

# Group 14 Metalated 6-Amino-1-Azafulvene Dimers. Evidence for a Double Intramolecular Nitrogen-Tin Interaction

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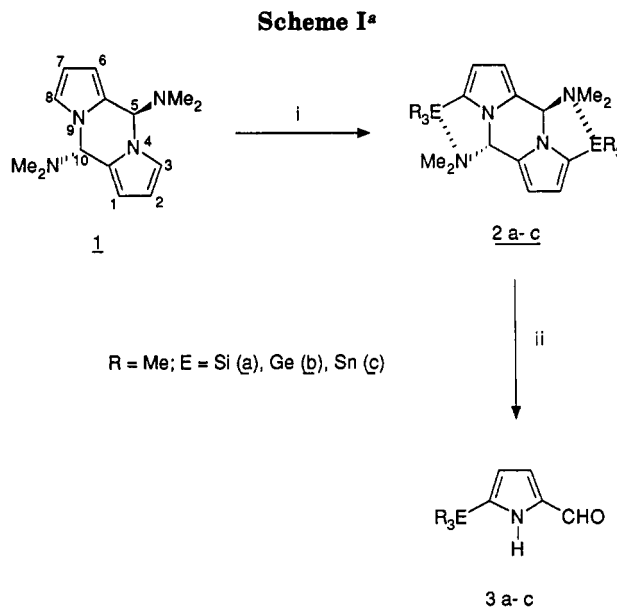
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**Summary:** The structures of group 14 C-metalated 6-amino-1-azafulvene dimers have been investigated in solution and in the solid state by NMR spectroscopy. For one of these compounds, 5,10-bis(dimethylamino)-3,8-bis(trimethylstannyl)-5H,10H-dipyrrolo[1,2-a:1',2'-d]-pyrazine (2c), the molecular structure in the solid state has been determined by X-ray diffractometry. The two tin centers have a distorted-trigonal-bipyramidal coordination geometry with the more electronegative N ligand at a pseudoaxial position, resulting in one of the longest known Sn—N interactions: 3.101 (5) Å. Moreover, the temperature-dependent <sup>13</sup>C CP-MAS NMR spectrum of this compound shows an appreciable narrowing of the Me<sub>3</sub>Sn signal between 296 and 333 K. By comparison with nonmetalated analogs or with isomer 5c, the nonreactivity of compound 2c toward hydrolytic decomposition into corresponding 5-(trimethylstannyl)-pyrrole-2-carbaldehyde (3c) may be the result of stabilization of the dimeric form 2c by a double Sn—N interaction. In silicon and germanium analogs (2a, 2b) the Si(Ge)—N interaction is weaker.

The simultaneous blocking of the aldehyde and amine functions of pyrrole-2-carbaldehyde by formation of the 6-amino-1-azafulvene dimer 1<sup>1</sup> allows the versatile synthesis of 5-substituted pyrrole-2-carbaldehydes.<sup>2a</sup> Recently, we prepared group 14 5-metalated pyrrole-2-carbaldehydes from 1 through intermediate 3,8-dimetalated derivatives 2<sup>3</sup> (Scheme I). However, although the C-metalation of 1 is easy, the deprotection of 2 to generate the aldehydes 3 appeared to be more difficult than with organic substituents,<sup>2a</sup> particularly when E = Sn. Thus, 3, having a tri-*n*-butylstannyl substituent, was obtained in moderate yield, and the hydrolysis of 2c into 3c failed.<sup>3</sup> This abnormal reactivity was ascribed to a possible double intramolecular nitrogen-heteroatom coordination in 2 (Me<sub>2</sub>N—E)<sup>4</sup> which would reduce the ease of monomerization of this dimer into the corresponding 6-amino-1-azafulvene<sup>5</sup> and consequently the latter's hydrolysis. A coordination of this type was considered for the lithiated derivative of 1,<sup>2a</sup> which can be prepared more easily than 2-lithiopyrroles<sup>6</sup> without addition of a complexing agent (i.e. TMEDA). However, structural data are not available



<sup>a</sup> Legend: i, (1) <sup>n</sup>BuLi/THF-hexane, (2) R<sub>3</sub>ECl; ii, for 3a,b THF/AcONa, H<sub>2</sub>O (reflux), for 3c MeI/MeCN, H<sub>2</sub>O (reflux).

for 1, either on its configuration (cis or trans) or on its conformation.

