Reaction of Ic in the Presence of Cp_2ZrCl_2/nBuLi. The reaction of Ic (511 mg, 2.4 mmol) with Cp_2ZrCl_2 (47 mg, 0.16 mmol) and nBuLi (0.20 mL, 1.6 M in hexane) at 90 °C for 47 h was conducted as described for Ib. A ^{1}H NMR spectrum of the reaction residue after workup showed only the presence of Ic.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Additional support from the Weldon Spring Fund of the University of Missouri—St. Louis is gratefully acknowledged. The Hewlett-Packard 5988A GC/MS system was purchased with the support of the National Science Foundation (Grant No. CHE-8813154). We appreciate helpful discussions with J. S. Chickos, T. D. Tilley, and K. Brown-Wensley and the technical assistance of S. Gonzales.

Intramolecular Penta- and Hexacoordinate Tetraorganotin Compounds Containing the 8-(Dimethylamino)-1-naphthyl Ligand

Johann T. B. H. Jastrzebski, Jaap Boersma, Peter M. Esch, and Gerard van Koten*

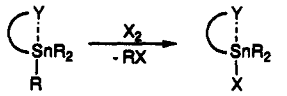
Debye Research Institute, Department of Metal-Mediated Synthesis, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received July 10, 1990

A series of novel tetraorganotin compounds, $Sn[(8\text{-}Me_2N)C_{10}H_6\text{-}1]RR'R''$, containing the 8-(dimethylamino)-1-naphthyl group, has been synthesized and characterized. For one of these compounds ($R = R' = R'' = Ph$) the molecular structure in the solid state has been determined by X-ray diffraction methods: $C_{30}H_{27}NSn$, monoclinic, space group $P2_1/a$, and $a = 24.8365$ (7) Å, $b = 12.3785$ (4) Å, $c = 17.1997$ (6) Å, $\beta = 109.102$ (3)°, and $Z = 8$; final $R = 0.031$ for 7920 observed reflections. The tin center has a distorted trigonal-bipyramidal coordination geometry with the nitrogen atom (Sn–N = 2.884 (3) Å) and one of the phenyl groups at approximately axial positions. The structure of this tetraorganotin compound was compared with that of [8-(dimethylamino)-1-naphthyl]methylphenyltin bromide, for which the structure in the solid state has been determined by X-ray diffraction methods: $C_{19}H_{20}BrNSn$, monoclinic, space group $P2_1/a$, with $a = 16.356$ (3) Å, $b = 13.922$ (4) Å, $c = 8.082$ (2) Å, $\beta = 102.91$ (2); and $Z = 4$; final $R = 0.042$ for 2804 observed reflections. The tin center has a trigonal-bipyramidal coordination geometry in which the organic ligands occupy the equatorial sites, while the more electronegative Br and N ligands are in the axial positions. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of the tetraorganotin compounds show that, most likely as a result of the fixed orientation of the nitrogen atom with respect to the tin atom, also in solution these species are pentacoordinate. This may be concluded from the observations that (i) the ^{1}H and ^{13}C NMR spectra of chiral [8-(dimethylamino)-1-naphthyl]methylphenylneopentyltin show two resonances for the diastereotopic NMe_2 group, indicating that pyramidal inversion of the nitrogen atom is blocked, and (ii) the increase of the $^1J(^{119}Sn-^{13}C(1)_{naphthyl})$ values compared to those of unsubstituted naphthyltin compounds points to a coordination number larger than 4. Moreover, the tetraorganotin compounds show an enhanced reactivity in redistribution reactions, which may be the result of the labilization of the Sn–C bond in a trans position with respect to the coordinating nitrogen atom.

Introduction

Although tetraorganotin compounds were previously regarded as being unable to extend their coordination number because of the poor acceptor properties of the tin center,[1] recently a few examples of tetraorganotin compounds have been reported in which the tin center may be regarded as penta-[2-4] or even hexacoordinate[5] as a result of intramolecular Sn–N coordination. Such coordination has been proposed to be responsible for the changes in the reactivity sequence observed in halodemetalation reactions of mixed tetraorganotin compounds, in which potentially coordinating groups (Y) are present in the γ-position with respect to the tin. It is thought that intramolecular assistance by those groups facilitates the cleavage of tin–carbon bonds trans to them (eq 1).[6-8]



(1)

The presence of pentacoordinate tin in such tetraorganotin compounds was confirmed by the X-ray crystal structure determination of (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin.[9]

Previously we have reported on the synthesis and characterization of pentacoordinate triorganotin halides containing the bidentate 8-(dimethylamino)-1-naphthyl group, and it was shown that these contain a configurationally stable tin center.[10] Moreover, it appeared that

---

(1) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982.

(2) Jurkschat, K.; Tzschach, A.; Meunier-Piret, J. *J. Organomet. Chem.* **1985**, *290*, 285.

(3) Tzschach, A.; Jurkschat, K. *Pure Appl. Chem.* **1986**, *58*, 639.

(4) Kumar Das, V. G.; Lo Kong Mun; Chen Wei; Blunden, S. J.; Mak, T. C. W. *J. Organomet. Chem.* **1987**, *322*, 163.

(5) Kumar Das, V. G.; Lo Kong Mun; Chen Wei; Mak, T. C. W. *Organometallics* **1987**, *6*, 10.

(6) Sanders, D.; Rosenberg, S. D.; Debreczeni, E.; Weinberg, E. L. *J. Am. Chem. Soc.* **1959**, *81*, 972.

(7) Jousseaume, B.; Villeneuve, P. *J. Chem. Soc., Chem. Commun.* **1987**, 513.

(8) Weichmann, H.; Schmoll, C. *Z. Chem.* **1984**, *24*, 390.

(9) Jousseaume, B.; Villeneuve, P.; Dräger, M.; Roller, S.; Chezeau, J. M. *J. Organomet. Chem.* **1988**, *349*, C1.

