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Bis(1°-amino)cyclodistib(III)azanes: the First Structural Characterization of cis and trans Isomers of a Single Cyclodipnict(III)azane

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The dichlorocyclodistib(III)azane $[ClSb(\mu\text{-}N^tBu)]_2$ (**1**) has been shown to exist as the cis isomer in the solid state. A series of bis(1°-amino)cyclodistib(III)azanes $[R'NHSb(\mu\text{-}N^tBu)]_2$ (**2**, R′ = ^{t}Bu; **3**, R′ = Dipp; **4**, R′ = Dmp) has been prepared by the reaction of **1** with 2 equiv. of LiNHR′. On the basis of NMR solution spectra, all three derivatives are formed as a mixture of cis and trans isomers. In the case of **3**, the structures of both the cis and trans isomers have been determined by X-ray crystallography; *cis*-**3** adopts an endo, endo arrangement for the amido protons of the DippNH groups. Isomerization of *trans*-**3** into *cis*-**3** occurs slowly in solution. Deprotonation of **2** with 2 equiv. of ^{n}BuNa or *trans*-**3** with ^{n}BuLi produces $[Na_2Sb_2(\mu\text{-}N^tBu)_4]$ (**5**) and $[Li_2Sb_2(\mu\text{-}N^tBu)_2(\mu\text{-}NDipp)_2]$ (**6**), whose solvated cubane structures were established by X-ray crystallography. In contrast, the reaction of *cis*-**3** with 2 equiv. of ^{n}BuLi produces the tricyclic compound $[Li_2Sb(\mu\text{-}N^tBu)_2(\mu\text{-}NDipp)(\mu\text{-}NHDipp)]$ (**7**).

Introduction

Cyclodipnict(III)azanes of the type $[XE(\mu\text{-}NR)]_2$ (E = P, As, Sb, Bi) are well-known inorganic heterocycles. The chemistry of these four-membered rings has attracted sustained interest for more than 40 years, and highlights of this research area have been well-summarized in several recent review articles.[1−3] Much of the current research on these systems has been directed toward the synthesis of anionic complexes of the type $[RNE(\mu\text{-}NR)]_2^{-2}$ and the bis(1°-amino)cyclodipnict(III)azanes, from which the anions are easily derived.[1−3] Expectedly, neutral cyclodiphosph(III)azanes, which have two available phosphorus donors, have been used to prepare coordination complexes with transition metals.[4] In addition, coordination complexes utilizing the nitrogen centers of the $[RNP(\mu\text{-}NR)]_2^{-2}$ dianions have been reported,[5] and it has been shown that group 4 metal complexes of this type can function as catalysts in the polymerization of ethene.[6] One intriguing new development in the chemistry of cyclodipnict(III)azanes has evolved from the work of Wright et al., who have used cyclodiphosph(III)azanes to prepare the first examples of a new class of inorganic macrocycles.[2,7]

Whereas cyclodiphosph(III)azanes have been extensively studied, the chemistry of the heavier pnictogen (As, Sb, Bi) analogues has been slower to develop.[1,3] This is in large part due to the difficulty in the systematic preparation of the

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heavier cyclodipnict(III)azanes, because the synthetic methods available for producing cyclodiphosph(III)azanes tend to give more disparate results when applied to the heavier elements.[1,3] Thus, the reaction of $SbCl_3$ with LiNHDmp (Dmp = 2,6-dimethylphenyl) produces the bis(1°-amino)-cyclodistib(III)azane $[DmpHNE(\mu\text{-}NDmp)]_2$, whereas the analogous reaction using LiNPh generates the macrocycle $Sb_{12}(NPh)_{18}$.[8] The difficulty in preparing these heterocycles is evidenced by the rarity of known examples; there are only two reported bis(1°-amino)cyclodistib(III)azanes, and $[DipNHBi(\mu\text{-}NDipp)]_2$ (Dipp = 2,6 di*iso*propylphenyl) is the sole bismuth analogue.[9,10] The related antimony dianion $[CyNSb(\mu\text{-}NCy)]_2^{-2}$ (Cy = cyclohexyl) is not synthesized directly from $[CyNHSb(\mu\text{-}NCy)]_2$ but is prepared in situ by the reaction of $[Me_2NSb(\mu\text{-}NCy)]_2^{-2}$ with LiNHCy, for example.[11]

In an effort to devise a cogent synthetic method for the generation of bis(1°-amino)cyclodistib(III)azanes, we surmised that the reaction of the known reagent $[ClSb(\mu\text{-}N^tBu)]_2$ with lithium amides would provide a suitable starting point.[12] In this contribution, we report a series of bis(1°-amino)cyclodistib(III)azanes generated by the successful application of this synthetic method. The compounds are shown to exist as a mixture of cis and trans isomers in solution. In the case of one derivative, the structures of both isomers in the solid state were established. Investigations of the metalation of these cis and trans isomers with ^{n}BuLi revealed an unanticipated difference in the type of product that is obtained.

Results and Discussion

X-ray Structure of $[ClSb(\mu\text{-}N^tBu)]_2$ (1). The cyclodistib(III)azane $[ClSb(\mu\text{-}N^tBu)]_2$ (**1**) was first prepared in 1979 via reaction of $SbCl_3$ with $LiN(SiMe_3)^tBu$.[12] More recently, Stahl has reported a convenient one-pot synthesis, albeit with slightly lower yields.[13] Although the structure of **1** has not been previously determined, it was originally assigned to be cis on the basis of the known structure of the phosphorus analogue.[12] Subsequent work demonstrated that the arsenic analogue also adopts a cis configuration in the solid state.[14] More recently, several derivatives of **1** have been shown to exist as the trans isomers in the solid state, which led to the suggestion that, in contrast to the phosphorus and arsenic compounds, **1** might also have a trans configuration.[13] To provide clarity on this subject, we have undertaken a crystallographic study on **1** that revealed that the compound adopts a cis configuration in the solid state (Figure 1). Compound **1** crystallizes with three independent but chemically equivalent molecules present in the asymmetric unit. The molecules are nearly identical with the exception of the puckering of the central Sb_2N_2 rings. Two of the molecules present in the asymmetric unit of **1** are noticeably puckered, with the angles between N−Sb−N planes being 168 and 170°. However, the third molecule is essentially planar, with an analogous angle of 177°. It has been previously shown that *cis*-cyclodipnict(III)azanes have puckered E_2N_2 rings, whereas the rings in the trans isomers are planar.[1] Regardless of the differences in the ring puckering, the molecules all have similar geometric parameters (Table 1). The Sb−N distances are equal within error, ranging from 2.009(7) to 2.022(7) Å. Not surprisingly, the endocyclic N−Sb−N angles are more acute (77.9(3)−78.6(3)°) than the exoxyclic N−Sb−Cl angles (97.5(2)−100.4(2)°).

