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Synthesis and Structural and Spectroscopic Characterization of the Germanazene $[GeN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$ and the Tin and Lead Tetramers $[SnN(BMes_2)]_4$, $[SnN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_4$, and $[PbN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_4$

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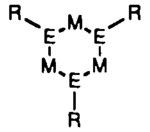
Received December 28, 1990

The reactions of $M[N(SiMe_3)_2]_2$ (M = Ge, Sn, Pb) with two bulky primary amines have been investigated. When $Ge[N(SiMe_3)_2]_2$ was treated with $H_2N(Dipp)$ (Dipp = $2,6\text{-}i\text{-}Pr_2C_6H_3$), the trimeric species $[GeN(Dipp)]_3$ (**1**) was formed in high yield. The reaction of $Sn[N(SiMe_3)_2]_2$ with $H_2N(Dipp)$ or the primary borylamine H_2NBMes_2 gives the tetrameric species $[SnN(Dipp)]_4$ (**2**) and $[SnN(BMes_2)]_4$ (**3**). The lead compound $[PbN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_4$ (**4**) was prepared in a similar manner. Details of the ^1H NMR spectroscopy and X-ray crystal structures of all compounds are reported. The trimer $[GeN(Dipp)]_3$ (**1**), which was described in a preliminary communication, has a planar Ge_3N_3 ring structure with stereochemically active Ge lone pairs. The structures of **2**–**4** are tetrameric, featuring Sn_4N_4 or Pb_4N_4 cubane skeletons. The data suggest considerable ionic character in the M–N bonds. Crystal data [Mo Kα (λ = 0.71069 Å)] at 130 K are as follows: **2**, a = 12.214 (2) Å, b = 19.129 (4) Å, c = 21.488 (4) Å, α = 84.27 (1)°, β = 76.15 (1)°, γ = 86.78 (1)°, Z = 4, triclinic, space group $P\bar{1}$, 9463 unique observed ($I > 2\sigma(I)$) data, $R(F)$ = 0.050; **3**, a = 28.185 (8) Å, c = 35.161 (11) Å, Z = 12, tetragonal, space group $I\bar{4}c2$, 5199 unique observed ($I > 3\sigma(I)$) data, $R(F)$ = 0.083; **4**, a = 12.330 (3) Å, b = 19.242 (4) Å, c = 21.435 (6) Å, α = 83.06 (2)°, β = 76.61 (2)°, γ = 85.97 (2)°, Z = 4, triclinic, space group $P\bar{1}$, 11095 unique observed ($I > 2\sigma(I)$) data, $R(F)$ = 0.074.

Introduction

Some recent work in this laboratory has focused on the synthesis and characterization of novel, potentially delocalized, quasi-aromatic inorganic rings that involve heavier main-group elements.[1] Examples of these include $(RBPR')_3$,[2] $(RAlNR')_3$,[3] $(RZnER)_3$ (E = S,[4] Se[5]), and $(RGaPR')_3$.[6] The common feature of these heterocycles is that the sum of the group numbers of adjacent atoms is 8. Many other combinations of group numbers that could give a Hückel 6-π-electron system are also possible. One example of such a system is a species defined by the formula $(MER)_3$ (M = divalent main group 4 element; E = N, P, As) as illustrated:



The first instance of such a compound $[GeN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$ was recently reported by this laboratory.[7] It was hoped that a range of such compounds would be accessible by the reaction between the readily available precursors $M[N(SiMe_3)_2]_2$ (M = Ge, Sn, Pb) and suitable primary amines, phosphines, or arsines. The work described in this paper focuses primarily on some reactions of the divalent metal amides with the bulky primary amine $H_2N(Dipp)$ (Dipp = $2,6\text{-}i\text{-}Pr_2C_6H_3$) and the borylamine $H_2N(BMes_2)$. The products of this reaction are oligomers of metal imines of formula $(MNR)_n$ (M = Ge, Sn, Pb). There has been a considerable amount of work on such compounds, particularly for the tin derivatives.[8,9] However, the effects of high steric requirements of the nitrogen substituent on the structure of the reaction product have received much less attention until recently.[7,10]

Experimental Section

General Procedures. All work was performed by using Schlenk techniques under N_2 or a Vacuum Atmospheres HE43-2 drybox under Ar. Solvents were freshly distilled under N_2 from Na/K alloy–benzophenone ketyl and degassed twice immediately before use. $H_2N(BMes_2)$,[11] $Ge[N(SiMe_3)_2]_2$, $Sn[N(SiMe_3)_2]_2$, and $Pb[N(SiMe_3)_2]_2$ were prepared via literature procedures.[12] $H_2N(Dipp)$ (Dipp = $2,6\text{-}i\text{-}Pr_2C_6H_3$) was obtained commercially and purified by distillation from CaH_2 under reduced pressure. ^1H and ^{11}B NMR spectra were obtained with a General Electric QE-300 spectrometer. The ^{11}B NMR data were referenced to external $BF_3{\cdot}Et_2O$. All compounds gave satisfactory C, H, and N elemental analysis.

