
C12A	0.6140 (2)	−0.1731 (4)	0.9997 (3)	3.24 (8)
C12B	0.1196 (2)	0.4450 (4)	1.0322 (3)	3.68 (8)
C13A	0.6708 (2)	−0.2512 (4)	0.9813 (3)	3.79 (9)
C13B	0.1808 (2)	0.5247 (4)	1.0257 (3)	4.3 (1)
C14A	0.6970 (2)	−0.2353 (4)	0.9004 (3)	3.51 (8)
C14B	0.2063 (2)	0.5211 (4)	0.9427 (3)	4.3 (1)
C15A	0.5715 (2)	0.1204 (4)	0.9956 (3)	3.13 (7)
C15B	0.0670 (2)	0.1581 (4)	0.9935 (3)	3.65 (8)
C16A	0.4821 (2)	−0.0341 (4)	1.0172 (2)	3.47 (8)
C16B	−0.0195 (2)	0.3078 (4)	1.0282 (3)	3.70 (8)
C17A	0.3554 (2)	−0.0291 (4)	0.7199 (2)	2.69 (7)
C17B	−0.1298 (2)	0.3716 (4)	0.7656 (2)	2.68 (7)
C18A	0.3788 (2)	−0.1645 (4)	0.7383 (2)	2.71 (7)
C18B	−0.1620 (2)	0.4575 (4)	0.6734 (2)	2.99 (7)
C19A	0.4277 (2)	−0.2130 (4)	0.6713 (3)	3.21 (7)
C19B	−0.0979 (2)	0.5167 (4)	0.6347 (3)	3.52 (8)
C20A	0.4731 (2)	−0.3290 (5)	0.7162 (3)	4.6 (1)
C20B	−0.0416 (2)	0.5997 (5)	0.7125 (3)	4.7 (1)
C21A	0.3792 (3)	−0.2336 (6)	0.5595 (3)	5.4 (1)
C21B	−0.1321 (3)	0.5850 (6)	0.5340 (3)	5.6 (1)
C22A	0.3061 (2)	−0.2443 (4)	0.7274 (3)	3.52 (8)
C22B	−0.2173 (2)	0.5521 (4)	0.6973 (3)	3.41 (8)
C23A	0.2564 (2)	−0.1993 (4)	0.7937 (3)	3.92 (8)
C23B	−0.2834 (2)	0.4938 (4)	0.7297 (3)	3.58 (8)
C24A	0.2295 (2)	−0.0679 (4)	0.7711 (3)	3.37 (8)
C24B	−0.2510 (2)	0.4147 (4)	0.8237 (3)	3.18 (8)
C25A	0.1807 (2)	−0.0236 (6)	0.8368 (3)	4.8 (1)
C25B	−0.3150 (2)	0.3553 (6)	0.8598 (3)	4.6 (1)
C26A	0.3023 (2)	0.0143 (4)	0.7828 (3)	3.28 (7)
C26B	−0.1966 (2)	0.3171 (4)	0.8015 (3)	3.03 (7)
H1A[b]	0.446 (2)	0.190 (4)	0.829 (3)	4.0
H1B[b]	−0.060 (2)	0.109 (4)	0.817 (2)	4.0

[a] $B_{eq} = (4\pi^2/3)\sum_i\sum_j U_{ij}a_ia_j\mathbf{a}_i\mathbf{a}_j$. [b] Positional parameters for H1A and H1B were refined in the least-squares procedure with $B_{eq,H}$ fixed to 4.0 Å^2.

To create a center of asymmetry at the tin atom, the methyl groups bound to tin have to be cleaved selectively by bromine and substituted by different ligands. In the first step, monobromodemetalation of **1** in methanol[33] yields **2**, a distillable liquid, almost quantitatively (Scheme I). After alkylation with *tert*-butyllithium, **3** is formed as a distillable liquid. In the next step, the remaining two methyl groups are split off by treating **3** with 2 equiv of bromine in methanol.[34] **4** is obtained as a colorless liquid after repeated distillation. The slow 1/1 addition of highly diluted 8-(dimethylamino)naphthyllithium etherate[29,35] to **4** results in monoalkylation, yielding **5**, which is isolated as colorless crystals in 60% yield. A solution of **5**, which has the optically active (−)-menthyl ligand linked to an asymmetric tin atom, contains both epimers, differing in the absolute configuration at the tin center, in a constant ratio of 45:55.

In the final step, the reduction of **5** with lithium aluminum hydride affords **6**. This compound crystallizes in excellent yield from pentane solution. A single-crystal

---

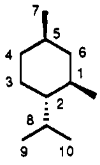
[32] Johnson, C. K. ORTEP, Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, Tennessee, 1965.

[33] Boué, S.; Gielen, M.; Nasielski, J.; Lieutenant, J.-P.; Spielmann, R. *Bull. Soc. Chim. Belg.* **1969**, *78*, 135.

[34] Sisido, K.; Miyanisi, T.; Isida, T.; Kozima, S. *J. Organomet. Chem.* **1970**, *23*, 117.

[35] Jastrzebski, J. T. B. H.; van Koten, G.; Goubitz, K.; Arlen, C.; Pfeffer, M. *J. Organomet. Chem.* **1983**, *246*, C75.

Table III. $^{13}C\{^1H\}$ NMR (67.93-MHz) Spectral Data: Chemical Shifts[a] and $^{13}C-^{117/119}Sn$ Coupling Constants[b,c] of the Menthyl, Methyl, and/or *tert*-Butyl Ligand in Compounds 1–6[d]