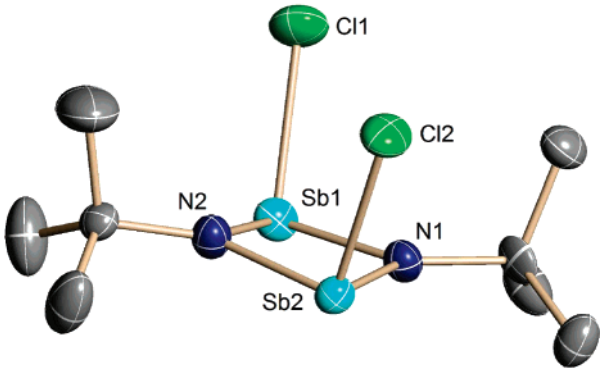
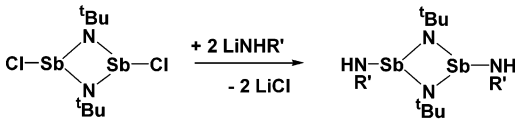


Figure 1. View of one of the molecules of *cis*-**1**. Hydrogen atoms have been removed for clarity.

Scheme 1. Synthesis of Bis(1°-amino)cyclodistib(III)azanes



1

2 R' = ^{t}Bu
3 R' = Dipp
4 R' = Dmp

Synthesis and Structures of Bis(1°-amino)cyclodistib-(III)azanes. The reaction of 2 equiv. of lithium amide with **1** readily produces the bis(1°-amino)cyclodistib(III)azanes **2**−**4** as outlined in Scheme 1. In each case, the products are isolated as a mixture of cis and trans isomers, with the cis isomer being favored in solution. The cis:trans isomer ratio that is initially isolated varies for each compound (**2**, 80:20; **3**, 60:40; **4**, 85:15). Interestingly, in the case of **3**, it was possible to separate the cis and trans isomers because of the large difference in their solubilities; *trans*-**3**, which is isolated as a yellow solid, is only sparingly soluble in *n*-hexane, whereas *cis*-**3** is freely soluble. Furthermore, *cis*-**3** is initially obtained as a viscous yellow oil that slowly crystallizes upon standing at −20 °C. Both compounds **2** and **4** are obtained as thick oils, presumably as a result of the high percentage

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Table 1. Selected Bond Distances (Å) and Angles (deg) for *cis*-**1**

molecule 1		molecule 2		molecule 3	
Sb1−N1	2.013(7)	Sb3−N3	2.014(7)	Sb5−N5	2.014(5)
Sb1−N2	2.017(7)	Sb3−N4	2.017(6)	Sb5−N6	2.014(5)
Sb2−N1	2.022(6)	Sb4−N3	2.022(7)	Sb6−N5	2.018(6)
Sb2−N2	2.009(7)	Sb4−N4	2.016(6)	Sb6−N6	2.020(6)
Sb1−Cl1	2.445(3)	Sb3−Cl3	2.456(7)	Sb5−Cl5	2.449(3)
Sb2−Cl2	2.450(3)	Sb4−Cl4	2.440(3)	Sb6−Cl6	2.434(3)
N1−Sb1−N2	77.9(3)	N3−Sb3−N4	78.6(3)	N5−Sb5−N6	78.1(3)
N1−Sb1−Cl1	99.9(2)	N3−Sb3−Cl3	99.4(3)	N5−Sb5−Cl5	98.9(2)
N2−Sb1−Cl1	99.7(2)	N4−Sb3−Cl3	97.7(3)	N6−Sb5−Cl5	97.5(2)
N1−Sb2−N2	77.9(3)	N3−Sb4−N4	78.4(3)	N5−Sb6−N6	77.9(3)
N1−Sb2−Cl2	99.8(2)	N3−Sb4−Cl4	100.4(2)	N5−Sb6−Cl6	97.7(2)
N2−Sb2−Cl2	100.0(2)	N4−Sb4−Cl4	98.1(2)	N6−Sb6−Cl6	98.0(2)

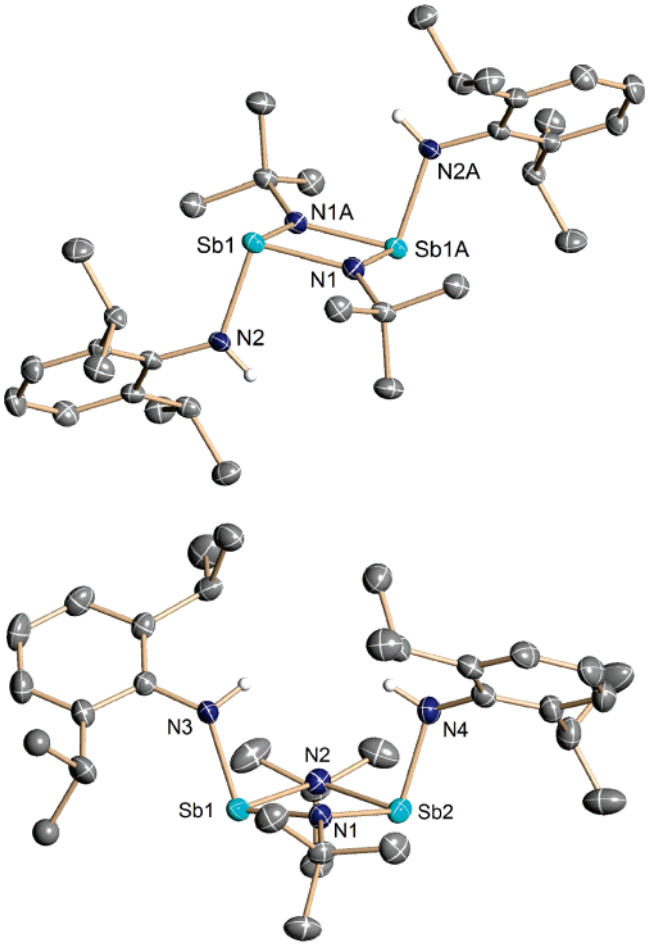

Figure 2. (top) View of the structure of *trans*-**3**. (bottom) View of the structure of *cis*-**3**. In each case, only the amido hydrogen atoms are shown.

of the cis isomer present in these samples. All attempts to separate the cis and trans isomers of **2** and **4** were unsuccessful. The identities of the two isomers *cis*-**3** and *trans*-**3** were unambiguously established by an X-ray structural determination of each isomer, as depicted in Figure 2. The structure of *cis*-**4** was also determined crystallographically and is shown in Figure 3.