$[GeN(Dipp)]_3$ (1). $Ge[N(SiMe_3)_2]_2$ (**1**) (0.84 g, 2.1 mmol) and $H_2N(Dipp)$ (0.39 g, 2.1 mmol) were heated together at 60 °C for 10 min. The eliminated amine $HN(SiMe_3)_2$ was removed under reduced pressure to afford the crude product **1** as a yellow solid. This was recrystallized from a minimum volume (~10 mL) of warm (50 °C) hexane to give the product **1** as large yellow crystals in >90% yield. Mp = 273–275 °C (turns orange at >250 °C); ^1H NMR (300 MHz, C_6D_6) δ 1.12 (d, 36 H, J = 7 Hz), 3.4 (septet, 6 H, J = 7 Hz), 7.14 (m, 9 H).

$[SnN(Dipp)]_4$ (2) and $[PbN(Dipp)]_4$ (4). These compounds were synthesized in an almost identical manner as follows: $Pb[N(SiMe_3)_2]_2$ (1.08 g, 2 mmol) was heated (50 °C) with $H_2N(Dipp)$ (0.355, 2 mmol) for 5 min. Removal of the volatile $HN(SiMe_3)_2$ under reduced pressure gave a yellow solid. Recrystallization from warm hexane gave the product **4** as orange-yellow crystals in >80% yield; mp = 150 °C dec (lead mirror). For **2**, mp = >255 °C dec. ^1H NMR (300 MHz, C_6D_6): **2**, δ 1.3 (d, 48 H, Me, J = 7 Hz), 3.47 (septet, 8 H, CH, J = 7 Hz), 6.92 (t, 4 H, p-H, J = 7 Hz), 7.14 (d, 8 H, m-H, J = 7 Hz); **4**, δ 1.26 (d, 48 H, Me, J = 7 Hz), 3.52 (septet, 8 H, CH, J = 7 Hz), 6.71 (t, 4 H, p-H, J = 8 Hz), 7.28 (d, 8 H, m-H, J = 8 Hz).

$[SnN(BMes_2)]_4$ (3). $Sn[N(SiMe_3)_2]_2$ (1.6 g, 3.6 mmol) was dissolved in hexane (20 mL), and solid H_2NBMes_2 (0.96 g, 3.6 mmol) was added slowly at room temperature. The solution was then refluxed for 1 h and cooled. The volatile materials were removed under reduced pressure. The residue was redissolved in hexane (30 mL). Filtration followed by reduction of the volume to ca. 10 mL afforded the product **3** as colorless crystals: yield 0.5 g, 35%; mp = 243–244 °C (turns opaque ~150 °C, orange ~215 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 48 H, o-CH_3), 2.24 (s, 24 H, p-CH_3), 6.67 (s, 16 H, m-H); ^{11}B NMR (96.46 MHz, C_6D_6) δ 47.1.

X-ray Data Collection and Solution and Refinement of the Structures. The crystals of **2**–**4** were transferred from the Schlenk tube onto a Petri dish and immediately covered with a layer of hydrocarbon oil.[13] A single crystal was selected, mounted on a glass fiber, and immediately placed in a low-temperature N_2 stream. The X-ray data for **2** and **4** were collected on a Siemens R3m/v diffractometer equipped with a locally modified Enraf-Nonius LT apparatus. Data collection for **3** was carried out on a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device. Computer programs were from SHELXTL-PLUS (Version 5), installed on a microVAX 3200 instrument.

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Table I. Selected Crystal Data for Compounds **2**–**4**

	2	**3**	**4**
compd	$[\text{SnN}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_4$	$[\text{SnN}(\text{BMes}_2)]_4$	$[\text{PbN}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_4$
formula	$C_{48}H_{68}N_4Sn_4$	$C_{72}H_{88}B_4N_4Sn_4$	$C_{48}H_{68}N_4Pb_4$
fw	1175.8	1527.5	1529.8
a, Å	12.214 (2)	28.185 (8)	12.330 (3)
b, Å	19.129 (4)		19.242 (4)
c, Å	21.488 (4)	35.161 (11)	21.435 (6)
α, deg	84.27 (1)		83.06 (2)
β, deg	76.15 (1)		76.61 (2)
γ, deg	86.78 (1)		85.97 (2)
V, Å^3	4848 (2)	27932 (15)	4906 (2)
Z	4	12	4
space group	$P\bar{1}$	$I\bar{4}c2$	$P\bar{1}$
T, K	130	130	130
λ, Å	0.71069	0.71069	0.71069
d(calcd), g/cm^3	1.61	1.09	2.07
μ(Mo Kα), cm^{-1}	20.80	10.96	138.23
transm fctr range	0.66–0.82	0.72–0.90	0.01–0.07
$R(F)$	0.050	0.083	0.074
$R_w(F)$	0.052	0.091	0.076

The atom form factors, including anomalous scattering factors, were from ref 14. Some details of data collection and refinement are given in Table I. Further details are provided in the supplementary material. Data for **1** were provided in a preliminary communication.[7] All structures were solved by direct methods. An absorption correction was applied[15] to all compounds. Hydrogen atoms were included in the refinement at calculated positions by using a riding model, with C–H of 0.96 Å and $U_H = 1.2U_C$ for compounds **2**–**4**. The metal atoms were refined anisotropically in the case of **2**–**4**. In **1**, all atoms were refined anisotropically. Atom coordinates and isotropic thermal parameters are given in Table II. Selected bond distances and angles are listed in Table III. The largest features on the final difference maps were 2.66, 1.15, and 6.09 e Å^{-3} for **2**–**4**.

