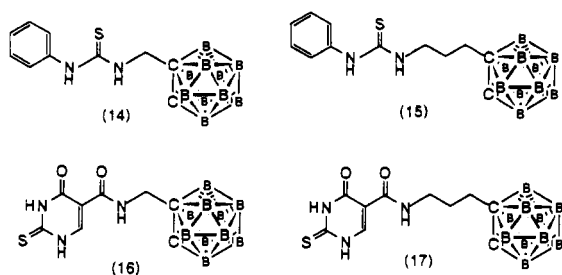


Scheme II



of a boron atom from the 3 or 6 position of the carborane cage.¹² Since these boron atoms are not equivalent, this may account for the observation that the methylene protons in the ¹H NMR spectrum appear as a pair of doublets at δ 2.85 and 2.65, $J = 13.3$ Hz. This nido anion was readily characterized as its tetramethylammonium salt.

A more recent and milder method for the removal of the phthalyl group has been reported.¹⁶ This is a stepwise method, employing the reduction of the phthalimido moiety by sodium borohydride to an *o*-(hydroxymethyl)benzoyl derivative which is then hydrolyzed under acidic conditions to generate the amine hydrochloride in excellent yield. By use of this method the (phthalimidomethyl)- and (phthalimidopropyl)carboranes **1** and **6** were respectively converted to the corresponding (aminoalkyl)carborane hydrochlorides **4** and **8** (Scheme I).

An alternative route for the preparation of alkylamines is by the displacement of a (*p*-tolylsulfonyl)oxy group or a halide by the nucleophilic azide ion and its subsequent catalytic hydrogenation to the amine.^{17,18} However, when either (chloromethyl) or (bromomethyl)carborane was subjected to such nucleophilic displacement by the azide moiety, starting material was recovered unchanged. Such a lack of reactivity of these halocarboranes is in sharp contrast to the reaction of the other alkyl halides but is in agreement with other studies whereby reactivity of the halides is enhanced following conversion to the nido analogue.¹⁹ This

has recently been described as being due to the unique stereoelectronic features of the carborane cage.⁸ Support for this hypothesis is found in the fact that degradation of the cage to its nido structure significantly increases the reactivity and displacability of halogens and other leaving groups. Progressively insulating these leaving groups from the carborane moiety, by inserting methylenes, produces halocarboranes which understandably more closely resemble alkyl halides. As the first example, we synthesized 1-(2-((*p*-tolylsulfonyl)oxy)ethyl)-*o*-carborane (**9**) from commercially-available 3-butylnyl tosylate and acetonitrile-decaborane complex. This carborane reacted readily with sodium azide in refluxing acetone displacing the tosyloxy function and yielding the corresponding azido structure (**10**). The same compound was also obtained from 1-(2-iodoethyl)-*o*-carborane (**11**).¹⁵ This azido compound was hydrogenated in the presence of acetic acid over 5% Pd on charcoal and gave the corresponding amine salt (**12**) which was readily characterized as the crystalline 1-(2-(acetamido)ethyl)-*o*-carborane (**13**) (Scheme I). Compound **13** was obtained in nearly quantitative yield by performing the hydrogenation reaction of **10** in the presence of acetic anhydride. Higher homologues containing both the carborane and amino moieties were readily obtained by the insertion of additional methylene groups.

In addition to acylation as a means of characterizing the aminocarboranes, it has been possible to characterize these amines as their corresponding phenylthioureas (**14** and **15**) and as amide derivatives of the thiouracil-5-carboxylic acid (**16** and **17**) (Scheme II). The latter reactions provide a very effective way of attaching a carborane moiety to thiouracil. Such boron-containing structures may have potential for becoming selectively incorporated into melanoma cells.²⁰

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Preparation of Tin Nitride via an Amide Imide Intermediate[†]

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Introduction

Binary nitrides of most elements can be prepared under appropriate conditions. These compounds show an extraordinary range of physical and chemical properties, more so than the oxides which they resemble in some respects. The nitrides are classified¹

as ionic, mostly represented by groups I and II; covalent, mostly represented by groups III and IV; and interstitial, formed by many metals. As the names imply, the properties of these materials are somewhat predictable, particularly those of the ionic nitrides, which are salt-like, and of the interstitial nitrides, which can be considered as metals with expanded lattices containing nitrogen in interstitial positions. The covalent nitrides show a wider range of properties. Some of the latter are solids with very high melting points and low electrical conductivities (such as BN, AlN, and Si₃N₄) while others are volatile or can form the basis of polymeric networks (such as (CN)₂ or PN). In addition to these covalent nitrides, there are some that are semiconductors and have limited thermal stabilities (such as Cu₃N, Zn₃N₂, and Sn₃N₄). It is the latter that appeared to be of interest because of potential applications in the development of electronic devices. Tin nitride was selected for