The central Sb_2N_2 ring of *trans*-**3**, which has a crystallographically imposed center of symmetry, is completely planar, as found for other structurally characterized cyclodipnict(III)azanes that have a trans configuration.[1,3] In contrast, there is considerable puckering of the Sb_2N_2 ring in *cis*-**3** and *cis*-**4**, with angles between the N−Sb−N planes

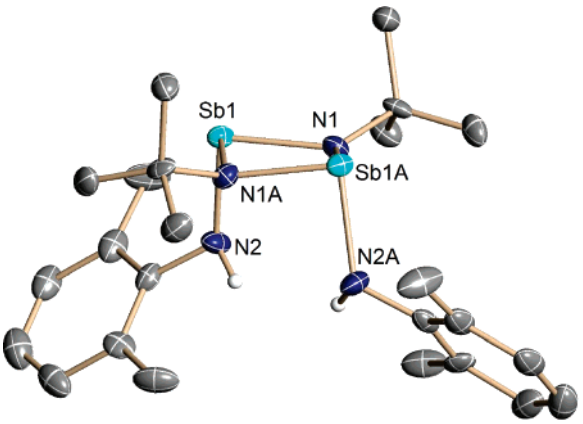

Figure 3. View of the structure of *cis*-**4**. Only the amido hydrogen atoms are shown.

of 161 and 163°, respectively. Presumably, the increased puckering observed in *cis*-**3** and *cis*-**4** in comparison to that in *cis*-**1** is due to the large increase in steric bulk arising from the introduction of the Dipp and Dmp substituents. There is little difference in the bond distances and angles observed for *cis*-**3**, *trans*-**3**, and *cis*-**4** (Table 2). Even the imido Sb−N and amido Sb−N distances show little variation, falling in the narrow range of 2.022(4)−2.067(7) Å. Similar to *cis*-**1**, the endocyclic N−Sb−N angles (range 77.5(3)−78.1(1)°) are in each case more acute than the exocyclic N−Sb−N angles (range 91.5(3)−99.6(1)°). For both of the cis isomers, the amido protons of the (H)NR substituents adopt an endo, endo configuration.

Solution NMR Studies of cis and trans Isomerism. Solution-state cis and trans isomerism has been well-established for cyclodiphosph(III)azanes, and it is possible to distinguish between the isomers from their markedly different ^{31}P NMR chemical shifts.[15] Unfortunately, there are no isotopes with $I = 1/2$ for the heavier pnictogens, and consequently, NMR studies on heavier cyclodipnict(III)azanes are limited. A solution-state equilibrium between cis and trans isomers has been observed for a series of cyclodistib(III)azanes $[RSb(\mu\text{-}N^tBu)]_2$ (R = alkyl, alkoxy, aryloxy, and silyl).[16] Furthermore, the possibility of solution-state cis and trans isomerism has been considered for bis(amino)cyclodistib(III)azanes, although definitive NMR data

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Table 2. Selected Bond Distances (Å) and Angles (deg) for *trans*-**3**, *cis*-**3**, and *cis*-**4**

trans-**3**		*cis*-**3**				*cis*-**4**	
Sb1−N1	2.022(4)	Sb1−N1	2.027(3)	Sb2−N2	2.031(3)	Sb1−N1	2.027(7)
Sb1−N1A	2.039(3)	Sb1−N2	2.050(3)	Sb2−N1	2.045(3)	Sb1−N1A	2.047(7)
Sb1−N2	2.058(3)	Sb1−N3	2.058(3)	Sb2−N4	2.052(3)	Sb1−N2	2.067(7)
N1−Sb1−N1A	77.9(2)	N1−Sb1−N2	78.1(1)	N1−Sb2−N2	78.1(1)	N1−Sb1−N1A	77.5(3)
N1−Sb1−N2	95.7(1)	N1−Sb1−N3	96.1(1)	N1−Sb2−N4	98.5(1)	N1−Sb1−N2	91.5(3)
N1A-Sb1−N2	99.6(1)	N2−Sb1−N3	98.7(1)	N2−Sb2−N4	93.3(1)	N1A-Sb1−N2	98.1(3)

are lacking.[8,17] Solution NMR studies on the series of cyclodistib(III)azanes **2**−**4** clearly demonstrated the presence of two compounds, which had very similar NMR spectra in each case. ^{1}H−^{13}C HMBC-correlated NMR spectra obtained for **3** and **4** indicated that, in each case, the amido protons were associated with the aromatic substituents, thus ruling out the possibility of the rearrangement isomers [Sb(μ-NAr)(NH^{t}Bu)]$_2$. The presence of cis and trans isomers was unambiguously established in the case of **3** by crystallographic studies, as discussed previously.

The ability to separate the two isomers of **3** by physical methods allowed for the collection of NMR data for each isomer separately. Although very similar ^{1}H NMR spectra are obtained for the two isomers, there is a significant difference in the chemical shifts observed for the amido protons of *cis*-**3** (δ = 5.01) and *trans*-**3** (δ = 5.23). The difference in shifts can be attributed to the endo, endo configuration of the amido protons in *cis*-**3** (Figure 2), which places them in a more shielded environment than that in *trans*-**3**; similar differences are observed in the ^{1}H NMR spectra of *cis*- and *trans*-**4**. For compound **2**, the difference in the chemical shifts is considerably smaller (cis, δ = 2.65; trans, δ = 2.69), although this is not surprising, as the *tert*-butyl amido substituents would not be as shielding as the aromatic rings of the Dipp and Dmp groups.

Initial NMR investigations on the isomer *trans*-**3** indicated the presence of small amounts of *cis*-**3**, and all attempts to obtain pure samples of *trans*-**3** were unsuccessful. Further NMR studies revealed that, in fact, *trans*-**3** isomerizes to *cis*-**3** in solution, over the course of ca. 10 days. This transformation can be easily followed by ^{1}H NMR spectroscopy, as shown in Figure 4. It should be noted that during this long time period, some decomposition of **3** occurs in solution. The solution NMR data for compound **3** clearly indicate that the trans isomer is the kinetic product, whereas the cis isomer is the thermodynamic product.

Similar long-term NMR solution studies were performed on **2** and **4**, and it was found that the initially observed cis:trans ratios do not change. During this work, it was noted that thick oily samples of **2** stored at −20 °C slowly transform to a mixture of an oil and a yellow solid. NMR spectra obtained on these semisolid samples revealed an increase in the quantity of the trans isomer (up to ca. 50%). However, within 48 h, the original cis:trans ratio of 80:20 is observed. Although it has not been possible to unambiguously establish the presence of cis and trans isomers for **2** and **4**, given the similarities in their physical properties and spectroscopic data, it seems the most probable explanation. Unfortunately, all attempts to grow crystals of compound **2** suitable for X-ray diffraction studies were unsuccessful.

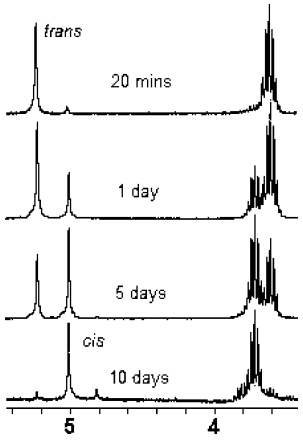

Figure 4. ^{1}H NMR spectra showing the transformation of *trans*-**3** to *cis*-**3** in solution. Only the regions containing the amido N−H and methine protons of the isopropyl groups are shown for clarity.

Several different mechanisms have been proposed for the interconversion of cis and trans isomers of cyclodiphosphazanes.[1,18] In particular, pyramidal inversion has been considered as the most likely mechanism for the phosphorus case.[1] For the heavier elements, however, pyramidal inversion is a considerably higher energy process,[18a] and so it is highly unlikely that this mechanism is operating at room temperature for the compounds **2**−**4**. The possibility of complete dissociation into iminopnictane monomers has also been considered.[1,18b] However, whereas this has been demonstrated to occur for both phosphorus and arsenic, such a dissociation is unknown for antimony.[18c] To probe the possibility that this mechanism was acting in the cis and trans interconversion for the compounds **2**−**4**, we monitored equal mixtures of **2** and **3** by ^{1}H NMR, and no evidence of a new mixed species was observed; only intact **2** and **3** were present even after one week in solution. A further conceivable possibility is a partial opening of the central Sb_2N_2 ring via cleavage of an Sb−N bond that allows for rotation around the geminal Sb−N bond and results in the formation of the other isomer upon ring closure.[1] This latter mechanism would appear to be the most likely possibility in the current systems.