0276-7333/91/2310-0930$02.50/0

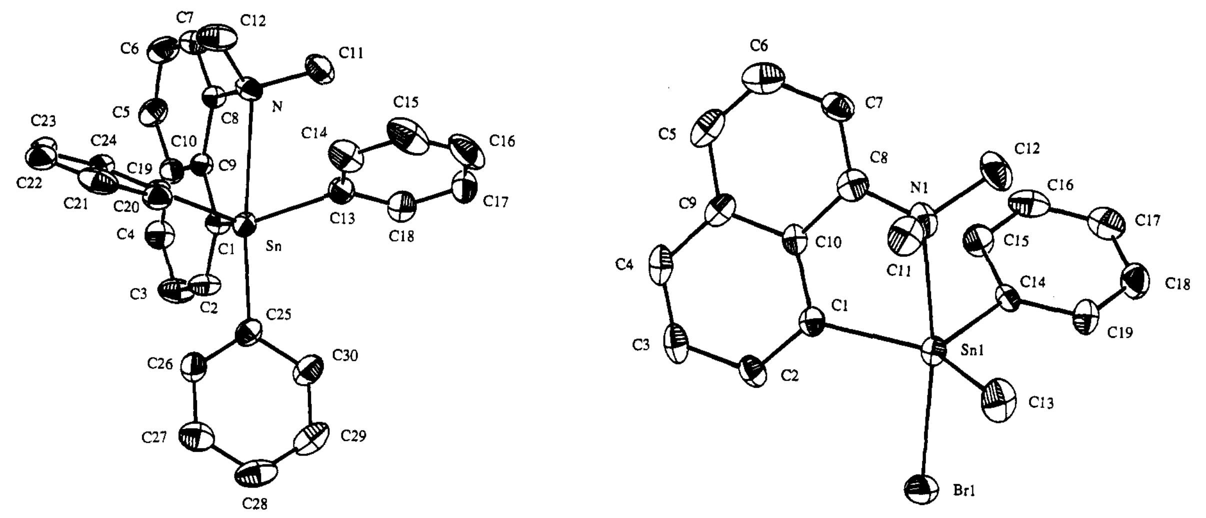
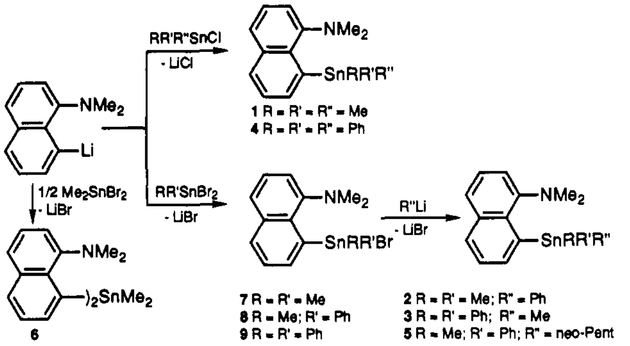


Figure 1. ORTEP (30% probability level) drawings of 4 (left) and 8 (right).

Scheme I



[8-(dimethylamino)-1-naphthyl]trimethyltin had an exceptional reactivity in the redistribution reaction with trimethyltin chloride or bromide. Also, other organometallic species derived from this ligand, such as tetrameric [8-(dimethylamino)-1-naphthyl]copper[11] and some [8-(dimethylamino)-1-naphthyl]platinum compounds,[12,13] have enforced geometries and special reactivities.

In this paper we report the synthesis and characterization of a series of tetraorganotin compounds and triorganotin halides containing the 8-(dimethylamino)-1-naphthyl group.

Results and Discussion

Synthesis of the Tetraorganotin Compounds 1–6. Reaction of [8-(dimethylamino)-1-naphthyl]lithium with trimethyltin chloride or triphenyltin chloride affords in high yield [8-(dimethylamino)-1-naphthyl]trimethyltin (1) and [8-(dimethylamino)-1-naphthyl]triphenyltin (4), respectively (cf. Scheme I). The tetraorganotin compounds 2, 3, and 5 were prepared by reaction of [8-(dimethylamino)-1-naphthyl]methylphenyltin bromide (8)[10] with an appropriate organolithium reagent. Finally bis[8-(dimethylamino)-1-naphthyl]dimethyltin (6) was prepared by the reaction of 2 equiv of [8-(dimethylamino)-1-naphthyl]lithium with dimethyltin dibromide.

Table I. Relevant Data on the Geometries of 4 and 8

4 (molecule A)		8	
	Bond Lengths (Å)		
Sn–N	2.884 (3)	Sn1–N1	2.496 (6)
Sn–C1	2.137 (4)	Sn1–C1	2.131 (6)
Sn–C13	2.148 (4)	Sn1–C14	2.151 (6)
Sn–C19	2.149 (4)	Sn1–C13	2.144 (9)
Sn–C25	2.183 (4)	Sn1–Br	2.667 (1)
	Bond Angles (deg)		
N–Sn–C25	168.5 (1)	N1–Sn1–Br1	171.5 (1)
C1–Sn–C25	101.8 (2)	C1–Sn1–Br1	96.6 (2)
C1–Sn–N	68.8 (1)	C1–Sn1–N1	74.9 (3)
C1–Sn–C13	124.0 (2)	C1–Sn1–C13	128.6 (4)
C1–Sn–C19	108.8 (2)	C1–Sn1–C14	116.1 (3)
C13–Sn–C19	114.4 (2)	C13–Sn1–C14	113.0 (4)
C13–Sn–C25	101.1 (2)	C13–Sn1–Br1	92.4 (4)
C19–Sn–C25	103.4 (2)	C14–Sn1–Br1	96.0 (2)
N–Sn–C13	80.0 (2)	N1–Sn1–C13	92.4 (4)
N–Sn–C19	86.3 (1)	N1–Sn1–C14	88.6 (3)

With the exception of 5, which is a colorless liquid, the new tetraorganotin compounds are white crystalline solids. They were characterized by elemental analysis and ^{1}H, ^{13}C, and ^{119}Sn NMR spectra. To enable a comparison to be made between the structures of the tetraorganotin compounds and those of the corresponding triorganotin halides, the X-ray structures of both [8-(dimethylamino)-1-naphthyl]triphenyltin (4) and [8-(dimethylamino)-1-naphthyl]methylphenyltin bromide (8) were determined.