Results and Discussion

Syntheses. The syntheses of compounds **1**–**4** are extremely facile. The general reaction is given by

$$\text{M(NR}_2)_2 + \text{H}_2\text{NR}' \rightarrow (1/n)(\text{MNR}')_n + 2\text{HNR}_2$$

Except in the case of **3**, no solvent was required for the reaction. The reaction between H_2N(Dipp) and $M(NR_2)_2$ (M = Ge, Sn, Pb; R = $SiMe_3$) proceeds spontaneously at room temperature. Warming slightly to ~60 °C ensured complete reaction within 10 min. The reactions appear to be quantitative, and yields of 75–85% were obtained routinely from one crop of crystals. More forcing (but still mild) conditions were used for the reaction involving H_2NBMes_2. A solvent was employed to promote the reaction in this case, since $H_2N(BMes_2)$ is a relatively high-melting solid and not readily miscible with $Sn[N(SiMe_3)_2]_2$. These synthetic methods are similar to those employed previously for the tin compounds using the starting material $\overline{\text{SnN}(t\text{-Bu})\text{SiMe}_2\text{N}}(t\text{-Bu})$.[8,9] In addition, solvents were usually employed in these syntheses.

Structural Descriptions. [GeN(Dipp)]$_3$ (1). The structure of compound **1** has been described in a preliminary communication.[7] It crystallizes in a triclinic space group with one molecule in the asymmetric unit, and therefore it has no symmetry restriction. Its structure may be described as a head-to-tail cyclic trimer of GeN(Dipp) monomers to give a planar Ge_3N_3 ring. The mean deviation from the averaged Ge_3N_3 plane is 0.03 Å. The ipso carbons from the three aromatic substituents are coplanar with the Ge_3N_3 plane. The Ge–N bonds are essentially equal and they average 1.859 (2) Å. The internal ring angles average 101.8 (1)° at germanium and 138.0 (2)° at nitrogen. The external Ge–N–C angles are symmetrical with an average deviation of 1.3° from a mean value of 110.9°. The planes of the Dipp rings subtend an average angle of 86.2° to the Ge_3N_3 core.

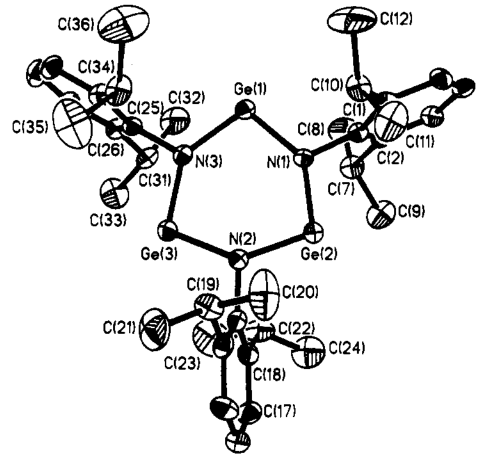

Figure 1. Computer-generated drawing of **1**. H atoms are not shown for clarity. Important bond distances and angles are given in Table III.

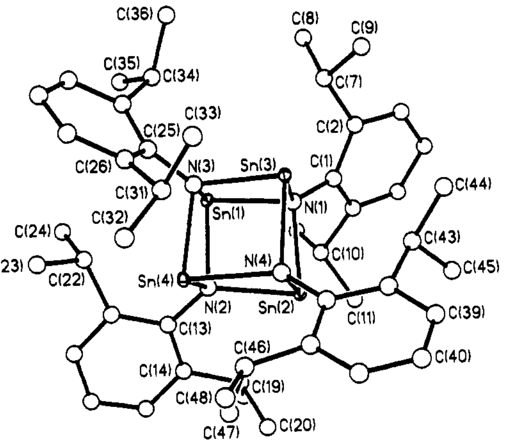

Figure 2. Computer-generated drawing of one of the molecules of **2**. H atoms are not shown for clarity. Important bond distances and angles are given in Table III.

[MN(Dipp)]$_4$ (M = Sn (2), Pb (4)). Compounds **2** and **4** form isomorphous crystals that crystallize in the triclinic space group $P\bar{1}$. The asymmetric unit contains two crystallographically independent but chemically identical tetrameric units. These comprise an M_4N_4 cubane-like core with a Dipp group bound to each nitrogen. The angles within the M_4N_4 units show considerable distortions from 90°. In **2**, the bond angles at tin vary from 80 to 84.8° and those at nitrogen from 94.2 to 100.2°. The corresponding variations in **4** are from 78.8 to 86.7° for lead and from 94.0 to 101.3° for nitrogen. The average Sn–N and Pb–N

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(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

(15) The absorption correction was made by using the program XABS by H. Hope and B. Moezzi. The program obtains an absorption from $F_o - F_c$ differences: Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