In this paper we report the structural analysis in solution and in the solid state by NMR spectroscopy of group 14 C-metalated 6-amino-1-azafulvene dimers; for the tin derivative 2c the molecular structure was determined by single-crystal X-ray diffraction.

**Synthesis of Compounds 2a-c, 3a-c, 5a,c and 6a,c.** The compounds 2a-c have been prepared by the previously

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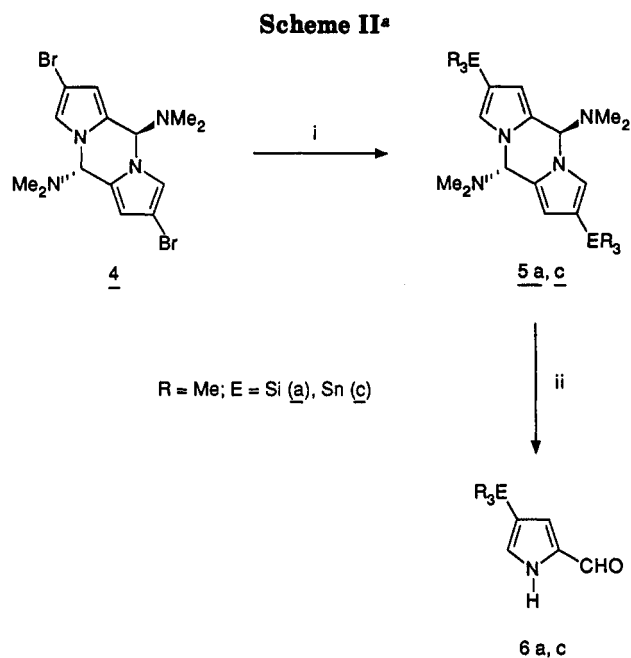
(5) Such dimers are in equilibrium with the azafulvene monomer at high temperatures;<sup>2</sup> see also: Mori, S.; Watanabe, M.; Kajigaeshi, S.; Kanemasa, S. *Heterocycles* **1976**, *4*, 957. Watanabe, M.; Kobayashi, T.; Kajigaeshi, S.; Kanemasa, S. *Chem. Lett.* **1975**, 607.

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(1) (a) Sammes, M. P. Physical and Theoretical Aspects, Synthesis, and Chemical Reactivity of 2H- and 3H-Pyrroles. In *Chem. Heterocycl. Compd.* **1990**, *48* (Pyrroles, Part 1), 549-728 (609, 610, 613). (b) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1.

(2) (a) Muchowski, J. M.; Hess, P. *Tetrahedron Lett.* **1988**, *29*, 777; (b) **1988**, *29*, 3215.

(3) Denat, F.; Gaspard-Illoughmane, H.; Dubac, J. *J. Organomet. Chem.* **1992**, *423*, 173.



<sup>a</sup> Legend: i, (1) <sup>t</sup>BuLi/THF-pentane, (2) R<sub>3</sub>ECl; ii, THF/NaHCO<sub>3</sub>, H<sub>2</sub>O (reflux).

described method<sup>3</sup> and have been enriched (>95%) as the trans isomers by recrystallization (AcOEt). 2a,b were hydrolyzed in THF with aqueous AcONa under reflux during 15 h for 2a and 35 h for 2b, to give the C-metalated pyrrole-2-carbaldehydes 3a,b in 85% and 76% yield, respectively (Scheme I). Under these conditions, the tin derivative 2c did not undergo hydrolysis, even in the presence of a potential complexing agent (KF, Et<sub>3</sub>N, pyridine, TMEDA, DABCO). On the other hand, when 2c was hydrolyzed with excess methyl iodide in 2% aqueous acetonitrile at reflux (3 h), the expected aldehyde 3c was formed in poor yield (20%).<sup>7a</sup> The products 5a,c were synthesized from the 3-bromo-6-(dimethylamino)-1-azafulvene dimer 4<sup>2b,7b</sup> (Scheme II) and hydrolyzed using