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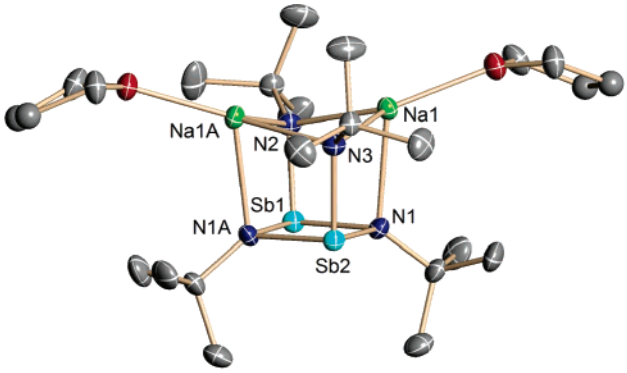


Figure 5. View of the structure of complex **5**. Hydrogen atoms have been removed for clarity.

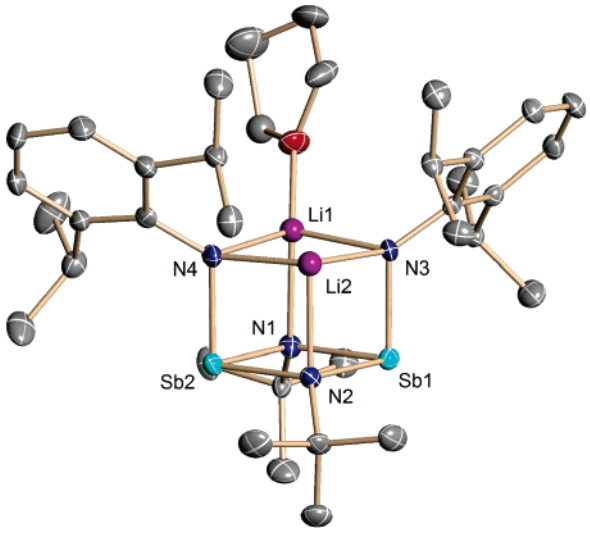
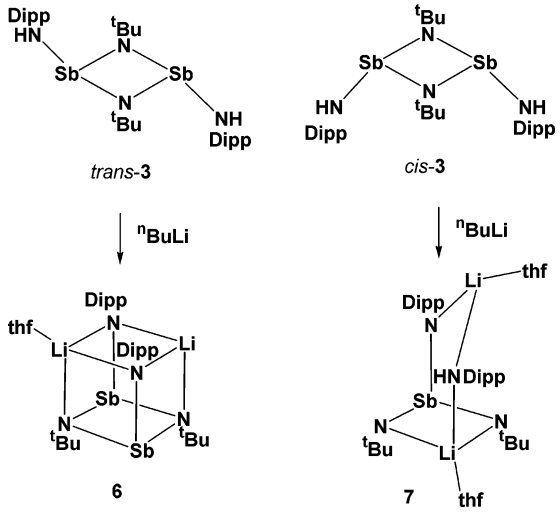


Figure 6. View of the structure of complex **6**. Hydrogen atoms have been removed for clarity.

Deprotonation of bis(1°-amino)cyclodistib(III)azanes. Bis(1°-amino)cyclodistib(III)azanes are obvious precursors for the formation of dianions of the type $[RNSb(\mu\text{-}NR)]_2^{2-}$. Indeed, the reaction of **2** or **3** with butyl-sodium or butyl-lithium, respectively, readily produces the heterometallic cubane complexes $[Na_2Sb_2(\mu\text{-}N^tBu)_4]$ (**5**) and $[Li_2Sb_2(\mu\text{-}N^t\text{-}Bu)_2(\mu\text{-}NDipp)_2]$ (**6**), which both contain dianions of the type $[RNSb(\mu\text{-}N^tBu)]_2^{2-}$ (Figures 5 and 6). The cyclohexyl derivative $[CyNSb(\mu\text{-}NCy)]_2^{2-}$ is the only other example of an antimony-containing dianion of this type that has been reported.[11,19] The observed solid-state structures of complexes **5** and **6** are analogous to that of the solvated bismuth complex $[Bi_2(NCy)_4Li_2(THF)_2]$.[20] In contrast, the unsolvated antimony complex $[\{Sb_2(NCy)_4\}_2Na_4]$ is tetrameric as a result of the face-to-face dimerization of two $[Sb(NCy)_4Na_2]$ cubanes.[19] A similar effect of alkali-metal solvation is evident in the structures of the analogous phosphorus-containing complexes

Scheme 2. Metalation of *trans*-**3** and *cis*-**3** with Butyl-lithium



$[P_2(N^tBu)_4Li_2(THF)_2]$ and $[\{P_2(N^tBu)_4\}_2Li_4]$.[21,22] The solid-structure structure of complex **5** contains two monosolvated sodium ions, whereas complex **6** contains only a single molecule of THF coordinated to one of the lithium centers (Li1). The second lithium center is too sterically shielded by the bulky Dipp substituents to allow for coordination of a second THF molecule. Furthermore, there are several agostic interactions between Li2 and the surrounding hydrogen atoms (range 2.17(1)−2.23(1) Å) as a result of this steric congestion. In both **5** and **6** it can be assumed that solvation prevents further aggregation of the cubane structures.[23]

Both of the complexes **5** and **6** adopt a distorted cubane structure, and there is considerable variation of the Sb−N bond distances (Table 3). In particular, the Sb−N distances of the Sb_2N_2 rings are considerably longer (2.088(4)−2.096(3) Å) than those in the $SbMN_2$ (M = Li, Na) rings [1.978(5)−2.015(4) Å]. In addition, direct comparison can be made in the case of **6** with *cis*-**3**, in which the analogous distances ranged from 2.027(3)−2.050(3) Å. Presumably, the differences in the distances observed in the cluster complexes **5** and **6** are in part a reflection of the higher ionic character of the bonding resulting from the generation of the $[RNSb(\mu\text{-}N^tBu)]_2^{2-}$ dianion. Furthermore, there is clearly an increase in steric crowding in **6** that may also contribute to the observed bond lengthening. As was observed in the structures of **3** and **4**, the endocyclic N−Sb−N angles of the Sb_2N_2 rings are more acute than the exocyclic N−Sb−N angles in **5** and **6**.