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Table I. Tin Amide Imide and Tin Nitride

	batch I		batch II		batch III		batch IV	
	amide imide	nitride ^a	amide imide	nitride ^a	amide imide	nitride ^a	amide imide ^b	nitride ^c
wt % Sn	55.73	66.57	60.6	69.37	58.07	65.9	67.6	80.6
wt % N	25.52	13.6	23.79	15.4	20.75	12.5	22.3	14.5
wt % K	14.40	17.2	9.66	11.0	8.07	9.2	6.0	4.4
wt % Br	1.86	1.9	3.33	3.8	11.0	12.5	<.3	<.1
wt % H	2.83	0.2	2.58	0.4	2.10		2.2	
N/Sn ^d	3.13	0.99	2.92	1.48	2.89	1.47	2.52	1.36

^a Nitride produced by thermal treatment of the amide imide at 300 (I, III) and 260 °C (II). ^b Combined batches I–III subjected to an additional NH₃ wash. ^c Thermal treatment of amide imide batch IV and an additional NH₃ wash. ^d Atom ratio derived after correction for the presence of KBr and KNH₂.

study to expand the rather limited information published in the literature,^{2,3} none of which relates to the preparation of bulk material other than by glow-discharge methods. Also noted are discrepancies such as the reported electrical conductivities that differ by as much as 10⁵.

Results and Discussion

Synthesis. Tin nitride, Sn₃N₄, was prepared by the thermal decomposition of tin amide imide, Sn(NH₂)₂NH, which is apparently a polymeric compound. The amide imide was prepared, in turn, from the reaction between tin(IV) bromide and potassium amide in liquid ammonia. Alternatively, tin bromide was first ammonolyzed to the amide bromide, SnBr(NH₂)₃, and then treated with potassium amide to eliminate the last bromide. The composition of the ammonolytic product is in agreement with the results of previous studies of the ammonolysis of tin halides.^{4,5} The results of three independent amide imide preparations are given in Table I. The idealized molecular formulas given above for the amide imide and the nitride are calculated compositions derived after corrections for the presence of residual potassium bromide byproduct and excess potassium amide. The former is readily removed as found by subjecting a combined mixture of all amide imide products to exhaustive ammonia washes. Excess potassium amide is more difficult to remove; some residue remains even after conversion of the amide imide into the nitride followed by exhaustive ammonia washings. The nitride finally isolated is about 95% pure. It is interesting to note that the nitride does not react with liquid ammonia. Tin nitride has been prepared in the past in glow-discharge systems^{2,3} and more recently⁶ by chemical vapor deposition in a system that utilized the decomposition of tetrakis(diethylamido)tin. Schwarz and Jeanmaire postulated⁴ the existence of tin nitride as an intermediate in the thermal decomposition of the chloro amide, but the nitride was not isolated.

Alternative synthetic pathways examined in the course of the present study, although not practical or successful, are described because of the insight gained into the chemistry of tin. These include the following pathways. (a) The first pathway is the use of a metal atom reactor to co-condense at 77 K vapors of ammonia and tin. The frozen deposit had a brownish color but melted into a finely divided suspension of tin in liquid ammonia. (b) The second pathway is direct synthesis between the elements. A sample of tin metal did not show any sign of reaction after being held in an autoclave at 500 °C under 10 MPa of nitrogen for a 36-h period; (c) The third pathway is vapor-phase ammonolysis. The vapor-phase reaction between tin bromide and ammonia at 330 °C produced a fine pale yellow powder. This material showed in the IR region the typical band at 1400 cm⁻¹ due to the NH₄⁺ ion, thus suggesting ammonolysis to produce NH₄Br and some mixed tin amide bromide. However, the solid could not be