Table II. Selected Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **2–4**

	x	*y*	*z*	*U*(eq)[a]
		Compound **2**		
Sn(1)	2278 (1)	2292 (1)	4585 (1)	13 (1)
Sn(2)	3474 (1)	1946 (1)	3071 (1)	12 (1)
Sn(3)	2045 (1)	3485 (1)	3331 (1)	13 (1)
Sn(4)	4521 (1)	3169 (1)	3713 (1)	13 (1)
N(1)	1805 (7)	2326 (4)	3660 (4)	14 (2)
N(2)	3989 (7)	2077 (4)	3992 (4)	11 (2)
N(3)	2714 (7)	3417 (4)	4195 (4)	12 (2)
N(4)	3752 (6)	3080 (4)	2867 (4)	9 (2)
C(1)	827 (9)	1969 (6)	3603 (5)	16 (3)
C(13)	4850 (9)	1727 (6)	4300 (5)	17 (3)
C(25)	2634 (9)	4007 (6)	4571 (5)	17 (3)
C(37)	4103 (8)	3249 (5)	2174 (5)	14 (2)
Sn(5)	390 (1)	8260 (1)	1227 (1)	14 (1)
Sn(6)	1754 (1)	6978 (1)	1991 (1)	13 (1)
Sn(7)	2518 (1)	7337 (1)	396 (1)	13 (1)
Sn(8)	3023 (1)	8475 (1)	1381 (1)	16 (1)
N(5)	901 (7)	7154 (4)	1167 (4)	12 (2)
N(6)	1381 (7)	8130 (4)	2013 (4)	12 (2)
N(7)	2113 (7)	8460 (5)	629 (4)	19 (2)
N(8)	3278 (7)	7290 (5)	1228 (4)	17 (2)
C(49)	208 (8)	6653 (5)	997 (5)	14 (2)
C(61)	1136 (8)	8318 (5)	2684 (5)	13 (2)
C(73)	2231 (9)	9106 (6)	191 (5)	19 (3)
C(85)	4229 (8)	6799 (5)	1137 (5)	15 (2)
		Compound **3**		
Sn(1)	9507 (1)	356 (1)	−319 (1)	27 (1)
N(1)	9587 (6)	286 (6)	340 (5)	26 (4)
B(1)	9246 (13)	443 (13)	606 (10)	51 (9)
C(1)	9376 (8)	986 (9)	792 (7)	27 (6)
Sn(2)	2197 (1)	1782 (1)	2074 (1)	37 (1)
Sn(3)	2173 (1)	2929 (1)	2268 (1)	38 (1)
N(2)	1677 (7)	2270 (7)	2324 (6)	37 (5)
N(3)	2709 (7)	2395 (7)	2154 (5)	28 (5)
B(2)	1175 (14)	2277 (14)	2197 (11)	57 (11)
B(3)	3045 (14)	2538 (14)	1858 (11)	55 (10)
C(19)	1088 (1)	2087 (10)	1761 (8)	41 (7)
C(37)	3574 (11)	2251 (10)	1870 (8)	46 (8)
		Compound **4**		
Pb(1)	2252 (1)	2257 (1)	4668 (1)	12 (1)
Pb(2)	3543 (1)	1912 (1)	3092 (1)	12 (1)
Pb(3)	2037 (1)	3521 (1)	3330 (1)	12 (1)
Pb(4)	4578 (1)	3172 (1)	3771 (1)	12 (1)
N(1)	1822 (17)	2302 (11)	3679 (10)	20 (5)
N(2)	4041 (14)	2030 (9)	4059 (8)	7 (4)
N(3)	2720 (16)	3429 (10)	4226 (9)	15 (4)
N(4)	3800 (14)	3068 (9)	2887 (9)	8 (4)
C(1)	848 (22)	1947 (14)	3604 (13)	25 (6)
C(13)	4885 (17)	1705 (11)	4406 (10)	6 (4)
C(25)	2633 (20)	4001 (13)	4582 (12)	20 (6)
C(37)	4147 (19)	3242 (12)	2165 (12)	15 (5)
Pb(5)	277 (1)	8276 (1)	1133 (1)	17 (1)
Pb(6)	1702 (1)	6960 (1)	1997 (1)	13 (1)
Pb(7)	2491 (1)	7282 (1)	318 (1)	15 (1)
Pb(8)	3005 (1)	8501 (1)	1292 (1)	21 (1)
N(5)	800 (15)	7103 (10)	1119 (9)	13 (4)
N(6)	1323 (17)	8166 (11)	1969 (10)	23 (5)
N(7)	2043 (18)	8497 (12)	504 (11)	26 (5)
N(8)	3240 (17)	7237 (11)	1211 (10)	20 (5)
C(49)	113 (20)	6623 (13)	974 (12)	19 (6)
C(61)	1061 (19)	8352 (13)	2627 (12)	17 (5)
C(73)	2203 (22)	9105 (15)	76 (14)	28 (6)
C(85)	4208 (19)	6763 (12)	1081 (11)	14 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

distances are 2.23 (2) and 2.34 (2) Å, respectively. The N–C distances in **2** and **4** average 1.45 (2) and 1.44 (3) Å. There are no unusual metric features within the aromatic substituent rings of either compound, and there are no interactions apparent between neighboring core units.