Comparison of the Reactions of *cis*- and *trans*-3 with ^{n}BuLi. The ability to separate the isomers *cis*-**3** and *trans*-**3** provided the intriguing opportunity to investigate the chemistry of the two isomers independently. The reaction of two equivalents of *n*-butyl-lithium with the two isomers produced some surprising results. We had initially surmised that the

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(20) Edwards, A. J.; Beswick, M. A.; Galsworthy, J. R.; Paver, M. A.; Raithby, P. R.; Rennie, M. A.; Russell, C. A.; Verhorevoort, K. L.; Wright, D. S. *Inorg. Chim. Acta* **1996**, *248*, 9.
(21) Schranz, I.; Stahl, L.; Staples, R. *Inorg. Chem.* **1998**, *37*, 1493.
(22) Brask, J. K.; Chivers, T.; Krahn, M. L.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 290.
(23) For a discussion of the influence of solvation on the structures of alkali-metal derivatives of polyimido anions of p-block elements, see: Brask, J. K.; Chivers, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3960.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **5** and **6**

complex **5**			complex **6**		
Sb1−N1	2.095(3)	Sb1−N1	2.119(4)	Sb2−N1	2.088(4)
Sb2−N1	2.096(3)	Sb1−N2	2.089(4)	Sb2−N2	2.095(4)
Sb1−N2[a]	1.978(5)	Sb1−N3	2.015(4)	Sb2−N4	2.002(4)
N1−Sb1−N1A[b]	80.2(2)	N1−Sb1−N2	80.4(2)	N1−Sb2−N2	81.0(2)
N1−Sb1−N2	94.0(1)	N1−Sb1−N3	91.7(2)	N1−Sb2−N4	90.6(2)
N1−Sb2−N3	94.6(1)	N2−Sb1−N3	88.9(2)	N2−Sb2−N4	90.2(2)
Na1−N1	2.445(3)	Li1−N1	2.154(9)	Li2−N2	2.084(10)
Na1−N2	2.421(3)	Li1−N3	2.101(10)	Li2−N3	2.008(10)
Na1−N3	2.419(3)	Li1−N4	2.082(9)	Li2−N4	2.063(10)

[a] Sb2−N3 = 1.988(5). [b] N1−Sb2−N1A = 80.1(2).

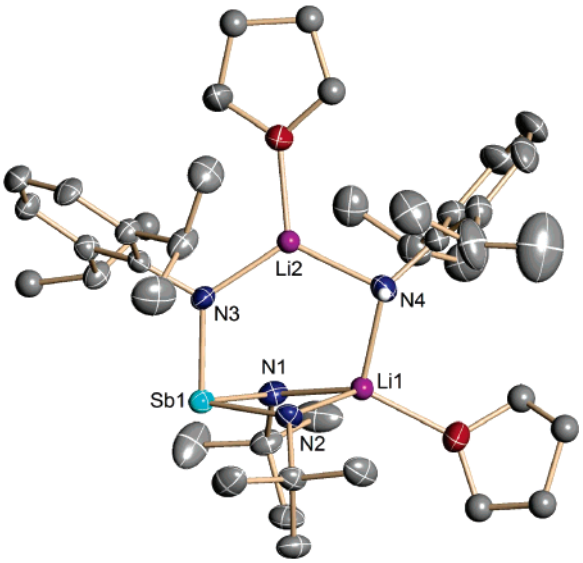


Figure 7. View of the structure of Complex **7**. Only the amido hydrogen atoms are shown.

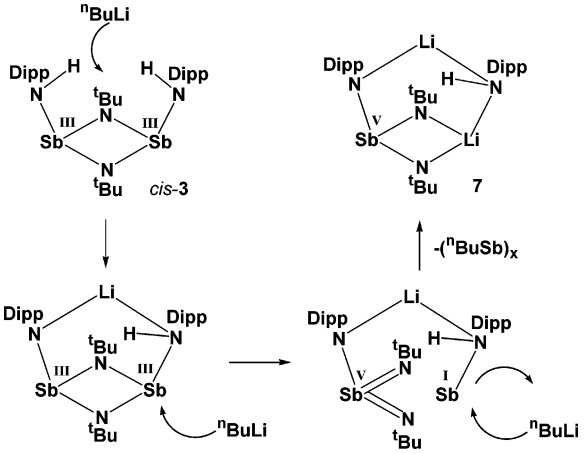
reaction with *cis*-**3** would readily form the cubane complex **6**, whereas *trans*-**3** might produce a new structural motif. However, only the reaction of 2 equiv. of *n*-butyl-lithium with *trans*-**3** resulted in the formation of the complex **6**; the analogous reaction with *cis*-**3** consistently resulted in destruction of the cyclodistib(III)azane to form the tricyclic complex [$Li_2Sb(\mu$-N^{t}Bu$)(\mu$-NDipp$)(\mu$-NH(Dipp)] (**7**), as depicted in Scheme 2. The ready formation of the cis-arranged cubane **6** from *trans*-**3** clearly requires a rapid isomerization to occur in solution. The NMR studies of **3** described earlier demonstrated that *trans*-**3** isomerizes to *cis*-**3** in solution, albeit slowly (days). Presumably, the formation of six Li−N bonds provides a thermodynamic driving force that increases the rate of isomerization in solution upon deprotonation of *trans*-**3**. It is also of interest to note that in the preparation of complex **5**, the highest yields are obtained when the reaction is carried out on samples enriched with *trans*-**2**; when freshly prepared samples of **2** (ratio of cis: trans isomers, 80:20) are used, yields of **5** are ca. 20%. Although these observations are consistent with the reactivity of compound **3**, they do not unambiguously prove that only *trans*-**2** leads to the formation of complex **5**.

Complex **7** crystallizes with two crystallographically independent but chemically equivalent molecules in the asymmetric unit; one molecule is depicted in Figure 7. The Sb−N^{t}Bu imido distances (2.089(4)−2.099(4) Å) are considerably longer than the Sb−NDipp imido distances (1.967-

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **7**

molecule 1		molecule 2	
Sb1−N1	2.093(4)	Sb2−N5	2.105(4)
Sb1−N2	2.097(4)	Sb2−N6	2.098(5)
Sb1−N3	1.970(4)	Sb2−N7	1.966(4)
Li1−N1	2.14(1)	Li3−N5	2.13(1)
Li1−N2	2.13(1)	Li3−N6	2.13(1)
Li1−N4	2.03(1)	Li3−N8	2.00(1)
Li2−N3	1.92(1)	Li4−N7	1.94(1)
Li2−N4	2.00(1)	Li4−N8	1.99(1)
N1−Sb1−N2	88.2(2)	N5−Sb2−N6	87.0(2)
N1−Sb1−N3	91.1(2)	N5−Sb2−N7	92.7(2)
N2−Sb1−N3	92.5(2)	N6−Sb2−N7	91.8(2)

Scheme 3. Possible Mechanism for the Formation of Complex **7**



(4)−1.970(4) Å), which was also observed in complex **6**. There is little difference in the Sb^V−N distances observed in **7** in comparison to the Sb^{III}−N distances found in **5** and **6**. Although it could be anticipated that the Sb^V−N distances would be shorter than the Sb^{III}−N distances, it has been previously demonstrated that there is little correlation between the oxidation state of antimony and Sb−N bond lengths.[24] Unsurprisingly, the N−Sb−N angles of the $LiSbN_2$ ring are similar to those observed in the cluster complex **6** (Table 4).

