

Table II. Comparison of $\nu(\text{CO})$ Frequencies of Some Hydrido Carbonyl Anionic Clusters Supported on Magnesia and in a CH_2Cl_2 Solution as Their PPN Salt

anion	adsorbed on magnesia	PPN salt	ref
$\text{HFeOs}_3(\text{CO})_{13}^-$	1788	1794	this work
$\text{HFeRu}_3(\text{CO})_{13}^-$	1772	1809	this work
$\text{FeCo}_3(\text{CO})_{12}^-$	1814	1811	this work
$\text{HFe}_3(\text{CO})_{11}^-$	1598	1709	15, 16

(Table II). It is unlikely that the adsorbed anions are bound to the magnesia through tight ion pairing since such an interaction generally produces a shift to a lower bridge carbonyl stretching frequency. Such behavior is observed for $[\text{HFe}_3(\text{CO})_{11}]^-$ on the surface of magnesia (Table II). Where the tight ion pairs have been formed, the OH group on the magnesia is believed to function as a nucleophile to attack the coordinated CO in the well-known reaction of a metal carbonyl with a hydroxyl group to generate

carbonate and hydrido carbonyl anion. In the present case it is reasonable to assume that proton abstraction results in the formation of adsorbed water which remains coordinated to the Mg^+ site and the interaction with the anion is not as strong or as specific as in the case of the tight ion pair.

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Registry No. $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$, 12563-74-5; $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$, 12375-24-5; $\text{HFeCo}_3(\text{CO})_{12}$, 21750-96-9; $[\text{PPN}]^+[\text{HFeOs}_3(\text{CO})_{13}]^-$, 89716-81-4; $\text{K}^+[\text{HFeOs}_3(\text{CO})_{13}]^-$, 102588-90-9; $[\text{HFeOs}_3(\text{CO})_{13}]^-$, 89716-80-3; $[\text{PPN}]^+[\text{HFeRu}_3(\text{CO})_{13}]^-$, 78571-90-1; $\text{K}^+[\text{HFeRu}_3(\text{CO})_{13}]^-$, 102588-91-0; $[\text{HFeRu}_3(\text{CO})_{13}]^-$, 74128-10-2; $[\text{PPN}]^+[\text{FeCo}_3(\text{CO})_{12}]^-$, 80883-51-8; $[\text{FeCo}_3(\text{CO})_{12}]^-$, 53240-35-0; $[\text{PPN}]^+[\text{Co}(\text{CO})_4]^-$, 53433-12-8; MgO , 1309-48-4; Fe , 7439-89-6; Ru , 7440-18-8; Os , 7440-04-2; Co , 7440-48-4.

Organotin(IV) Compounds Derived from 2-Me₂NC₆H₄CH₂Li and Its Chiral α -Me₃Si Derivative. X-ray Structure of Pentacoordinate [$\{2\text{-(Dimethylamino)phenyl}\}$ (trimethylsilyl)methyl-C,N]methylphenyltin Bromide Having a Chiral Sn Center

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A series of triorganotin halides, $\text{RR}'\text{SnBr}(C-N)$, and a series of tetraorganotin compounds, $\text{R}_3\text{Sn}(C-N)$, have been synthesized in which $C-N$ is either monoanionic 2-Me₂NC₆H₄CH₂⁻ or novel, monoanionic 2-Me₂NC₆H₄CH(SiMe₃)⁻. ¹H and ¹³C NMR data indicate that the tin center in the $\text{R}_3\text{Sn}(C-N)$ compounds is tetraordinate whereas this center in the $\text{RR}'\text{SnBr}(C-N)$ derivatives is pentacoordinate as a result of intramolecular Sn-N coordination. Pentacoordination in a trigonal-bipyramidal manner with axial N and Br atoms has also been established by the X-ray structure determination of 2-Me₂NC₆H₄CH(SiMe₃)-SnMePhBr (**4c**): C₁₉H₂₅BrNSiSn; monoclinic; $P2_1/n$, $a = 13.085$ (4) Å, $b = 16.127$ (5) Å, $c = 10.437$ (3) Å; $\beta = 99.88$ (2)°; $V = 2170$ (1) Å³; $Z = 4$; $\mu(\text{Mo K}\alpha) = 29.4$ cm⁻¹; $R = 0.0307$ for 3185 [$I \geq 2.5\sigma(I)$] reflections. Compound **4c** contains two chiral centers, which are formed stereospecifically during the reaction of 2-Me₂NC₆H₄CH(SiMe₃)Li with PhMeSnBr₂ and have either the R_C, R_{Sn} or the S_C, S_{Sn} combination of configurations at the benzylic C and five-coordinate Sn centers. The structure shows that the chelate ring conformation is such that it places the bulky Me₃Si substituent both out of the plane of the aryl ring and, furthermore, at the side of the less bulky methyl ligand. It is suggested that the unusual high configurational stability of the $\text{RR}'\text{SnBr}(C-N)$ compounds arises from the rigidity of the 2-Me₂NC₆H₄CH(Z)⁻ ligand which holds the 2-Me₂N group in close proximity of the tin center. If Z is the bulky SiMe₃ group also, the SnR₂Br grouping is locked in a fixed position with respect to the N donor site.

Introduction

It has been well-established that the configurational stability of the tin center in triorganotin halides can be increased considerably by using potentially bidentate organo ligands $\text{C}\text{---}\text{Y}$,¹ in which Y is a heteroatom-containing substituent, e.g., $-\text{NR}_2$,² $-\text{P}(=\text{O})\text{R}_2$,³ $-\text{C}(=\text{O})\text{R}$,⁴ or

$-\text{NOR}$.⁵ These compounds, $\text{SnC}_2(\text{C}\text{---}\text{Y})\text{X}$ (X = halide), have a trigonal-bipyramidal structure²⁻⁵ in which the electronegative ligands Y and X occupy apical sites and the three carbon ligands C equatorial sites.

The existence of an equilibrium in solution between the two possible situations, i.e., with and without intramo-

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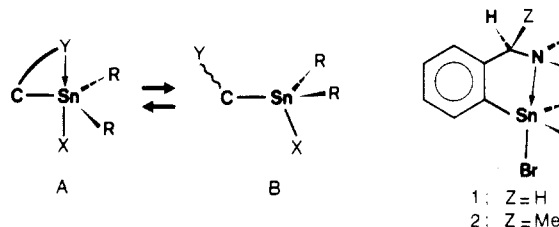
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Table I. Physical Data for the Triorganotin Bromides 3 and 4

compd	yield, ^a %	mp, °C	elemental anal. ^b					M _r ^c
			C	H	N	Br		
3a	37	107–110	37.2 (36.4)	5.1 (5.0)	3.7 (3.8)	21.2 (22.0)	403 (363)	
3b	57	157–158	45.3 (45.2)	4.7 (4.7)	3.2 (3.3)	18.6 (18.8)	432 (425)	
3c	45	125–127	52.7 (51.8)	4.8 (4.6)	2.8 (2.9)	16.9 (16.4)	506 (487)	
4a	64	125–127	38.7 (38.7)	6.1 (6.0)	3.1 (3.2)	18.3 (18.4)	475 (435)	
4b	60	170–172	46.0 (45.9)	5.6 (5.7)	2.8 (2.8)	16.1 (16.1)	521 (497)	
4c	62	150–152	51.3 (51.6)	5.3 (5.4)	2.5 (2.5)	14.2 (14.3)	587 (559)	