Molecular Geometry and Crystal Structure of 4 and 8. The crystal structure of 8 involves the packing of four discrete mononuclear molecules in the unit cell. Figure 1 shows an ORTEP view of 8 together with the adopted numbering scheme. Selected geometrical data are given in Table I. In 8 the tin atom has a trigonal-bipyramidal coordination as a result of C,N-chelate bonding of the 8-(dimethylamino)-1-naphthyl group. The tin–carbon bonds are at the equatorial sites, and the more electronegative nitrogen and bromine atoms are at the axial positions. The overall structural geometry, i.e. the bond distances and bond angles around the tin atom, is well in line with that in other pentacoordinate triorganotin bromides where intramolecular coordination of a neutral nitrogen-containing substituent leads to a five-membered chelate ring.[14,15] Although the N–Sn–Br angle is almost

---

(10) Jastrzebski, J. T. B. H.; Knaap, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287.

(11) Wehman, E.; van Koten, G.; Knotter, D. M.; Spelten, H.; Heijdenrijk, D.; Mak, A. N. S.; Stam, C. H. *J. Organomet. Chem.* **1987**, *325*, 293.

(12) Wehman, E.; van Koten, G.; Jastrzebski, J. T. B. H.; Ossor, H.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2975.

(13) Wehman, E.; van Koten, G.; Knaap, C. T.; Ossor, H.; Pfeffer, M.; Spek, A. L. *Inorg. Chem.* **1988**, *27*, 4409.

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

linear (171.5 (1)°), the C(1)–Sn–N angle (74.9 (3)°) deviates considerably from the value of an ideal trigonal bipyramid (90°), but that is to be expected, since this angle is determined by the fairly inflexible values of the Sn–N and Sn–C bond lengths. This phenomenon is common for trigonal-bipyramidal arrays in which a ligand forms a five-membered chelate ring bridging an equatorial and an axial site (see ref 14 and 15 and references cited therein).

The crystal structure of **4** comprises the packing of eight discrete mononuclear molecules in the unit cell. The asymmetric unit contains the two independent molecules A and B, which are chemically identical but which differ slightly but not significantly in structure. An ORTEP view of one of these molecules (A) is shown in Figure 1, which reveals a configuration at tin that is intermediate between a tetrahedron and a trigonal bipyramid. The bond angles given in Table I are in accord with this. Recently the X-ray structure determination of [3-(2-pyridyl)-2-thienyl-*C,N*]-tri-4-tolyltin has been reported,[4] and the structural features of this compound are very closely related to those of **4**. In **4** a distortion toward a higher coordination geometry becomes particularly evident when the bond angles around the tin atom in **4** are compared with those in e.g. tetraphenyltin[16] and tetra-2-thienyltin.[17] In these last two compounds a distorted-tetrahedral coordination geometry at tin is present, as is apparent from an opening of the C–Sn–C bonds, i.e. from 109.5° in tetraphenyltin to 112.6° in tetrakis(2-thienyl)tin, while in **4** two sets of C–Sn–C bond angles may be discerned, one of about 102° (101.1, 101.8, and 103.4°) and one much larger, i.e 108.8, 114.4, and 124.0°. The first set of angles is of those subtended at tin by C25 with each of the other ipso carbon atoms. Also noteworthy is the longer Sn–C25 bond distance relative to the other Sn–C_{ipso} bond distances in the molecule. If these geometrical data are interpreted in terms of a pseudo-trigonal-bipyramidal coordination geometry at tin, the nitrogen atom and C25 would then occupy approximately axial positions, consistent with the C25–Sn–N bond angle of 168.5 (1)°. However, the absence of a well-defined trigonal plane comprising the atoms C1, C13, and C19 is implied in the sum of only 347.2° for the equatorial bond angles and a displacement of 0.45 (2) Å of the Sn atom from this quasi basal plane in the direction of C25. It must be noted that the Sn–N distance in **4** is extremely long (2.884 (3) Å) for a Sn–N coordination bond, while this value is almost the same as that found in [3-(2-pyridyl)-2-thienyl-*C,N*]tri-4-tolyltin.[4] However, the observed Sn–N distance is shorter than the longest one found in Ph_2SnCl_2·pyrazine,[18] 2.965 (11) Å, which is the longest Sn–N coordinate bond known. That the Sn–N distance of 2.884 (3) Å in **4** is indicative of Sn–N bonding can be deduced from our recent finding that in bis[8-(dimethylamino)-1-naphthyl]methyltin iodide there is one Sn–N coordinate bond (2.542 (9) Å) while the other nitrogen atom is 3.10 (1) Å from the Sn atom and is definitely not coordinatively bonded.[19]

Table II. Relevant $^1H^a$ NMR Data of the Tetraorganotin Compounds Sn[8-(Me_2N)$C_{10}H_6$-1]RR′R″ (1–6)

	R	R′	R″	$SnCH_3$^{b}	$H2_{naphthyl}$^{c}	$N(CH_3)_2$
1	Me	Me	Me	0.27 (50, 52)	7.95 (61, 63)	2.33
2	Me	Me	Ph	0.43 (51, 53)	7.85 (61, 63)	2.15
3	Me	Ph	Ph	0.70 (54, 56)	7.98 (64, 66)	2.03
4	Ph	Ph	Ph		8.00 (64, 66)	1.83
5	Me	Ph	neo-Pent^d	0.52 (50, 52)	7.85 (63, 66)	2.10, 2.15^e
6	Me	Me	[8-(Me_2N)-$C_{10}H_6$-1]	0.53 (45, 47)	8.00 (64, 66)	1.93^f

^{a} All values are in δ relative to Me_4Si; toluene-d_8 solvent; at 25 °C. ^{b} $^2J(^{117,119}Sn-^1H)$ in parentheses. ^{c} $^3J(^{117,119}Sn-^1H)$ in parentheses. ^{d} The neo-Pent CH_2 resonances were observed as an AB pattern at δ 1.30 and 1.40; J_{AB} = 13 Hz; $^2J(^{117,119}Sn-^1H)$ = 58, 60 Hz; no coalescence occurs up to 120 °C. ^{e} No coalescence occurs up to 120 °C. ^{f} At −30 °C two resonances at δ 1.65 and 2.25; T_{coal} = −30 °C.

