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Synthetic and Structural Studies of Cyclodistib(V)azanes

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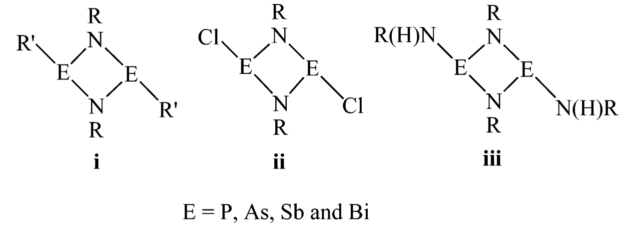
High-yielding syntheses of complexes based around the cyclodistibazane (Sb_2N_2) core are described from the reaction of organoantimony(V) chlorides with varying stoichiometric amounts of lithiated primary amines, LiN(H)R. Thus, mixing Ph_3SbCl_2 with 2 equiv of LiN(H)R (R = CH_2Ph) produces $Ph_3Sb(\mu\text{-NR})_2SbPh_3$ (**1**). Mixed amido/imido complexes of formula $\{R(H)N\}Ph_2Sb(\mu\text{-NR})_2SbPh_2\{N(H)R\}$ (**2**) (R = CH_2Ph, 2-OMe-5-^{t}Bu-C_6H_3, and Cy) are made from the corresponding 3:1 molar ratio combination of LiN(H)R with Ph_2SbCl_3. A similar reaction employing only 2 equiv of LiN(H)R (R = CH_2Ph) with 1 equiv of Ph_2SbCl_3 yields $ClPh_2Sb(\mu\text{-NR})_2SbPh_2Cl$ (**3**). Compounds **2a**–**c** and **3** possess reactive functionality which may make them useful synthetic reagents in the preparation of more complex main group imido architectures. All of the complexes have been characterized by ^{1}H NMR spectroscopy, elemental analysis (CHN), and X-ray crystallography. An investigation of all known crystallographically characterized Sb–N fragments from the Cambridge Structural Database highlights a series of parameters that appear to influence the observed Sb–N bond lengths.

Introduction

Over recent years there has been an increasing number of main group imido macrocyclic structures reported with potential uses both as bulky counterions to transition metal complexes and also as ligands themselves. The ongoing interest in such compounds is due to their diverse structural and electronic features, as well as having potential uses as precursors for solid-state materials.[1] Many group 15 imido frameworks contain a basic E_2N_2 four-membered ring (Chart 1) which can then be linked together by a variety of spacer units.[2−4] These E_2N_2 rings are formed by amine condensation reactions of ECl_3 with a primary amine or metalated amide. The products can take a variety of forms as illustrated in Chart 1, depending on the organic substituents and also the stoichiometry employed. The principal focus of previous work has been on the lighter elements of group 15, presumably on account of the stronger bond strengths that would be anticipated. Similar condensation reactions have been observed for the corresponding arsenic, antimony, and bismuth analogues[5] but almost exclusively in oxidation state +3.

Chart 1. Some Dimeric Architectures of Pnictazanes



The imido chemistry of antimony in its highest oxidation state is an area which has received relatively little attention, and the ready preparation and structural characterization of these species would be of considerable value. Investigations into the synthesis of fundamental antimony(V) imido species is also of interest in the continued search for precursors to solid-state materials such as antimony nitride. Initial studies on the preparation of compounds containing Sb(V)−N bonds

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suggested that they can only be formed if the basicity of the nitrogen is reduced by the use of electron-withdrawing groups or by mesomeric effects.[6] Furthermore, single valence products were only obtained from using trimethylsilyl-substituted amines. Preparative methods were enlarged in the 1995 report of the synthesis of $Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)_2SbPh_3$,[7] prepared from the reaction of $Ph_3Sb(NMe_2)_2$ with phenylethylamine. This complex was described in terms of having two imido groups linking the Sb(V) centers together. Since that report, there have only been a handful of structurally characterized examples of related compounds. Most notably, the elegant experimental studies of Matano et al. of a series of monomeric iminopnictoranes resulted in imino-λ^5-stibane complexes containing formal $Sb(V){=}N$ bonds.[8] They reported a series of (acylimino)triaryl-λ^5-pnictoranes, $Ar_3M{=}NCOR$, and also a similar series of the type $Ar_3M{=}NSO_2CF_3$, where the formation of dimers and higher oligomers was blocked by delocalizing the negative charge of the imido nitrogen center and by employing the steric bulk of the system to prevent further aggregation.

Herein we report syntheses of a range of cyclodistib(V)-azanes, which are potentially useful building blocks for larger antimony imido frameworks. This work provides further evidence that antimony(V)−nitrogen bonds can be readily formed with a range of substituents on the nitrogen center. Importantly, it has been found that subtle variations in the reagents employed in the synthesis lead to products offering reactive functionalities at the antimony center, which may prove to be valuable synthetic reagents for the preparation of further novel main group architectures.