^a After recrystallization from hot benzene/hexane (50/50). ^b Found (calcd). ^c By osmometry in benzene: found (calcd).

lecular Sn–Y coordination (A and B, respectively) could be monitored in many cases by following the temperature dependence of the ¹H NMR patterns of prochiral groupings present in these compounds, e.g., the CH₂ and NMe₂ groups in 1. Disappearance of the diastereotopism of the



(N)Me groups occurred in 1 at 30 °C, whereas the diastereotopism of the CH₂ group remained unaltered up to 123 °C.¹² This showed that Sn–N bond dissociation occurred (A ⇌ B process) but that racemization at the Sn center was still slow on the NMR time scale even at 123 °C. Later we established^{2a} by using the chiral labeling approach,^{2a,6} i.e., by using 2 which contains a chiral benzylic group,⁷ that on a much slower time scale inversion of configuration at the tin center does occur in the coordinated situation A.

A factor that so far has not been considered in the discussions concerning the influence of intramolecular coordination (cf. A) on the configurational stability of triorganotin halides is the steric bulkiness the heteroatom-containing group represents when it is not coordinated. If one compares the stereochemistry of the coordinated and noncoordinated situations A and B, respectively, for compounds 1 and 2, both having two sp² C atoms in the five-membered chelate ring, one comes to the conclusion that the noncoordinated *o*-CH(Z)NMe₂ substituent represents a group with considerable steric bulkiness. This bulkiness destabilizes situation B with respect to the five-coordinate-situation A. In the latter situation this bulkiness has been completely removed by the Sn–N coordination. In a forthcoming report we will demonstrate the importance of this factor by a study in which we have increased the size of group Z from Me to Et to *i*-Pr to *t*-Bu.⁹

In this paper we report on the synthesis and structural characterization of a series of triorganotin compounds derived from *N,N*-dimethyl-*o*-toluidine. This ligand has

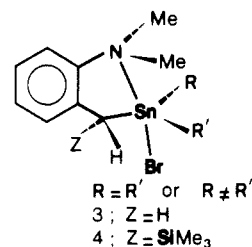
(6) We developed this approach for the detection of M–NR₂ coordination in compounds containing a build-in –NR₂ ligand: e.g., van der Ploeg, A. F. M. J.; van der Kolk, C. E. M.; van Koten, G. *J. Organomet. Chem.* 1981, 212, 283.

(7) Whereas in the coordinated situation A the diastereotopism of the coordinated NMe₂ group reflects the chirality at the benzylic C atom, this diastereotopism is completely absent in the noncoordinated situation B because then inversion at nitrogen and concomitant rotation about the C–N bond can occur.^{2a} Recently Corriu et al.⁹ used this method for a detailed study of the inversion processes at silicon in the corresponding pentacoordinate silicon compounds.

(8) Corriu, R. J. P.; Kpotou, A.; Poixier, M.; Royo, G.; Corey, J. Y. *J. Organomet. Chem.* 1984, 277, C25.

(9) van Koten, G.; Jastrzebski, J. T. B. H., to be submitted for publication.

already been used with much success for the syntheses of numerous cyclometalated compounds.¹⁰ Triorganotin halides derived from this ligand were recently prepared,¹¹ but details concerning the ¹¹⁹Sn NMR data exclusively were reported. As compared with the C–Y ligands used in 1 and 2, the presence of the *o*-toluidine ligand, as in 3, is interesting for the following two reasons: i, the Sn center is bonded to a sp³-C atom but the number of sp²-C atoms in the chelate ring remains unaltered as compared with 1 and 2; ii, the steric interference has now directly been introduced at the carbon atom to which the Sn center is bonded. In connection with the latter aspect we synthesized a new bidentate ligand containing an α -SiMe₃ substituent; see 4.¹² The influence of this substituent on the configurational stability of the tin center in compounds of type 4 will be discussed. An X-ray crystal structure determination of one diastereomer, i.e., [2-Me₂NC₆H₄CH(SiMe₃)]SnMePhBr, will be described.



Experimental Section

General Data. All reactions were carried out under dry, oxygen-free nitrogen. ¹H NMR spectra were recorded on Varian A 60 and XL 100 spectrometers. ¹³C NMR spectra on a Bruker WP 80 spectrometer. Molecular weights were determined osmotically by using a HP 302B vapor pressure osmometer. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands (see Table I).

{[2-(Dimethylamino)phenyl]methyl}lithium (5) was prepared according to procedures reported in the literature.¹³

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(12) (a) Lappert et al.^{12b} and Raston et al.^{12c} have extensively explored the organometallic compounds derived from ligands containing α -SiMe₃ groups. The recently reported organocopper and -silver compounds derived from (2-pyridyl)CH(SiMe₃)^{12c} demonstrate the stabilizing influence of the α -SiMe₃ group^{12d} on the metal–C bond and the metal–nitrogen coordination leading to the dimeric structure of these compounds. (b) Lappert, M. F.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* 1981, 173. Lappert, M. F.; Leung, W. P.; Raston, C. L.; Thorne, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* 1982, 233, C28. Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1982, 14. (c) Leung, W.-P.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1984, 1801 and references cited therein. (d) For an explanation of the stabilizing effect of α -SiMe₃ groups on the C–Li bonding, see: Schleyer, P. v. R.; Kos, A. J.; Wilhelm, D.; Clark, T.; Boche, G.; Decher, G.; Etzrodt, H.; Dietrich, H.; Mahdi, W. *J. Chem. Soc., Chem. Commun.* 1984, 1495.

Syntheses. [2-(Dimethylamino)phenyl](triorgano-M)-methane [M = Si (7a and 7b); M = Sn (10a and 10c)]. To a suspension of [2-(dimethylamino)phenyl]methyl]lithium (5) (40 mmol) in diethyl ether (80 mL) was added 40 mmol of trimethylsilyl chloride. The mixture was refluxed for 4 h. The solid material (LiCl) was filtered off, and the filtrate was concentrated at reduced pressure. The resulting oily residue was distilled at reduced pressure yielding 6.7 g (80%) of 7a as a colorless oil, bp 94–96 °C (8 mmHg). The triphenylsilyl compound 7b was obtained similarly by reacting 5 (10 mmol) in 20 mL of diethyl ether with triphenylsilyl chloride: yield 80% after recrystallization from *n*-hexane; mp 72 °C.

The corresponding trimethyltin derivative 10a was prepared in a similar way starting from 5 and trimethyltin chloride: yield 80%; bp 120 °C (8 mmHg).