		1	2	3	4	5	6
menthyl	δ C_1 ($\lvert {}^1J \rvert$)	31.9 (393.4/411.7)	39.1 (415.6/435.0)	33.6 (345.3/361.5)	51.5 (302.0/316.0)	48.3 (438.0/458.3) 48.2 (430.5/450.6)	37.9 (395.5/413.9) 36.2 (378.1/395.8)
	δ C_2 ($\lvert {}^2J \rvert$)	46.9 (15.7)	46.2 (18.4)	47.1 (14.5)	46.2 (15.7)	45.5 (28.4) 44.5 (17.7)	47.0 (8.9) 46.8 (14.1)
	δ C_3 ($\lvert {}^3J_{trans} \rvert$)	26.9 (61.5)	26.6 (77.9/81.5)	27.1 (57.7)	26.8 (92.9/97.2)	27.2 (79.6) 26.8 (86.9)	27.1 (60.3) 26.9 (65.8)
	δ C_4 ($\lvert {}^4J \rvert$)	35.9 (6.3)	35.3 (8.9)	35.9 (6.0)	34.7 (12.1)	35.2 35.15	35.9 35.8
	δ C_5 ($\lvert {}^3J_{trans} \rvert$)	35.5 (64.6)	35.1 (79.5/83.2)	35.7 (59.7)	35.4 (85.3/89.2)	35.9 (88.0/92.1) 35.5 (75.7/79.2)	36.1 (68.7) 35.6 (66.8)
	δ C_6 ($\lvert {}^2J \rvert$)	41.1 (17.0)	39.9 (23.6)	42.2 (17.2)	40.8 (32.5)	42.5 (23.1) 41.1 (35.2)	44.2 (15.5) 42.5 (16.5)
	δ C_7 ($\lvert {}^4J \rvert$)	22.9	22.6	22.9	22.5 (7.6)	22.9 22.7	23.0 22.9
	δ C_8 ($\lvert {}^3J_{gauche} \rvert$)	33.6 (20.1)	34.0 (25.7)	34.0 (17.2)	36.4 (30.8)	35.1 (23.5) 33.7 (19.6)	34.2 (19.4) 33.0 (18.7)
	δ C_9	22.2	22.0	22.3	21.9	22.4 22.1	22.0 21.9
	δ C_{10}	15.7	15.7	16.1	16.0	16.7 16.5	16.1 14.7
methyl	δ CH_3 ($\lvert {}^1J \rvert$)	−10.3 (287.9/301.3)	−1.8 (288.4/301.8) −2.1 (288.4/301.8)	−11.7 (248.5/260.0) −12.2 (248.3/259.7)			
tert-butyl	δ C_{Sn} ($\lvert {}^1J \rvert$)			23.8 (374.0/394.1)	44.3 (378.8/396.5)	39.6 (423.6/443.3) 38.8 (435.0/455.2)	28.0 (326.4/341.5) 27.3 (343.2/359.1)
	δ CH_3 ($\lvert {}^2J \rvert$)			31.0 (16.1)	29.0 (8.1)	32.2 32.1	32.5 32.1

[a] δ in ppm. [b] $\lvert {}^nJ \rvert$ in Hz. [c] A single value quoted means unresolved $^{117/119}Sn$ satellites. [d] In C_6D_6.

Scheme I

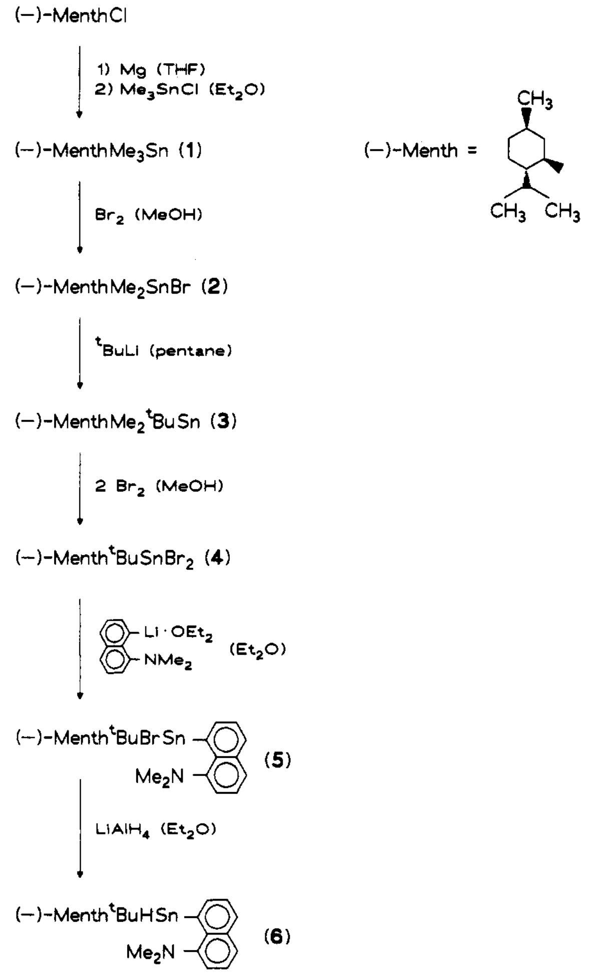
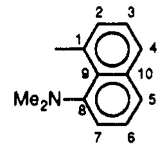


Table IV. $^{13}C\{^1H\}$ NMR (67.93-MHz) Spectral Data: Chemical Shifts[a] and $^{13}C-^{117/119}Sn$ Coupling Constants[b,c] of the 8-(Dimethylamino)naphthyl Ligand in Compounds 5 and 6[d]

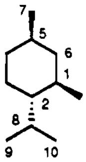
		5	6
	δ C_1 ($\lvert {}^1J \rvert$)	139.6 (435.6/455.9) 137.6 (416.3/435.6)	139.3 (402.5/421.3) 138.1 (414.3/433.5)
	δ C_2 ($\lvert {}^2J \rvert$)	139.4 (23.1) 138.3 (25.7)	136.6 (33.2) 135.7 (34.6)
	δ C_3 ($\lvert {}^3J \rvert$)	127.4 (56.9) 127.2 (53.1)	125.85 (52.7) 125.7 (53.9)
	δ C_4 ($\lvert {}^4J \rvert$)	129.2 (12.5) 129.0 (13.6)	129.2 (11.5) 129.0 (11.3)
	δ C_5	126.6 126.3	125.9 125.85
	δ C_6	125.7 125.5	125.62 125.58
	δ C_7 ($\lvert {}^4J \rvert$)	114.3 (7.0) 113.8 (6.7)	116.3
	δ C_8 ($\lvert {}^3J \rvert$)	151.4 (13.0) 151.0 (16.0)	152.5 (14.6) 152.2 (15.9)
	δ C_9 ($\lvert {}^2J \rvert$)	135.2 (31.1) 134.3 (34.0)	135.2 (17.9)
	δ C_{10} ($\lvert {}^3J \rvert$)	135.1 (35.9) 134.9 (38.2)	135.9 (28.5) 135.8 (29.6)
	δ CH_3	51.5 51.0 46.4 46.0	49.8 47.9 46.1 43.5

[a] δ in ppm. [b] $\lvert {}^nJ \rvert$ in Hz. [c] A single value quoted means unresolved $^{117/119}Sn$ satellites. [d] In C_6D_6.

X-ray investigation of 6 shows 1:1 pairs of both epimers. In solution, the epimers of 6 are detectable in a constant ratio of 40:60. Steric crowding has to be held responsible for the stability of the triorganotin hydride containing a *tert*-amino functionality.

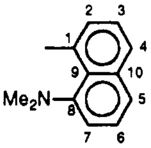
NMR Spectroscopy. The broad-band-decoupled $^{13}C\{^1H\}$ NMR spectra of all compounds synthesized have been recorded in d_6-benzene. They show distinguishable peaks for all carbon atoms with Sn satellite lines surrounding the signals for carbons separated from tin by up to four bonds. The magnitude of the coupling constants $\lvert {}^nJ({}^{13}CSn) \rvert$ provides valuable information regarding the structure and conformation of the compounds. The ^1H NMR spectra, which show Sn satellites only for intense, well-separated signals, supplement the information obtained from the ^{13}C NMR spectra. In addition, the inverse-gated broad-band-decoupled $^{117}Sn\{^1H\}$ NMR spectra allow the quantitative determination of the epimers formed by integration of the two single resonances observed. Detailed NMR spectral data for 1–6 are given in Tables III–VIII.

