Syntheses and Structures of Bis(azido)- and Bis(*tert*-butoxy)cyclodistibazanes

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Introduction

Small inorganic heterocycles[1] are generally not only more stable than similar carbocycles (cf. cyclobutane)[2] but are also often formed in preference to their acyclic counterparts. This is especially true for heterocycles of the types $(E-N)_2$,[3] or $(E-E')_2$,[4] where E and E′ are main-group elements. Interest in these ring systems has increased in the recent past, mainly because such species are good starting materials for polycyclic inorganic and organometallic compounds.[3,4] Like their carbon analogues, however, these inorganic rings do exhibit cis−trans isomerism, which may impact their applications.

We are interested in heterocycles with a central $(E-N)_2$ ring, E = P, Si, as building blocks for chelating ligands.[5] Particularly useful for this purpose are dichloro-substituted species, such as *cis*-[ClP(μ-N^{t}Bu)$_2$PCl],[6] because they can be systematically modified by substitutions and oxidations to afford chelating diamide ligands. Analogous dichloro species exist for the higher group 15 homologues, arsenic[7] and antimony,[8] and these molecules are also potentially good source materials for bis(amino)-substituted heterocycles. But while [ClP(μ-N^{t}Bu)$_2$PCl] and [ClAs(μ-N^{t}Bu)$_2$AsCl] were shown be cis isomers, a definitive structural investigation of [ClSb(μ-N^{t}Bu)$_2$SbCl] is still lacking. Herein we report an improved synthesis of [ClSb(μ-N^{t}Bu)$_2$SbCl] and the syntheses and solid-state structures of two of its simplest derivatives, namely, [N$_3$Sb(μ-N^{t}Bu)$_2$SbN$_3$] and [^{t}BuOSb(μ-N^{t}Bu)$_2$SbO^{t}Bu].

Results and Discussion

The synthesis of the 2,4-dichlorocyclodistibazane [ClSb(μ-N^{t}Bu)$_2$SbCl] (**1**) was reported more than 20 years ago, but its solid-state structure was not determined.[8] On the basis of the known structure of [ClP(μ-N^{t}Bu)$_2$PCl],[6b] the authors suggested that **1** had a cis geometry, and this assumption was later strengthened when it was demonstrated that the arsenic analogue was also a cis isomer.[7]

Very recently a number of substituted cyclodistibazanes were prepared from the reactions of Sb(NMe$_2$)$_3$ with amines, alcohols, and antimony trichloride.[3a−f] X-ray diffraction studies revealed that most of these products are trans isomers, and this raised our suspicion that [ClSb(μ-N^{t}Bu)$_2$SbCl], contrary to earlier assumptions, is really a trans isomer.

Because only *cis*-substituted heterocycles are useful chelating ligands, it was important to determine the dichloride's stereochemistry prior to further modifications. The previously reported synthesis of **1** was unnecessarily complicated, and we therefore developed an easier one-step procedure, using SbCl$_3$ and *tert*-butylamine (Scheme 1). Just as in the original work, however, the crystals isolated from this reaction were unsuitable for single-crystal X-ray diffraction studies, leaving the compound's configuration in doubt. We thought that structural analyses of simple derivatives of **1** might provide clues about the stereochemistry of the dichloride.

The pseudohalide azide, N_3^-, appeared to be a good substitute, because molecular azides are often isostructural with their chloride analogues.[5c,d,9b] Treatment of **1** with 2 equiv of sodium azide (Scheme 1) produced **2** as thin, colorless, X-ray quality crystals.

The cyclodistibazane diazide **2**, whose crystal and refinement data are collected in Table 1, forms a layer structure of associated molecules, with intermolecular Sb···N contacts (3.226 Å), which are significantly shorter than the sum of van der Waals radii of these elements (3.7 Å).[10] Figure 1 shows that **2** is a trans isomer in which the azide substituents adopt an endo conformation. The C_i-symmetric molecule consists of a planar

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(1) *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vols. I and II.

(2) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005−8025. (b) Cox, J. D. *Tetrahedron* **1963**, *19*, 1175−1184.