In a similar way the triphenyltin compound 10c was obtained by reacting 5 with triphenyltin chloride: yield 75%; mp 114 °C. 7a: ¹H NMR (in CDCl₃, δ) NMe₂ 2.95 (6 H), CH₂Si 2.45 (2 H), SiMe₃ 0.22 (9 H), aromatic H 7.28 (4 H). 7b: ¹H NMR (in CDCl₃, δ) NMe₂ 2.20 (6 H), CH₂Si 2.95 (2 H), aromatic H 6.60–7.40 (19 H).

[2-(Dimethylamino)phenyl](triorganosilyl)methyl]lithium (6). To a solution of 10 mmol of 7 in diethyl ether (10 mmol) was added 10 mmol of *n*-butyllithium in *n*-hexane (7 mL). The resulting pale yellow solution was stirred for 2 days. The solvents were removed in vacuo, yielding a yellow solid. This solid was washed with two 10-mL portions of *n*-pentane and dried in vacuo, yielding 1.8 g (84%) of 6a as a yellow solid. ¹H and ¹³C spectra of the product obtained from the reaction of 6a with D₂O showed the exclusive formation of [2-(dimethylamino)phenyl](trimethylsilyl)monodeuteriomethane.

The triphenylsilyl analogue 6b was prepared in the same way, giving 80% yield of yellow solid of 6b.

[2-(Dimethylamino)phenyl]bis(trimethylsilyl)methane (9) and [2-(Dimethylamino)phenyl](trimethylsilyl)(trimethylstannyl)methane (10b). To a solution of 10 mmol of 6 in diethyl ether (20 mL) was added 10 mmol of either trimethylsilyl chloride or trimethyltin chloride. The mixture was refluxed for 2 h. The solvent was removed at reduced pressure, and the resulting oily residue was extracted with 2 × 10 mL of benzene (removal of LiCl). The combined benzene extracts were evaporated at reduced pressure giving pure 9 and 10b, respectively, as colorless oils in quantitative yield. 9: ¹H NMR (in CDCl₃, δ) NMe₂ 2.60 (6 H), Si₂CH 2.75 (1 H), SiMe₃ 0.18 (9 H), aromatic H 7.28 (4 H).

Synthesis of the Triorganotin Bromides 3 and 4. To a solution of the respective diorganotin dibromide (10 mmol) (dimethyl-, diphenyl-, or methylphenyltin dibromide) in diethyl ether (25 mL) was added 10 mmol of the solid organolithium compound (5 or 6) in small portions in 0.5 h. The resulting suspension or solution was stirred for 2 h. The solvent was removed in vacuo, and the resulting solid was extracted with three 20-mL portions of hot benzene (removal of LiBr). The combined benzene extracts were evaporated at reduced pressure, yielding the almost pure triorganotin bromides as white solids in quantitative yield. For analytical purposes the compounds were recrystallized from a hot benzene/hexane (50/50) mixture. Yields, melting points, analytical data, and molecular weight data are in Table I.

X-ray Structure Determination of 4c (C₁₉H₂₃BrNSiSn). **Data Collection and Refinement.** A crystal of the title compound was glued on top of a glass fiber and transferred to an Enraf-Nonius CAD4F diffractometer for data collection. Unit cell dimensions, their corresponding standard deviations, and a unique data set were obtained by procedures standard at our laboratory¹⁴ using zirconium-filtered Mo Kα radiation. The crystal data and details of the data collection and structure refinement are summarized in Table II. The intensities of two reflections were monitored after every 2 h of X-ray exposure time. A small decay of up to 1% at the end of the data collection was observed. The data were subsequently corrected for absorption, Lorentz, and polarization effects and the small decay.¹⁴ The validity of

Table II. Crystal Data and Details of the Structure Analysis of 4c

a. Crystal Data	
empirical formula	C ₁₉ H ₂₃ BrNSiSn
M _r	497.12
space group	P2 ₁ /n
cryst system	monoclinic
a, Å	13.085 (4)
b, Å	16.127 (5)
c, Å	10.437 (3)
β, deg	99.88 (2)
V, Å ³	2170 (1)
Z	4
D(calcd), g·cm ⁻³	1.522
F(000), electrons	992
μ(Mo Kα), cm	29.4
crystal	elongated prism
face <i>h</i> , <i>k</i> , <i>l</i> , (<i>d</i> , mm)	-1,-1,1 (0.07); -2,3,2 (0.06); 1,1,-1 (0.08); 1,-1,-1 (0.06); 0,-1,0 (0.01); -1,0,1 (0.06); 2,0,1 (0.46); -2,2,-1 (0.36); -2,-4,-1 (0.30)
cryst volume, mm ³	0.018
no. of grid points	268
max transmissn	0.744
min transmissn	0.522
b. Data Collection	
θ(min), θ(max)	0.1, 27.5
radiatn, Å	0.710 69 (Mo Kα), Zr filtered
ω-2θ scan, deg	0.40 + 0.35 tan θ
data set	+ <i>h</i> ,+ <i>k</i> ,± <i>l</i>
horizontal and vertical aperture, mm	2.0, 3.0
max time/reflectn, s	90
reflctns	0,2,0 and 1,1,-2
total reflctn data	5062
total unique reflctns	4955
obsd data (<i>I</i> ≥ 2.5σ(<i>I</i>))	3185
c. Refinement	
no. of refined parameters	286
weighting scheme	w ⁻¹ = (σ ² (<i>F</i>) + 0.000 855 <i>F</i> ²)/1.1718
final R _F and R _{wF}	0.0307, 0.0346
min, max residual density, e·Å ⁻³	-0.45, 0.51
rms deviatn of a reflctn of unit wt	1.10
max shift/error	0.13

the crystal description was checked by its application to the absorption correction of the Ψ-scan data for the reflection 221: the maximum variation about the mean diminished from 19% to 8%. The structure was solved via location of the Sn and Br from the Patterson synthesis, followed by standard difference Fourier techniques; all the hydrogen atoms were found from a difference Fourier map except for the methyl hydrogen atoms of the trimethylsilyl moiety, which were introduced at calculated positions (C-H : 1.08 Å) and refined as rigid groups with their carrier carbon atoms.

Refinement on *F* by full-matrix least-squares techniques converged at *R* = 0.0307. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with individual isotropic thermal parameters, except for the methyl hydrogen atoms that were refined with one overall isotropic thermal parameter for those on Si (C(17), C(18), and C(19), *U* = 0.25 (2) Å²) and one for those remaining (C(8), C(15), and C(16), *U* = 0.108 (7) Å²). Weights based on counting statistics were introduced in the final stages of the refinement. The final values of the refined positional parameters are given in Table III.

Analysis of the thermal motion of the three methyl groups of the trimethylsilyl moiety indicated a strong librational motion about the Si-C(1) bond (see deposited Ortep plot).