Further evidence for the presence of Sn–N coordination in **4** is the observation that the atoms (N and Sn) present at the 1- and 8-positions of the naphthalene rings are perfectly in the plane of these rings, while in other 1,8-disubstituted naphthalenes, as a result of steric repulsion, these substituents are twisted out of the plane of the naphthalene rings and even the planarity of the naphthalene skeleton in these compounds is significantly distorted.[22]

The axial arrangement of N and Br in **8** and N and C25 in **4** can be seen as a "snapshot" of a S_N2 pathway for substitution with inversion at tetrahedral Sn with the NMe_2 lone pair as the incoming nucleophile and Br and C25, respectively, as the leaving group. The relevant geometrical data (bond distances and angles) around Sn in **4** and **8** match perfectly well with the curves deduced by Britton and Dunitz for such a process.[23] The observation that the Sn atom is still below the equatorial plane of a hypothetical trigonal-bipyramidal transition state is in line with the small leaving-group ability of a phenyl anion. Moreover, it is most probably the fixed orientation of the N lone pair that induces the trigonal-bipyramidal arrangement in **4**.

Structure in Solution of the Tetraorganotin Compounds 1–6. The relevant ^1H NMR spectroscopic data of **1–6** are given in Table II (^1H NMR spectroscopic data of the triorganotin bromides **7–9** were reported earlier[10]). The ^{13}C and ^{119}Sn NMR spectroscopic data of the tetraorganotin compounds **1–6** and the triorganotin bromides **7–9** are given in Table III. The observed $^2J(^{117,119}Sn-^1H)$ values of about 52 Hz for the methyl (Sn) protons of the methyltin derivatives **1–3** and **5** suggest a tetrahedral rather than a trigonal-bipyramidal geometry at tin.[14,15,24,25] On the other hand, the observation of two resonances for the NMe_2 group in **5**, which contains a stable chiral tin center, indicates that pyramidal inversion at nitrogen of this NMe_2 group is blocked, possibly as a result of Sn–N coordination. It must be noted, however, that even when Sn–N coordination would not occur, pyramidal inversion at nitrogen could be blocked for steric reasons. In this case also two resonances for the NMe_2 group would be observed.

The ^1H and ^{13}C chemical shift values of the NMe_2 resonances in **1–5** are not sensitive to the anticipated Sn–N

---

(15) 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.

(16) Chieh, P. C.; Trotter, J. *J. Chem. Soc. A* **1970**, 911.

(17) Karipides, A.; Reed, A. T.; Haller, D. A.; Hayes, F. *Acta Crystallogr., Sect. B* **1977**, *33*, 950.

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

(19) Bis[8-(dimethylamino)-1-naphthyl]methyltin iodide was obtained from the oxidative addition of methyl iodide to bis[8-(dimethylamino)-1-naphthyl]tin(II).[20] The X-ray structure determination[21] of this compound showed that one of the 8-(dimethylamino)-1-naphthyl ligands is C,N-chelate bonded to tin, while the nitrogen atom of the other 8-(dimethylamino)-1-naphthyl group is not coordinated to tin, resulting in a trigonal-bipyramidal coordination geometry at tin with a nitrogen and an iodine atom at the axial positions.

(20) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; Heijdenrijk, D.; Goubitz, K.; de Ridder, D. J. A. *J. Organomet. Chem.* **1989**, *367*, 55.

(21) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; Heijdenrijk, D.; de Ridder, D. J. A. To be submitted for publication.

(22) Blount, J. F.; Cozzi, F.; Damewood, J. R.; Iroff, L. D.; Sjöstrand, U.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 99.

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

(24) Mitchell, T. N. *J. Organomet. Chem.* **1973**, *59*, 189.

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

Table III. Relevant $^{13}C^a$ and $^{119}Sn^b$ NMR Data for the Tetraorganotin Compounds $Sn[8\text{-}(Me_2N)C_{10}H_6\text{-}1]RR'R''$ (1–6) and the Triorganotin Bromides $SnBr[8\text{-}(Me_2N)C_{10}H_6\text{-}1]RR'$ (7–9)

	R	R′	R″	$SnCH_3{}^c$	$C1_{naphthyl}{}^c$	$N(CH_3)_2$	$\delta(^{119}Sn)$
1	Me	Me	Me	−5.2 (348, 364)	138.6 (538, 558)	47.4	−46.7
2	Me	Me	Ph	−6.6 (382, 400)	137.0 (562, 588)	47.4	−81.7
3	Me	Ph	Ph	−7.4 (427, 446)	135.2 (570, 595)	47.6	−110.4
4	Ph	Ph	Ph		133.4 (612, 637)	48.6	−155.3
5	Me	Ph	neo-Pent[d]	−4.2 (340, 356)	137.7 (524, 545)	46.7, 47.6[e]	−97.3
6	Me	Me	$[8\text{-}(Me_2N)C_{10}H_6\text{-}1]$	−1.7 (341, 357)	141.5 (623, 652)	47.9	−98.0
(1-naphthyl)trimethyltin				−8.4 (333, 348)	142.5 (451, 465)		−38.6
di-1-naphthyldimethyltin				−7.4 (344, 360)	141.6 (462, 482)		−65.2
7	Me	Me		1.5 (486, 509)	135.9 (698, 714)	48.1	−38.7
8	Me	Ph		1.3 (575, 540)	134.1 (*f*)	47.9, 48.6	−97.5
9	Ph	Ph			134.0 (*f*)	48.9	−165.1

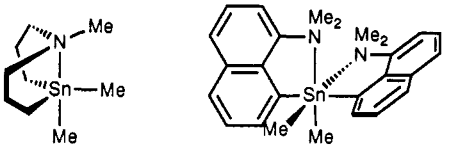
[a] All values are in δ relative to Me_4Si; toluene-d_8 solvent; at 25 °C. [b] δ values relative to Me_4Sn; toluene-d_8 solvent; at 25 °C. [c] $^1J(^{117,119}Sn-^{13}C)$ in parentheses. [d] The neo-Pent CH_2 resonances were observed at δ 31.2; $^1J(^{117,119}Sn-^1H)$ = 401, 421 Hz. [e] No coalescence occurred up to 120 °C. [f] Not observed.

coordination. The ^{13}C δ values of the NMe_2 group carbons of all compounds under study (**1**–**9**) are found at almost the same position (about 48 ppm), i.e. very close to that of 1-(dimethylamino)naphthalene (46.2 ppm). In contrast to this insensitivity, a distinct influence of the substitution of Ph for Me groups at the tin center is found on the $\delta(NMe_2)$ value (see Table II). An upfield shift of this resonance when methyl groups at the tin center are substituted by phenyl groups is also found in tetraorganotin compounds containing the [2-(dimethylamino)phenyl]methyl group.[14]