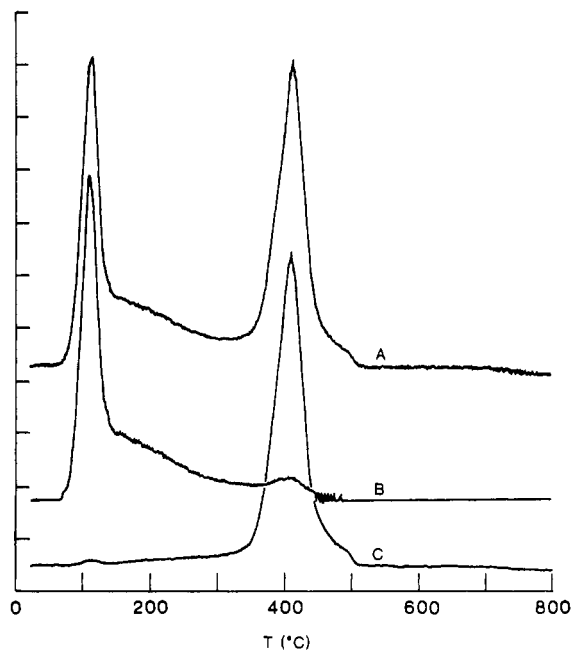
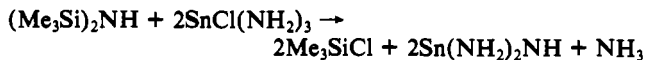


Figure 1. Temperature-programmed thermal decomposition profile of tin amide imide: (A) total ion current; (B) ammonia evolved; (C) nitrogen evolved.

fractionated by partial sublimation. Chemical analysis is suggestive of a material formulated as (NH₄)₂SnBr₄(NH₂)₂. (Anal. Calcd: Sn, 23.44; Br, 63.21. Found: Sn, 22.84; Br, 62.2.) Mass spectral analysis showed fragmentation typical of SnBr₄, with no fragments incorporating both bromide and amide. It appears that this material readily reverts to the starting reactants. (d) The fourth pathway is anodic oxidation of tin in the presence of an amine. Tin metal readily oxidizes to a Sn(II) species in an electrochemical cell containing an electrolyte mixture⁷ of propylamine, acetonitrile, and tetrabutylammonium bromide. The electrolyte has been used in the anodic oxidation of aluminum and titanium as an intermediate step in the preparation of the corresponding nitrides.^{7,8} In the case of tin, this approach is not as convenient because it requires a two-compartment cell to prevent redeposition of tin metal at the cathode and because the relative thermal stability of tin nitride prevents pyrolytic elimination of the electrolyte as is done in the case of aluminum and titanium. (e) The final pathway is halide elimination from the ammonolytic product via a volatile species. The following reaction below was examined as a possible way to eliminate the residual halide as a volatile species:



Thermodynamic considerations⁹ suggested that the reaction does

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not proceed as written. On the other hand, a similar reaction has been reported¹⁰ to occur. There was no trimethylsilyl chloride produced in an ampule holding the reactants at 100 °C for 20 h.

Characterization. Temperature programmed thermal decomposition (TPTD) examination of the amide imide revealed (Figure 1) two well-defined events with maxima at 125 and 420 °C. The profiles of the TPTD of three independent samples, containing different levels of impurities, were essentially the same. This is an indication that the KBr and KNH₂ are dispersed in the amide with little or no chemical interaction. The maxima in the TPTD corresponded with the evolution of ammonia and nitrogen, respectively, and served to establish the conditions for the preparation of the nitride which was conducted subsequently at 300 °C. The final residue in the TPTD was metallic tin. The volatile evolution is well-defined, and at 300 °C, prior to any significant evolution of nitrogen, the ammonia loss is almost complete with very little hydrogen left as evidenced by the absence of any NH vibration in the IR spectrum of the nitride. The IR spectrum of the nitride is very simple. It contains a single prominent band at 620 cm⁻¹, in agreement with previous observations³ on material obtained in a glow-discharge system. It is interesting to note the difference in thermal behavior between bulk powder nitride, which decomposes significantly at 420 °C, and glow-discharge films, which decompose only at >720 °C.³ Evidently the activation energy for decomposition is greatly enhanced in the film.