Table V. ^{1}H NMR (270-MHz) Spectral Data: Chemical Shifts^a and ^{1}H–$^{117/119}$Sn Coupling Constants^b of the Menthyl, Methyl, and/or *tert*-Butyl Ligand and Hydride in Compounds 1–6^c

		1	2	3	4	5	6
menthyl	δ H–C$_1$	1.18 m			2.17 ddd^{e,e,f}		1.83 ddd^{e,e,f} 1.59 ddd^{e,e,f}
	δ H–C$_2$	1.25 m					
	δ H$_e$–C$_3$	1.59 m		1.66 dddd^{d,f,f,f}			
	δ H$_a$–C$_3$	0.90 m	0.86 dddd^{d,e,e,f}				
	δ H$_e$–C$_4$	1.70 m		1.74 ddddd^{d,f,f,f,g}			
	δ H$_a$–C$_4$						
	δ H–C$_5$	1.15 m					
	δ H$_e$–C$_6$	1.77 m	1.88 dddd^{d,f,f,g}	1.91 dddd^{d,f,f,g}	2.20 dddd^{d,f,f,g}		2.33 dddd^{d,f,f,g} 1.93 dddd^{d,f,f,g}
	δ H$_a$–C$_6$	0.98 ddd^{d,e,e}	1.06 ddd^{d,e,e}				
	δ H–C$_7$	0.83 d^h	0.78 d^h	0.87 d^h	0.76 d^h	0.93 d^h 0.72 d^h	0.92 d^h 0.80 d^h
	δ H–C$_8$	1.56 m		1.59 dqq^{f,i,i}			
	δ H–C$_9$	0.89 d^i	0.84 d^i	0.94 d^i	0.85 d^i	1.10 d^i 1.09 d^i	0.75 d^i 0.63 d^i
	δ H–C$_{10}$	0.71 d^i	0.67 d^i	0.76 d^i	0.68 d^i	0.93 d^i 0.39 d^i	0.72 d^i –0.17 d^i
	[δ other H]	0.92–0.80 m	1.70–0.90 m	1.50–0.85 m	1.60–1.05 m	2.35–0.95 m	1.75–0.84 m
methyl	δ CH$_3$ ($\lvert ^2J \rvert$)	0.03 s (47.8/50.0)	0.484 s (48.4/50.6) 0.480 s (48.4/50.6)	0.03 s (43.2/45.2) 0.01 s (43.1/45.0)			
tert-butyl	δ CH$_3$ ($\lvert ^3J \rvert$)			1.15 s (59.8/62.5)	1.27 s (116.2/121.6)	1.21 s (82.6/86.4) 1.13 s (88.0/92.1)	1.57 s (57.7/60.4) 1.43 s (58.8/61.5)
hydride	δ H$_{Sn}$ ($\lvert ^1J \rvert$)						6.37 s (1722.7/1802.8) 6.20 s (1716.9/1796.8)

^{a} δ in ppm. ^{b} $|^nJ|$ in Hz. ^{c} In C$_6$D$_6$. ^{d} $|^2J(^1H^1H)| \approx 12$ Hz. ^{e} $|^3J(^1H^1H)| \approx 12$ Hz. ^{f} $|^3J(^1H^1H)| \approx 3$ Hz. ^{g} $|^4J(^1H^1H)| \approx 3$Hz. ^{h} $|^3J(^1H^1H)| \approx 6$ Hz. ^{i} $|^3J(^1H^1H)| \approx 7$ Hz.

Table VI. ^{1}H NMR (270-MHz) Spectral Data: Chemical Shifts^a and ^{1}H–$^{117/119}$Sn Coupling Constants^{b,c} of the 8-(Dimethylamino)naphthyl Ligand in Compounds 5 and 6^d

		5	6
	δ H–C$_2$ ($\lvert ^3J \rvert$)	8.92 dd^{e,g} (56.3) 8.88 dd^{e,g} (61.5)	8.00 dd^{e,g} (51.4) 7.95 dd^{e,g} (52.1)
	δ H–C$_3$	7.35 dd^{e,f} 7.32 dd^{e,f}	7.33 dd^{e,f} 7.31 dd^{e,f}
	δ H–C$_4$	7.58 d^f 7.55 d^f	7.65 dd^{f,g} 7.64 dd^{f,g}
	δ H–C$_5$	7.48 d^f 7.45 d^f	7.48 dd^{f,g}
	δ H–C$_6$	7.22 dd^{e,f} 7.21 dd^{e,f}	7.24 dd^{e,f}
	δ H–C$_7$	6.89 dd^{e,g} 6.86 dd^{e,g}	7.00 dd^{e,g}
	δ CH$_3$	2.52 s 2.47 s 2.36 s 2.26 s	2.55 s 2.52 s 2.42 s 2.34 s

^{a} δ in ppm. ^{b} $|^nJ|$ in Hz. ^{c} A single value quoted means unresolved $^{117/119}$Sn satellites. ^{d} In C$_6$D$_6$. ^{e} $|^3J(^1H^1H)| \approx 7$ Hz. ^{f} $|^3J(^1H^1H)| \approx 8$ Hz. ^{g} $|^4J(^1H^1H)| \approx 1$ Hz.

Table VII. ^{1}H NMR (400-MHz) Spectral Data: Chemical Shifts^a and ^{1}H–^{1}H Coupling Constants^b of the Menthyl Ligand in (–)-Menthyltrimethyltin (1)^c