Although the ^{119}Sn chemical shift values of **1**–**5** are close to those of the corrresponding triorganotin bromides **7**–**9** (Table III), it is not possible to correlate these values with the coordination geometry at tin. The chemical shift of **1** is only shifted 8 ppm upfield compared to that of 1-naphthyltrimethyltin. This upfield shift may be an indication of a distortion toward a higher coordination geometry at tin, but normally this upfield shift lies in a range of about 100 ppm.[26,27]

More informative, however, from the standpoint of structural assignment, are the ^{13}C NMR data and in particular the one-bond coupling constants $^1J(^{117,119}Sn-^{13}C)$. Studies on *n*-butyl-[28,29] and aryltin[30-32] compounds have demonstrated that these one-bond couplings are a sensitive measure of the state of hybridization at tin and increase with increasing coordination number in these compounds.

The data show that the $^1J(^{117,119}Sn-^{13}C)$ values of the naphthyl C1 resonances, obtained for the tetraorganotin compounds **1**–**5**, are smaller than those of the triorganotin bromides **7** and **8**, for which a trigonal-bipyramidal coordination geometry at tin was unambiguously proven, both in the solid state (vide supra) and in solution.[10] However, as compared to the $^1J(^{117}Sn-^{13}C)$ value of trimethyl-1-naphthyltin (451 Hz), the values for **1**–**5** are now considerably larger (538–612 Hz). An increase in coupling constant is ascribed to an increase of s character in the C1–Sn bond. In the present naphthyl compounds this increased $^1J(^{117}Sn-^{13}C)$ could likewise be caused by an increase in s character and so point to the presence of a distorted trigonal-bipyramidal arrangement at the Sn atom in **1**–**5** in solution. Such an arrangement was found for **4** in the solid; i.e., the coordinating NMe_2 group and one of the organic groups are in the axial positions, and the naphthyl–Sn bond and the two remaining organic groups are in the equatorial positions. In principle the equatorial and axial substituents in the ^1H and ^{13}C NMR spectra of these compounds should be distinguishable, as was found for the dimethyldiptychstannolidine **10** (Figure 2).[3,33] In the latter compound the ^1H NMR spectrum recorded at low temperature shows the equatorial Me group at −0.04 ppm and the axial Me group at −0.40 ppm.[3,33] However, at low temperature (−80 °C), both the ^1H and the ^{13}C NMR spectra of the trimethyl- and triphenyltin derivatives **1** and **5** show only one resonance pattern for the methyl or phenyl groups, indicating that a fluxional process is still operative which is fast on the NMR time scale and makes the equatorial and axial substituents equivalent. Although for the equatorial and axial substituents an increase and decrease, respectively, in the $^2J(^{117,119}Sn-^1H)$ and $^1J(^{117,119}Sn-^{13}C)$ values is expected, most likely the same fluxional process causes the observation of averaged values that are close to those for tetraorganotin compounds having a tetrahedral geometry at tin. This phenomenon was also observed for the $^2J(^{117,119}Sn-^1H)$ values of the methyl–Sn groups in **10**.[3,33]



10 **6**

Figure 2. Schematical representation of the dimethyldiptychstannolidine **10** and proposed structure for **6**.

The observation that the ^1H resonances for the NMe_2 groups of bis[8-(dimethylamino)-1-naphthyl]dimethyltin (**6**) decoalesce at −25 °C into two resonances (Table II), while no further changes are observed in the ^1H NMR spectrum upon lowering the temperature down to −90 °C, indicates that (i) the molecule lacks a plane of symmetry containing the N atom of the NMe_2 substituent and (ii) pyramidal inversion at the nitrogen atoms is blocked. On the basis of these results we propose a distorted-octahedral coordination geometry at tin for **6**. In principle five geo-

---

(26) Smith, P. J.; Tupciauskas, A. P. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1978; Vol. 8, p 291.

(27) Wrackmeyer, B. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1985; Vol. 16, p 291.

(28) Domazetis, G.; Magee, R. J.; James, B. D. *J. Organomet. Chem.* **1978**, *148*, 339.

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

(30) Holecek, J.; Nadvornik, M.; Handlir, K.; Lycka, A. *J. Organomet. Chem.* **1983**, *241*, 177.

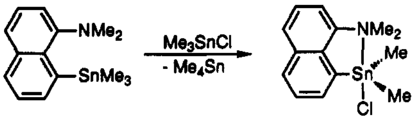
(31) Holecek, J.; Handlir, K.; Nadvornik, M.; Lycka, A. *J. Organomet. Chem.* **1983**, *258*, 147.

(32) Kumar Das, V. G.; Yap, C. K.; Ng, S. W.; Chen Wei; Mak, T. C. W. *J. Organomet. Chem.* **1986**, *311*, 289.

(33) Jurkschat, K.; Schilling, J.; Mügge, C.; Tzschach, A.; Meunier-Piret, J.; Gielen, M.; Willem, R. *Organometallics* **1988**, *7*, 38.

metrically different isomers exist for such an octahedral coordination geometry involving two identical chelating ligands and two other identical groups. For **6**, three of these may be excluded on the basis of the observed ^1H NMR spectra and we propose the structure with the C1-(naphthyl)–Sn bonds in trans positions and both Me (Sn) and NMe_2 groups in cis positions as schematically shown in Figure 2. However, the alternative structure with both the C1(naphthyl)–Sn bonds and Me (Sn) groups in cis positions and the NMe_2 groups in trans positions may not be excluded. Octahedral coordination geometries have recently been established at silicon in tetraorganosilicon compounds containing the 8-(dimethylamino)-1-naphthyl ligand, in the solid state[34] as well in solution,[35] and at tin in bis[3-(2-pyridyl)-2-thienyl]diphenyltin.[5] Further evidence of the structure proposed for **6** is the extremely large $^1J(^{117}Sn-^{13}C_{naphthyl})$ value (623 Hz), compared to the value of dinaphthyldimethyltin (462 Hz) (see Table III). Furthermore, the high-field shift of the ^{119}Sn resonance of **6** (δ −97.5), compared to the value for dinaphthyldimethyltin (δ −65.2), indicates a distortion toward a higher coordination geometry at tin (vide supra).

