The relative stabilities of Ph*E*(NH-*t*-Bu)$_2$ and Ph*E*(μ-N-*t*-Bu)$_2$*E*Ph (*E* = As, Sb, and Bi): X-ray structures of {Li$_2$[PhAs(N-*t*-Bu)$_2$]}$_2$ and Ph*E*(μ-N-*t*-Bu)$_2$*E*Ph (*E* = Sb, Bi)

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Abstract: The reaction of Ph*E*Cl$_2$ with 2 equiv of LiHN-*t*-Bu has been studied for the series *E* = As, Sb, and Bi to determine the effect of the phenyl group on subsequent amine condensation processes. For PhAsCl$_2$, the metathesis product PhAs(NH-*t*-Bu)$_2$ **4** was obtained as a colourless oil. Similar reactions involving Ph*E*Cl$_2$, where *E* = Sb or Bi, yielded the cyclodipnict(III)azanes Ph*E*(μ-N-*t*-Bu)$_2$*E*Ph **5** (*E* = Sb) and **6** (*E* = Bi), respectively. Treatment of **4** with 2 equiv of *n*-BuLi produced the dilithium salt Li$_2$[PhAs(N-*t*-Bu)$_2$] **7a**. Products **4**, **5**, **6**, and **7a** were characterized by ^{1}H, ^{7}Li (**7a**), and ^{13}C NMR spectra, while **5**, **6**, and **7a** were also structurally characterized by X-ray crystallography. Compound **7a** is dimeric in the solid state via intermolecular Li···N and η^6-Li···Ph interactions. The cyclodipnict(III)azanes **5** and **6** have similar structures, with the exocyclic phenyl groups in *trans* positions relative to the E_2N_2 ring. This synthetic approach provides a new route to the four-membered rings *RE*(μ-N-*t*-Bu)$_2$*ER* (*E* = Sb, Bi) and the first example of a bis(organyl)cyclodibism(III)azane.

Key words: arsenic, antimony, bismuth, amides, imides.

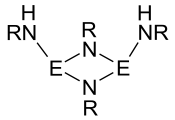
Résumé : Afin de pouvoir déterminer l'effet du groupe phényle sur les processus subséquents de condensation de l'amine, on a étudié la réaction de Ph*E*Cl$_2$ (*E* = As, Sb et Bi) avec deux équivalents de LiHN-*t*-Bu. Dans le cas du PhAsCl$_2$, le produit de dismutation, PhAs(NH-*t*-Bu)$_2$ (**4**), a été obtenu sous la forme d'huile incolore. Les réactions semblables de Ph*E*Cl$_2$ dans lesquelles *E* = Sb ou Bi conduisent respectivement aux cyclodipnict(III)azanes, Ph*E*(μ-N-*t*-Bu)$_2$*E*Ph (**5**, *E* = Sb) et (**6**, *E* = Bi). Le traitement du composé **4** avec deux équivalents de BuLi conduit à la formation du sel dilithié Li$_2$[PhAs(N-*t*-Bu)$_2$] (**7a**). Les produits **4**, **5**, **6** et **7a** ont été caractérisés par leurs spectres RMN du ^{1}H et du ^{7}Li (**7a**) et des spectres RMN du ^{13}C alors que les produits **5**, **6** et **7a** ont aussi été caractérisés par diffraction des rayons X. À l'état solide, le composé **7a** existe à l'état trimère par le biais d'interactions Li···N et η^6-Li···Ph. Les cyclodipnict(III)azanes **5** et **6** ont des structures semblables avec des groupes phényles exocycliques en positions *trans* par rapport au cycle E_2N_2. Cette approche fournit une nouvelle voie de synthèse vers les cycles à quatre chaînons R*E*(μ-N-*t*-Bu)$_2$*E*R (*E* = Sb, Bi) et le premier exemple d'une bis(organyl)cyclodibism(III)azane.

Mots clés : arsenic, antimoine, bismuth, amides, imides.

[Traduit par la Rédaction]

Introduction

Pnicogen(III) compounds of secondary amines have been employed extensively as reagents for the preparation of compounds containing other functional groups (1). Homoleptic species *E*(N*R*$_2$)$_3$ (*E* = P, As, Sb, Bi) are synthesized via simple metathesis reactions of a pnicogen(III) halide with the appropriate amine or alkali metal amide. Analogous studies involving primary amines, on the other hand, have proven to be less predictable as a result of the remaining acidic amino proton after initial *E*—N bond formation. Reactions involving primary amines and PCl$_3$ do not afford tris(amino)pnictines P(NH*R*)$_3$; rather, further amine elimination occurs to yield [cyclodiphosph(III)azanes] **1**, **2**, cyclic systems (ClPN*R*)$_3$, P$_4$(N*R*)$_6$ cages, or other condensation products, depending on the choice of amine substituent and reaction stoichiometry (2, 3). Although there have been fewer such studies involving *E*Cl$_3$ (*E* = As, Sb, Bi), similar condensation reactions are observed (4–12).