Neutral scattering factors were taken from ref 15a and corrected for anomalous dispersion effects.^{15b} All calculations were carried out with the programs SHELX76¹⁶ and EUCLID¹⁷ on the CY-

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Table III. Positional Parameters and Their Estimated Standard Deviations^a

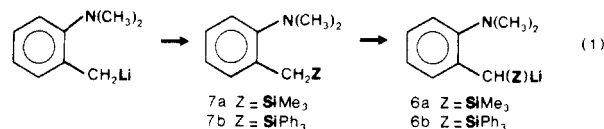
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} , Å ²
Sn	0.24102 (2)	0.18402 (2)	0.46264 (3)	0.0475 (1)
Br	0.15707 (5)	0.18629 (3)	0.21135 (4)	0.0764 (2)
Si	0.26301 (8)	-0.03033 (7)	0.4285 (1)	0.0523 (4)
N	0.3073 (3)	0.1607 (2)	0.6983 (3)	0.056 (1)
C(1)	0.1942 (3)	0.0595 (2)	0.4957 (3)	0.044 (1)
C(2)	0.1792 (3)	0.0517 (2)	0.6354 (4)	0.049 (1)
C(3)	0.2318 (3)	0.1032 (3)	0.7339 (4)	0.055 (1)
C(4)	0.2119 (5)	0.0982 (4)	0.8598 (5)	0.077 (2)
C(5)	0.1416 (4)	0.0412 (5)	0.8891 (6)	0.094 (3)
C(6)	0.0899 (5)	-0.0107 (4)	0.7967 (6)	0.085 (2)
C(7)	0.1087 (4)	-0.0057 (3)	0.6703 (5)	0.064 (2)
C(8)	0.3883 (4)	0.2318 (4)	0.4373 (6)	0.076 (2)
C(9)	0.1387 (3)	0.2740 (2)	0.5180 (4)	0.054 (1)
C(10)	0.1643 (4)	0.3581 (3)	0.5170 (5)	0.068 (2)
C(11)	0.1035 (6)	0.4172 (4)	0.5576 (6)	0.090 (2)
C(12)	0.0154 (6)	0.3951 (4)	0.6003 (5)	0.095 (3)
C(13)	-0.0144 (5)	0.3131 (4)	0.6037 (5)	0.082 (2)
C(14)	0.0491 (4)	0.2520 (3)	0.5613 (4)	0.067 (2)
C(15)	0.4109 (4)	0.1220 (3)	0.7154 (6)	0.072 (2)
C(16)	0.3159 (5)	0.2401 (4)	0.7730 (6)	0.086 (2)
C(17)	0.3498 (6)	0.0049 (4)	0.3188 (8)	0.145 (4)
C(18)	0.1647 (6)	-0.0986 (5)	0.336 (1)	0.210 (6)
C(19)	0.3407 (6)	-0.0930 (4)	0.5589 (6)	0.128 (3)

$$^a U_{eq} = \frac{1}{3} \sum_i \mu_i a_i^* a_j^* \bar{a}_i \bar{a}_j$$

BER-175 computer of the University of Utrecht.

Results and Discussion

2-Me₂NC₆H₄CH₂Li (5) and 2-Me₂NC₆H₄CH(SiMe₃)Li (6). The in situ preparation of 2-Me₂NC₆H₄CH₂Li and subsequent use for the synthesis of a variety of interesting organometallic compounds has been well documented.¹⁰ In our recent study of the structure and reactivity of organolithium compounds with heteroatom-containing substituents,¹⁸ we isolated 5 from the reaction of 2-Me₂NC₆H₄CH₃ with *n*-butyllithium in an exact 1/1 molar ratio. Structural characterization of pure 5 is, however, hampered by its low solubility in weakly or noncoordinating solvents like benzene or diethyl ether. The α-Me₃Si- and α-Ph₃Si-substituted lithium derivatives 6 have been prepared by the route shown in eq 1.



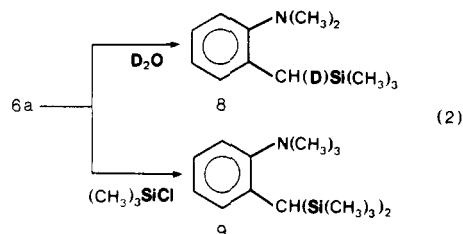
Conversion of 5 with R₃SiCl into 7 occurred almost quantitatively. The tetraorganosilicon compounds 7a (a distillable oil) and 7b (a crystalline solid) react smoothly with *n*-butyllithium in diethyl ether to give the novel α-lithiated benzyl lithium derivatives 6. Pure diethyl ether free 6 can be isolated from the reaction mixture as yellow solids in 80% yield.¹⁹ Contrary to the insolubility of 5 the α-silylated derivatives dissolve readily in ethers and hydrocarbons. Reactions with both D₂O and Me₃SiCl afforded the expected α-deuterio- and α-bis(triorganosilyl)-substituted compounds, respectively, which is shown in eq 2 for the conversion of 6a. Their isolation in about 95% yield established that the α-lithiation of 7 occurs

(16) Sheldrick, G. SHELX 76, a program for crystal structure determination; Anorganisch-Chemisches Institut der Universität Göttingen: Göttingen, FRG, 1976.

(17) Spek, A. L. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon: Oxford, 1982; p 528.

(18) Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* 1982, 104, 5490. Jastrzebski, J. T. B. H.; van Koten, G.; Goubitz, K.; Arlen, C.; Pfeffer, M. *J. Organomet. Chem.* 1983, 246, C75.

(19) Attempts to obtain suitable single crystals of 6 are underway.

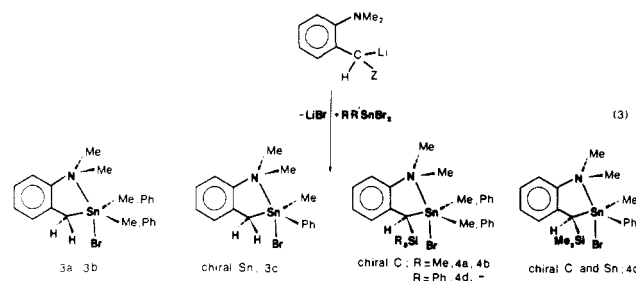


quantitatively. Attempts to convert 9 into the corresponding α-lithiated bis(trimethylsilyl) derivative with either *n*-butyllithium or *n*-butyllithium-TMEDA were unsuccessful.

The new compounds were characterized by their elemental analysis, molecular weight data, and ¹H NMR spectra (vide infra), see Tables I and IV.

2-Me₂NC₆H₄CH(R)SnR'₃ [R' = Me, R = H (10a) or SiMe₃ (10b); R = H, R' = Ph (10c)] and 2-Me₂NC₆H₄CH(R)SnR'R''Br (4). Both lithiated compounds 5 and 7 react quantitatively with Me₃SnCl to give the corresponding trimethyltin derivatives 10a and 10b while the triphenyltin derivative 10c and the triphenylsilyl derivative 10d were obtained from the reaction of 5 with Ph₃SnCl and Ph₃SiCl, respectively. These reactions are analogous to the formation of the trimethylsilyl derivatives 7 and 9; see eq 1. For the interpretation of their NMR spectra and fluxional behavior (vide infra), it is important to note that the benzylic C atoms in 10b and 10d are chiral.