δ H–C$_1$	1.18	ddd; $\lvert ^3J_{aa} \rvert = 12$, $\lvert ^3J_{aa} \rvert = 12$, $\lvert ^3J_{ae} \rvert = 3$
δ H–C$_2$	1.25	dddd; $\lvert ^3J_{aa} \rvert = 12$, $\lvert ^3J_{aa} \rvert = 12$, $\lvert ^3J_{ae} \rvert = 3$, $\lvert ^3J \rvert = 2.5$
δ H$_e$–C$_3$	1.59	dddd; $\lvert ^2J \rvert = 12$, $\lvert ^3J_{ea} \rvert = 3$, $\lvert ^3J_{ea} \rvert = 3$, $\lvert ^3J_{ee} \rvert = 3$
δ H$_a$–C$_3$	0.90	dddd; $\lvert ^2J \rvert = 12$, $\lvert ^3J_{aa} \rvert = 12$, $\lvert ^3J_{aa} \rvert = 12$, $\lvert ^3J_{ae} \rvert = 3$
δ H$_e$–C$_4$	1.70	ddddd; $\lvert ^2J \rvert = 12$, $\lvert ^3J_{ea} \rvert = 3$, $\lvert ^3J_{ea} \rvert = 3$, $\lvert ^3J_{ee} \rvert = 3$, $\lvert ^4J \rvert = 2.5$
δ H$_a$–C$_4$	0.86^d	
δ H–C$_5$	1.15	m
δ H$_e$–C$_6$	1.77	dddd; $\lvert ^2J \rvert = 12.5$, $\lvert ^3J_{ea} \rvert = 3$, $\lvert ^3J_{ea} \rvert = 3$, $\lvert ^4J \rvert = 2.5$
δ H$_a$–C$_6$	0.98	ddd; $\lvert ^2J \rvert = 12.5$, $\lvert ^3J_{aa} \rvert = 12$, $\lvert ^3J_{aa} \rvert = 11$
δ H–C$_7$	0.83	d; $\lvert ^3J \rvert = 6.5$
δ H–C$_8$	1.56	dqq; $\lvert ^3J \rvert = 2.5$, $\lvert ^3J \rvert = 7$, $\lvert ^3J \rvert = 7$
δ H–C$_9$	0.89	d; $\lvert ^3J \rvert = 7$
δ H–C$_{10}$	0.71	d; $\lvert ^3J \rvert = 7$

^{a} δ in ppm. ^{b} $|^nJ|$ in Hz. ^{c} In C$_6$D$_6$. ^{d} Masked by resonances of H–C$_7$ and H–C$_9$.

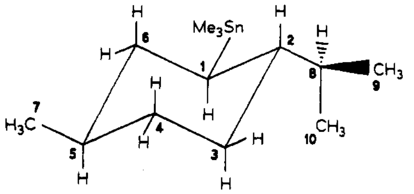


Figure 1. (–)-Menthyltrimethyltin (1).

The ^{13}C{^{1}H} NMR spectrum of 1 reveals the stereospecificity of the Grignard reaction forming the bond between the menthyl ligand and tin. The assignment of the 10 menthyl resonance lines is based upon (a) the analysis of multiplicity by means of DEPT experiments, (b) comparison of the chemical shifts with those of (–)-menthol[36] considering the respective shift differences between cyclohexyltrimethyltin and cyclohexanol,[37] and (c) the magnitude of the coupling constants $|^nJ(^{13}C^{117/119}Sn)|$. According to $|^1J| > |^3J| > |^2J| > |^4J|$, the menthyl carbon atom directly attached to tin (C$_1$) shows by far the largest coupling constant: $|^1J(^{13}C^{117/119}Sn)| = 393.4/411.7$ Hz. The coupling constants $|^3J(^{13}CSn)|$ of the menthyl carbons in the γ position to tin (C$_3$, C$_5$, C$_8$) reflect the conformation of the molecule with a Karplus-type relationship existing between $|^3J(^{13}CSn)|$ and the dihedral angle of the coupling nuclei.[38] C$_3$ and C$_5$ have coupling constants of 61.5 and 64.5 Hz, indicating γ trans positions with respect to the trimethylstannyl group; C$_8$ shows a Sn coupling of 20.1 Hz, indicating a γ gauche position. Such spatial arrangement is exclusively realized with the Me$_3$Sn group in equatorial position as present in the (–)-menthyltin derivative (see Figure 1). The coupling constants $|^2J(^{13}CSn)|$ of C$_2$ and C$_6$ are 15.7 and 17.0 Hz, and $|^4J(^{13}CSn)|$ observed for C$_4$ has a value of 6.3 Hz. A further coupling constant $|^4J(^{13}CSn)|$ is suggested by a broadened base of its resonance line only for C$_7$, positioned in a W arrangement to tin, whereas the respective couplings of C$_9$ and C$_{10}$ are not

---

[36] Bohlmann, F.; Zeisberg, R.; Klein, E. *Org. Magn. Reson.* **1975**, *7*, 426.

[37] Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1984; Chapter 3.4.6.

[38] Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpitt, M.; Lee, C.-H.; Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640.

Table VIII. ^{117}Sn{^{1}H Inverse Gated} NMR (28.552-MHz) Spectral Data: Chemical Shifts^a of Compounds 1–6^b

	1	2	3	4	5	6
δ Sn	−6.9	124.7	1.3	91.9	10.4 (55:45)^c −20.8	−91.3 (40:60)^c −94.8

^{a} δ in ppm. ^{b} In C_6D_6. ^{c} Relative integral ratio.

detectable at all. The proton resonances of 1 have been assigned with the aid of a ^{1}H–^{13}C shift-correlation 2-D experiment. The menthyl ^{1}H,^{1}H coupling constants determined from the 400-MHz ^{1}H NMR spectrum verify the conformation of the compound.

The (−)-menthylstannyl derivatives 2–6 produce menthyl resonances assigned accordingly by comparison with 1. The ^{13}C NMR chemical shift value of C_1 especially reflects the replacement of the methyl groups at tin in 1: Substitution by bromine and substitution by *tert*-butyl or by naphthyl (to a smaller extent) each result in a deshielding of C_1.

For the two methyl groups bound to the prochiral tin center in 2 and 3, respectively, there is diastereotopic nonequivalence detectable in both the ^{1}H and the ^{13}C NMR spectrum.

The ^{13}C{^{1}H} NMR spectrum of 5 represents a superposition of the different spectra of the two diastereomers differing in the absolute configuration at tin. Each of the 24 different carbons present in the molecule shows 2 distinct signals, the separation of which decreases with increasing spatial distance between the respective carbon and the asymmetric tin center. The separation $\Delta\delta$ ranges from 1.4 to 0.05 ppm with the larger values observed for the menthyl C_2, C_6, and C_8 in β and γ gauche positions to tin, the naphthyl ipso and ortho carbons, and the quarternary *tert*-butyl carbon.