Previously we reported that the synthesis of **1** should be carried out carefully and that it is essential to avoid the use of an excess of trimethyltin chloride, since it appeared that **1** undergoes a fast redistribution reaction at room temperature with Me_3SnCl, leading to the quantitative formation of [8-(dimethylamino)-1-naphthyl]dimethyltin chloride and tetramethyltin[10] (eq 2).



(2)

This type of redistribution reaction is rather uncommon and normally proceeds only at elevated temperatures.[36,37] Preliminary experiments have shown that the tetraorganotin compounds **1–6** undergo this redistribution reaction with several types of organotin halides. When compounds are used that have different organic groups at tin, a very complex situation arises, since transfer of different groups may, and indeed does, occur. Furthermore, it appeared that the ratio of the different redistribution products depends on the reaction temperature and on the type of halogen atom present in the organotin halide. A more detailed study of this redistribution reaction will be the subject of a forthcoming paper.

Conclusions. It has been shown that by use of the rigid geometry of the 8-(dimethylamino)-1-naphthyl group, in particular through the fixed orientation of the nitrogen lone pair, it is possible to enforce intramolecular coordination to the tin atom in tetraorganotin compounds. As a result of this coordination such tetraorganotin compounds have enhanced reactivities, as was shown by the reaction of these compounds with several organotin halides. A possible explanation for this enhanced reactivity may be the labilization of the Sn–C bond in a trans position with respect to the coordinating nitrogen atom, which may be concluded from the observation that this Sn–C distance in [8-(dimethylamino)-1-naphthyl]triphenyltin (**4**) is significantly elongated compared to the other Sn–C distances (cf. ref 38 and references cited therein). Furthermore, preliminary experiments have shown that reactions of [8-(dimethylamino)-1-naphthyl]trimethyltin (**1**) and [8-(dimethylamino)-1-naphthyl]diphenylmethyltin (**3**) with $PtCl_2$(1,5-cyclooctadiene) give rise to the formation of methyl- and phenylplatinum compounds, respectively (transfer of organic groups from tin to platinum has been reported earlier[39]). This observation indicates that the novel tetraorganotin compounds **1–6** might be interesting starting materials for the synthesis of novel organometallic compounds.

Experimental Section

General Data. All reactions were carried out under dry, oxygen-free nitrogen. ^1H, ^{13}C, and ^{119}Sn spectra were recorded on a Bruker AC 200 spectrometer. [8-(Dimethylamino)-1-naphthyl]lithium[40] and [8-(dimethylamino)-1-naphthyl]methylphenyltin bromide[10] were prepared according to procedures reported in the literature.

Synthesis of [8-(Dimethylamino)-1-naphthyl]trimethyltin (1) and [8-(Dimethylamino)-1-naphthyl]triphenyltin (4). To a solution of 10 mmol of [8-(dimethylamino)-1-naphthyl]lithium in diethyl ether (20 mL) was added a solution of 10 mmol of trimethyl- or triphenyltin chloride, dissolved in diethyl ether (30 mL), over 1 h. The resulting suspension was refluxed for 3 h and stirred for 12 h, after which the solid material (LiCl) was filtered off. The solvent was removed in vacuo, and the remaining solid was dissolved in warm (60 °C) hexane. The warm turbid solution was filtered and set aside at −30 °C for 24 h, during which time a white crystalline solid was formed. The solid material was filtered off, washed with cold pentane, and dried in vacuo, giving the tetraorganotin compounds **1** and **4**, analytically pure, as white crystalline solids in 76 and 62% yield (after recrystallization from pentane), respectively. **1**: mp 35 °C. Anal. Calcd for $C_{15}H_{21}NSn$: C, 53.9; H, 6.3, N, 4.2. Found: C, 53.8; H, 6.4; N, 4.2. **4**: mp 162 °C. Anal. Calcd for $C_{30}H_{27}NSn$: C, 69.3; H, 5.2; N, 2.7. Found: C, 69.1; H, 5.3; N, 2.7.

Synthesis of [8-(Dimethylamino)-1-naphthyl]dimethylphenyltin (2), [8-(Dimethylamino)-1-naphthyl]methyldiphenyltin (3), and [8-(Dimethylamino)-1-naphthyl]methylphenylneopentyltin (5). To a suspension of 5 mmol of [8-(dimethylamino)-1-naphthyl]methylphenyltin bromide (**8**) in diethyl ether (25 mL) was added, over 1 h at −20 °C, a solution of 5 mmol of methyllithium, phenyllithium, or neopentyllithium in 10 mL of diethyl ether. The reaction mixture was refluxed for 3 h and worked up as described for **1** and **4**, giving the tetraorganotin compounds **2** and **3** as white crystalline solids in 97 and 91% yield (after recrystallization from pentane), respectively. Compound **5** was obtained as a colorless liquid, which was used without further purification. **2**: mp 67 °C. Anal. Calcd for $C_{20}H_{23}NSn$: C, 60.7; H, 5.8; N, 3.5. Found: C, 60.5; H, 6.0; N, 3.4. **3**: mp 147 °C. Anal. Calcd for $C_{25}H_{25}NSn$: C, 65.5; H, 5.5; N, 3.1. Found: C, 65.3; H, 5.5; N, 2.9.

Synthesis of Bis[8-(dimethylamino)-1-naphthyl]dimethyltin (6). To a solution of 5 mmol of dimethyltin bromide in diethyl ether (20 mL) was added a solution of 10 mmol of [8-(dimethylamino)-1-naphthyl]lithium in diethyl ether (20 mL). After it was stirred for 3 h, the reaction mixture was worked up as described for **1–5** giving **6** as a white crystalline solid in 85% yield: mp 96 °C. Anal. Calcd for $C_{26}H_{30}N_2Sn$: C, 63.8; H, 6.1; N, 5.7. Found: C, 63.6; H, 6.2; N, 5.6.