The triorganotin bromides 3 and 4 were obtained by reacting either a suspension of 5 in diethyl ether with the diorganotin dibromide or a solution of 6 with these tin dibromides; see eq 3. Whereas the 2-Me₂NC₆H₄CH(R)-



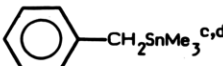
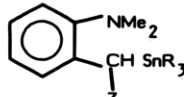
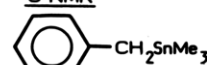
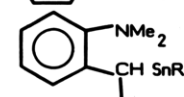
SnMe₃ compounds (10a and 10b) are distillable oils, the novel triorganotin bromides appeared to be crystalline solids. Like the tetraorganotin compounds these triorganotin bromides exist in benzene as monomers (see Table I).

The structures of the triorganotin compounds in solution were studied by ¹H and ¹³C NMR spectrometry. Main questions which had to be answered were as follows: i, does intramolecular Sn-N coordination occur; ii, what is the configurational stability of the various chiral centers in these compounds. In order to facilitate the interpretation of the NMR data, an X-ray structure determination of 2-Me₂NC₆H₄CH(SiMe₃)SnMePhBr (4c) was carried out.

Molecular Geometry and Crystal Structure of 2-Me₂NC₆H₄CH(SiMe₃)SnMePhBr (4c). The crystal structure of 4c consists of four discrete molecules per monoclinic unit cell (Figure 1). The molecular geometry of one diastereomer is shown in a Pluto drawing (Figure 2) while selected data on the molecular geometry are listed in Table V. The tin center has a distorted trigonal-bipyramidal coordination geometry. The organo ligands occupy the equatorial sites while the more electronegative Br and N ligands are in the axial positions.

Figure 1 shows that the unit cell contains, as a requirement of the space group symmetry, two enantiomeric pairs of diastereomers R_CR_{Sn} and S_CS_{Sn}. The isomer

Table IV. Relevant ¹H^a and ¹³C NMR^a Data of the Tetraorganotin Compounds 10

	NMe ₂	SiMe ₃	CHZ ^b	SnMe ₃ ^b
¹H NMR				
			2.40 (59, 62)	0.16 (50, 52)
				
10a, Z = H, R = Me ^c	2.82		2.42 (62, 64)	0.15 (52, 54)
10b, Z = SiMe ₃ , R = Me ^c	2.83	0.25	2.90 (78, 82)	0.32 (49, 52)
10c, Z = H, R = Ph ^e	1.63		2.30 (68, 72)	
10d, Z = SiPh ₃ , R = Me	2.60		3.80 (86, 91)	0.0 (52, 50)
¹³C NMR				
			20.5 (285)	-10.1 (322)
				
10a, Z = H, R = Me ^c	44.3		18.3 (327)	-8.9 (331)
10b, Z = SiMe ₃ , R = Me ^c	44.9	0.30	17.3 (235)	-8.2 (320)
10c, Z = H, R = Ph ^e	44.2		18.4 (373)	
10d, Z = SiPh ₃ , R = Me ^c	44.8		14.2 (220)	-7.3 (330)

^a All values in δ relative to Me₄Si (internal standard); at ambient temperature; singlet unless otherwise stated. ^b ¹H NMR data ²J (¹¹⁷,¹¹⁹Sn, ¹H), Hz. ¹³C NMR data ¹J(¹¹⁹Sn,¹³C) Hz. ^c In CCl₄. ^d See ref 22. ^e In CDCl₃.

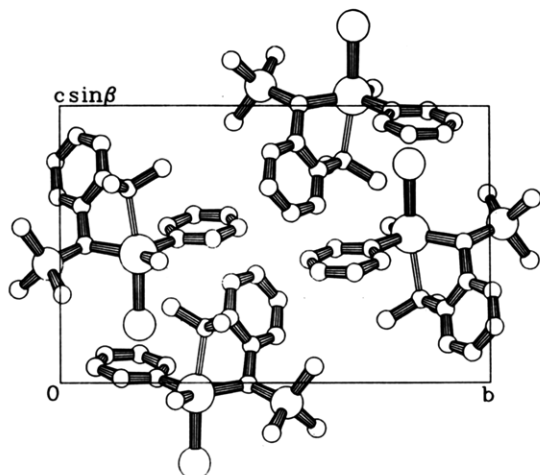


Figure 1. Monoclinic unit cell (projection down the *a* axis) of **4c** containing four discrete molecules: two *R_C,R_{Sn}* (see Figure 2) and two *S_C,S_{Sn}* diastereomers.

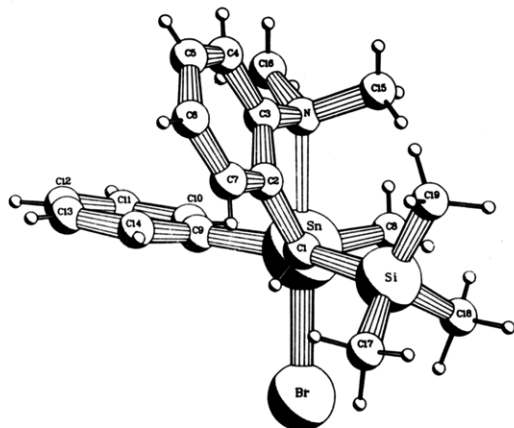


Figure 2. Molecular geometry of the *R_C,R_{Sn}* diastereomer of MePh[2-Me₂NC₆H₄CH(SiMe₃)]SnBr (**4c**). For an Ortep stereo plot (stereoview) see Figure A deposited.

Table V. Relevant Data on the Geometry of C₁₉H₂₃BrNSiSn (**4c**)