(7) (a) Procedure for 3c: This compound was obtained by hydrolysis of 2c with excess methyl iodide (12 equiv) in 2.5% aqueous acetonitrile (reflux 3 h) and purified by chromatography on silica gel with pentane/ethyl acetate/triethylamine (100:8:1) as eluent: mp 88 °C; 20% yield. <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 0.35 (s, SnMe), 6.42 (dd, *J* = 3.6, 2.3 Hz, H<sub>3</sub>), 7.00 (dd, *J* = 3.6, 2.3 Hz, H<sub>3</sub>), 9.51 (s, CHO). Anal. Calcd for C<sub>8</sub>H<sub>13</sub>ONSn: C, 37.26; H, 5.08. Found: C, 37.3; H, 5.1. (b) Procedure for 5a: To a stirred solution of 0.2 g (0.5 mmol) of 4 in 30 mL of anhydrous THF cooled to -78 °C was added 2 mmol of *tert*-butyllithium (1.7 M in pentane). The mixture was stirred for 30 min at -78 °C, and then 0.217 g (2 mmol) of Me<sub>3</sub>SiCl was added. The solution was stirred for 1 h at -50 °C and then for 30 min at room temperature. Hydrolysis, extraction (Et<sub>2</sub>O), drying (Na<sub>2</sub>SO<sub>4</sub>), and concentration gave 5a (70% yield). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 0.23 (s, SiMe), 2.27 (s, NMe), 5.88 (d, *J* = 0.8 Hz, H<sub>5,10</sub>), 6.23 (dd, *J* = 1.7, 0.8 Hz, H<sub>1,6</sub>), 6.97 (d, *J* = 1.7 Hz, H<sub>3,8</sub>). Anal. Calcd for C<sub>20</sub>H<sub>36</sub>N<sub>4</sub>OSi<sub>2</sub>: C, 61.79; H, 9.37. Found: C, 61.9; H, 9.3. An identical procedure was followed for the preparation of 5c from Me<sub>3</sub>SnCl (90% yield). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 0.22 (s, SnMe), 2.25 (s, NMe), 5.88 (d, *J* = 0.9 Hz, H<sub>5,10</sub>), 6.18 (dd, *J* = 1.6, 0.9 Hz, H<sub>1,6</sub>), 6.87 (d, *J* = 1.6 Hz, H<sub>3,8</sub>). Anal. Calcd for C<sub>20</sub>H<sub>36</sub>N<sub>4</sub>OSn<sub>2</sub>: C, 42.15; H, 6.37. Found: C, 42.2; H, 6.4. (c) Procedure for 6a: 5a in THF was hydrolyzed with a saturated aqueous NaHCO<sub>3</sub> solution under reflux for 15 h. After extraction (Et<sub>2</sub>O), drying (Na<sub>2</sub>SO<sub>4</sub>), and concentration, 6a was recrystallized from hexane and the residue was chromatographed on silica gel with pentane/ethyl acetate/triethylamine (100:10:1) as eluent (90% yield): mp 74 °C. <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 0.23 (s, SiMe), 7.08 (dd, *J* = 2.3, 1.4 Hz, H<sub>3</sub>), 7.21 (m, H<sub>5</sub>), 9.51 (d, *J* = 1 Hz, CHO), 10.5 (bs, NH). <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>): -0.4 (SiMe), 121.7 (C<sub>2</sub>), 127.8 (C<sub>3</sub>), 132.4 (C<sub>5</sub>), 134.5 (C<sub>2</sub>), 179.6 (CHO). IR (CCL<sub>4</sub>): 1650 (C=O), 3267 cm<sup>-1</sup> (N-H). Anal. Calcd for C<sub>8</sub>H<sub>11</sub>ONSi: C, 57.44; H, 7.83. Found: C, 57.5; H, 7.8. An identical procedure was followed from the preparation of 6c (40% yield from 5c): mp 70 °C. <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 0.27 (s, SnMe), 7.03-7.17 (m, H<sub>3</sub> and H<sub>5</sub>), 9.53 (d, *J* = 1.1 Hz, CHO), 9.9 (bs, N-H). <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>): -9.2 (SnMe), 118.8 (C<sub>4</sub>), 128.9 (C<sub>3</sub> or C<sub>5</sub>), 132.6 (C<sub>5</sub> or C<sub>3</sub>), 134.7 (C<sub>2</sub>), 179.2 (CHO). IR (CCL<sub>4</sub>): 1651 (C=O), 3264 cm<sup>-1</sup> (N-H). Anal. Calcd for C<sub>8</sub>H<sub>11</sub>OSn: C, 37.26; H, 5.08. Found: C, 37.3; H, 5.0.