Results and Discussion

Two equivalents of LiN(H)R ($R = CH_2Ph$) were reacted with Ph_3SbCl_2 in tetrahydrofuran (THF) to give a pale yellow solution. Reduction of the solvent volume to ca. 10 mL followed by storage for 24 h at 25 °C gave a good yield of colorless, crystalline material. The ^1H NMR spectrum of this material showed a singlet at $\delta = 3.88$ ppm, indicating the presence of methylene protons. The NMR spectrum and IR spectroscopy confirmed the absence of NH units in the product. Single-crystal X-ray structure analysis revealed that the complex formed was $Ph_3Sb(\mu\text{-}NCH_2Ph)_2SbPh_3$ (**1**) as shown in Figure 1. Selected bond lengths and angles are given in Table 1. In this synthesis, it is noteworthy that the Sb(V)−N bonds are formed under very mild conditions using reagents that are readily available in the modern laboratory.

Given the similarities in the amines employed, it was unsurprising to find that complex **1** (where $R = CH_2Ph$) is closely related to the previous example reported by Wright (where $R = CH_2CH_2Ph$).[7] The Sb_2N_2 core has a rhombic shape (N−Sb−N 74.67(8), Sb−N−Sb 105.33(8)°) in which the Sb(V) centers have highly distorted trigonal bipyramidal geometries. The dimensions of the Sb_2N_2 core are similar to those observed in cyclodistib(III)azanes.[5,9] The molecule has a center of inversion, and the Sb−N lengths have an alternate "long/short" arrangement (2.128(2)/1.995(2) Å). A ready explanation of this observation and a detailed analysis of Sb−N bond lengths is discussed below.

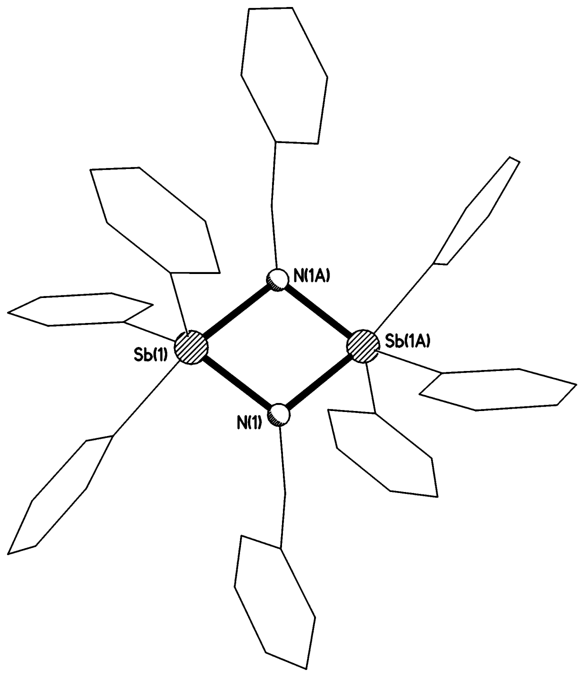

Figure 1. Molecular structure of $Ph_3Sb(\mu\text{-}NCH_2Ph)_2SbPh_3$ (**1**). Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Ph_3Sb(\mu\text{-}NCH_2Ph)_2SbPh_3$ (**1**)

bond lengths (Å)			
Sb(1)−N(1)	1.995(2)	Sb(1)−C(7)	2.141(2)
Sb(1)−N(1A)[a]	2.128(2)	Sb(1)−C(13)	2.131(2)
Sb(1)−C(1)	2.199(2)	C(19)−N(1)	1.457(2)

bond angles (deg)			
N(1)−Sb(1)−N(1A)	74.67(8)	N(1A)−Sb(1)−C(13)	92.45(7)
N(1)−Sb(1)−C(1)	95.46(8)	C(7)−Sb(1)−C(1)	92.96(8)
N(1)−Sb(1)−C(7)	122.40(7)	C(13)−Sb(1)−C(1)	92.87(8)
N(1)−Sb(1)−C(13)	124.38(7)	C(13)−Sb(1)−C(7)	111.89(7)
N(1A)−Sb(1)−C(1)	170.12(6)	Sb(1)−N(1)−Sb(1A)	105.33(8)
N(1A)−Sb(1)−C(7)	92.78(7)		

[a] Symmetry transformations used to generate equivalent atoms denoted "A": $x + 2, -y + 2, -z$.