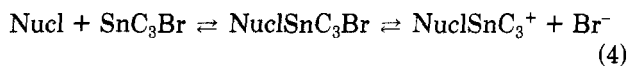
Bond Distances, Å			
Sn-Br	2.663 (1)	Sn-N	2.492 (3)
Sn-C(1)	2.144 (3)	Sn-C(8)	2.134 (5)
Sn-C(9)	2.121 (4)	N-C(3)	1.449 (6)
N-C(15)	1.475 (6)	N-C(16)	1.493 (7)
C(1)-C(2)	1.509 (5)	C(1)-Si	1.902 (4)
C(2)-C(3)	1.406 (6)	Si-C(17)	1.836 (8)
Si-C(18)	1.836 (8)	Si-C(19)	1.853 (7)
Bond Angles, deg			
Br-Sn-N	171.3 (1)	Br-Sn-C(1)	95.2 (1)
Br-Sn-C(8)	95.8 (2)	Br-Sn-C(9)	94.9 (1)
N-Sn-C(1)	76.1 (1)	N-Sn-C(8)	90.4 (2)
N-Sn-C(9)	87.9 (1)	C(1)-Sn-C(8)	130.3 (2)
C(1)-Sn-C(9)	112.7 (1)	C(8)-Sn-C(9)	114.3 (2)
Sn-N-C(3)	102.3 (2)	Sn-N-C(15)	109.9 (3)
Sn-N-C(16)	111.6 (3)	C(3)-N-C(15)	110.5 (3)
C(3)-N-C(16)	114.1 (4)	C(15)-N-C(16)	108.4 (3)
Sn-C(1)-C(2)	108.8 (2)	Sn-C(1)-Si	119.2 (2)
C(2)-C(1)-Si	116.2 (2)	C(1)-C(2)-C(3)	121.9 (3)
N-C(3)-C(2)	117.4 (4)	C(1)-Si-C(17)	112.2 (2)
C(1)-Si-C(18)	108.5 (3)	C(1)-Si-C(19)	112.3 (2)
C(17)-Si-C(18)	108.1 (4)	C(17)-Si-C(19)	107.9 (3)
C(18)-Si-C(19)	107.7 (4)		
Torsion Angles, deg			
Sn-C(1)-Si-C(17)	-9.2 (4)	C(2)-C(1)-Si-C(17)	-142.4 (4)
Sn-C(1)-Si-C(18)	-128.6 (4)	C(2)-C(1)-Si-C(18)	98.2 (4)
Sn-C(1)-Si-C(19)	112.4 (3)	C(2)-C(1)-Si-C(19)	-20.8 (4)
Br-Sn-C(9)-C(10)	-89.7 (4)	Br-Sn-C(9)-C(14)	93.5 (4)
C(4)-C(3)-N-C(15)	89.5 (6)	C(4)-C(3)-N-C(16)	-32.8 (6)
Si-C(1)-C(2)-C(3)	111.8 (4)		

which has the *R* configuration at the benzylic C atom combines this with the *R* configuration²⁰ at the five-coordinate tin center. Figure 2 reveals a possible reason for the preference for these particular sets of configurations at the neighboring C and Sn centers. The five-membered

(20) The assignment of the configuration at the tin center is according to the convention for the designation of five-coordinate complexes: *Pure Appl. Chem.* 1971, 28, 1; cf. section 7.514.

chelate ring is puckered as is indicated by the average absolute torsion angle which amounts to 23.7°. The actual ring conformation is such that it places the bulky Me₃Si substituent in the sterically most favorable position, i.e., out of the plane of the phenyl ring (vide infra). This ring conformation is furthermore combined with the configuration at Sn in which this Me₃Si substituent is on the side of the less bulky Me ligand. As a result the Si atom is only -0.41 (1) Å out of the equatorial plane defined by C(1), C(8), and C(9) on the side of the Sn atom (-0.20 (1) Å).

These structural features also provide an explanation for the observed diastereoselectivity during the formation of **4c** (see eq 3) which involves the simultaneous formation of two chiral centers. The organolithium compound **6a**, from which **4c** is derived, very likely has a polynuclear structure involving multicenter C-Li bonding. Such carbon centers have low configurational stability,²¹ and in principle it must be expected that the reaction of **6** with MePhSnBr₂ provides the enantiomeric pairs of both diastereoisomers. The ¹H and ¹³C NMR spectra of reaction mixtures of **4** showed exclusively one resonance pattern which indicates that most likely the R_C,S_{Sn}/S_C,R_{Sn} pair is not formed or this pair after its formation is converted in a subsequent, fast stereoisomerization process in the actually isolated S_C,S_{Sn}/R_C,R_{Sn} pair. However, earlier studies on **2** showed that the latter processes for this type of compounds with intramolecular coordination are slow,^{2a} which makes the first possibility, that the selective formation of the diastereoisomers is a kinetically controlled process, most likely. The structure of **4** is one of a series of related triorganotin halide compounds we have studied containing a five-membered chelate ring with intramolecular Sn-N coordination.²² Also in the case of **4c** the relevant geometrical data, i.e., the Sn-N and Sn-Br bond lengths and the C-Sn-Br bond angles, match perfectly well with the curve deduced from crystallographic evidence, by Britton and Dunitz,²³ that maps the pathway for the S_N2 reaction of triorganotin bromides with nucleophiles:



Furthermore, it is interesting to note that the sum of the bond angles in the equatorial plane is 357.2° with the Sn atom on the side opposite to the attacking nitrogen atom (i.e., the nucleophile).

Structures in Solution. The Tetraorganotin Compounds 2-Me₂NC₆H₄CH(Z)SnR₃ (10**).** Comparison of the ²J(¹¹⁹SnC¹H) values on the methyl (Sn) protons of the trimethyltin derivatives **10a**, **10b**, and **10d** with those of the parent compound trimethylbenzyltin (see Table IV) established that the tin center in these *o*-Me₂N-substituted compounds are tetracoordinate. They all have the characteristic ²J(¹¹⁹Sn,C¹H) value for tetracoordinate tin of about 50 Hz.^{24,25} Accordingly, the built-in ligand does not interact with the tin center in these compounds. Most conclusive in this respect is the observation of a singlet resonance for the NMe₂ protons (at 2.83 ppm vs. 2.70 ppm for *N,N*-dimethyltoluidine) in **10b** which contains a chiral benzylic carbon center. Sn-N coordination would have resulted in diastereotopism of the NMe₂ grouping (vide

supra and ref 2). Therefore the singlet resonance is a second, direct proof that the NMe₂ group is not coordinated to the tin center in the tetraorganotin compounds **10**.

The data of **10a** and Me₃SnCH₂Ph also reveal that the introduction of a Me₂N group has little effect on the δ-(CH₃) and δ(CH₂) values in both the ¹H and ¹³C NMR spectra. That, however, the *o*-Me₂N substituent has a considerable influence on the electron density in the σ-skeleton of the benzylic group is indicated by the increase of the ²J(^{117,119}Sn,CH) by 40 Hz.

Rather large and specific changes are observed on introducing a SiMe₃ or SiPh₃ group (i.e., **10b** and **10d**) at the benzylic carbon atom or by replacing an α-SnMe₃ by an α-SnPh₃ group (i.e., **10c**). The C(benzyl) resonances in the silylated compounds **10b** and **10d** are shifted to higher field which indicates that introduction of the more electropositive Si groupings makes the C(benzyl) center slightly more negative in part by polarization.^{12d} A considerable decrease of the ¹J(^{117,119}Sn,¹³C(benzyl)) by 88 Hz in **10b** and 107 Hz in **10d** is observed. The ¹H NMR data of **10b** are likewise affected: the benzylic H resonance shifts downfield by 0.5 ppm, while the ²J(¹¹⁹Sn,C¹H) on this proton increases by 16 Hz.