The coupling constants $|^1J(^{13}C^{117/119}Sn)|$ evidence a pentacoordinate structure of 5 in solution as has been established for the solid-state structures of 8-(dimethylamino)naphthyl-(−)-menthylmethyltin bromide[39] and 8-(dimethylamino)naphthylmethylphenyltin bromide.[40,41] The trigonal bipyramidal coordination geometry around tin with bromine and nitrogen in axial positions is reflected by an increase of the coupling constants $|^1J(CSn)|$, indicating the increased s character of the hybrid orbitals participating in the equatorial Sn–C bonds as compared to a tetrahedral arrangement with four-coordinate tin.[42] As those coupling constants are enlarged by around 100 Hz for 8-(dimethylamino)naphthyl-(−)-menthylmethyltin bromide ($|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 516.5/540.5$ Hz, $|^1J(^{13}C^{117/119}Sn)_{methyl}| = 419.0/438.5$ Hz) in comparison to (−)-menthylmethylnaphthyltin bromide ($|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 421.0/440.6$ Hz, $|^1J(^{13}C^{117/119}Sn)_{methyl}| = 297.2/311.0$ Hz),[43] a difference of the same order of magnitude should be observed for the $|^1J|$ values of 5 (e.g., $|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 434.2/454.4$ Hz)[44] and its analogue lacking the N-donor site, *tert*-butyl-(−)-menthylnaphthyltin bromide. With the latter compound not being available, the $|^1J|$ values of (−)-menthylmethylnaphthyltin bromide reduced in the same way as observed for the replacement of a methyl by a *tert*-butyl group in 2 (e.g., $|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 415.6/435.0$ Hz) vs *tert*-butyl-(−)-menthylmethyltin bromide[26] (e.g., $|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 332.4/347.9$ Hz) serve as values for comparison.

The Sn–N coordination in 5 renders the two methyls of the NMe_2 group diastereotopic. Both the ^{13}C{^{1}H} and the ^{1}H NMR spectrum of 5 show four dimethylamino resonances, two for each diastereomer. In a high-temperature 80-MHz proton NMR experiment, there is no coalescence observable up to 105 °C, the highest temperature studied. The ^{1}H NMR spectrum of 5, again with doubled resonance lines as in the ^{13}C NMR spectrum, provides additional evidence for a pentacoordinate structure. The trigonal bipyramidal arrangement around tin with nitrogen and bromine in axial positions places the naphthyl C_2 proton near the bromine, causing a downfield shift[29] of its resonances ($\delta\ ^1H_{naphthyl\ C_2} = 8.92$ and 8.88 ppm) compared to the four-coordinate (−)-menthylmethylnaphthyltin bromide ($\delta\ ^1H_{naphthyl\ C_2} = 8.03$ and 7.99 ppm).

5 gives rise to two ^{117}Sn{^{1}H} resonances at 10.4 and −20.8 ppm with a relative integral ratio of 55:45. They appear significantly upfield of the signals of (−)-menthylmethylnaphthyltin bromide at 68.9 and 68.4 ppm, indicating an increase in the coordination number[45,46] in 5.

The NMR spectra of 6 also reveal the existence of two diastereomers. Twenty-two of the 24 ^{13}C{^{1}H} NMR signals are doubled with separations $\Delta\delta$ up to 1.7 ppm (see Figure 2); the ^{1}H and ^{117}Sn{^{1}H} resonances for the two diastereomers are different as well. The ^{13}C and ^{1}H NMR spectral parameters of 6 show the N-donor atom function positioned in the coordination sphere of the tin center, even though the replacement of the electronegative bromine in 5 by hydrogen suggests highly diminished Lewis acidity of the metal in 6, not being sufficient anymore for a strong Sn–N coordination as indicated by ^{117}Sn NMR.

The coupling constants $|^1J(^{13}C^{117/119}Sn)|$ as well as $|^1J(^1H^{117/119}Sn)|$ in 6 reflect the distortion of the tetrahedral coordination geometry around Sn caused by the amino group of the potentially bidentate ligand. As seen by direct comparison of 8-(dimethylamino)naphthyl-(−)-menthylmethyltin hydride ($|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 455.1/476.3$ Hz, $|^1J(^{13}C^{117/119}Sn)_{methyl}| = 267.8/280.3$ Hz) and (−)-menthylmethylnaphthyltin hydride ($|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 410.7/429.8$ Hz, $|^1J(^{13}C^{117/119}Sn)_{methyl}| = 310.8/325.3$ Hz),[43] the $|^1J|$ values of 6 ($|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 386.8/404.8$ Hz, $|^1J(^{13}C^{117/119}Sn)_{tert\text{-}butyl}| = 334.8/350.3$ Hz)[44] should show the same trend of increase or decrease when compared with the corresponding tin hydride without the amine function, *tert*-butyl-(−)-menthylnaphthyltin hydride, which is unknown. The menthyl coupling $|^1J|$ of the latter compound can be estimated by reducing the value observed for (−)-menthylmethylnaphthyltin hydride by the difference observed between those couplings of (−)-menthyldimethyltin hydride[26] ($|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 405.1/423.8$ Hz) and *tert*-butyl-(−)-menthylmethyltin hydride[26] ($|^1J(^{13}C^{117/119}Sn)_{menthyl}| = 353.9/370.2$ Hz). The *tert*-butyl

---

(39) Schumann, H.; Wassermann, B. C.; Pickardt, J. In *Chemistry and Technology of Silicon and Tin*; Kumar Das, V.G., Ng Seik Weng, Gielen, M., Eds.; Oxford University Press: Oxford, Great Britain, 1992; pp 532–543.

(40) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681.

(41) Jastrzebski, J. T. B. H.; Boersma, J.; Esch, P. M.; van Koten, G. *Organometallics* **1991**, *10*, 930.

(42) Nadvornik, M.; Holecek, J.; Handlir, K.; Lycka, A. *J. Organomet. Chem.* **1984**, *275*, 43.

(43) Wassermann, B. C. Dissertation TU Berlin, 1992. Schumann, H.; Wassermann, B. C. To be published.

(44) The tin coupling constants of corresponding signals of the two diastereomers differ in magnitude. The mean value has been cited in the text.

(45) Otera, J. *J. Organomet. Chem.* **1981**, *221*, 57.

(46) Jastrzebski, J. T. B. H.; Grove, D. M.; Boersma, J.; van Koten, G.; Ernsting, J.-M. *Magn. Reson. Chem.* **1991**, *29*, S25.