One interesting difference between **1** and $Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)_2SbPh_3$ is that the benzyl groups of the bridging imido centers adopt a trans orientation with respect to the planar Sb_2N_2 ring in **1**, whereas the cis conformation is observed for the phenylethyl example. The steric bulk and electronic properties of the two imido ligands are very similar, suggesting that the energy difference between the cis and the trans forms of these compounds is very small and that crystal packing forces may account for the differences in the solid-state geometries observed. Interestingly, the ^1H NMR spectrum of **1** shows only a sharp singlet for the CH_2

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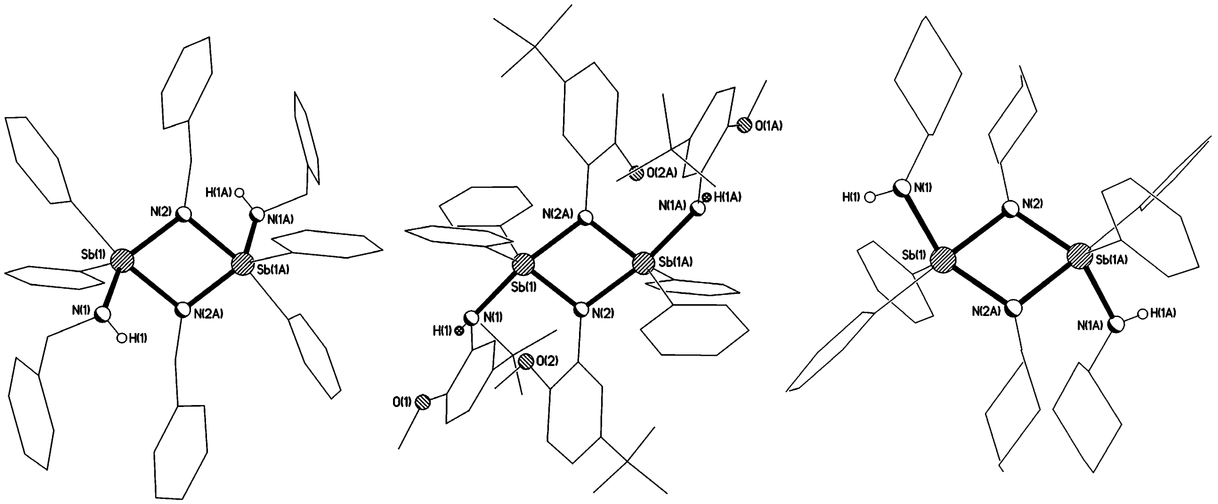

2a **2b** **2c**

Figure 2. Molecular structures of $\{N(H)CH_2Ph\}Ph_2Sb(\mu\text{-}NCH_2Ph)_2SbPh_2\{N(H)CH_2Ph\}$ (**2a**), $\{N(H)C_6H_4(OMe)^tBu\}Ph_2Sb(\mu\text{-}N(H)C_6H_4(OMe)^tBu)_2SbPh_2\text{-}\{N(H)C_6H_4(OMe)^tBu\}$ (**2b**), and $\{N(H)Cy\}Ph_2Sb(\mu\text{-}NCy)_2SbPh_2\{N(H)Cy\}$ (**2c**). Hydrogen atoms (except for those on nitrogen), and a lattice THF molecule in the case of **2c**, have been omitted for clarity.

protons which is consistent with either a conformationally rigid structure or one where the cis and trans isomers are interconverting rapidly on the NMR time scale. Further work will be required to differentiate these two possibilities.

The synthesis of **1** represents a new high-yielding synthesis of a cyclodistib(V)azane. To further explore the potential of this simple method to cyclodistibazane complexes, diphenylantimony(V) trichloride, which could be synthesized in high yield based on the literature procedure,[10] was chosen as an alternative antimony reagent to prepare complexes possessing additional reactive functionalities attached to the antimony center.

Ph_2SbCl_3 was reacted with 3 equiv of lithiated amine LiN(H)R (R = CH_2Ph (**2a**), (2-OMe-5-^{t}Bu)C_6H_3 (**2b**), Cy (**2c**)) in THF. A good yield of crystalline material was obtained from each reaction by the reduction of solvent and overnight storage at 25 °C. Resonances at δ = 4.38 and 4.10 ppm in the ^1H NMR spectrum of **2a** and **2b**, respectively, indicated the presence of a N−H proton; a similar peak was not observed for **2c**, presumably because it is incorporated in the morass of peaks associated with the cyclohexyl and phenyl groups present in this molecule. Single-crystal X-ray diffraction experiments on **2a**−**c** confirmed the crystalline complexes to be of the general formula $\{R(H)N\}Ph_2Sb(\mu\text{-}NR)_2SbPh_2\{N(H)R\}$ as shown in Figure 2, with selected bond lengths and angles for these molecules given in Table 2.