In both **10a** and **10b** the Sn sp³ center of a tetrahedral SnMe₃ group is bonded to C(benzyl). Accordingly the specific changes of these ¹J and ²J values must arise from a change of the s orbital contribution in the C(benzyl) hybrids which take part in the C-H bonding (i.e., an increased contribution) and in the C-Sn bonding (i.e., a considerable decrease).²⁶

Finally, the replacement of Me (**10a**) by Ph (**10c**) groups results in an increase of the ¹J(^{117,119}Sn,¹³C(benzyl)) by almost 50 Hz while the δ(NMe₂) is shifted upfield by almost 1.2 ppm by this replacement (see Table IV). In particular the latter observation is of interest for the interpretation of the structural features of the triorganotin halides **3** and **4** in solution (vide infra).

The Triorganotin Bromides 2-Me₂NC₆H₄CH₂SnRR'/Br (3**) and 2-Me₂NC₆H₄CH(SiMe₃)SnRR'/Br (**4**).** The ¹H and ¹³C NMR data of **3** and **4** are given in Tables VI and VII. For the methyltin derivatives **3a**, **3c**, **4a**, and **4c** ²J(^{117,119}Sn,C¹H) amounts to about 60 Hz (vs. about 50 Hz in **10a** and **10b**) which is a value normally observed for triorganotin halides with five-coordination at tin.^{24,25} The increase of ¹J(^{117,119}Sn,¹³C) in the ¹³C NMR spectra from about 325 Hz in **10a** and **10b** to about 450 Hz in these triorganotin bromides seems to be in agreement with this: i.e., Sn-N coordination results in a trigonal-bipyramidal structure for these compounds as has been found for **4c** in the solid (vide supra).

The absolute values for the ²J(^{117,119}Sn,C¹H) and ¹J(¹¹⁹Sn,¹³C) on the benzylic C and H atoms (vide supra for **10b** and **10d**) are rather extreme. However, the observed trends are consistent with the increased s orbital participation in the Sn-C bond of a planar C₃Sn arrangement of the *trans*-C₃SnNBr complexes **3** and **4** as compared with sp³-hybrid orbital of Sn taking part in a Sn-C bond of the tetrahedral C₄Sn grouping of **10** (cf. ref 27).

The ¹³C chemical shift values of the NMe₂ C resonances are not sensitive to the anticipated Sn-N coordination. A downfield shift would be expected for the species in the slow-exchange limit of the Sn-N bond association-disso-

(21) van den Berghe, E. V.; van der Kelen, G. P. *J. Organomet. Chem.* **1968**, *11*, 479.

(22) See ref 2a. 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. Jastrzebski, J. T. B. H.; Knaap, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287.

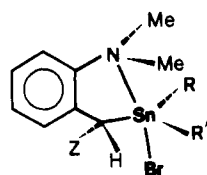
(23) Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2971.

(24) See ref 1, 2a, and 2b.

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

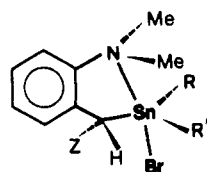
(26) An ¹¹⁹Sn NMR study of these and related compounds is underway in order to clarify the origin of this decrease of the ¹J(¹¹⁹Sn,¹³C) with the benzylic C atom.

(27) Nádvořník, M.; Holeček, J.; Handlíř, K.; Lyčka, A. *J. Organomet. Chem.* **1984**, *275*, 43.

Table VI. Relevant ¹H NMR Data of the Triorganotin Bromides 3 and 4

	Z	R	R'	NMe ₂	SiMe ₃	CHZ ^b	SnCH ₃
3a	H	Me	Me	2.80		2.90 (76, 80)	0.90 (58, 61)
3b	H	Ph	Ph	2.00		2.90 (80, 83)	
3c	H	Me	Ph	2.35; 2.25/2.65 ^c		2.95/3.05 ^d (78, 82) ^e	0.95 (60, 63)
4a	SiMe ₃	Me	Me	2.59; 2.50/2.68 ^f	0.18	0.43 (56, 58)/0.98 (60, 63)	0.43 (56, 58)/0.98 (60, 63)
4b	SiMe ₃	Ph	Ph	2.21; 2.11/2.30 ^g	0.21	3.05 (114, 119)	
4c	SiMe ₃	Me	Ph	2.41; 2.26/2.56 ^h	0.30	2.79 (110, 115)	1.24 (62, 65)
4d	SiPh ₃	Me	Me	2.50; 2.25/2.65 ⁱ		3.55 (108/113)	0.50 (68, 72)/0.80 (65, 68)

^a All values are in δ relative to Me₄Si (internal standard); in CDCl₃; at ambient temperature; singlets unless otherwise stated. ^b ²J(^{117,119}Sn, ¹H), Hz. ^c At -50 °C, $T_{\text{coal}} = 4$ °C. ^d $J_{\text{AB}} = 14$ Hz. ^e Both ²J_{Sn-HA} and ²J_{Sn-HB}. ^f At -12 °C, $T_{\text{coal}} = 4$ °C. ^g At -22 °C, $T_{\text{coal}} = -13$ °C. ^h At -27 °C, $T_{\text{coal}} = 10$ °C. ⁱ At -20 °C, $T_{\text{coal}} = 0$ °C.

Table VII. Relevant ¹³C NMR Data of the Triorganotin Bromides 3 and 4

	Z	R	R'	NMe ₂	SiMe ₃	CHZ	CH ₃
3a	H	Me	Me	45.2		23.8 (482) ^b	-0.8 (446) ^b
3b	H	Ph	Ph	45.6		24.4 (524) ^b	
3c	H	Me	Ph	46.0; 4.55/45.9 ^d		24.5 (518) ^b	1.5 (479) ^b
4a	SiMe ₃	Me	Me	46.9; 44.5/49.2 ^e	1.6 (16) ^b [51] ^c	26.4 (417) ^b [46] ^c	-0.2 (427), ^b 3.2 (473) ^b
4b	SiMe ₃	Ph	Ph	47.2; 45.1/49.4 ^f	2.1 (18) ^b [53] ^c	28.4 (452) ^b [45] ^c	
4c	SiMe ₃	Me	Ph	47.0; 44.8/49.3 ^g	1.7 (18) ^b [52] ^c	25.4 (442) ^b [44] ^c	1.4 (511) ^b
4d	SiPh ₃	Me	Me	46.4; 44.4/48.2 ^h		25.9 (420) ^b [...] ⁱ	0.3 (448) ^b /3.3 (501) ^b

^a All values are in δ relative to Me₄Si (internal standard); CDCl₃ solvent; at ambient temperature. ^b ¹J(¹¹⁹Sn, ¹³C), Hz. ^c ¹J(²⁹Si, ¹³C), Hz. ^d At -30 °C, $T_{\text{coal}} = -10$ °C. ^e At -30 °C, $T_{\text{coal}} = 20$ °C. ^f At -20 °C, $T_{\text{coal}} = 5$ °C. ^g At -30 °C, $T_{\text{coal}} = 20$ °C. ^h At -20 °C, $T_{\text{coal}} = 5$ °C. ⁱ Not observed.

ciation process (vide infra) with respect to the chemical shift for the NMe₂ C atoms in the tetraorganotin derivatives. A similar conclusion can be drawn for the shifts of the NMe₂ H resonances. Contrary to this insensitivity of the ¹H and ¹³C chemical shifts of the NMe₂ grouping for N-to-Sn coordination a distinct influence of the substitution of Ph for Me groups at the tin center is found on the δ (NMe₂) (see Table V; about 0.4 ppm per substituted Me group in 3 and about 0.2 ppm for a similar substitution in 4).