The formation of complex **7** can be considered to result from the monolithiation of *cis*-**3** followed by nucleophilic attack at the second antimony center, which results in replacement of one Sb in the Sb_2N_2 ring by Li (Scheme 3). This difference in reactivity in relation to *trans*-**3** can be attributed to the endo, endo configuration of the amido protons in *cis*-**3**. Presumably, the two bulky Dipp substituents

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sterically shield the amido protons, making them less accessible to approach by *n*-butyl-lithium. This would allow nucleophilic attack by *n*-butyl-lithium at one of the antimony centers to become a viable alternative reaction that initiates the opening of the Sb_2N_2 ring in *cis*-**3**. Competition between deprotonation and nucleophilic substitution has been observed previously for amido-arsenic and amido-boron systems.[25,26] In the current case, the byproduct is presumably the antimony oligomer $(^n\text{BuSb})_n$.[27]

Solution NMR Studies of Complexes 5−7. The NMR data obtained for complexes **5**−**7** were in keeping with the solid-state structures of the complexes. In the case of **5**, two separate resonances are observed in the ^{1}H NMR spectrum for the methyl protons of the two different *tert*-butyl imido groups. For complex **6**, one resonance is observed for the *tert*-butyl groups, and one doublet and one septet are present for the *iso*-propyl groups of the Dipp substituents. The ^{1}H NMR spectrum of **7** is, as anticipated, more complex because of the presence of the two different Dipp substituents. However, the appropriate resonances are clearly distinguishable, such as the two separate doublets for the methyl protons of the isopropyl groups. The amido N−H proton resonance is also clearly visible and is markedly shielded ($\delta = 2.63$) relative to that observed in *cis*-**3** ($\delta = 5.01$) presumably as a result of an increase in negative charge at the amido nitrogen center in the complex **7**.

Conclusions

The metathetical reaction of lithium amides with $[ClSb(\mu\text{-}N^tBu)]_2$ was used successfully to prepare the first series of bis(1°-amino)cyclodistib(III)azanes. In all cases, the compounds were found to exist in solution as a mixture of cis and trans isomers. In the case of $[NHDippSb(\mu\text{-}N^tBu)]_2$, it was possible to separate the two isomers and compare their reactivity with ^{n}BuLi. Surprisingly, the trans-isomer gave rise to the cis-arranged heterometallic cubane $[LiNDippSb(\mu\text{-}N^tBu)]_2$ (**6**). In contrast, the cis isomer was found to be susceptible to nucleophilic attack at antimony, resulting in destruction of the cyclodistib(III)azane ring and the formation of the tricyclic complex $[Li_2Sb(\mu\text{-}N^tBu)(\mu\text{-NDipp})(\mu\text{-NHDipp})]$ (**7**). These unexpected results have significant implications for the study of cyclodistib(III)azanes, and could help to shed light on the multifarious results that have been previously observed in the chemistry of these compounds.[1,3]

Although we have demonstrated the applicability of this approach to the synthesis of bis(1°-amino)cyclodistib(III)azanes, further application of this methodology suffers from the lack of availability of other $[ClSb(\mu\text{-NR})]_2$ dimers, **1** being the only known isolated example. The development of a general synthetic route to dichloro reagents of the type $[ClE(\mu\text{-NR})]_2$ (E = Sb, Bi) remains a significant challenge.

Experimental Section

All reactions and the manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glovebox. Solvents were freshly distilled, dried, and degassed prior to use. NMR spectra were obtained on C_6D_6 solutions at 25 °C using a Bruker AMX 300 spectrometer, unless otherwise noted. All lithium amides were prepared by reaction of *n*-butyl-lithium with the respective amine, isolated as solids, dried under vacuum, and subsequently stored in an inert atmosphere glovebox. The reagent $[ClSb(\mu\text{-}N^tBu)]_2$ (**1**) was prepared by the literature methods.[13] X-ray quality crystals of **1** were grown by slow diffusion of *n*-hexane into a concentrated solution of the compound in THF at −20 °C.

2: A mixture of $LiNH^tBu$ (0.693 g, 8.76 mmol) and **1** (2.000 g, 4.38 mmol) was placed in a 100 mL Schlenk flask and cooled to −78 °C. To this was added 50 mL of cold toluene (−78 °C), and the reaction mixture was stirred for 0.5 h at −78 °C. The solution was warmed to room temperature and stirred for an additional 1.5 h. The mixture was then filtered through Celite and the solvent was removed under a vacuum, to give primarily *cis*-**2** as a thick yellow oil (2.05 g, 88%) that solidifies after storage at −20 °C for 12 h. Anal. Calcd for $C_{16}H_{38}N_4Sb_2$: C, 36.26; H, 7.23; N, 10.57. Found: C, 35.34; H, 7.16; N, 10.08. (*cis*-**2**) ^{1}H NMR: δ 1.27, 1.34 (s, 36H, C(CH_3)$_3$) 2.65 (s, 2H, NH^tBu). ^{13}C NMR: δ 35.86, 36.44 (C(CH_3)$_3$), 53.31, 54.81 (C(CH$_3$)$_3$). (*trans*-**2**) ^{1}H NMR: δ 1.28, 1.29 (s, 36H, C(CH_3)$_3$), 2.69 (s, 2H, NH^tBu). ^{13}C NMR: δ 35.63, 35.69 (C(CH_3)$_3$), 53.09, 55.85 (C(CH$_3$)$_3$).

3: A solution of **1** (4.000 g, 8.76 mmol) in 70 mL of cold toluene (−78 °C) was added to a suspension of LiNHDipp (3.210 g, 17.52 mmol) in 20 mL of cold toluene (−78 °C), and the mixture was stirred for 30 min at −78 °C. The solution was allowed to warm to room temperature and stirred for an additional 2h. The mixture was then filtered through Celite and the solvent was removed under a vacuum. The residue was washed with *n*-hexane (15 mL), leaving *trans*-**3** as a yellow solid (2.75 g, 43%). The *n*-hexane washings were collected and the solvent removed under a vacuum to give *cis*-**3** as a thick yellow oil (2.65 g, 41%). Storage of the oil at −20 °C for 24 h resulted in the formation of X-ray quality crystals of *cis*-**3**. A small amount of *trans*-**3** could be dissolved into hot *n*-hexane, and storage of this solution at −20 °C for several hours produced X-ray quality crystals of *trans*-**3**. Anal. Calcd for $C_{32}H_{54}N_4Sb_2$: C, 52.06; H, 7.37; N, 7.59. Found: C, 51.90; H, 7.67; N, 7.32. (*cis*-**3**) ^{1}H NMR: δ 1.17 (s, 18H, C(CH_3)$_3$), 1.35 (d, 24H, $^3J_{HH}$ = 8 Hz, CH(CH_3)$_2$), 3.72 (sept, 4 H, $^3J_{HH}$ = 8 Hz, CH(CH$_3$)$_2$), 5.01 (s, 2 H, NHDipp), 6.97, (t, 2 H, $^3J_{HH}$ = 8 Hz, Ar-H), 7.18 (d, 4 H, $^3J_{HH}$ = 8 Hz, Ar-H). ^{13}C NMR: δ 24.71 (CH(CH_3)$_2$), 29.49 (CH(CH$_3$)$_2$), 36.11 (C(CH_3)$_3$), 54.08 (C(CH$_3$)$_3$), 121.09, 124.11, 138.22, 143.42 (Ar-C). (*trans*-**3**) ^{1}H NMR: δ 1.06 (s, 18H, C(CH_3)$_3$), 1.34 (d, 24H, $^3J_{HH}$ = 8 Hz, CH(CH_3)$_2$), 3.62 (sept, 4 H, $^3J_{HH}$ = 8 Hz, CH(CH$_3$)$_2$), 5.23 (s, 2 H, NHDipp), 6.95, (t, 2 H, $^3J_{HH}$ = 8 Hz, Ar-H), 7.19 (d, 4 H, $^3J_{HH}$ = 8 Hz, Ar-H). ^{13}C NMR: δ 24.28 (CH(CH_3)$_2$), 29.89 (CH(CH$_3$)$_2$), 35.18 (C(CH_3)$_3$), 53.65 (C(CH$_3$)$_3$), 120.33, 124.15, 136.83, 144.51 (Ar-C).