(3) (a) Edwards, A. J.; Paver, M. A.; Rennie, M.-A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1994**, 2963−2966. (b) Edwards, A. J.; Leadbeater, N. E.; Paver, M. A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1994**, 1479−1482. (c) Alton, R. A.; Barr, D.; Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Rennie, M.-A.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Chem. Commun*. **1994**, 1481−1482. (d) Bashall, A.; Beswick, M. A.; Harmer, C. N.; McPartlin, M.; Paver, M. A.; Wright, D. S. J. *Chem. Soc., Dalton Trans.* **1998**, 517−518. (e) Beswick, M. A.; Wright, D. S. *Coord. Chem. Rev.* **1998**, *176*, 373−406. (f) Bryant, R.; James, S. C.; Jeffery, J. C.; Norman, N. C.; Orpen, A. G.; Weckenmann, U. *J. Chem. Soc., Dalton Trans.* **2000**, 4007−4009. (g) Björgvinsson, M.; Roesky, H. W.; Pauer, F.; Sheldrick, G. M. *Chem. Ber.* **1992**, *125*, 767−769. (h) Chivers, T.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 540−545. (i) Chivers, T.; Parvez, M.; Schatte, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 2217−2219. (j) Tarassoli, A.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1982**, *21*, 2684−2690. (k) Tarassoli, A.; Thompson, M. L.; Haltiwanger, R. C.; Hill, T. G.; Norman, A. D. *Inorg. Chem.* **1988**, *27*, 3382−3386.

(4) (a) Chen, T. Q.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Inorg. Chem.* **1997**, *36*, 802−808. (b) Chen, T. Q.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Inorg. Chem.* **1997**, *36*, 1070−1075. (c) Chen, T. Q.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Inorg. Chem.* **1997**, *36*, 1534−1535.

(5) (a) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203−250. (b) Schranz, I.; Grocholl, L. P.; Stahl, L.; Staples, R. J.; Johnson, A. *Inorg. Chem.* **2000**, *39*, 3037−3041. (c) Schranz, I.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **1999**, *38*, 5814−5819. (d) Moser, D. F.; Schranz, I.; Gerrety, M. C.; Stahl, L.; Staples, R. J. *J. Chem. Soc., Dalton* Trans. **1999**, 751−757. (e) Grocholl, L.; Schranz, I.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **1998**, *37*, 2496−2499. (f) Schranz, I.; Stahl, L.; Staples, R. J. *Inorg. Chem.* **1998**, *37*, 1493−1498. (g) Grocholl, L.; Stahl, L.; Staples, R. J. *Chem. Commun.* (*Cambridge*) **1997**, 1465−1466.

(6) (a) Scherer, O. J.; Klusmann, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 752−753. (b) Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 259−262.

(7) Bohra, R.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *Acta Crystallogr.* **1984**, *C40*, 1150−1152.

(8) Kuhn, N.; Scherer, O. J. *Z. Naturforsch.* **1979**, *34b*, 888−889.

(9) (a) Aubauer, C.; Klapötke, T. M.; Nöth, H.; Schulz, A.; Suter, M.; Weigand, J. *Chem. Commun. (Cambridge)* **2000**, 2491−2492. (b) Scherer, O. J.; Wolmershäuser, G.; Conrad, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 404−405.

(10) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960.