**Table I.** <sup>1</sup>H NMR at Variable Temperatures for Compounds 1, 2a-c, and 5a,c<sup>a,b</sup>

	1	2a	2b	2c	5a	5c
<i>T</i> <sub>c</sub> (°C)	<-100	-76	-80	-66	<-100	<-100
δ(NMe) (ppm)		1.91	1.77	1.94		
Δ <i>ν</i> (Hz) <sup>c</sup>		255	252	252		
Δ <i>G</i> <sup>‡</sup> (kcal mol <sup>-1</sup> ) <sup>d</sup>		8.9	8.7	9.4		

<sup>a</sup> <sup>1</sup>H NMR spectra for 1 and 2a-c have been previously described.<sup>2a,3</sup>

<sup>b</sup> Conditions: *ν*<sub>0</sub> = 200.133 MHz; solvent CD<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Δ*ν* = chemical shift difference of the methyl signals below the coalescence temperature.

<sup>d</sup> Using the Eyring equation.<sup>18</sup>

a THF-aqueous HCO<sub>3</sub>Na mixture, giving 6a,c in 90% and 40% yield, respectively.<sup>7c</sup> Aside from the demetalation of 5c (or 6c),<sup>8</sup> it is clear that the compounds 5a,c are easily decomposed under alkaline conditions, unlike 2a,c, which are much more stable under the same conditions.

**Variable-Temperature NMR Data.** When nitrogen inversion is prevented at low temperature, the two diastereotopic methyl groups bonded to it in 1 and its derivatives should give two different <sup>1</sup>H resonances. The possible coordination N—E in 2a-c should give higher coalescence temperatures than for 1 (*T*<sub>c</sub> < -100 °C). This was observed (Table I), with *T*<sub>c</sub> = -66 °C in the case of the tin compound 2c, which is higher than for the silicon 2a (*T*<sub>c</sub> = -76 °C) or germanium 2b (*T*<sub>c</sub> = -80 °C) derivatives. Nevertheless, the calculated free energies, which are almost the same for 2a,c, agree with either a weak coordination effect or steric blocking of pyramidal inversion at nitrogen, which has been often observed.<sup>4</sup>

Pentacoordination of silicon<sup>4a-e</sup> and tin<sup>4b-j</sup> cause an upfield shift in the <sup>29</sup>Si and <sup>119</sup>Sn NMR spectra compared to a tetracoordinated model molecule in which additional coordination is not possible. When 1-methyl-5-(trimethylsilyl)pyrrole-2-carbaldehyde (δ(<sup>29</sup>Si) -10.9 ppm) is compared with 2a (δ(<sup>29</sup>Si) -13.5 ppm (CDCl<sub>3</sub>) relative to Me<sub>4</sub>Si), a weak upfield shift is evident, but in the case of weak nitrogen-silicon interactions, differences of 1-12 ppm have been reported.<sup>4e</sup> Between 1-methyl-5-(trimethylstannyl)pyrrole-2-carbaldehyde (δ(<sup>119</sup>Sn) -48.0 ppm) and 2c (δ(<sup>119</sup>Sn) -61.6 ppm (CDCl<sub>3</sub>) relative to Me<sub>4</sub>Sn) the upfield shift is greater. Moreover, chemical shifts in 2a,c do not change on cooling from ambient temperature to -100 °C.