Crystal Structure Determination of [8-(Dimethylamino)-1-naphthyl]triphenyltin (4). Transparent colorless crystals of **4**, $C_{30}H_{27}NSn$, are monoclinic, space group $P2_1/a$, with eight molecules in a unit cell of dimensions a = 24.8365 (7) Å, b = 12.3785 (4) Å, c = 17.1997 (6) Å, and β = 109.102 (3)°. A total of 9911 independent intensities (2.7 < θ < 65°; h, −29 to +27; k, 0–14; l, 0–20) were measured at 25 °C on a Nonius CAD4 diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.5418 Å); 1991 of these were below the 2.5$\sigma(I)$ level and were

---

(34) Brelière, C.; Carré, F.; Corriu, R. J. P.; Poirier, M.; Royo, G.; Zwecker, J. *Organometallics* **1989**, *8*, 1831.

(35) Brelière, C.; Corriu, R. J. P.; Royo, G.; Zwecker, J. *Organometallics* **1989**, *8*, 1834.

(36) Moedritzer, K. *Adv. Organomet. Chem.* **1968**, *6*, 171.

(37) Gielen, M.; Nasielski, J. *Organotin Compounds*; Marcel Dekker: New York, 1972.

(38) Aprahamian, S. L.; Shechter, H. *Tetrahedron Lett.* **1990**, *31*, 1089.

(39) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978**, 357.

(40) Jastrzebski, J. T. B. H.; van Koten, G.; Goubitz, K.; Arlen, C.; Pfeffer, M. *J. Organomet. Chem.* **1983**, *246*, C75.

Table IV. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å) and Their Esd's in Parentheses for the Non-H Atoms of 4

atom	x	y	z	U_{eq}[a]
Sn	0.13143 (1)	0.49976 (2)	0.42282 (2)	0.0394 (2)
N	0.1550 (2)	0.2849 (3)	0.3776 (3)	0.046 (2)
C1	0.1808 (2)	0.5044 (3)	0.3418 (3)	0.039 (2)
C2	0.1935 (2)	0.6056 (4)	0.3192 (3)	0.052 (3)
C3	0.2328 (3)	0.6210 (4)	0.2766 (4)	0.061 (3)
C4	0.2607 (2)	0.5348 (5)	0.2585 (3)	0.053 (3)
C5	0.2799 (2)	0.3408 (4)	0.2635 (3)	0.051 (3)
C6	0.2705 (2)	0.2398 (5)	0.2849 (4)	0.061 (3)
C7	0.2296 (2)	0.2218 (4)	0.3228 (3)	0.051 (3)
C8	0.1992 (2)	0.3038 (3)	0.3414 (3)	0.039 (2)
C9	0.2090 (2)	0.4133 (3)	0.3217 (3)	0.037 (2)
C10	0.2496 (2)	0.4300 (4)	0.2808 (3)	0.042 (2)
C11	0.1040 (2)	0.2420 (5)	0.3142 (4)	0.068 (4)
C12	0.1725 (3)	0.2096 (5)	0.4481 (4)	0.070 (4)
C13	0.0478 (2)	0.4301 (4)	0.3911 (3)	0.051 (3)
C14	0.0311 (3)	0.3741 (5)	0.4486 (4)	0.069 (4)
C15	−0.0228 (3)	0.3317 (6)	0.4311 (5)	0.092 (5)
C16	−0.0616 (3)	0.3459 (6)	0.3555 (7)	0.106 (6)
C17	−0.0471 (3)	0.4024 (6)	0.2968 (6)	0.099 (5)
C18	0.0074 (3)	0.4455 (5)	0.3148 (4)	0.073 (4)
C19	0.1866 (2)	0.4609 (4)	0.5446 (3)	0.040 (2)
C20	0.1678 (2)	0.4705 (4)	0.6120 (3)	0.051 (3)
C21	0.2060 (3)	0.4545 (5)	0.6915 (3)	0.069 (4)
C22	0.2617 (3)	0.4276 (4)	0.7031 (4)	0.068 (3)
C23	0.2806 (3)	0.4177 (5)	0.6369 (4)	0.068 (3)
C24	0.2425 (2)	0.4328 (4)	0.5581 (3)	0.051 (3)
C25	0.1124 (2)	0.6706 (4)	0.4318 (3)	0.046 (3)
C26	0.1457 (2)	0.7346 (5)	0.4947 (3)	0.052 (3)
C27	0.1327 (3)	0.8426 (5)	0.5023 (4)	0.069 (4)
C28	0.0861 (3)	0.8905 (5)	0.4438 (5)	0.077 (4)
C29	0.0531 (3)	0.8269 (6)	0.3803 (4)	0.076 (4)
C30	0.0654 (2)	0.7193 (5)	0.3746 (3)	0.062 (3)
Sna	0.12567 (1)	0.09576 (2)	−0.00414 (2)	0.0429 (2)
Na	0.1239 (2)	0.2446 (4)	−0.1343 (3)	0.057 (3)
C1a	0.0845 (2)	0.0276 (4)	−0.1233 (3)	0.046 (3)
C2a	0.0584 (2)	−0.0721 (4)	−0.1265 (3)	0.057 (3)
C3a	0.0380 (3)	−0.1328 (5)	−0.1986 (4)	0.073 (4)
C4a	0.0462 (3)	−0.0954 (5)	−0.2687 (4)	0.075 (4)
C5a	0.0814 (3)	0.0409 (7)	−0.3441 (4)	0.077 (4)
C6a	0.1050 (3)	0.1376 (7)	−0.3453 (4)	0.084 (5)
C7a	0.1194 (3)	0.2078 (6)	−0.2761 (4)	0.073 (4)
C8a	0.1124 (2)	0.1739 (5)	−0.2044 (3)	0.053 (3)
C9a	0.0898 (2)	0.0702 (4)	−0.1983 (3)	0.046 (3)
C10a	0.0728 (2)	0.0053 (5)	−0.2707 (3)	0.056 (3)
C11a	0.0755 (4)	0.3181 (6)	−0.1455 (4)	0.085 (5)
C12a	0.1769 (4)	0.3076 (6)	−0.1160 (4)	0.091 (5)
C13a	0.1153 (2)	−0.0319 (4)	0.0769 (3)	0.049 (3)
C14a	0.1368 (3)	−0.1356 (5)	0.0749 (3)	0.062 (3)
C15a	0.1279 (3)	−0.2164 (5)	0.1249 (4)	0.073 (4)
C16a	0.0978 (3)	−0.1959 (6)	0.1774 (4)	0.077 (4)
C17a	0.0767 (3)	−0.0956 (6)	0.1801 (4)	0.075 (4)
C18a	0.0848 (2)	−0.0138 (5)	0.1299 (4)	0.060 (3)
C19a	0.0893 (2)	0.2322 (4)	0.0377 (3)	0.045 (2)
C20a	0.1222 (2)	0.3120 (5)	0.0879 (3)	0.058 (3)
C21a	0.0970 (3)	0.3983 (5)	0.1130 (4)	0.073 (4)
C22a	0.0389 (3)	0.4081 (5)	0.0888 (4)	0.074 (4)
C23a	0.0051 (3)	0.3273 (6)	0.0403 (5)	0.079 (4)
C24a	0.0306 (3)	0.2414 (5)	0.0151 (4)	0.065 (3)
C25a	0.2156 (2)	0.1014 (4)	0.0162 (3)	0.050 (3)
C26a	0.2536 (3)	0.1585 (7)	0.0786 (5)	0.092 (5)
C27a	0.3111 (3)	0.1591 (8)	0.0891 (6)	0.112 (6)
C28a	0.3313 (3)	0.1064 (7)	0.0368 (6)	0.098 (6)
C29a	0.2960 (3)	0.0484 (7)	−0.0237 (5)	0.092 (5)
C30a	0.2376 (3)	0.0457 (6)	−0.0361 (4)	0.068 (4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table V. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) and Their Esd's in Parentheses for the Non-H Atoms of 8