The X-ray crystal structures of **2a**, **2b**, and **2c** show the three compounds to be essentially isostructural, with each possessing a crystallographic center of inversion which makes the two halves of each molecule identical in the solid state. The Sb_2N_2 cores of **2a**−**c** are formed by two imido groups and two antimony centers. Each antimony center is additionally bound to two phenyl groups and a pendant amido arm. As with the structure of **1**, the imido bridges are arranged in a trans orientation. Similarly the amido arms are mutually trans. The central Sb_2N_2 units are rhombic in shape (within the Sb_2N_2 cores, av N−Sb−N 75.62° and av Sb−N−Sb 104.36°). The antimony centers have distorted trigonal bipyramidal geometries, although it should be noted that one of the −OMe groups of each monomer unit of **2b** form long-range contacts with its respective Sb center (Sb−O 3.175 Å).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **2a**−**c**

	(**2a**)	(**2b**)	(**2c**)
	bond lengths (Å)		
Sb(1)−N(1)	2.038(2)	2.094(3)	2.034(2)
Sb(1)−N(2)	2.006(2)	2.000(3)	2.104(2)
Sb(1)−N(2A)	2.107(2)	2.128(3)	2.008(2)
Sb(1)−C(1)	2.180(3)	2.120(3)	2.133(3)
Sb(1)−C(7)	2.137(3)	2.163(4)	2.198(3)
	bond angles (deg)		
N(1)−Sb(1)−N(2)	130.99(9)	96.05(12)	89.82(9)
N(1)−Sb(1)−N(2A)	87.65(9)	171.00(11)	138.31(10)
N(2)−Sb(1)−N(2A)	75.23(9)	75.04(12)	76.60(10)
Sb(1)−N(2)−Sb(1A)	104.72(9)	104.96(12)	103.40(10)
N(1)−Sb(1)−C(1)	90.50(10)	90.14(13)	107.98(10)
N(1)−Sb(1)−C(7)	112.39(9)	89.29(13)	87.39(10)
N(2)−Sb(1)−C(1)	95.66(9)	120.24(13)	94.64(9)
N(2)−Sb(1)−C(7)	114.80(9)	123.81(13)	171.07(9)
N(2A)−Sb(1)−C(1)	165.96(9)	95.37(12)	112.22(10)
N(2A)−Sb(1)−C(7)	95.92(9)	94.72(12)	100.00(9)
C(1)−Sb(1)−C(7)	97.65(10)	115.62(14)	94.29(10)

The imposed tight bond angle at the Sb centers in the Sb_2N_2 core is most readily accommodated by having one imido group in an axial site and one in an equatorial site. This is indeed the case in **2a**−**c**, but the positioning of the other substituents is dependent on the organic group present. Hence, in the structures of **2a** and **2c**, one imido group, one phenyl group, and the pendant amide arm lie equatorially (sum of equatorial angles about Sb are 358.2° for **2a** and 358.51° for **2c**), while the other phenyl ring and imido bridge occupy the axial positions (C(1)−Sb−N(2A) 165.96° for **2a**, 171.1° for **2c**). Complex **2b** has the more sterically demanding organic group (2-OMe-5-^{t}Bu)C_6H_3 on the nitrogen centers and also possesses the possibility of sidearm donation from the −OMe groups, and hence the positioning of the substit-

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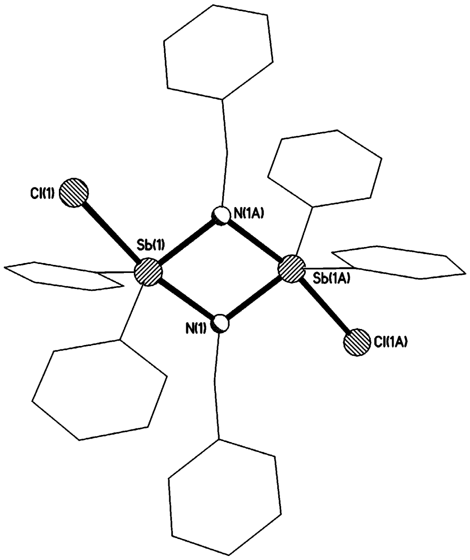

Figure 3. Molecular structure of $Ph_2(Cl)Sb(\mu\text{-}NCH_2Ph)_2Sb(Cl)Ph_2$ (**3**). Hydrogen atoms have been omitted for clarity.

uents on antimony is different for this complex. The pendant amide arm and one of the imido bridges occupy the axial positions (N(1)−Sb(1)−N(2A) 171.00(11)°), while the two phenyl rings and the remaining imido group are arranged equatorially (sum of angles 359.67°).

Complexes **2** all possess reactive N−H functionality that should prove to be a useful tool in seeking to link the Sb_2N_2 units together. An alternative approach to this same goal is to leave proreactive functionality at the Sb center. This is readily achieved in this instance by variation of the stoichiometry employed in the reaction. The use of 2 equiv of LiN(H)R to 1 equiv of Ph_2SbCl_3 resulted in the isolation of a good yield of the mixed imido/chloro-substituted dimer (**3**) shown in Figure 3.