4: In a manner similar to that described for **2**, this was prepared from **1** (3.000 g, 6.57 mmol) and LiNHDmp (1.670 g 13.14 mmol) in 50 mL of cold toluene (−78 °C) to give primarily *cis*-**4** as a thick, deep yellow oil (3.58 g, 87%). Storage of the oil for several hours at room temperature resulted in the formation of X-ray quality crystals of *cis*-**4**. Anal. Calcd for $C_{24}H_{38}N_4Sb_2$: C, 46.04; H, 6.12;

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(26) Brask, J. K.; Chivers, T.; Schatte, G. *Chem. Commun.* **2000**, 1805.
(27) The reaction of $BuSbBr_2$ with magnesium has been reported to produce yellow solutions that contain a mixture of cyclic oligomers $(BuSb)_n$ (primarily $n = 5$) on the basis of solution NMR data. Evaporation of these solutions gives black solids. Ates, M.; Breunig, H. J.; Gulec, S.; Offermann, W.; Hanerle, K.; Drager, M. *Chem. Ber.* **1989**, *122*, 473.

Table 5. Crystallographic Data for Complexes *cis*-**1**, *cis*-**3**, *trans*-**3**, *cis*-**4**, **5**, **6**, and **7**[a]

	cis-**1**	*cis*-**3**	*trans*-**3**	*cis*-**4**	**5**	**6**	**7**
formula	$C_8H_{18}Cl_2N_2Sb_2$	$C_{32}H_{54}N_4Sb_2$	$C_{32}H_{54}N_4Sb_2$	$C_{24}H_{38}N_4Sb_2$	$C_{24}H_{52}N_4Na_2O_2Sb_2$	$C_{36}H_{60}Li_2N_4OSb_2$	$C_{40}H_{69}Li_2N_4O_2Sb$
fw	456.64	738.29	738.29	626.08	718.18	822.26	773.62
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	*Pbcn*	*Pnma*	$P2_1/c$	$P\bar{1}$
a (Å)	5.965(1)	9.955(2)	12.111(2)	11.254(2)	17.305(4)	18.353(4)	10.705(2)
b (Å)	14.331(3)	11.433(2)	9.339(2)	12.092(2)	16.439(3)	10.586(2)	20.816(4)
c (Å)	51.65(1)	31.723(6)	15.749(3)	19.741(4)	11.772(2)	21.552(4)	20.970(4)
α (deg)	90	90	90	90	90	90	107.63(3)
β (deg)	91.77(3)	95.71(3)	103.10(3)	90	90	112.16(3)	92.50(3)
γ (deg)	90	90	90	90	90	90	91.08(3)
V (Å^3)	4413(2)	3593(1)	1735.0(6)	2684.4(8)	3349(1)	3878(2)	4447(2)
Z	12	4	2	4	4	4	4
d_{calcd} (g cm^{-3})	2.062	1.365	1.413	1.548	1.424	1.408	1.156
μ (mm^{-1})	4.008	1.528	1.582	2.028	1.663	1.424	0.654
R^b	0.0268	0.0338	0.0362	0.0535	0.0391	0.0429	0.525
$R_w{}^c$	0.0499	0.0742	0.0949	0.1612	0.1020	0.0880	0.1376

[a] T = 173(2) K; wavelength = 0.71073 Å. [b] $R = \sum|F_o| - |F_c||/\sum|F_o|$ ($I > 2.00\sigma(I)$). [c] $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$ (all data).

N, 8.95. Found: C, 45.72; H, 6.05; N, 8.72. (*cis*-**4**) ^{1}H NMR: δ 1.09 (s, 18H, C(C*H*$_3$)$_3$), 2.42 (s, 12H, Ar(C*H*$_3$)), 4.74 (s, 2 H, N*H*Dmp), 6.76, (t, 2 H, $^3J_{HH}$ = 9 Hz, Ar-*H*), 7.05 (d, 4 H, $^3J_{HH}$ = 9 Hz, Ar-*H*). ^{13}C NMR: δ 21.51 (Ar(*C*H$_3$)), 36.22 (C(*C*H$_3$)$_3$), 53.92 (*C*(CH$_3$)$_3$), 119.41, 125.64, 129.74, 147.21 (Ar-*C*). (*trans*-**4**) ^{1}H NMR: δ 0.99 (s, 18H, C(C*H*$_3$)$_3$), 2.32 (s, 12H, Ar(C*H*$_3$)), 4.94 (s, 2 H, N*H*Dmp), 6.76 (t, 2 H, $^3J_{HH}$ = 9 Hz, Ar-*H*), 7.02 (d, 4 H, $^3J_{HH}$ = 9 Hz, Ar-*H*). ^{13}C NMR: δ 21.34 (Ar(*C*H$_3$)), 36.13 (C(*C*H$_3$)$_3$), 53.71 (*C*(CH$_3$)$_3$), 118.90, 124.76, 129.70, 147.95 (Ar-*C*).

5: A suspension of butyl-sodium (0.725 g, 9.06 mmol) in *n*-hexane (15 mL) was cooled to −78 °C, and cold THF (−78 °C, 20 mL) was added to dissolve the butyl-sodium. This solution was added dropwise by using a cannula to a cold solution of **2** (2.400 g, 4.53 mmol) in THF (−78 °C, 25 mL), and the mixture was stirred for 0.5 h at −78 °C. The solution was allowed to warm to room temperature and stirred for an additional 1h. The solution was filtered through Celite; the solvent was then removed under a vacuum, and the residue was dissolved in *n*-hexane (ca. 5 mL). Storage of the solution at −20 °C for 12 h resulted in the formation of X-ray quality yellow crystals of **5** (1.78 g, 55%). Anal. Calcd for $C_{24}H_{52}N_4Na_2O_2Sb_2$: C, 40.14; H, 7.30; N, 7.80. Found: C, 40.36; H, 7.61; N, 7.64. ^{1}H NMR: δ 1.33 (m, 8H THF), 1.44, 1.53 (s, 36H, C(C*H*$_3$)$_3$), 3.52 (s, 8H, THF). ^{13}C NMR: δ 25.92 (THF), 35.15, 42.15 (C(*C*H$_3$)$_3$), 55.37, 56.23 (*C*(CH$_3$)$_3$), 68.40 (THF).