[SnN(BMes$_2$)]$_4$ (3). This compound crystallizes in the tetragonal space group *I*$\bar{4}$*c*2. Two chemically identical but crystallographically independent molecules featuring distorted Sn_4N_4 cubes are apparent. One molecule is defined by one SnN(BMes$_2$) unit, the three remaining SnN(BMes$_2$) moieties being generated by symmetry. Its overall point symmetry is $\bar{4}$. The remaining cubane-like molecules may be generated from a unique dimeric {SnN(BMes$_2$)}$_2$ unit and has 2-fold symmetry. As in **2** and **4**, there are no interactions between the tetrameric units. There is a rather large range in the Sn–N distances, which may vary from 2.15 (2) to 2.34 (2) Å. The longest distances, for example Sn(1)–N(1), Sn(2)–N(3), and Sn(3)–N(2), indicate elongation of the Sn_4N_4 core along these directions. The B–N distances average 1.45 (4) Å. Distortions from the cubane structure are indicated by the angles at tin and nitrogen, which range from 75.8 (9) to 86.8 (7)° for the former and from 92.2 (6) to 104.1 (9)° for the latter.

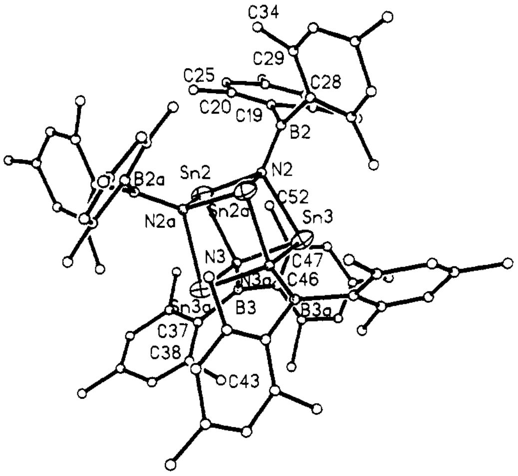

Figure 3. Computer-generated drawing of one of the molecules of **3**. H atoms are not shown for clarity. Important bond distances and angles are given in Table III.

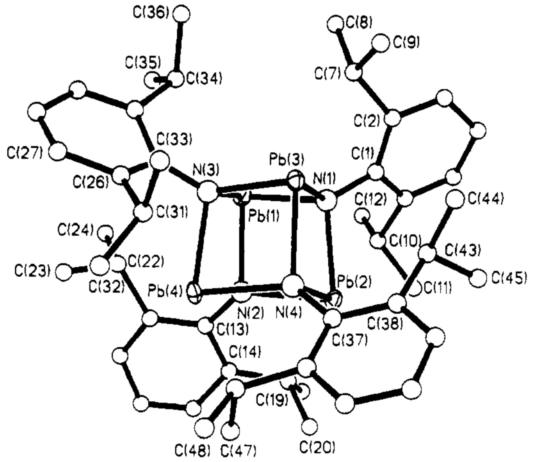

Figure 4. Computer-generated drawing of one of the molecules of **4**. H atoms are not shown for clarity. Important bond distances and angles are given in Table III.

Discussion

The easily synthesized divalent amides M[N(SiMe$_3$)$_2$]$_2$ (M = Ge, Sn, Pb)[12] combined with one of the bulkier commercially available primary amines provide a facile high-yield route to compounds **1**, **2**, and **4**. The reaction between Sn[N(SiMe$_3$)$_2$]$_2$ and the borylamine H$_2$N(BMes$_2$)[11] was also investigated because it was felt that this would throw some light on the character of the Sn–N bonding. As already mentioned, interest in these reactions arose because of recent work on quasi-aromatic cyclic systems involving heavier main-group-element ring members. The reaction between Ge[N(SiMe$_3$)$_2$]$_2$ and H$_2$N(Dipp) gave the trimeric product in essentially quantitative yield:

$$\mathrm{Ge[N(SiMe_3)_2]_2 + H_2N(Dipp) \rightarrow \tfrac{1}{3}[GeN(Dipp)]_3 + 2HN(SiMe_3)_2}$$