The X-ray crystal structure of **3** shows a Sb_2N_2 ring with benzylimido ($-NCH_2Ph$) groups linking the two antimony centers. Each antimony center is also bound to two phenyl groups and a chlorine atom. The organic substituents on the imido groups are arranged in a trans orientation as are the two chloride ligands. The antimony centers display distorted trigonal bipyramidal geometry, with the imido group and the chlorine atom occupying the axial sites (N(1)−Sb(1)−Cl(1) 169.39(5)°) and the two phenyl groups and the remaining imido group in the equatorial positions (sum of angles between these groups is 359.98°) (see Table 3). As with the structures of **1**, **2a**−**c**, and $Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)_2SbPh_3$,[7] there is a pattern of alternating long/short Sb−N bond lengths in the core (2.081(2) and 1.987(2) Å in **3**). In other species involving Sb(V)−N bonds, such variations are not commonly observed. These typically have relatively uniform Sb−N bond lengths that are greater than those observed in **1**, **2a**−**c**, and **3**, for example, Sb−N 2.15−2.19 Å in $[Cl_3SbNMe]_4$,[6] 2.18−2.19 Å in $[Cl_4SbN_3]_2$,[11] and 2.11−2.14 Å in $[Cl_4SbNCNSiMe_3]_2$.[12] However, in each of these example complexes, antimony has distorted octahedral geometry, whereas it has a distorted trigonal bipyramidal arrangement of ligands in the structures of **1**, **2a**−**c**, **3**, and $Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)_2SbPh_3$. The pattern of alternating short and long Sb−N bonds in all of the latter set of cyclodistibazane complexes is readily explained by the different geometrical positions occupied by these groups about their distorted trigonal bipyramidal Sb centers. Hence, the equatorial Sb−N contacts are relatively short, whereas the axial contacts are longer in a way that is commonly encountered in this geometry.

Table 3. Selected Bond Lengths and Angles for $Ph_2Sb(Cl)(\mu\text{-}NCH_2Ph)_2Sb(Cl)Ph_2$ (**3**)

bond lengths (Å)			
Sb(1)−N(1)	2.081(2)	Sb(1)−C(1)	2.125(2)
Sb(1)−N(1A)[a]	1.987(2)	Sb(1)−C(7)	2.113(2)
Sb(1)−Cl(1)	2.450(1)	N(1)−C(13)	1.471(2)
bond angles (deg)			
N(1)−Sb(1)−N(1A)	77.04(7)	N(1A)−Sb(1)−Cl(1)	92.45(5)
Sb(1)−N(1)−Sb(1A)	102.96(7)	N(1)−Sb(1)−Cl(1)	169.39(5)
N(1)−Sb(1)−C(1)	96.66(7)	C(1)−Sb(1)−Cl(1)	90.19(5)
N(1A)−Sb(1)−C(1)	122.24(7)	C(7)−Sb(1)−Cl(1)	88.74(6)
N(1)−Sb(1)−C(7)	95.70(7)	C(13)−N(1)−Sb(1)	126.8(1)
N(1A)−Sb(1)−C(7)	122.99(8)	C(13)−N(1)−Sb(1A)	129.9(1)
C(1)−Sb(1)−C(7)	114.75(8)		

[a] Symmetry transformations used to generate equivalent atoms denoted "A": $-x + 1, -y + 1, -z$.

In summary, the reaction of 2 equiv of LiN(H)R (R = CH_2Ph) with Ph_3SbCl_2 leads to the formation in good yield of the condensation product $Ph_3Sb(\mu\text{-}NCH_2Ph)_2SbPh_3$ with the elimination of LiCl and $PhCH_2NH_2$. Similar condensation reactions occur when the antimony reagent is changed to Ph_2SbCl_3. Isolation of the amino-substituted product, $\{N(H)R\}Ph_2Sb(\mu\text{-}NR)_2SbPh_2\{N(H)R\}$, or the chloro-substituted product, $ClPh_2Sb(\mu\text{-}NR)_2SbPh_2Cl$, is dependent on the stoichiometry of the reaction as shown in Scheme 1.

The data presented as part of this study and those found in the literature showed large variations in Sb−N bond lengths. To probe this feature, a search was undertaken of Sb−N fragments present in the November 2002 edition of the Cambridge Structural Database. A summary of the results and subsequent categorization of the hits of this search are shown below in Table 4. A more detailed analysis is described in Supporting Information.

Although it is recognized that much of the analysis is not based on sufficient data to have real statistical vigor, some general patterns emerge that are interesting in light of the current report. Factors that were investigated included the oxidation sate of the antimony, the coordination number at the antimony, and the nature of the nitrogen center. Few easily discernible trends could be seen from the coordination number investigation save that those with three-coordinate Sb tended to be shorter than higher coordination numbers. The effect of the nitrogen center was clearer, with Sb−NR bond lengths tending to be shorter than comparable $Sb-NR_2$ bond lengths. Most significantly, it would ordinarily be expected that Sb(V)−N bonds would be shorter than corresponding Sb(III)−N bonds, but curiously, it was observed that the oxidation state of the antimony has little effect on the Sb−N bond length. A ready explanation may lie in the fact that steric influences must also be considered,

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Scheme 1. Preparation of **1**, **2**, and **3**