These results lead us to think that the interactions between silicon, germanium, and tin atoms and nitrogen of the dimethylamino group are too weak to cause significant changes in solution NMR spectra.

**Solid-State CP-MAS Spectra.** Solid-state NMR spectra have been obtained with CP-MAS techniques (cross polarization, magic-angle spinning at 3000 Hz) on sealed samples (Kel-F tubes<sup>10</sup> in 7-mm ZrO<sub>2</sub> rotors) of 1 and 2a-c (Table II). <sup>29</sup>Si CP-MAS of 2a (δ -12.9 ppm relative to Me<sub>4</sub>Si in solution) and <sup>119</sup>Sn CP-MAS of 2c (δ -76.6 ppm relative to Me<sub>4</sub>Sn in solution) have been measured, and each consists of a single resonance line. These values compare well with those obtained in solution, but for the <sup>119</sup>Sn signal an upfield shift of 15 ppm was observed.

(8) The hydrolysis of 5c gives mainly the pyrrole-2-carbaldehyde corresponding to demetalation of 6c. The hydrolytic lability of the Sn-C bond in 6c (or 5c) is not surprising, owing to the electronic effect of the formyl group, which is known to favor electrophilic substitution meta on the pyrrole ring.<sup>9</sup>

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Table II.  $^{13}\text{C}$  CP-MAS Data for 1 and 2a-c<sup>a,b</sup>

	1	2a	2b	2c
EMe		2.9	3.4	-3.4 <sup>c</sup>
NMe	37.6/39.2 (qs)	35.0/36.6 (qs)	35.7 (qb)	37.0/38.4 (qs)
	44.8/46.3 (qs)	42.0/43.7 (qs)	42.8 (qb)	43.7/45.3 (qs)
CH	72.4/73.7 (qs)	72.5 (qb)	73.8 (qb)	72.9 (qb)
C $_{\beta}'$	108.6	107.6	108.4	109.3
C $_{\beta}$	112.7	122.1	120.3	122.9
		123.9	122.1	
C $_{\alpha}'$	123.0/124.2 (qs)	127.4 (qb)	127.1 (qb)	128.5/130.0 (qs)
		128.9 (qb)	128.7 (qb)	
C $_{\alpha}$	125.6/127.0 (qs)	132.6 (qb)	133.9 (qb)	131.7/133.0 (qb)

<sup>a</sup> Legend: CH, C<sub>5,10</sub>H; C $_{\alpha}$ , C<sub>3,8</sub>H; C $_{\alpha}'$ , C<sub>5a,10a</sub>H; C $_{\beta}$ , C<sub>2,7</sub>H; C $_{\beta}'$ , C<sub>1,6</sub>H (cf. 1 in Scheme I). <sup>b</sup> qs/qb = quadrupole splitting/broadening due to  $^{14}\text{N}$  quadrupolar moment. <sup>c</sup>  $^1J(^{119}/^{117}\text{Sn}^{13}\text{C}) = 375$  Hz.

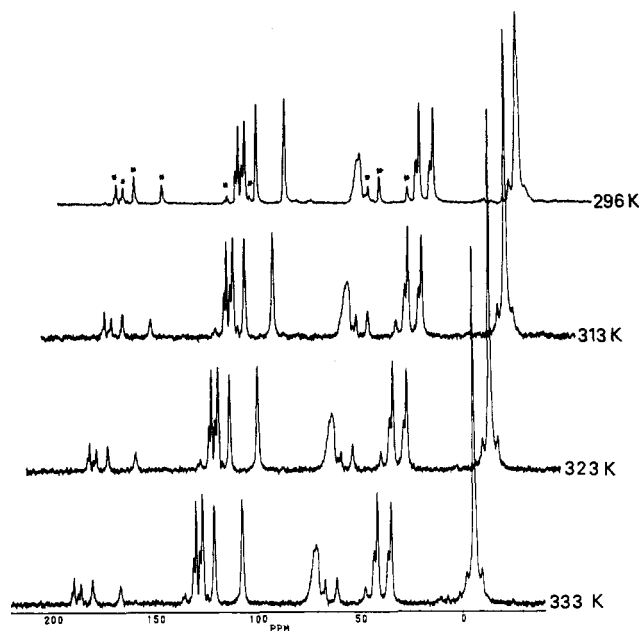


Figure 1.  $^{13}\text{C}$  CP-MAS spectrum of 2c and its temperature dependence between 296 and 333 K. The peaks marked with asterisks are spinning sidebands. Notice the unsymmetrical quadrupole splitting by  $^{14}\text{N}$ .