Table III. Important Bond Distances (Å) and Angles (deg) for **1-4**

		Compound **1**			
Ge(1)-N(1)	1.858 (2)	Ge(2)-N(2)	1.852 (3)	N(1)-C(1)	1.455 (5)
Ge(1)-N(3)	1.859 (3)	Ge(3)-N(2)	1.858 (2)	N(2)-C(13)	1.446 (5)
Ge(2)-N(1)	1.859 (2)	Ge(3)-N(3)	1.861 (2)	N(3)-C(25)	1.455 (5)
N(1)-Ge(1)-N(3)	101.7 (1)	N(2)-Ge(3)-N(3)	101.9 (1)	Ge(2)-N(2)-Ge(3)	138.0 (2)
N(1)-Ge(2)-N(2)	101.7 (1)	Ge(1)-N(1)-Ge(2)	138.2 (1)	Ge(1)-N(3)-Ge(3)	137.9 (2)
		Compound **2**[a]			
Sn(1)-N(1)	2.185 (9)	Sn(1)-N(2)	2.251 (8)	Sn(1)-N(3)	2.247 (8)
Sn(2)-N(1)	2.250 (9)	Sn(2)-N(2)	2.243 (9)	Sn(2)-N(4)	2.216 (8)
Sn(3)-N(1)	2.272 (8)	Sn(3)-N(3)	2.222 (9)	Sn(3)-N(4)	2.207 (9)
Sn(4)-N(2)	2.217 (8)	Sn(4)-N(3)	2.210 (9)	Sn(4)-N(4)	2.290 (9)
N(1)-C(1)	1.444 (14)	N(2)-C(13)	1.474 (14)	N(3)-C(25)	1.454 (14)
N(4)-C(37)	1.448 (13)				
N(1)-Sn(1)-N(2)	82.2 (3)	N(1)-Sn(1)-N(3)	82.4 (3)	N(2)-Sn(1)-N(3)	81.1 (3)
N(1)-Sn(2)-N(2)	80.9 (3)	N(1)-Sn(2)-N(4)	82.6 (3)	N(2)-Sn(2)-N(4)	84.6 (3)
N(1)-Sn(3)-N(3)	81.0 (3)	N(1)-Sn(3)-N(4)	82.3 (3)	N(3)-Sn(3)-N(4)	83.4 (3)
N(2)-Sn(4)-N(3)	82.7 (3)	N(2)-Sn(4)-N(4)	83.5 (3)	N(3)-Sn(4)-N(4)	81.7 (3)
Sn(1)-N(1)-Sn(2)	99.0 (4)	Sn(1)-N(1)-Sn(3)	97.8 (4)	Sn(2)-N(1)-Sn(3)	95.7 (3)
Sn(1)-N(2)-Sn(2)	97.2 (3)	Sn(1)-N(2)-Sn(4)	97.6 (3)	Sn(2)-N(2)-Sn(4)	96.0 (3)
Sn(1)-N(3)-Sn(3)	97.5 (4)	Sn(1)-N(3)-Sn(4)	97.9 (3)	Sn(3)-N(3)-Sn(4)	98.0 (3)
Sn(2)-N(4)-Sn(3)	98.6 (4)	Sn(2)-N(4)-Sn(4)	94.7 (3)	Sn(3)-N(4)-Sn(4)	96.1 (3)
Sn(2)-N(4)-C(37)	113.2 (6)	Sn(3)-N(4)-C(37)	112.4 (7)	Sn(4)-N(4)-C(37)	135.2 (7)
		Compound **3**			
Sn(1)-N(1)	2.34 (2)	Sn(1)-N(1A)	2.25 (2)	Sn(1)-N(1B)	2.20 (2)
N(1)-B(1)	1.41 (4)	Sn(1A)-N(1)	2.20 (2)	Sn(1B)-N(1)	2.25 (2)
Sn(2)-N(2)	2.19 (2)	Sn(2)-N(3)	2.27 (2)	Sn(2)-N(2A)	2.15 (2)
Sn(3)-N(2)	2.33 (2)	Sn(3)-N(3)	2.17 (2)	Sn(3)-N(3A)	2.21 (2)
N(2)-B(2)	1.48 (4)	Sn(2A)-N(2)	2.15 (2)	N(3)-B(3)	1.46 (4)
Sn(3A)-N(3)	2.21 (2)				
N(1)-Sn(1)-N(1A)	85.8 (7)	N(1)-Sn(1)-N(1B)	86.8 (7)	N(1A)-Sn(1)-N(1B)	79.1 (7)
Sn(1)-N(1)-B(1)	124 (2)	Sn(1)-N(1)-Sn(1A)	93.3 (6)	B(1)-N(1)-Sn(1A)	113 (2)
Sn(1)-N(1)-Sn(1B)	92.2 (6)	B(1)-N(1)-Sn(1B)	127 (2)	Sn(1A)-N(1)-Sn(1B)	100.8 (7)
N(2)-Sn(2)-N(3)	84.1 (7)	N(2)-Sn(2)-N(2A)	75.8 (9)	N(3)-Sn(2)-N(2A)	85.5 (7)
N(2)-Sn(3)-N(3)	83.1 (7)	N(2)-Sn(3)-N(3A)	82.5 (7)	N(3)-Sn(3)-N(3A)	77.2 (8)
Sn(2)-N(2)-Sn(3)	93.7 (8)	Sn(2)-N(2)-B(2)	122 (2)	Sn(3)-N(2)-B(2)	122 (2)
Sn(2)-N(2)-Sn(2A)	104.1 (9)	Sn(3)-N(2)-Sn(2A)	94.4 (8)	B(2)-N(2)-Sn(2A)	115 (2)
Sn(2)-N(3)-Sn(3)	96.2 (7)	Sn(2)-N(3)-B(3)	122 (2)	Sn(3)-N(3)-B(3)	113 (2)
Sn(2)-N(3)-Sn(3A)	94.4 (7)	Sn(3)-N(3)-Sn(3A)	102.8 (8)	B(3)-N(3)-Sn(3A)	123 (2)
		Compound **4**[a]			
Pb(1)-N(1)	2.30 (2)	Pb(1)-N(2)	2.38 (2)	Pb(1)-N(3)	2.36 (2)
Pb(2)-N(1)	2.35 (2)	Pb(2)-N(2)	2.33 (2)	Pb(2)-N(4)	2.26 (2)
Pb(3)-N(1)	2.39 (2)	Pb(3)-N(3)	2.34 (2)	Pb(3)-N(4)	2.31 (2)
Pb(4)-N(2)	2.32 (2)	Pb(4)-N(3)	2.30 (2)	Pb(4)-N(4)	2.40 (2)
N(1)-C(1)	1.44 (4)	N(2)-C(13)	1.47 (3)	N(3)-C(25)	1.39 (3)
N(4)-C(37)	1.48 (3)				
N(1)-Pb(1)-N(2)	81.7 (7)	N(1)-Pb(1)-N(3)	82.8 (7)	N(2)-Pb(1)-N(3)	80.6 (7)
N(1)-Pb(2)-N(2)	81.5 (8)	N(1)-Pb(2)-N(4)	82.5 (7)	N(2)-Pb(2)-N(4)	84.8 (7)
N(1)-Pb(3)-N(3)	81.1 (8)	N(1)-Pb(3)-N(4)	80.8 (7)	N(3)-Pb(3)-N(4)	83.2 (8)
N(2)-Pb(4)-N(3)	83.1 (7)	N(2)-Pb(4)-N(4)	82.1 (7)	N(3)-Pb(4)-N(4)	82.1 (8)
Pb(1)-N(1)-Pb(2)	98.9 (8)	Pb(1)-N(1)-Pb(3)	97.5 (8)	Pb(2)-N(1)-Pb(3)	95.5 (7)
Pb(1)-N(2)-Pb(2)	97.2 (8)	Pb(1)-N(2)-Pb(4)	97.2 (7)	Pb(2)-N(2)-Pb(4)	96.1 (7)
Pb(1)-N(3)-Pb(3)	97.3 (8)	Pb(1)-N(3)-Pb(4)	98.3 (8)	Pb(3)-N(3)-Pb(4)	97.7 (8)
Pb(2)-N(4)-Pb(3)	100.5 (7)	Pb(2)-N(4)-Pb(4)	95.8 (7)	Pb(3)-N(4)-Pb(4)	95.7 (7)
Pb(2)-N(4)-C(37)	115.1 (14)				