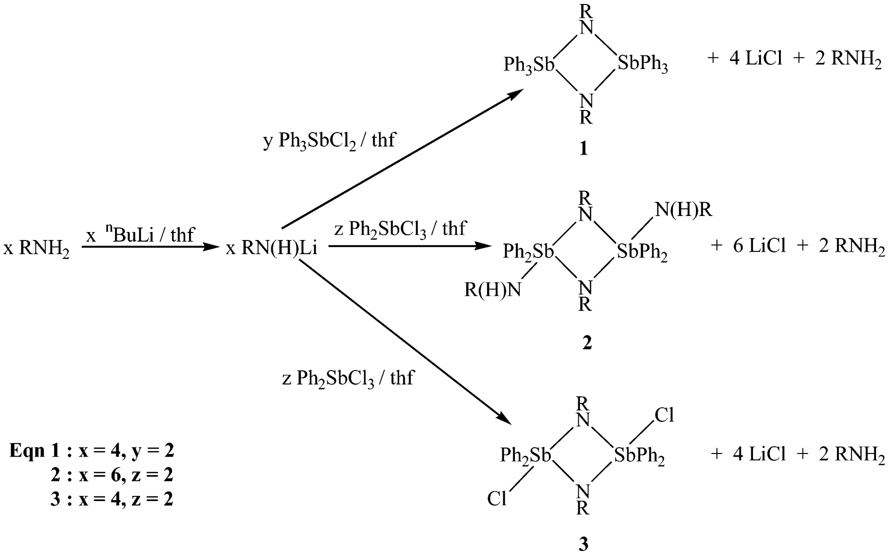

Table 4. Summary of Analysis of Sb−N Bond Lengths Generated from a Cambridge Structural Database Search

	set **A**[a]	set **B**	set **C**	set **D**	set **E**	set **F**	set **G**	set **H**	set **I**	set **J**
no. fragments	493	308	241	68	140	87	44	35	135	148
mean bond length	2.240	2.105	2.103	2.115	2.062	2.148	2.149	2.119	2.070	2.129
standard deviation	0.218	0.084	0.083	0.088	0.047	0.100	0.087	0.060	0.055	0.088

[a] The sets correspond to **A**, all of the data fitting the search criteria; **B**, all of the data less those assessed as being dative bonds; **C**, with Sb(III); **D**, with Sb(V); **E**, Sb coord no. 3; **F**, Sb coord no. 4; **G**, Sb coord no. 5; **H**, Sb coord no. 6; **I**, Sb−NR; **J**, Sb−NR$_2$.

and the higher coordination numbers associated with antimony(V) centers may cause a lengthening of the Sb−N bond. A combination of these opposing factors probably dictates the relatively similar lengths of the Sb(III)−N and Sb(V)−N bonds.

Conclusions

Cyclodistib(V)azane complexes may be synthesized from the reaction of organoantimony(V) chlorides with varying stoichiometric amounts of lithiated primary amines. The synthetic protocol may be used to produce “saturated” dimers or those which contain potentially reactive amide or chloride functionalities.

An analysis of the results of Sb−N fragments from the Cambridge Structural Database shows that no single factor determines the observed bond length, but the oxidation state and coordination number at the antimony center and the nature of the nitrogen moiety all play a role.

Experimental Section

Reagents and General Procedures. All of the reactions and manipulation of products were carried out using standard inert atmosphere techniques under an atmosphere of nitrogen. Air- and moisture-sensitive materials were weighed out, isolated, and stored in an argon-filled Saffron Beta glovebox. Unless otherwise stated, all of the chemicals used were readily available from commercial sources and used as supplied. Solvents used were distilled HPLC grade and were dried using sodium wire (water content below 5 ppm) and then further dried and degassed using a commercially available solvent purification system from Anhydrous Engineering. Diethyl ether and THF were passed through two alumina-packed columns, while dichloromethane, hexane, and toluene were passed through an alumina-packed column followed by a copper redox catalyst.[13]

Instrumentation. ^{1}H NMR spectra were measured at 25 °C in C_5D_5N on a JEOL Eclipse 300 MHz spectrometer. Chemical shifts reported were referenced to internal solvent peaks. IR spectra were obtained as Nujol mulls between NaCl plates on a Perkin-Elmer Spectrum 1 FT-IR spectrophotometer. Elemental analyses were recorded on a Carlo Erba EA1108 CHN elemental analyzer.

Preparation of $Ph_3Sb(\mu\text{-}NCH_2Ph)_2SbPh_3$ (1). Li^{n}Bu (2.5 mL, 1.6 M solution in hexanes, 4 mmol) was added dropwise to an ice-cooled solution of $PhCH_2NH_2$ (0.44 mL, 4 mmol) in THF (30 mL) and stirred for 30 min to give a bright pink solution. The solution was cooled in ice, and Ph_3SbCl_2 (0.85 g, 2 mmol) was added. The resulting pale yellow solution was stirred for 1 h at room temperature. Colorless, crystalline blocks of (**1**) were obtained by reduction of the solvent volume in vacuo to approximately 10 mL and stored at room temperature for 24 h (0.70 g, 76% yield). Anal. Calcd for $C_{25}H_{22}NSb$: C, 65.53; H, 4.84; N, 3.06. Found: C, 64.97; H, 4.69; N, 2.86. ^{1}H NMR data (C_5H_5N, 300 MHz, 25 °C): δ = 8.00−8.10 and 7.22−7.44 (collection of m, 20H, $-NCH_2C_6\mathbf{H_5}$, and $-Sb(C_6\mathbf{H_5})_2$), 3.88 (s, 2H, $-NC\mathbf{H_2}C_6H_5$). Mp 153−156 °C (yellow oil).