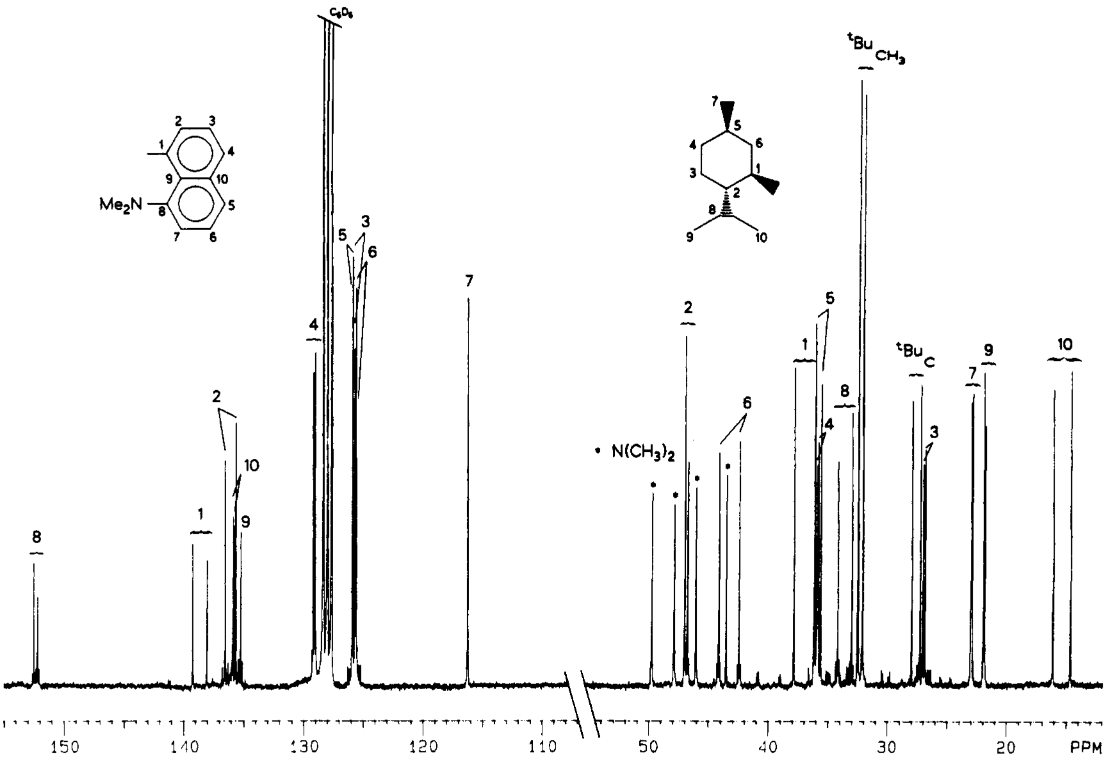


Figure 2. $^{13}C\{^1H\}$ NMR spectrum (67.93 MHz) of *tert*-butyl-8-(dimethylamino)naphthyl-(−)-menthyltin hydride (6) in C_6D_6.

coupling $|^1J|$ of *tert*-butyl-(−)-menthylnaphthyltin hydride amounts of a value larger than that detected for *tert*-butyl-(−)-menthylmethyltin hydride[26] ($|^1J(^{13}C^{117/119}Sn)_{tert\text{-butyl}}$ = 386.3/404.2 Hz) as can be estimated comparing the magnitude of the coupling constants of (−)-menthyldimethyltin hydride and (−)-menthylmethylnaphthyltin hydride. Therefore, there is a slight increase of the menthyl and a decrease of the *tert*-butyl coupling constant $|^1J|$ in 6. This slightly increased or decreased s orbital participation[47] in the $Sn-C_{menthyl}$ or $Sn-C_{tert\text{-butyl}}$ bond, respectively, indicates the beginning distortion of the tetrahedral into a trigonal bipyramidal structure with the menthyl ligand in quasi-equatorial position and the *tert*-butyl group in quasi-axial position. The hydrogen atom bound to tin occupies a quasi-equatorial position as reflected by its coupling constant $|^1J(^1H^{117/119}Sn)|$ with a value of 1719.8/1799.8 Hz[44] for 6 clearly larger than that found for (−)-menthylmethylnaphthyltin hydride (1615.8/1690.9 Hz). The (dimethylamino)naphthyl ligand spans the remaining quasi-equatorial and -axial sites, with the electronegative nitrogen approaching the tin from the latter site.

The diastereotopicity detected for the dimethylamino group of 6 by means of four $^{13}C\{^1H\}$ or ^1H NMR signals, respectively, illustrates a blocked exchange of the two methyl groups bound to nitrogen, i.e., a fixed orientation of its lone pair of electrons toward the tin atom. There are mainly steric reasons—originating in the geometry of the rigid 1,8-disubstituted naphthalene skeleton—responsible for this arrangement of the NMe_2 groups. The absence of an upfield shift of the $^{117}Sn\{^1H\}$ resonances of 6 at −91.3 and −94.8 ppm with respect to the dialkylaryltin hydride lacking the donor atom function (δ ^{117}Sn [(−)-menthylmethylnaphthyltin hydride] = −117.0 and −121.6 ppm) suggests the absence of a significant donor–acceptor interaction between tin and nitrogen. The relative integral ratio of the two ^{117}Sn signals was determined to be 40:60.

The "doubly chiral" triorganotin compounds 5 and 6 both reveal the influence of the optically active ligand on the asymmetric tin center by their diastereomeric ratios being unequal to 1 in solution. The metal configuration is controlled by optical induction from the (−)-menthyl ligand. This control can be considered either kinetic, with the diastereomers being stable toward interconversion, or thermodynamic, with the diastereomers configurationally labile at the tin center. Freshly prepared solutions of crystalline 5 or 6 in benzene each show a constant diastereomeric ratio: neither its optical rotation nor the integral ratio of its doubled NMR signals changes with time. Even dissolution of the crystals and immediate ^1H NMR investigation at low temperature—at −50 °C for 5 and at −80 °C for 6 in toluene—only allow the detection of both epimers in the constant ratio of 45:55 or 40:60, respectively. There are two interpretations possible, consistent with the findings. (a) Crystalline 5 or 6 consists of both epimers—configurationally stable—in the same ratio as observed in solution; out of the different species of crystals (pure R_{Sn} diastereomer, pure S_{Sn} diastereomer, R_{Sn}/S_{Sn} pairs), the latter has arbitrarily been picked for carrying out the single-crystal structure analysis of 6. (b) 5 or 6—configurationally instable at the tin center—crystallizes diastereomerically pure, as has been detected for 8-(dimethylamino)naphthyl-(−)-menthylmethyltin bromide[39] and for 2-[1-(*S*)-(dimethylamino)ethyl]phenylmethylphenyltin bromide,[23] or solely in diastereomeric pairs and, when dissolved again, epimerizes to reach the R_{Sn}/S_{Sn} equilibrium observed in a stereoisomerization process very fast on the laboratory time scale yet slow on the NMR time scale. For the tin hydride 6, interpretation (a) seems to be more likely.

Crystal Structure of 6. The single-crystal X-ray diffraction study of 6 reveals a crystal structure consisting of discrete mononuclear molecules. The asymmetric unit contains two crystallographically independent molecules, which show identical configuration of the chiral ligand but different configuration at the asymmetric tin center. The absolute configuration is assigned to R_{Sn} for molecule A

---

[47] Jurkschat, K.; Tzschach, A. *J. Organomet. Chem.* **1984**, *272*, C13.