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Scheme 1

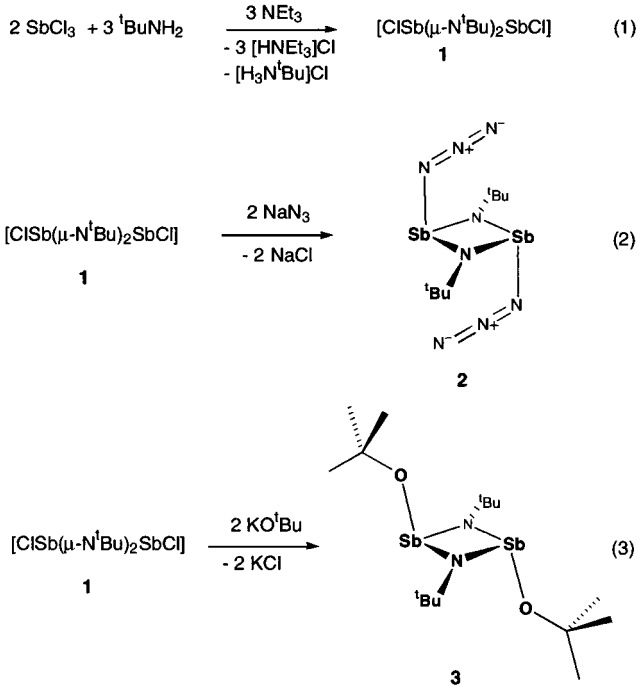

Table 1. Crystallographic Data for **2** and **3**

empirical formula	$C_8H_{18}N_8Sb$	$C_{16}H_{36}N_2O_2Sb$
fw	469.80	531.97
space group	$P\bar{1}$	$P2_1/c$
T (°C)	−60	−60
a, Å	6.6242(9)	11.2460(3)
b, Å	6.9198(9)	8.9360(2)
c, Å	8.969(1)	11.9367(1)
α, deg	99.401(6)	
β, deg	97.796(5)	109.995(2)
γ, deg	100.969(5)	
V, Å^3	392.26(9)	1129.81(4)
Z	1	2
ρ, g cm^{-3}	1.989	1.564
λ, Å	0.710 73	0.710 73
μ, cm^{-1}	34.42	23.99
$R(F)^a$ ($I > 2\sigma(I)$)	0.0276	0.0309
$R_w(F^2)^b$ (all data)	0.0650	0.0901

^{a} $R = \sum|F_o - F_c|/\sum|F_o|$. ^{b} $R_w(F^2) = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Sb−N heterocycle, bearing two linear (178.7(4)°) azide moieties, which are inclined toward the ring with a dihedral angle of 15.3°. The unusually long antimony−azide bond (2.188(4) Å), which is almost perpendicular (94.39(13)°) to the heterocycle, may be due to donation of the imino-nitrogen lone pair electrons into the Sb−N1 antibonding orbital. Both nitrogen−nitrogen bonds of the azide ligands have typical lengths,[5c,d,11] but the symmetrical endocyclic Sb−N bonds are slightly shorter (2.015(3) and 2.027(3) Å) than those in related compounds (av 2.050 Å).[3a−f]

While, at first glance, the endo conformation appears to be due to an intramolecular bond between the antimony atom and the terminal nitrogen of the azide moiety, the Sb···N separation (3.678 Å) is not short enough to suggest even a weak interaction. The more efficient packing of the molecules is a more likely cause for the adoption of this conformation.

The pronounced Lewis acidity of antimony(III) species, particularly when substituted with halogens, has been noted previously.[3e] It may have caused the association of **2** in the solid state, which, in turn, is reflected in the broadness and the low

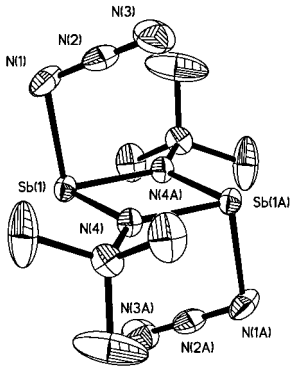

Figure 1. Thermal ellipsoid (35% probability) plot and partial numbering scheme of **2**. Selected bond lengths (Å) and angles (deg): Sb(1)−N(1) = 2.118(4), Sb(1)−N(4A) = 2.015(3), Sb(1)−N(4) = 2.027(3), N(1)−N(2) = 1.222(5), N(2)−N(3) = 1.133(5) Å, N(4)−Sb(1)−N(4A) = 77.48(11), Sb(1)−N(4)−Sb(1A) = 102.52(11), N(1)−N(2)−N(3) = 178.7(4).

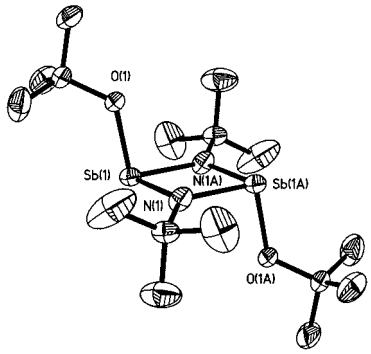

Figure 2. Thermal ellipsoid (35% probability) plot and partial numbering scheme of **3**. Selected bond lengths (Å) and angles (deg): Sb(1)−N(1) = 2.027(3), Sb(1)−N(1A) = 2.014(3), Sb(1)−O(1) = 1.983(2), N(1)−Sb(1)−N(1A) = 78.35(12), Sb(1)−N(1)−Sb(1A) = 101.65(12).

energy of the antisymmetric stretching vibration of the azide groups (2043 cm^{-1}).[11]

To gain further insight into the influence of substituent size on the stereochemistry, we also synthesized [^{t}BuOSb(μ-N^{t}Bu)$_2$SbO^{t}Bu] (**3**) (Scheme 1), whose much greater solubility suggests a lack of intermolecular bonding. The X-ray analysis confirmed this assumption, because **3** crystallizes free of unusual intermolecular contacts. It also showed that the configuration of these heterocycles is not controlled by intermolecular forces. Crystal and data collection parameters for **3** appear in Table 1. Like the diazide, **3** is C_i symmetric (Figure 2), implying a perfectly planar, trans-substituted (Sb−N)$_2$ ring. In notable contrast to **2**, however, the two *tert*-butoxy groups adopt an exo conformation, a difference which is readily explained in terms of the steric bulk of these substituents. The endocyclic Sb−N bonds are equidistant with those of **2**, but the antimony−alkoxide bonds are comparatively much shorter than the antimony−azide bonds.