Preparation of $\{N(H)CH_2Ph\}Ph_2Sb(\mu\text{-}NCH_2Ph)_2SbPh_2\{N(H)CH_2Ph\}$ (2a). Li^{n}Bu (3.75 mL, 1.6 M solution in hexanes, 6 mmol) was added dropwise to an ice-cooled solution of $PhCH_2Ph$ (0.66 mL, 6 mmol) in THF (30 mL) and stirred for 30 min to give a bright pink solution. The solution was cooled in ice, and Ph_2SbCl_3 (0.77 g, 2 mmol) was added to give a bright yellow solution. The solvent was removed in vacuo to give a white solid. Colorless, crystalline rods of **2a** were obtained from a saturated solution in

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(13) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

Table 5. Selected Crystal Data and Data Collection Parameters for **1**, **2a**, **2b**, **2c**, and **3**

	1	**2a**	**2b**	**2c**	**3**
formula	$C_{25}H_{22}NSb$	$C_{26}H_{25}N_2Sb$	$C_{38}H_{49}N_2O_3Sb$	$C_{24}H_{33}N_2Sb$	$C_{19}H_{17}ClNSb$
fw	458.19	487.23	703.54	471.27	416.54
space group	$P\bar{1}$	$P2(1)/c$	P-1	$C2/c$	$P2(1)/n$
a (Å)	9.0485(1q8)	11.989(1)	10.639(1)	16.7385(6)	11.664(2)
b (Å)	10.702(2)	17.422(2)	11.332(1)	13.1417(4)	10.549(2)
c (Å)	11.459(2)	10.350(1)	15.558(2)	21.3540(7)	14.024(3)
α (deg)	70.90(3)	90	77.251(2)	90	90
β (deg)	74.33(3)	92.874(2)	75.600(2)	112.542(2)	109.34(3)
γ (deg)	71.59(3)	90	84.373(2)	90	90
V (Å^3)	977.5(3)	2159.1(5)	1770.2(4)	4338.4(2)	1628.1(6)
Z	2	2	2	8	4
T (K)	173(2)	173(2)	100(2)	173(2)	100(2)
$d_{\text{calcd (g cm}^{-3})}$	1.557	1.499	1.320	1.443	1.699
μ (mm^{-1})	1.420	1.292	0.816	1.283	1.854
R^a	0.0206	0.0209	0.0395	0.0267	0.0210
wR^b	0.0479	0.0645	0.0980	0.0781	0.0505

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $(I > 2.00\sigma(I)$. [b] $R_w = \{[\Sigma\omega(F_o^2 - F_c^2)^2]/[\Sigma\omega(F_o^2)^2]\}^{1/2}$ (all data).

THF at room temperature (0.63 g, 65% yield). Despite repeated attempts, we have been unable to obtain satisfactory C analysis—we are unable to easily account for this but presume that it may be a result of carbide formation. Anal. Calcd for $C_{26}H_{25}N_2Sb$: C, 64.09; H, 5.17; N, 5.75. Found: C, 60.19; H, 5.12; N, 5.20. ^{1}H NMR data (CD_2Cl_2, 300 MHz, 25 °C): $\delta = 6.34-8.10$ (collection of m, 20H, $-N(H)CH_2C_6\mathbf{H_5}$, $-NCH_2C_6\mathbf{H_5}$, and $-Sb(C_6\mathbf{H_5})_2$), 4.38 (s, 1H, $-N(\mathbf{H})CH_2C_6H_5$), 2.26 (s, 2H, $-NC\mathbf{H_2}C_6H_5$), 1.18 (s, 2H, $-N(H)C\mathbf{H_2}C_6H_5$). Mp 142−145 °C (yellow oil).