Temperature-dependent  $^{13}\text{C}$  CP-MAS NMR of 2a and 2c show different changes of the Me<sub>3</sub>E signals between 296 and 333 K: while the Me<sub>3</sub>Si signal remains unchanged (half-width 40 Hz), the half-width of the Me<sub>3</sub>Sn signal decreases from 110 to 43 Hz, indicating some gain of rotational freedom around the sp<sup>2</sup> C-Sn bond as the temperature increases (Figure 1). As may be seen from Table II, the spectral data for 1 and 2c as well as for 2a,b are very similar to one another. In all spectra the Me<sub>2</sub>N group shows up as two distinct signals. In the spectra of 1 and 2c half of the carbon atoms in the azafulvene dimer nucleus appear as single lines, thus indicating a 2-fold symmetry operation (2-fold axis, mirror plane, or inversion center) in the molecule. This 2-fold symmetry element is confirmed by X-ray diffraction data for 2c: the molecules in the crystal are placed with their gravity points on inversion centers of the space group (see below). The spectra of 2a,b differ from that of 2c. They show two signals for the C $_{\alpha}'$  and C $_{\beta}$  atoms, thus indicating crystallographically different molecules in the lattice or a lower point symmetry in the solid phase compared to 1 and 2c. Unfortunately we have not been able to obtain single crystals of 2a and 2b in order to establish the reason for the observed signal splitting.

Table III. X-ray Data Collection Parameters for 2c

formula:	C <sub>20</sub> H <sub>36</sub> N <sub>4</sub> Sn <sub>2</sub>
cryst syst:	P2 <sub>1</sub> /c
lattice constants:	a = 6.660(4), b = 12.418(8), c = 14.387(9) Å;
	β = 93.51(5)°
V	= 1187.6(9) Å <sup>3</sup>
Z	= 2
D <sub>exptl</sub>	= 1.594 g/cm <sup>3</sup>
AED-2 (Siemens) diffractometer	
2θ limit:	3–48°
μ(Mo Kα)	= 21.14 cm <sup>-1</sup>
structure solution:	direct methods
anisotropic and isotropic (H atoms) temperature factors	
1486 unique obsd rflns	
146 params	
R	= 0.0212
R <sub>w</sub>	= 0.0202
max difference Fourier peak:	0.28 e/Å <sup>3</sup>

The asymmetric quadrupole splitting<sup>11</sup> of the carbon atoms which have direct bonds to nitrogen can be used to verify the exact assignments of the  $^{13}\text{C}$  atoms in the rings. As can be seen from the comparison of Table II with  $^{13}\text{C}$  NMR spectra in solution, there is a perfect matching.

**X-ray Structure of 2c and Molecular Mechanics.** Single crystals of 2c were obtained from saturated toluene solutions by cooling. The most relevant data of the X-ray structure analysis are collected in Table III, while positional parameters and the most important bond lengths and angles are assembled in Table IV.<sup>12</sup> As a result of the X-ray structure analysis, the molecule 2c is drawn together with the atomic labeling in Figure 2. From inspection of that figure it is clear that the molecule is centrosymmetric, the center of symmetry being placed in the middle of the six-membered central N<sub>2</sub>C<sub>4</sub> cycle to which two five-membered pyrrole cycles are condensed. The atoms of the rings are all in a plane which has no distortion within the standard deviations. At the carbon atoms C5 and C5' two dimethylamino groups are attached in a trans orientation with respect to the ring plane. As expected, the nitrogen atoms N1 and N1' are trigonal planar and the tendency toward a mesomeric system (6π) in the five-membered rings can be seen from the bonding distances in Table IV. There are only two bonds which are slightly distorting the planar arrangement: the Me<sub>3</sub>Sn groups are not coplanar with the ring system. The torsional angle C5-N1-C1-Sn is found to be 7.9°, the Me<sub>3</sub>Sn groups being tilted toward the dimethylamino groups. The reason for this must be due to an intramolecular donor-acceptor bond between N2 and Sn (dotted line in Figure 2). The separation between the two atoms is 3.101(5) Å, which is only 0.65 Å smaller than the sum of the van der Waals radii of the two elements.<sup>13</sup> In tetraorganotin compounds with transannular Sn-N bonds the distances between tin and nitrogen are 2.63 Å;<sup>14</sup> however, longer Sn-N coordinate bonds have been reported,<sup>4h</sup> the longest being 3.10(1) Å in a triorganotin halide containing two 8-(dimethylamino)-1-naphthyl ligands.<sup>15</sup> Equally long is the