atom	x	y	z	U_{eq}[a]
Sn1	0.30109 (4)	0.30204 (4)	0.03008 (8)	0.0365 (3)
Br1	0.23229 (7)	0.39880 (8)	−0.25145 (14)	0.0572 (6)
N1	0.3775 (6)	0.2337 (6)	0.3072 (10)	0.046 (4)
C1	0.3884 (5)	0.4104 (6)	0.1406 (11)	0.036 (4)
C2	0.3891 (6)	0.5027 (6)	0.0826 (13)	0.042 (5)
C3	0.4575 (7)	0.5648 (7)	0.1467 (15)	0.052 (6)
C4	0.5269 (7)	0.5318 (7)	0.2574 (14)	0.051 (6)
C5	0.6018 (6)	0.3976 (10)	0.4310 (14)	0.058 (6)
C6	0.6018 (8)	0.3083 (10)	0.4921 (15)	0.063 (7)
C7	0.5295 (7)	0.2500 (8)	0.4490 (12)	0.048 (5)
C8	0.4588 (6)	0.2837 (7)	0.3428 (11)	0.044 (5)
C9	0.5300 (5)	0.4358 (8)	0.3193 (11)	0.042 (5)
C10	0.4579 (5)	0.3770 (6)	0.2678 (10)	0.033 (4)
C11	0.3308 (8)	0.2662 (10)	0.4371 (14)	0.059 (7)
C12	0.3844 (10)	0.1262 (8)	0.3071 (15)	0.068 (7)
C13	0.1811 (7)	0.2697 (10)	0.0818 (18)	0.067 (8)
C14	0.3503 (5)	0.1868 (5)	−0.0960 (10)	0.033 (4)
C15	0.4358 (6)	0.1779 (7)	−0.0879 (14)	0.049 (5)
C16	0.4664 (7)	0.0985 (9)	−0.1615 (16)	0.063 (7)
C17	0.4119 (8)	0.0299 (9)	−0.2427 (15)	0.061 (7)
C18	0.3271 (8)	0.0391 (8)	−0.2524 (14)	0.058 (6)
C19	0.2968 (6)	0.1164 (7)	−0.1789 (12)	0.044 (5)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

treated as unobserved. The Sn positions were derived from a Patterson synthesis, and the C and N atoms were found from subsequent ΔF synthesis. After isotropic block-diagonal least-squares refinement, an empirical absorption correction (DIFABS)[41] was applied (crystal dimensions 0.25 × 0.25 × 0.25 mm; μ(Cu Kα) = 84.3 cm^{-1}). Continued anisotropic refinement converged to R = 0.040. At this stage all hydrogen atoms were found from a ΔF synthesis. Hydrogen positions were introduced, and continued refinement, anisotropic for C, N, and Sn and isotropic for H, converged to R = 0.031 (R_w = 0.042). The anomalous dispersion of Sn was taken into account. An extinction correction was applied, and the weighting scheme $w = 1/(7.0 + F_o + 0.01F_o^2)$ was employed. Fractional coordinates of the non-hydrogen atoms are given in Table IV.

Crystal Structure Determination of [8-(Dimethylamino)-1-naphthyl]methylphenyltin Bromide (8). Transparent colorless crystals of 8, $C_{19}H_{20}BrNSn$, are monoclinic, space group $P2_1/a$, with four molecules in a unit cell of dimensions a = 16.356 (3) Å, b = 13.922 (4) Å, c = 8.082 (2) Å, and β = 102.91 (2)°. A total of 5399 independent intensities (1.9 < θ < 30°; h, −22 to +21; k, 0–19; l, 0–11) were measured at 25 °C on a Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å); 2595 of these were below the 2.5$\sigma(I)$ level and were treated as unobserved. The Sn and Br positions were derived from a Patterson synthesis, and the C and N atoms were found from subsequent ΔF synthesis. After isotropic block-diagonal least-squares refinement, an empirical absorption correction (DIFABS)[41] was applied (crystal dimensions 0.25 × 0.28 × 0.30 mm; μ(Mo Kα) = 36.3 cm^{-1}). Continued anisotropic refinement converged to R = 0.047. At this stage all hydrogen atoms were found from a ΔF synthesis. Hydrogen positions were introduced, and continued refinement, anisotropic for C, Br, N, and Sn and isotropic for H, converged to R = 0.042 (R_w = 0.051). The anomalous dispersion of Sn and Br was taken into account. An extinction correction was applied, and the weighting scheme $w = 1/(4.8 + F_o + 0.03F_o^2)$ was employed. Fractional coordinates of the non-hydrogen atoms are given in Table V.

Supplementary Material Available: Tables of fractional coordinates of the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles of the non-hydrogen and hydrogen atoms (15 pages); listings of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

---

(41) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.