Preparation of {N(H)C$_6$H$_4$(OMe)^{t}Bu}Ph$_2$Sb(μ-NC$_6$H$_4$(OMe)-^{t}Bu)$_2$Ph$_2$Sb{N(H)C$_6$H$_4$(OMe)^{t}Bu} (2b). LiBu^n (7.5 mL, 1.6 M solution in hexanes, 12 mmol) was added dropwise to an ice-cooled solution of (2-OMe-5-^{t}Bu) $C_6H_3NH_2$ (2.15 g, 12 mmol) in THF (50 mL) to give a dark blue solution. Ph_2SbCl_3 (1.53 g, 4 mmol) was added and stirred for 20 min to give a dark brown solution. The solvent was removed in vacuo to give a pale yellow solid. Yellow crystalline blocks were obtained from the storage of saturated solution in THF (30 mL) at −18 °C overnight (2.06 g, 82%). Anal. Calcd for $C_{38}H_{49}N_2O_3Sb$: C, 64.78; H, 6.80; N, 4.20. Found: C, 65.08; H, 6.65; N, 4.48. ^{1}H NMR data (C_4D_8O, 300 MHz, 25 °C): $\delta = 7.15-7.84$ (m, 10H, $-Sb(C_6\mathbf{H_5})_2$), 6.49−6.61 (m, 6H, $-N(H)C_6\mathbf{H_3}(OCH_3)C_4H_9$), and $-NC_6\mathbf{H_3}(OCH_3)C_4H_9$), 4.10 (s, 1H, $-N(\mathbf{H})C_6H_3(OCH_3)C_4H_9$), 3.69 (s, 3H, $-NC_6H_3(OC\mathbf{H_3})$-C_4H_9), 3.68 (s, 3H, $-N(H)C_6H_3(OC\mathbf{H_3})C_4H_9$), 1.18 (s, 9H, $-NC_6H_3$-$(OCH_3)C_4\mathbf{H_9}$), 1.17 (s, 9H, $-N(H)C_6H_3(OCH_3)C_4\mathbf{H_9}$). Mp 198−200 °C (to a yellow oil; at >210 °C, this changes to a dark red liquid).

Preparation of {N(H)Cy}Ph$_2$Sb(μ-NCy)$_2$SbPh$_2${N(H)Cy} (2c). LiBu^n (3.75 mL, 1.6 M solution in hexanes, 6 mmol) was added dropwise to an ice-cooled solution of $CyNH_2$ (0.69 mL, 6 mmol) in toluene (30 mL). The solution was stirred for 30 min at room temperature. Ph_2SbCl_3 (0.77 g, 2 mmol) was added to the solution and stirred for 3 h. A white precipitate was observed. The reaction mixture was filtered (porosity 3 sinter with Celite) to give a clear yellow solution. The solution was reduced in vacuo to approximately 10 mL in volume and stored at −5 °C for 24 h, yielding colorless, crystalline blocks (0.59 g, 63%). Anal. Calcd for $C_{24}H_{33}N_2Sb$: C, 61.16; H, 7.06; N, 5.94. Found: C, 61.08; H, 7.48; N, 5.78. ^{1}H NMR data (CD_2Cl_2, 300 MHz, 25 °C): $\delta = 7.03-7.66$ (m, 10H, $-Sb(C_6\mathbf{H_5})_2$), 1.45−1.76 and 0.77−1.24 (m, 22H, $-N(H)C_6\mathbf{H_{11}}$, and $-NC_6\mathbf{H_{11}}$). Mp 164−166 °C (to an orange oil).

Preparation of Ph$_2$Sb(Cl)(μ-NCH$_2$Ph)$_2$Sb(Cl)Ph$_2$ (3). A solution of $LiN(H)CH_2Ph$ (3 mmol) in THF (30 mL) was prepared as previously described for **2a**. Ph_2SbCl_3 (0.77 g, 2 mmol) was added and stirred for 1 h resulting in a pale yellow solution. Colorless, crystalline blocks were obtained by the reduction of solvent in vacuo to approximately 10 mL in volume and stored at room temperature for 24 h (0.62 g, 75%). Anal. Calcd for $C_{19}H_{17}ClNSb$: C, 54.78; H, 4.11; N, 3.36. Found: C, 54.44; H, 3.99; N, 3.28. ^{1}H NMR data (CD_2Cl_2, 300 MHz, 25 °C): $\delta = 7.34-7.87$ (m, 15H, $-NCH_2C_6\mathbf{H_5}$, and $-Sb(C_6\mathbf{H_5})_2$), 2.49 (s, 2H, $-NC\mathbf{H_2}C_6H_5$). Mp 148−150 °C (to a yellow oil).

X-ray Analyses. Single crystals of **1**, **2a**, **2b**, **2c**, and **3** (colorless blocks) were coated with perfluoropolyether oil under a stream of N_2 and mounted onto thin glass fibers. Measurements were made on a Bruker-Nonius SMART (**1**, **2a**, and **2c**) or Bruker-Nonius APEX (**2b** and **3**) CCD area-detector three-circle diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å).[14,15] Relevant parameters for the data collections and crystallographic data are summarized in Table 5. The structures were solved by direct methods (SHELXL-97) and refined by a full-matrix least-squares method based on F^2 using SHELXL-97.[16] Absorption corrections were applied based on multiple and symmetry-equivalent measurements.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The hydrogen atoms on nitrogen were initially located in the difference Fourier map and then included at geometrically idealized positions.

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Supporting Information Available: Histograms relating to the results of the CSD search and associated statistical analysis of these data together with X-ray crystallographic files (CIF) for the complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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