Both derivatives (**2** and **3**) of the dichloride appear to be thermodynamic products, because in no instance (even on heating) were NMR signals attributable to other isomers observed. The trans geometries of **2** and **3** do not prove that

(11) (a) Klapötke, T. M.; Schulz, A.; McNamara, J. *J. Chem. Soc., Dalton Trans.* **1996**, 2985−2987. (b) Klapötke, T. M. *Chem. Ber.* **1997**, *130*, 443−451. (c) Nag, H. G.; Kwik, W. L.; Lee, Y. W.; Oberhammer, H. *Inorg. Chem.* **1994**, *33*, 4425−4426. (d) Klapötke, T. M.; Geisler, P. *J. Chem. Soc., Dalton Trans.* **1995**, 3365−3366. (e) Fenske, D.; Dörner, H.-D.; Dehnicke, K. *Z. Naturforsch.* **1983**, *38b*, 1301−1303.

the dichloride **1** also has this configuration, because isomerization upon substitution is conceivable and has been observed elsewhere.[12] Together with the strikingly different physical properties of **1** (when compared to those of its P and As analogues), however, they strongly suggest it. Thus, for example, the melting point of **1** is much higher (141−143 °C), than those of the cis-isomeric phosphorus (42 °C) and arsenic (61−64 °C) analogues, while its solubility is much lower.

The appearance of opposite stereoisomers in homologous group 15 heterocycles raises the question, whether electronic or steric factors are responsible for these differences. If the bulk of the exocyclic group 15 substituents controlled the stereochemistry, the heterocycle with the smallest E···E separation, namely, the cyclodiphosphazane, should adopt the trans geometry, while the one with the largest separation, **1**, should exist as a cis isomer. The opposite is observed, however, suggesting that steric repulsion between the group 15 substituents cannot be the reason. Insight into the factors which control the stereochemistry would clearly be useful for future work, and perhaps high-level computational studies may shed new light on the configurational preferences of these group 15 heterocycles.

Experimental Section

All operations were performed under an atmosphere of argon or purified nitrogen on conventional Schlenk lines. The hydrocarbon or ethereal solvents were predried over molecular sieves or CaH_2 and distilled under a nitrogen atmosphere from sodium or potassium benzophenone ketyl immediately before use. Sodium azide, antimony trichloride, and potassium *tert*-butoxide were obtained from Aldrich and used as received.

NMR spectra were recorded on a Bruker Avance-500 spectrometer. The ^{1}H and ^{13}C spectra are referenced relative to C_6D_5H (7.15 ppm) and C_6H_6 (128.0 ppm), respectively. Melting points were recorded on a Mel-Temp melting point apparatus; they are uncorrected. E&R Microanalytical Laboratory, Inc., Parsippany, NJ, and Desert Analytics, Tucson, AZ, performed the elemental analyses.

Syntheses. [ClSb(*μ*-N^{t}Bu)$_2$SbCl], 1. A solution of $SbCl_3$ (2.23 g, 9.78 mmol) and Et_3N (2.05 mL, 14.7 mmol) in 60 mL of toluene was treated at 0 °C with ^{t}BuNH$_2$ (1.54 mL, 14.7 mmol), and the mixture was stirred at room temperature for 18 h. The initially clear, colorless reaction mixture gradually turned yellow with the formation of a white precipitate. It was filtered through a medium-porosity frit, and the ensuing yellow filtrate was concentrated in vacuo and stored at −21 °C. After several days, fine, yellow needles (2.46 g, 54.9%) formed.

Mp: 141−143 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 25 °C): δ = 1.00 (s). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 25 °C): δ = 55.3 (s), 33.8 (s).

***trans*-[N$_3$Sb(*μ*-N^{t}Bu)$_2$SbN$_3$], 2.** To sodium azide (0.130 g, 2.00 mmol) in 10 mL of THF was added dropwise a THF solution of **1** (0.457 g, 1.00 mmol). The yellow mixture was stirred for 18 h, while it gradually turned colorless with the formation of a white precipitate. The suspension was filtered through a medium-porosity frit, and the ensuing colorless solution was concentrated in vacuo and stored at −21 °C. After several days colorless plates (0.356 g, 75.7%) were isolated.