A similar observation is made when these values for the tetraorganotin compounds 10a and 10c are compared, i.e., 1.20 ppm for the substitution of three methyl groups by phenyl.

These distinct chemical shifts arise from the rigidity of the 2-Me₂NC₆H₄CH(Z) ligand. The Newman projection along the C(aryl)-C(benzyl) bond (Figure 3) as well as Figure 2 show that the C(1), C(2), C(3), and N atoms, which in the triorganotin halides constitute four of the five atoms of the chelate ring, are held in one plane by the aryl nucleus. This is also the case in the tetraorganotin compounds. Furthermore, this projection shows that the rotamer population will be largely determined by the bulkiness of the SnR₃ group and the nature of Z. For example in the case of 10a and 10c the rotamer with the R₃Sn group perpendicular to the aryl nucleus is occupied predominantly. Accordingly the NMe₂ methyl groups are in close proximity of the R substituents and, because of unhindered rotation about the C-N axis as well as free inversion at N, can equally experience the shielding influence of the phenyl rings.

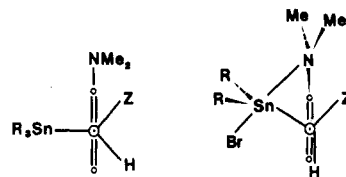


Figure 3. Newman projection along the C(aryl)-C(benzyl) bond in the RR'[2-Me₂NC₆H₄CH(Z)]SnBr compounds.

Detailed information concerning the Sn-N association-dissociation process as well as the configurational stability of the tin centers (on the NMR time scale) is obtained from the ¹H and ¹³C NMR spectra of 3 and 4 at different temperatures.

The spectra of 3c and 4a-c are temperature-dependent. At low temperatures the NMe₂ methyl resonances appear as two singlets in both the ¹H and the ¹³C NMR spectra of the compounds having either a chiral tin (3c) or a chiral benzylic carbon center (4a,b) or both chiral tin and benzylic carbon centers (4c). Sn-N coordination in these compounds renders the NMe₂ group a stable tetrahedral assembly and thus diastereotopic because it blocks inversion at N and rotation around the C-N bond. Above the coalescence temperatures (see Tables VI and VII) this diastereotopism disappears and the NMe₂ groups are homotopic; i.e., one singlet is observed, which indicates that the process A \rightleftharpoons B (vide supra) has become fast on the NMR time scale.

It is important to note that over the whole temperature range (-50 to +130 °C in toluene-d₆) the Sn center in the triorganotin halides has a relatively high configurational

stability. This is unambiguously shown by the following observations: i, the benzylic H atoms in 2-Me₂NC₆H₄CH₂SnMePhBr (**3c**) are diastereotopic establishing that inversion at the neighboring chiral tin center is slow or is even blocked on the NMR time scale; ii, the SnR₂ (R = Me in **4a** and Ph in **4b**) groupings, which are bonded to the chiral benzylic carbon center, are diastereotopic in both ¹H and ¹³C NMR spectra which shows conclusively that inversion at the tin center is in the slow-exchange limit; iii, for **4c**, which has two chiral centers, only one resonance pattern, both in the ¹H and ¹³C NMR spectra is observed over the whole temperature range studied (-50 to +125 °C in toluene) which points to the presence of only one enantiomeric pair of diastereomers in solution (*R_CR_{Sn}/S_CS_{Sn}* pair; cf. structure in the solid).

It is well-known in organotin chemistry that the configurational stability of a chiral tin center in triorganotin halides increases on introduction of highly hindering groups. Examples are MePhSn(CH₂CMe₂Ph)Cl²⁸ and Me[(SiMe₃)₂CH]₂SnCl.²⁹ It has been suggested that attack of nucleophiles at tin is the rate-determining step in the inversion of configuration process. The configurational stability of the highly hindered triorganotin compounds then has been attributed to the shielding of the tin atom for attack by nucleophiles.²⁸ Another approach which may give rise to increased configurational stability comprises the introduction of coordinating groups which can coordinate with the tin center, an approach which also has been successful for other group IV (14³²) metals such as Si, Ge,^{8,30} Pb, and Bi.³¹ We^{2,22} and others³ have shown that the flexibility of the five- or six-membered chelate ring is

of prime importance for the configurational stability of the metal center in these compounds. Thus in the triorganotin halides containing the benzylamine ligand (cf. **2**) the NMe₂ group is held in the neighborhood of the tin center even if it is not coordinated.⁹ The importance of this fact can be deduced from the observation that whereas the configurational stability is not affected by external nucleophiles,² inversion of configuration at tin in RRSn-[(CH₂)₂PO(Ph)R'']Br containing a very flexible chelate ring (all sp³C centers) occurs already even with very small amounts of nucleophiles.³

As has been indicated above (see Figures 2 and 3) the 2-Me₂NC₆H₄CH(Z) ligand is extremely rigid with the 2-Me₂N group held in close proximity of the tin center because of the rigid stereochemistry. If Z is a SiR₃ group, rotation about the C(benzyl)-C(aryl) bond most probably is blocked which locks the SnR₂Br group in a fixed position with respect to the N donor site. It is most probably for these stereochemical reasons that the configuration of the tin centers in the compounds **3** and **4** is stabilized to such a large extent.

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Registry No. **3a** (coordination entry), 102588-78-3; **3a**, 102615-61-2; **3b** (coordination entry), 102588-79-4; **3b**, 102630-15-9; **3c** (coordination entry), 84365-33-3; **3c**, 84457-47-6; **4a** (coordination entry), 102588-80-7; **4a**, 102615-62-3; **4b** (coordination entry), 102588-81-8; **4b**, 102615-63-4; **4c** (coordination entry), 102588-82-9; **4c**, 102615-64-5; **4d** (coordination entry), 102615-66-7; **4d**, 102615-65-6; **5**, 96454-49-8; **6a**, 93184-81-7; **6b**, 102615-59-8; **7a**, 102615-56-5; **7b**, 102615-57-6; **9**, 102615-60-1; **10a**, 84457-45-4; **10b**, 102615-53-2; **10c**, 102615-54-3; **10d**, 102615-55-4; PhCH₂SnMe₃, 4314-94-7; Me₂SnBr₂, 2767-47-7; Ph₂SnBr₂, 4713-59-1; MePhSnBr₂, 21247-36-9.

Supplementary Material Available: Tables of observed and calculated structure factors, final anisotropic thermal parameters, hydrogen atoms parameters, planes, and angles between planes as well as between bonds and planes and an Ortep plot (22 pages). Ordering information is given on any current masthead page.

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