The nitride was subjected to XPS analysis for qualitative purposes. Binding energies, referenced to C(1s) at 284.6 eV, were 396.2 and 485.1 eV for N(1s) and Sn(3d_{5/2}) respectively. The intensity ratio expressed as atomic concentrations (N/Sn) is 0.92, a figure which differs from the idealized value of 1.33. This situation is not unusual considering the empirical sensitivity factors used to convert intensities to concentrations and the fact that the technique analyzes the surface of the material, which may have a composition that departs from that of the bulk. In agreement with the bulk chemical analysis, the XPS analysis detected potassium but no bromide. The values for the N and Sn binding energies are in accordance with those of other nitrides^{11,12} although the nitrogen value is at the low end of the range, more in line with the interstitial nitrides than the covalent ones. This suggests considerable electron density shift from the metal to the nitrogen. A moderate shift in the tin value to a higher energy (compared with tin metal) is observed here as in the case of titanium nitride.¹³

The tin nitride powder prepared in the course of this study was found to be amorphous by X-ray diffraction. The nitride is brick red while the amide is pale yellow.

Attempts were made to determine the electrical resistivity of the nitride. A portion of the material was compressed into a pellet at room temperature under 550 MPa. The apparent density of the pellet at that stage was 3.16 g/cm³, which is about 62% of the value determined by Janeff² with a pycnometer. The void space in the pellet is approximately correct for the packing of spheres. The pellet was subjected to a thermal treatment of 8 h at 500 °C with the expectation of promoting sintering and additional densification. The treatment was conducted in an autoclave at 10 MPa nitrogen to prevent nitrogen loss from the nitride. The pellet had a marginal weight loss of 1.2%, but densification proceeded only slightly to 3.29 g/cm³. The electrical resistivity of the pellet at this stage was excessive, apparently due to poor contact among the particles of the material. A purer specimen, appropriate for resistivity measurements, was prepared as a film by CVD at atmospheric pressure under anaerobic conditions according to ref 6. Briefly, a stream of argon was used

to sweep a source containing (Et₂N)₄Sn, held at 150 °C, into a reaction zone, held at 300 °C, which contained the specimens to be coated. A side stream of anhydrous ammonia was also introduced to the hot reaction zone. The thickness of the coating on a quartz plate, used for the resistivity measurements, was derived from the gain in weight and assuming a density of 5.1 g/cm³. The coating on quartz was light brown in color. Those on silicon were iridescent because of interference with visible light. The resistivity at room temperature was 0.15 Ω cm, compared with 1.4 × 10⁻⁴ Ω given in ref 2 and 66-5.6 Ω cm on crude films that decreased to 6.3-1.4 Ω cm after annealing as reported in ref 3b. It is seen that the result found in the present work would support those given in ref 3b. It is possible that the specimen examined by Janeff² might have been contaminated with metallic tin, which would explain the higher conductivity. It is not uncommon to sputter free metal in a glow-discharge system. The IR spectrum of the material obtained in the CVD setup was identical with that of bulk powder from the amide imide intermediate. It did not show evidence of oxide species such as bands at 660 or 510 cm⁻¹ due to SnO₂ and SnO or a band that develops at 545 cm⁻¹ upon long exposure of bulk nitride to air. Furthermore, thermal decomposition at 800 °C of the film left a bright metallic coating, suggesting little or no oxygen on the initial film.

Experimental Section

All manipulations were conducted in a vacuum line and in an inert-gas glovebox (H₂O and O₂ <1 ppm). Ammonia was further dried by contact with metallic sodium. Liquid-ammonia reactions and product washing were conducted in sealed heavy-walled ampules provided with a side arm separated from the body of the ampule by a glass frit. In a typical reaction, about 2 mmol of tin(IV) bromide and a slight excess over the stoichiometric amount of potassium amide were loaded into an ampule together with about 15 mL of liquid ammonia. Washing of solids was done with ammonia recovered by a thermal gradient from the side arm that collected the soluble fraction being filtered. The TPTD analysis was conducted in a system containing a furnace, ramped at 10 °C/min. The volatiles evolved were continuously swept by high-purity helium into a Model 5970 Hewlett-Packard mass selective detector. The XPS analysis was conducted with a McPherson Model 36 electron spectrometer using Al Kα radiation at 250 W. Sample preparation for XPS was conducted in an inert-gas glovebox. Electrical resistivities were measured by the four-probe method. Infrared spectra were obtained with a Digilab FTIR 60 spectrophotometer.

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Bond Lengths in Covalent Fluorides. A New Value for the Covalent Radius of Fluorine

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From a consideration of observed bond lengths, we propose a new value of 54 pm for the covalent radius of fluorine. Pauling¹ originally gave a value of 64 pm, but after the determination of the bond length in the F₂ molecule,² the value of 72 pm, half the F-F bond length, was generally adopted. However, the observed bond lengths in many covalent fluorides are considerably shorter than those calculated from either of these values. More recently

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