Mp: 206 °C dec. ^{1}H NMR (500.13 MHz, benzene-d_6, 25 °C): δ = 0.88 (s). ^{13}C{^{1}H} NMR (125.76 MHz, benzene-d_6, 25 °C): δ = 53.7 (s), 33.2 (s). IR (Nujol mull): N_3 ν(asym) = 2043 cm^{-1} (m). Anal. Calcd for $C_8H_{18}N_8Sb_2$: C, 20.45; H, 3.86; N, 23.85. Found: C, 20.21; H, 3.93; N, 23.50.

***trans*-[^{t}BuOSb(*μ*-N^{t}Bu)$_2$SbO^{t}Bu], 3.** A sample of **1** (0.913 g, 2.00 mmol), dissolved in 10 mL of toluene, was added dropwise to a potassium *tert*-butoxide (0.449 g, 4.00 mmol) suspension at 0 °C. The mixture was stirred at room temperature for 18 h, while the initially yellow mixture gradually turned pale yellow with the formation of a white precipitate. After the solvent had been removed in vacuo, the remaining solid was taken up in 10 mL of toluene and the extract was filtered through a medium-porosity frit. The ensuing pale-yellow filtrate was concentrated in vacuo and stored at −21 °C until light-yellow plates (0.712 g, 66.9%) had formed.

Mp: 111−120 °C. ^{1}H NMR (500.13 MHz, benzene-d_6, 25 °C): δ = 1.38 (s, 18 H), 1.25 (s, 18 H). ^{13}C NMR (125.76 MHz, benzene-d_6, 25 °C): δ = 73.0 (s), 54.1 (s), 34.8 (s), 34.5 (s). Anal. Calcd for $C_{16}H_{36}N_2O_2Sb_2$: C, 36.13; H, 6.82; N, 5.27. Found: C, 35.94; H, 7.08; N, 5.03.

X-ray Crystallography. Intensity data of **2** and **3** were collected on a Bruker SMART CCD diffractometer. Using ω-scans of 0.3° per frame for 30 s, 2461 (7179 for **3**) reflection data with indices $-8 \le h \le 8$, $-8 \le k \le 15$, $-11 \le l \le 10$ ($-14 \le h \le 13$, $-10 \le k \le 11$, $-13 \le l \le 15$) in the range $4.7° \le 2\Theta \le 55.5°$ ($6.0° \le 2\Theta \le 56.5°$) were collected, of which 1581 (2720) were unique, R_{int} = 0.0958 (0.0247), and observed ($I > 2\sigma(I)$). A final difference map revealed no features greater than +1.093 (1.179) or less than −1.149 (−0.689) e Å^{-3}. Cell parameters were retrieved using SMART[13] software and refined with SAINT[14] on all observed reflections. Data were reduced with SAINT, which corrects for Lp and decay. An empirical absorption correction was applied with SADABS.[15] The structures were solved by direct methods with the SHELXS-90[16] program and refined by full-matrix least-squares methods on F^2 with SHELXL-97,[17] incorporated in SHELXTL-PC, Version 5.10.[18]

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Supporting Information Available: Packing diagram for **2**. Two X-ray crystallographic files for compounds **2** and **3**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) (a) Zeiss, W.; Weis, J. *Z. Naturforsch.* **1977**, *32b*, 485−487. (b) Chen, H.-J.; Haltiwanger, R. C.; Hill, T. G.; Thompson, M. L.; Coons, D. E.; Norman, A. D. *Inorg. Chem.* **1985**, *24*, 4725−4730. (c) Kamil, W. A.; Bond, M. R.; Willett, R. D.; Shreeve, J. M. *Inorg. Chem.* **1987**, *26*, 2829−2833.

(13) *SMART V 5.050 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(14) *SAINT V 5.01 Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(15) SADABS program for absorption corrections using the Bruker CCD Detector System. Based on: Blessing, R. *Acta Crystallogr.* **1995**, *A 51*, 33−38.

(16) Sheldrick, G. M. *SHELXS-90, Program for the Solution of Crystal Structures;* University of Göttingen: Göttingen, Germany, 1990.

(17) Sheldrick, G. M. *SHELXL-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(18) *SHELXTL 5.10 (PC-Version), Program Library for Structure Solution and Molecular Graphics*; Siemens Analytical Instruments Division: Madison, WI, 1995.