[a] Average values for the two crystallographically independent molecules.

The planar nature of the $Ge_3N_3\{C(ipso)\}_3$ array raises the question of the extent of delocalization in ring π orbitals. The average Ge-N distance is 1.859 (2) Å, which is marginally shorter than the lengths (~1.89 Å) observed in the acyclic GeN compounds $Ge[N(SiMe_3)_2]_2$[16] and $Ge[\overline{NCMe_2(CH_2)_3CMe_2}]_2$.[17] However, Ge-N bond lengths (1.856 (6) Å) very similar to those in **1** have been observed in the strained four-membered-ring system Ge[N(*t*-Bu)SiMeN(*t*-Bu)][N(*t*-Bu)SiMeN(*t*-Bu)][18] and in the recently reported closely related Ge_2N_2 ring compound $[GeN(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_2$ (1.849 (4) Å).[10] In addition, the length of a Ge-N double bond in the system $(>N-)_2(>N^+-)Ge{=}NSiMe_3$ is 1.688 (9) Å.[19] The lack of a significant shortening in the Ge-N bonds in **3** suggests that the amount of multiple bonding present in the Ge_3N_3 ring is small.[3] Most probably, the bonding is primarily ionic and there is little stabilization due to delocalization. In this respect, **1** resembles the "alumazene" ring $(MeAlN(Dipp))_3$ for which calculations,[20] based upon homodesmotic reactions, have indicated that little delocalization stability is present. This is in sharp contrast to the π-bonding in isoelectronic $(RBPR')_3$ rings,

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which are calculated to have more than half of the delocalization stabilization of benzene. The differences are thought to be primarily due to higher polarity of the Al–N bond. It seems safe to assume that a ring based upon Ge–N bonding, which has polarity similar to that of Al–N, would have similar characteristics. An interesting feature of the Ge_3N_3 ring is the very wide (~138°) internal ring angle seen at the nitrogens and the correspondingly narrow angle (~102°) seen at the germaniums. The latter angle may be due to the reluctance of the heavier main-group elements to hybridize. The high angle at the nitrogens then becomes necessary if the planarity of the Ge_3N_3 array is to be maintained. Models indicate that such strain could be avoided if the ring were to assume other conformations, i.e. a twist conformation. Wide internal angles have been observed in other six-membered rings featuring three-coordinate members. However, the reasons for this remarkable structural feature remain obscure. It is true, however, that π-overlap of the six p orbitals is maximized in a planar ring, but the relatively normal Ge–N distances observed in **1** are not consistent with an important role for this type of bonding. The trimeric structure of **1** is maintained in benzene solution (cryoscopy). In addition, the ^{1}H NMR spectrum (C_7D_8) of **1** shows little dynamic behavior in the range −90 to +90 °C.