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(12) Programs used: (a) SHELXTL-PLUS (Sheldrick, G. M. A Program for Crystal Structure Determination, Version 4.0; Siemens Analytical X-ray Instruments: Madison, WI, 1989). (b) SCHAKAL 88 (Keller, E. A Fortran Program for the Graphic Representation of Molecular and Crystallographic Models; Freiburg, Germany, 1988).

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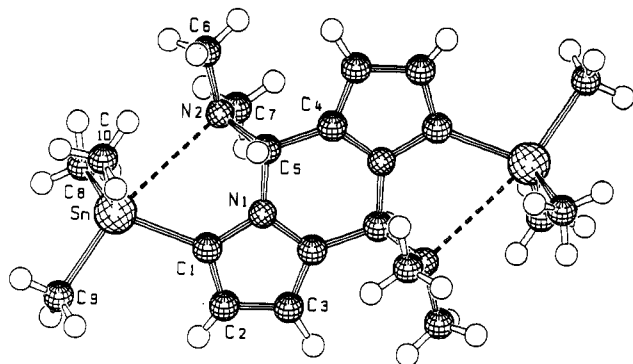


Figure 2. SCHAKAL<sup>12</sup> drawing of the molecular structure of **2c** after X-ray structure analysis.

Table IV. Atomic Coordinates ( $\times 10^4$ ), Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ), Bond Lengths ( $\text{\AA}$ ), and Bond Angles (deg) for **2c**

	x	y	z	U(eq)
Sn	935(1)	3887(1)	7946(1)	39(1)
N1	734(5)	4885(3)	5921(2)	31(1)
N2	-1023(5)	3248(3)	6013(2)	40(1)
C1	1730(6)	4842(3)	6794(3)	37(1)
C2	3453(7)	5416(4)	6715(3)	46(2)
C3	3546(7)	5797(4)	5804(3)	48(2)
C4	-1835(6)	4536(3)	4684(3)	35(1)
C5	-1195(6)	4366(3)	5692(3)	33(1)
C6	-2996(8)	2719(4)	6078(3)	69(2)
C7	340(7)	2610(4)	5470(3)	62(2)
C8	1875(8)	2249(4)	7843(3)	63(2)
C9	2686(8)	4562(4)	9114(3)	62(2)
C10	-2149(7)	4047(5)	8260(3)	68(2)
Sn-C1	2.131(4)	Sn-C8	2.136(5)	
Sn-C9	2.156(5)	Sn-C10	2.139(5)	
Sn-N2	3.101(5)	N1-C1	1.385(5)	
N1-C5	1.457(5)	N1-C4A	1.375(5)	
N2-C5	1.465(5)	N2-C6	1.477(6)	
N2-C7	1.467(6)	C1-C2	1.361(6)	
C2-C3	1.398(6)	C3-C4A	1.365(6)	
C4-C5	1.501(5)	C4-N1A	1.375(5)	
C4-C3A	1.365(6)			
C1-Sn-C8	112.9(2)	C1-Sn-C9	104.0(2)	
C8-Sn-C9	106.1(2)	C1-Sn-C10	113.6(2)	
C8-Sn-C10	113.1(2)	C9-Sn-C10	106.2(2)	
N2-Sn-C1	63.9(2)	N2-Sn-C8	78.6(2)	
N2-Sn-C9	167.4(2)	N2-Sn-C10	81.5(2)	
C1-N1-C5	123.8(3)	C1-N1-C4A	110.4(3)	
C5-N1-C4A	125.8(3)	C5-N2-C6	112.9(3)	
C5-N2-C7	112.5(3)	C6-N2-C7	112.1(3)	
Sn-C1-N1	126.8(3)	Sn-C1-C2	127.4(3)	
N1-C1-C2	105.3(3)	C1-C2-C3	110.0(4)	
C2-C3-C4A	107.2(4)	C5-C4-N1A	123.6(3)	
C5-C4-C3A	129.2(4)	N1A-C4-C3A	107.1(3)	
N1-C5-N2	107.3(3)	N1-C5-C4	110.5(3)	
N2-C5-C4	116.8(3)			