Table IX. Selected Bond Distances and Bond Angles for 6

	molecule A	molecule B
	Bond Distances, Å	
Sn-N	2.931 (3)	2.885 (3)
Sn-C1	2.212 (5)	2.212 (5)
Sn-C5	2.163 (4)	2.151 (4)
Sn-C17	2.187 (4)	2.180 (4)
Sn-H1	1.52 (5)[a]	1.63 (5)[a]
	Bond Angles, deg	
N-Sn-C1	162.5 (2)	162.6 (2)
N-Sn-C5	66.84 (11)	67.74 (12)
N-Sn-C17	91.34 (12)	82.62 (12)
N-Sn-H1	66 (2)	70 (2)
C1-Sn-C5	109.4 (2)	109.7 (2)
C1-Sn-C17	105.4 (2)	113.7 (2)
C1-Sn-H1	103 (2)	98 (2)
C5-Sn-C17	114.8 (2)	109.8 (2)
C5-Sn-H1	117 (2)	116.6 (14)
C17-Sn-H1	107 (2)	109 (2)
Sn-C5-C6	116.8 (3)	118.5 (3)
Sn-C5-C10	123.7 (3)	122.6 (3)
C6-C5-C10	118.1 (4)	117.5 (4)
N-C11-C10	116.6 (3)	117.2 (3)
N-C11-C12	122.7 (4)	122.0 (4)
C10-C11-C12	120.6 (4)	120.7 (4)

[a] See footnote *b* in Table II.

and to S_{Sn} for molecule B while confirming the 1*R*,2*S*,5*R* configuration of the (−)-menthyl ligand. ORTEP drawings of the two diastereomeric molecules A and B (different perspectives) in the asymmetric unit are shown in Figure 3 along with the adopted atomic numbering scheme. Selected bond distances and angles are summarized in Table IX.

The molecular structure of **6** corresponds with the conclusions from the NMR data. The coordination geometry around tin is that of a distorted monocapped tetrahedron. The nitrogen atom caps the triangular face built up by the two carbon atoms of the menthyl and naphthyl ligand and the hydrogen atom bound to tin, in trans position to the *tert*-butyl carbon. Alternatively, the coordination polyhedron can be regarded as a heavily distorted trigonal bipyramid with the menthyl C, naphthyl C, and hydrogen atom in a quasi-equatorial position and *tert*-butyl C and nitrogen atom in a quasi-axial position, suggesting an early stage of a S_N2-like approach of the donor atom toward the metal atom trans to the most polarizable bond.[48] A measurement for the position of a structure along the pathway from a tetrahedron to a trigonal bipyramid is given by the difference between the sums of the equatorial and axial angles with values between 0 (ideal tetrahedron) and 90° (ideal trigonal bipyramid).[49] The value of 21° [14°] for the present structure (molecule A [molecule B]) illustrates its closeness to the tetrahedral geometry. The quasi-equatorial angles C5-Sn-C17, C5-Sn-H1, and C17-Sn-H1 (mean 113° [112°]) match the tetrahedral angle more than an angle of 120°; likewise, the quasi-axial angles C1-Sn-C5, C1-Sn-C17, and C1-Sn-H1 show a mean value of 106° [107°], which is closer to the tetrahedral than to an angle of 90°. The deviation of the tin atom from the quasi-equatorial plane toward the *tert*-butyl group is 0.52 Å [0.57 Å].

Looking at the bond distances, the trend toward pentacoordination at the tin atom can be seen. The Sn-N distance of 2.931 (3) Å [2.885 (3) Å] indicates a very weak donor-acceptor interaction. It lies in the upper range of values reported in the literature for coordinative Sn-N bonds,[50] the longest distance being 2.965 (11) Å, found in the diphenyltin dichloride pyrazine adduct.[51] Dräger defines the limiting nonbonding distance between tin and nitrogen as the Sn-N single bond distance augmented by 1.0 Å, giving 3.08 Å.[52]

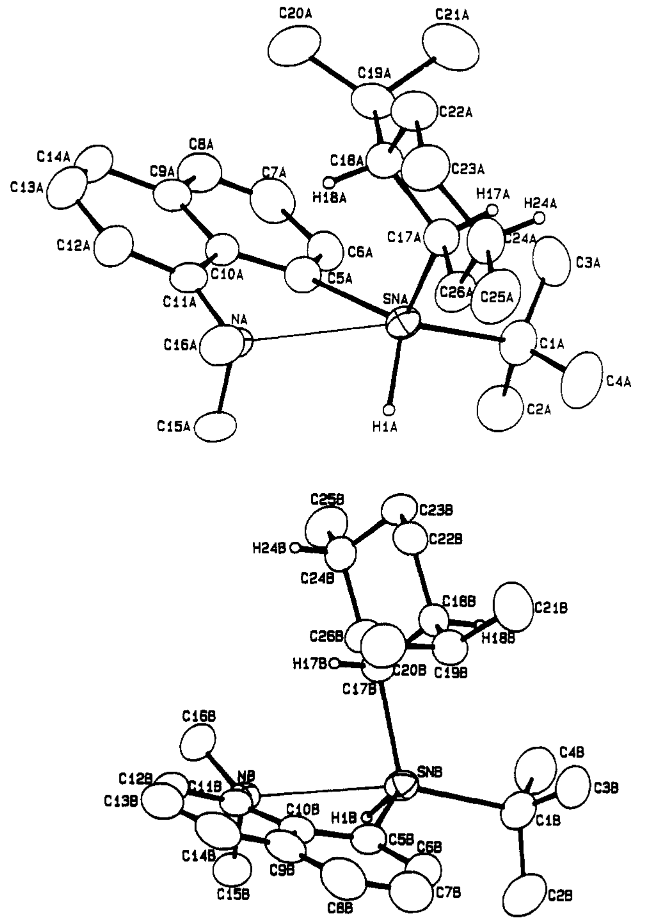


Figure 3. ORTEP drawings of *tert*-butyl-8-(dimethylamino)-naphthyl-(−)-menthyltin hydride (**6**) (upper molecule A, lower molecule B). Most hydrogens are omitted for clarity.

According to the structure correlation principle described by Britton and Dunitz for the S_N2 reaction pathway of Sn(IV) species,[53] the Sn-N interaction should cause some lengthening of the opposite Sn-C bond. The *tert*-butyl C-Sn bond distance of 2.212 (5) Å [2.212 (5) Å] is slightly longer than, e.g., in 3,3-di-*tert*-butyl-*N*,4,5,6,7-pentaphenyl-1,2-dihydro-1,2,3-diazastannepine-1,2-dicarboximide (2.164 (11), 2.185 (7) Å),[54] di-*tert*-butyl-[ethylenebis(dithiocarbamato)]tin (2.182 (8), 2.186 (8) Å),[55] hexakis-*tert*-butyldistannoxane (2.193 (4), 2.198 (4), 2.200 (4) Å),[56] or di-*tert*-butyltin oxide trimer (2.194 (6) Å),[57] yet due to the lack of structurally characterized *tert*-butyl-substituted tetraorganotin or triorganotin hydride compounds, an exact judging is not possible. The menthyl and naphthyl C-Sn bond distances of 2.187 (4) Å [2.180 (4) Å]

---

(48) Boyer, J.; Brelière, C.; Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Young, J. C. *J. Chem. Soc., Dalton Trans.* **1989**, 43.