6: A solution of *n*-butyl-lithium (2.20 mL, 2.5 M, 5.50 mmol) in cold THF (−78 °C, 5 mL) was added using a cannula to a solution of *trans*-**3** (2.000 g, 2.71 mmol) in cold THF (−78 °C, 60 mL). The solution was held at −78 °C for ca. 2 min and then allowed to warm to room temperature and stirred for an additional 40 min. The solvent was removed under a vacuum and the residue was dissolved in 5 mL of *n*-hexane, resulting in the immediate precipitation of yellow crystals of **6**. Deposition of the crystals was allowed to continue for 30 min; the solvent was then decanted and the crystals dried under a vacuum (1.78 g, 80%). Bulk samples of **6** were contaminated with small amounts of **7** because of the *cis*−*trans* equilibration of **3** (see Results and Discussion). However, analytically pure **6** can be obtained by sequential recrystallizations. Anal. Calcd for $C_{36}H_{60}Li_2N_4OSb_2$: C, 52.58; H, 7.36; N, 6.81. Found: C, 52.06; H, 7.66; N, 6.99. ^{1}H NMR: δ 1.32 (s, 18H, C(C*H*$_3$)$_3$), 1.35 (d, 24H, $^3J_{HH}$ = 8 Hz, CH(C*H*$_3$)$_2$), 3.16 (m, 4H, THF), 3.44 (sept, 4 H, $^3J_{HH}$ = 8 Hz, C*H*(CH$_3$)$_2$), 6.91, (t, 2 H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.20 (d, 4 H, $^3J_{HH}$ = 8 Hz, Ar-*H*). ^{13}C NMR: δ 25.32 (CH(*C*H$_3$)$_2$), 25.48 (THF), 29.76 (*C*H(CH$_3$)$_2$), 34.39 (C(*C*H$_3$)$_3$), 54.74 (*C*(CH$_3$)$_3$), 68.32 (THF), 117.37, 123.65, 139.81, 157.29 (Ar-*C*).

7: A solution of *n*-butyl-lithium (1.21 mL, 2.5 M, 3.03 mmol) in cold THF (−78 °C, 20 mL) was added using a cannula to a solution of *cis*-**3** (1.130 g, 1.53 mmol) in cold THF (−78 °C, 20 mL). The solution was held at −78 °C for 30 min and then allowed to warm to room temperature and stirred for an additional 1 h. The solvent was removed under a vacuum and the residue was dissolved in 5 mL of *n*-hexane. Storage of the solution at −20 °C for 12 h resulted in the formation of X-ray quality yellow crystals of **7** (0.580 g, 50%). Anal. Calcd for $C_{40}H_{71}Li_2N_4O_2Sb$: C, 61.94; H, 9.23; N, 7.22. Found: C, 61.10; H, 8.96; N, 7.39. ^{1}H NMR: δ 1.08 (m, 8H, THF), 1.32 (s, 18H, C(C*H*$_3$)$_3$), 1.34, 1.38 (d, 24H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)$_2$), 2.63 (s, 1H, N*H*Dipp), 3.06 (m, 8H, THF), 3.42 (m, br, 2H, C*H*(CH$_3$)$_2$), 4.04 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 6.62, 6.86 (t, 2H, $^3J_{HH}$ = 7 Hz, Ar-*H*), 7.10, 7.17 (d, 4H, $^3J_{HH}$ = 7 Hz, Ar-*H*). ^{13}C NMR: δ 24.21 (CH(*C*H$_3$)$_2$), 24.96 (THF), 25.53 (CH(*C*H$_3$)$_2$), 28.48, 28.80 (*C*H(CH$_3$)$_2$), 35.05 (C(*C*H$_3$)$_3$), 52.37 (*C*(CH$_3$)$_3$), 68.72 (THF), 111.60, 118.21, 122.94, 123.25, 132.05, 143.35, 158.11, 158.35 (Ar-*C*).

X-ray Analyses. Individual crystals of *cis*-**1** (pale yellow rod), *cis*-**3** (yellow needle), *trans*-**3** (yellow plate), *cis*-**4** (yellow plate), **5** (yellow block), **6** (yellow rod), and **7** (yellow plate) were coated with Paratone 8277 oil (Exxon) and mounted onto thin glass fibers. Data were collected on a Nonius Kappa CCD diffractometer via ω and ϕ scans. Cell parameters, data reduction, and absorption corrections were performed with the Nonius software (DENZO and SCALEPACK, B. V. Nonius, 1998). The structures were solved by direct methods as implemented in SHELXS-97, and refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method using the SHELXL-97 program (G. M. Sheldrick). The hydrogen atoms were calculated geometrically and refined using a riding model unless otherwise specified. Except as mentioned, all non-hydrogen atoms were refined with anisotropic thermal parameters. Relevant parameters for the data collections and crystallographic data are summarized in Table 5. Thermal ellipsoid plots are shown at the 30% probability level.

cis-**1**: The complex crystallizes with three independent but chemically equivalent molecules in the asymmetric unit. The refinement was complicated by twinning of the data, although all non-hydrogen atoms were refined with anisotropic thermal parameters. There were many indications of twinning, including the fact that the refinement stalled at 21.18%. Application of the program ROTAX[28] determined

that twinning occurred around the [100] direct lattice axis, and the program WinGX[29] was used to prepare an HKLF5 file for further refinement. The *R* values, *K* values, esds, and background noise were all significantly improved, indicating the correct twin assignment.

cis-**3**: The molecule was well-ordered with the exception of one of the isopropyl groups, which was modeled as a 50:50 isotropic mixture. The amido hydrogen atoms were located in the difference map.

trans-**3**: The molecule was well-ordered and no special considerations for the refinement were necessary. The amido hydrogen atoms were located in the difference map. Only one-half of the molecule was located in the difference Fourier map as the molecule is situated on a crystallographic center of symmetry.

cis-**4**: The molecule was well-ordered, and no special considerations for the refinement were necessary. The amido hydrogen atoms were located in the difference map. Only one-half of the molecule was located in the difference Fourier map, as the molecule is situated on a crystallographic 2-fold rotation axis.

5: The molecule was well-ordered with the exception of the coordinated THF molecule, which was modeled as a 60:40 mixture; two of the disordered carbon atoms were refined with isotropic thermal parameters.

6: The molecule was well-ordered, with the exception of one carbon position of the coordinated THF molecule, which was modeled as a 65:35 isotropic mixture. The lithium atoms were refined with isotropic thermal parameters.

7: There are two chemically equivalent but crystallographically independent molecules in the asymmetric unit. The molecules were well-ordered with the exception of the coordinated THF molecules and one isopropyl group, the latter of which was modeled as a 60:40 isotropic mixture. Three of the THF molecules were modeled as 50:50 isotropic mixtures, whereas the fourth THF molecule was severely disordered, and the best model that could be refined was a 25:25:20:15:15 isotropic mixture. For all the disordered portions, light geometric restraints were applied. The amido hydrogen atoms were located in the difference map.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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