The reaction between $Sn[N(SiMe_3)_2]_2$ or $Pb[N(SiMe_3)_2]_2$ and $H_2N(Dipp)$ results not in trimers but instead a high yield of the isostructural tetramers **2** and **4**. The reaction sequence leading to tin tetramers similar to **2**, but derived from different starting materials, has been investigated thoroughly.[8,9] The detailed structures of $[SnN(t\text{-Bu})]_4$[21] (**5**) and the hydrazine derivative $[Sn(NNMe_2)]_4$[22] (**6**) as well as the structure of several related heterometallic cubane[8,9] species have been described. The structures of **5** and **6** possess distorted cubane structures. In the case of the former compound, the Sn–N distances are close to ~2.2 Å and the NSnN angles and SnNSn angles for the most part within 2° of 81 and 98°, respectively. These Sn–N bond lengths are significantly longer than those observed for $Sn[N(SiMe_3)_2]_2$[16] (Sn–N = 2.096 (1) Å), which is, presumably, a consequence of the increase in the coordination number at Sn from 2 to 3. The distances and angles within the Sn_4N_4 cube of the hydrazine derivative **6** show somewhat more variation. Although the Sn–N distance averages 2.22 Å, it may vary from 2.15 (1) to 2.28 (1) Å. The NSnN angles are in the range 71.1 (4)–83.1 (4)°, and the SnNSn angles may vary from 95.0 (5) to 103.5 (5)°. The structure of **6** is further distinguished by the presence of long (~3.5 Å) interactions between tin atoms of neighboring cores. With the exception of the latter characteristic, the structural parameters seen in **2** are in close agreement with the values observed in **5** and **6**. The use of the larger Dipp substituent induces little change in the overall structure. It was originally hoped that this group might afford a trimeric product like **1**. The significantly larger size of Sn in comparison to Ge (0.2 Å larger radius) accounts for the higher degree of aggregation. The use of the more crowding amine $H_2N(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ in a reaction with $Sn[N(SiMe_3)_2]_2$ has not yet afforded crystalline material suitable for an X-ray data collection (cf. ref 10 for the Ge derivative).

The lead compound **4** has structural characteristics very similar to those seen in **2**, **5**, and **6**. The major difference concerns the Pb–N bond lengths, which at 2.34 (2) Å are a little more than 0.1 Å greater than the Sn–N distances in **2**. As a consequence of the increased lead coordination number, the Pb–N bonds are considerably longer than the 2.26 (1) Å distance observed for two-coordinate Pb(II) in $Pb[N(SiMe_3)_2]_2$.[16] It appears that no structures of a lead–nitrogen cubane had been published previously. However, the synthesis and characterization (by molecular weight determination and mass spectrum) of $[PbN(t\text{-Bu})]_4$ have been reported.[23]

The remaining structure in this discussion concerns the species $[SnN(BMes_2)]_4$ (**3**). This compound is derived from the reaction of $Sn[N(SiMe_3)_2]_2$ with the borylamine $H_2N(BMes_2)$. The corresponding reactions using Ge or Pb in the place of lead were attempted, but to date, no material suitable for X-ray crystallography has been isolated from these reactions. Interest in $H_2N(BMes_2)$ derives, in part, from its analogy to alkenes (the B–N distance in the free ligand is indicative of strong multiple bonding).[11] In addition, it was hoped that the involvement of the nitrogen lone pair in π-bonding to boron might reduce its bridging tendency and thereby give a less highly associated species. The isolation of the cubane species **3** did not realize the goal. The average Sn–N distance in **3** is not markedly different from those observed in **2**, **5**, and **6**. However, there is a slight elongation along one axis of the Sn_4N_4 cubes in **3**, which is suggestive of incipient dissociation into dimers. The B–N bond is lengthened somewhat in comparison to the B–N distance in $H_2N(BMes_2)$, but this is to be expected owing to the higher coordination number of nitrogen. The similarity in the average Sn–N distances in **2**, **3**, **5**, and **6** suggests that the Sn–N bonding in all these cubes has considerable ionic character. In addition, the elongation of the Sn_4N_4 cubes in **3** along one axis is indicative that, with suitable alteration of these ligands, lower aggregates, both dimeric[10] and trimeric,[7] might be obtained.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. **1** (coordination compound entry), 126423-24-3; **1** (salt entry), 126423-25-4; **2** (coordination compound entry), 134756-57-3; **2** (salt entry), 134735-40-3; **3** (coordination compound entry), 134735-38-9; **3** (salt entry), 134735-41-4; **4** (coordination compound entry), 134735-39-0; **4** (salt entry), 134735-42-5; $Ge[N(SiMe_3)_2]_2$, 55290-25-0; $Pb[N(SiMe_3)_2]_2$, 55147-59-6; $Sn[N(SiMe_3)_2]_2$, 55147-78-9; $H_2N(Dipp)$, 24544-04-5; H_2NBMes_2, 75018-24-5.

Supplementary Material Available: Full tables of structural parameters and refinement data, atom coordinates, and anisotropic thermal parameters (26 pages); complete listings of structure factors (127 pages). Ordering information is given on any current masthead page.

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