(49) Dräger, M. *J. Organomet. Chem.* **1983**, *251*, 209.

(50) Kumar Das, V. G.; Mun, L. K.; Wei, C.; Mak, T. C. W. *Organometallics* **1987**, *6*, 10.

(51) Cunningham, D.; Higgins, T.; McArdle, P. *J. Chem. Soc., Chem. Commun.* **1984**, 833.

(52) Dräger, M. *Z. Anorg. Allg. Chem.* **1976**, *423*, 53.

(53) Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2971.

(54) Preut, H.; Marx, R.; Neumann, W. P. *Acta Crystallogr., Sect. C* **1984**, *40*, 1793.

(55) Jung, O.-S.; Sohn, Y. S.; Ibers, J. A. *Inorg. Chem.* **1986**, *25*, 2273.

(56) Kerschl, S.; Wrackmeyer, B.; Männing, D.; Nöth, H.; Staudigl, R. *Z. Naturforsch., B: Chem. Sci.* **1987**, *42*, 387.

(57) Puff, H.; Schuh, W.; Sievers, R.; Wald, W.; Zimmer, R. *J. Organomet. Chem.* **1984**, *260*, 271.

and 2.163 (4) Å [2.151 (4) Å] match the values observed for 8-(dimethylamino)naphthyl-(–)-menthylmethyltin bromide (2.19 (1) Å [2.16 (1) Å] and 2.13 (1) Å [2.18 (1) Å]).[39] Thus, a nondirectional electronic influence of the Sn-bound hydrogen onto all neighboring ligand–tin bonds[58] causing a possible lengthening of the *tert*-butyl C–Sn bond can be ruled out.

The Sn–H bond distance is 1.52 (5) Å [1.63 (5) Å], which is the first time determination[59] of a length of a tin–hydrogen bond by X-ray crystallography. Only the Sn–H bond lengths determined by gas-phase electron diffraction on trimethyltin hydride, 1.705 (67) Å,[60] or predicted by force-field calculations, 1.698[61] and 1.695 Å,[62] are available for comparison until today. The shorter bond distances found in the present molecule may be due to the quasi-equatorial position of the Sn–H bond resulting from the beginning pentacoordination around tin.

The structural parameters of the 1,8-disubstituted naphthyl system indicate the responsibility of steric reasons for the Sn–N interaction observed. In 8-(dimethylamino)naphthyl-(–)-menthylmethyltin bromide,[39] the bond angles at the naphthyl carbons bearing the tin and nitrogen atoms are distorted such as to minimize the distance between tin and nitrogen—a consequence of the high Lewis acidic character of the tin atom in this compound. In the present tin hydride, however, the bond angle distortion detected results in an increase of the Sn–N distance. With angles Sn–C5–C6 of 116.8 (3)° [118.5 (3)°] and Sn–C5–C10 of 123.7 (3)° [122.6 (3)°] in **6**—exactly opposite in size as compared to the tin bromide mentioned—the naphthyl ligand is rotated around an axis on C5 perpendicular to the ligand plane so that the nitrogen atom is turned away from the tin center. In addition, the C–Sn and C–N bonds are bent toward opposite sides of the buckled naphthyl system. A twist of the C5–C10–C11 and C8–C9–C14 planes around the C9–C10 axis of the naphthalene skeleton with deviations from the best least-squares plane through carbon atoms C5–C14 of ≤ 0.08 Å causes a displacement of the tin and the nitrogen atoms to either side of the naphthyl mean plane by +0.71 Å [+0.69 Å] and –0.28 Å [–0.30 Å], respectively. This reluctance[63] of the tin center toward interaction with the donor atom rules out a significant Lewis acidity of the tin atom in **6**—in accordance with the lack of an electronegative substituent at tin. The weak Sn–N interaction yet observable must therefore be ascribed to the remaining steric constraints imposed by the peri-disubstitution of naphthalene.

The coordination geometry of a "trigonal bipyramidal-like monocapped tetrahedron", as found for the triorganotin hydride **6**, has also been described for N-donor-substituted tetraorganotin compounds. The molecule structures of 1-aza-5-stanna-5-methyltricyclo[3.3.3.0^{1,5}]undecane,[64] [3-(2-pyridyl)-2-thienyl]tri-*p*-tolyltin,[65] and 8-(dimethylamino)naphthltriphenyltin[40,41] each show weak Sn–N interaction ($d_{\mathrm{Sn-N}}$ = 2.624 (8), 2.841 (7), or 2.884 (3) Å, respectively) and a prolonged quasi-axial Sn–C bond.

Acknowledgment. Financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. This work was also supported by special grants of the TU Berlin within the exchange program TU Berlin/University of Oklahoma.

Registry No. **1**, 125002-46-2; **2**, 125002-47-3; **3**, 125002-48-4; **4**, 142189-15-9; **5** (organic entry, isomer 1), 142189-19-3; **5** (organic entry, isomer 2), 142189-16-0; **5** (coordinate entry), 142189-17-1; **6** (organic entry, isomer A), 142211-52-7; **6** (organic entry, isomer B), 142211-53-8; **6** (coordinate entry, isomer A), 142189-18-2; **6** (coordinate entry, isomer B), 142291-59-6; (–)-MenthCl, 16052-42-9; Me_3SnCl, 1066-45-1; 8-(dimethylamino)naphthyllithium etherate, 86526-70-7.

Supplementary Material Available: Tables listing all bond distances and angles, anisotropic thermal parameters, and hydrogen positions and ORTEP plots of both molecules of **6** in the asymmetric unit (8 pages). Ordering information is given on any current masthead page.

OM9200969

---

[58] Steinborn, D. *Wiss. Z. Tech. Hochsch. "Carl Schorlemmer" Leuna-Merseburg* **1986**, *28*, 203.

[59] Weidenbruch, M.; Schäfers, K.; Pohl, S.; Saak, W.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1989**, *570*, 75.

[60] Beagley, B.; McAloon, K.; Freeman, J. M. *Acta Crystallogr., Sect. B* **1974**, *30*, 444.

[61] Ouellette, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 7674.

[62] Allinger, N. L.; Quinn, M. I.; Chen, K.; Thompson, B.; Frierson, M. R. *J. Mol. Struct.* **1989**, *194*, 1.

[63] Carré, F.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Nayyar, N. K.; Reyé, C. *Organometallics* **1990**, *9*, 1989.

[64] Jurkschat, K.; Tzschach, A.; Meunier-Piret, J. *J. Organomet. Chem.* **1986**, *315*, 45.

[65] Kumar Das, V. G.; Mun, L. K.; Wei, C.; Blunden, S. J.; Mak, T. C. W. *J. Organomet. Chem.* **1987**, *322*, 163.