tin-nitrogen distance (3.101(5)  $\text{\AA}$ ) in **2c**. This interaction of the two atoms must, therefore, be considered as quite weak in terms of usual  $\sigma$ -bonds but, nevertheless, quite remarkable in terms of secondary bonding. Moreover, the  $\text{Me}_3\text{Sn}$  group which should display tetrahedral angles is seriously distorted; the coordination around the tin atom,

when the N2 interaction is taken into account, approaches a trigonal bipyramid, as may be deduced from the distances and angles of Table IV. For example, the longer Sn-C9 bond compared to Sn-C8 and Sn-C10 can be understood as an axial to equatorial situation in a trigonal bipyramid. The N2-Sn-C9 angle (167.4(2) $^\circ$ ) approaches linearity, and the C9-Sn-C8 and C9-Sn-C10 angles are about 3.5 $^\circ$  less than the tetrahedral angles. Not only are the  $\text{Me}_3\text{Sn}$  parts of the molecule distorted from ideal geometry but also the  $\text{Me}_2\text{N}$  ligands. The N2-C5-C5' angle, which should be about 120 $^\circ$ , is considerably widened to 131.2(3) $^\circ$  (H-C5-C5' = 116.7(3) $^\circ$ ), and the N2-C5-C4 (116.8(3) $^\circ$ ) and N2-C5-N1 (107.3(3) $^\circ$ ) angles are remarkably different, consistent with and indicative of the N2-Sn interaction.

Qualitative molecular mechanics calculations were performed on the molecules **2a-c** in the gas phase, taking the coordinates of the X-ray structure as starting points and refining the structures also with Si and Ge in place of Sn; E-N interactions were excluded.<sup>16</sup> The E-N2 distances found from these simulations are 3.30 (Si), 3.35 (Ge), and 3.32 (Sn)  $\text{\AA}$ , thus being 0.20-0.25  $\text{\AA}$  longer than that for **2c** found by experiment in the solid state. It seems reasonable to estimate the Si-N distance in **2a** to be about 3.0-3.10  $\text{\AA}$ , which is greater than 2.69  $\text{\AA}$ , the "minimal nonbonded distance"<sup>17</sup> between Si and N. However, in silicon compounds weak Si-N interactions have been reported up to 3.19  $\text{\AA}$ .<sup>4e</sup> It is clear that the estimated Si-N distance in compound **2a** is close to this value, and consequently, a weak Si-N interaction cannot be excluded. Molecular mechanics calculations also show that the rotations around the C5-N2 and C1-E bonds are hindered, with the order being **2c** > **2b** > **2a**, which fits well with our findings for the crystal structure.

In conclusion, group 14 element-nitrogen interactions in compounds **2a-c**, although weak, are probably responsible for the surprising resistance of these species to hydrolytic deprotection of N-H and formyl groups.

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**Supplementary Material Available:** Tables of crystal data and data collection and refinement details, positional parameters, bond lengths and angles, and anisotropic thermal parameters for **2c** and of <sup>13</sup>C NMR data in solution for *cis*- and *trans*-**1** and **2a-c** (6 pages). Ordering information is given on any current masthead page.

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(16) Alchemy III by Tripos Associates, St. Louis, MO, 1992 (customized to Si, Ge, and Sn with appropriate parameters by M. Veith).

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