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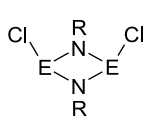

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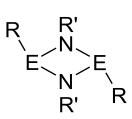

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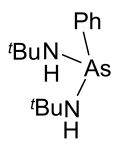
In contrast to reactions involving PCl_3, metathesis products of H_2N-*t*-Bu and *R*PCl_2 (*R* = Ph, Me, -*t*-Bu, C_5Me_5) yield *R*P(NH-*t*-Bu)$_2$ rather than the condensation products **3** (*E* = P) (6*c*, 13). The intermediates *R*P(NH-*t*-Bu)Cl (*R* = Me, *t*-Bu) are also isolable, given the appropriate reaction stoichiometry (14). Similar observations have been made for reactions of H_2N-*t*-Bu and *R*$AsCl_2$, which yield *R*As(NH-*t*-Bu)$_2$ and *R*AsCl(NH-*t*-Bu) with formation of minor amounts of **3** (*E* = As; *R′* = *t*-Bu) (15). To our knowledge, related studies involving *RE*Cl_2 (*E* = Sb, Bi) have not been reported. They are of interest in determining the effect of the pnicogen organyl substituent on condensation processes in these systems. We now report the results of an investigation of the reaction between LiNH-*t*-Bu and Ph*E*Cl_2 for the series *E* = As, Sb, and Bi, which gives the metathesis product **4** for arsenic and the condensation products **5** and **6** for antimony and bismuth, respectively. Further, we describe the metallation of **4** to give **7a**, and the solid-state structures of **5**, **6**, and **7a**.



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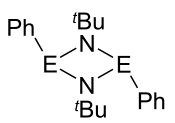
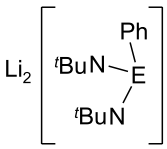


5, E = Sb
6, E = Bi



7a, E = As
7b, E = P

Experimental section

Reagents and general procedures

Solvents were dried and distilled over Na/benzophenone prior to use: diethyl ether and *n*-hexane. Phenylarsonic acid, triphenylantimony, and thionyl chloride were used as received from Aldrich. Antimony(III) chloride, triphenylbismuth, and bismuth(III) chloride were used as received from Strem. $PhAsCl_2$ (16), $PhSbCl_2$ (17), [$PhBiCl_2$(thf)](18), and LiHN-*t*-Bu (19) were prepared according to literature procedures (thf = tetrahydrofuran). Compound **4** has been reported previously, but was prepared via a different route and characterized by elemental analysis only (15*a*).

Instrumentation

^1H, ^{13}C, ^{31}P, and ^7Li NMR spectra were recorded on a Bruker DRX 400 NMR spectrometer at 298 K. Chemical shifts are reported relative to Me_4Si in C_6D_6 (^1H and ^{13}C), 85% H_3PO_4 in D_2O (^{31}P), and 1 M LiCl in D_2O (^7Li). Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Preparation of PhAs(NH-*t*-Bu)$_2$, 4

A slurry of LiHN-*t*-Bu (4.134 g, 52.29 mmol) in diethyl ether (40 mL) was added dropwise to a solution of $PhAsCl_2$ (5.828 g, 26.14 mmol) in diethyl ether (15 mL) at –90°C to give a cloudy white mixture. The mixture was allowed to warm to 23°C, and after 18 h, the solvent was removed under vacuum. Hexane (30 mL) was added and the mixture was centrifuged. The supernatant was decanted and the solvent removed under vacuum to give **4** as a yellow oil, which was distilled (10^{-3} mm, ~80°C) to give a colourless oil (5.140 g, 17.35 mmol, 66%). NMR data (thf-d_8): ^1H NMR δ: 1.25 (s, 18 H, N-*t-Bu*), 1.85 (s, 2 H, N*H*), 7.21–7.25 (m, 1 H, As*Ph-p*), 7.28–7.32 (m, 2H, As*Ph-o*), 7.69–7.72 (m, 2 H, As*Ph-m*). ^{13}C NMR δ: 33.7 (NC*Me*$_3$), 52.5 (N*C*Me$_3$), 128.9 (As*Ph*), 129.0 (As*Ph*), 131.6 (As*Ph*), 150.1 (As*Ph*).

Preparation of PhSb(μ-N-*t*-Bu)$_2$SbPh, 5

A slurry of LiHN-*t*-Bu (2.108 g, 26.67 mmol) in diethyl ether (20 mL) was added dropwise to a solution of $PhSbCl_2$ (3.597 g, 13.33 mmol) in diethyl ether (5 mL) at 0°C to give a cloudy yellow mixture, which was allowed to warm to 23°C. After 18 h, the solvent was removed under vacuum. Hexane (20 mL) was added, and the mixture was centrifuged. The supernatant was decanted, and the solvent was removed under vacuum to give **5** as a yellow-orange oil (3.071 g, 5.69 mmol, 85%). The oily product crystallized on standing at 23°C for 1 day. NMR data (thf-d_8): ^1H NMR δ: 1.26 (s, 18 H, N-*t-Bu*), 7.25–7.31 (m, 6 H, Sb*Ph-p*/*o*), 7.54–7.72 (m, 4 H, Sb*Ph-m*). ^{13}C NMR δ: 35.1 (NC*Me*$_3$), 52.4 (N*C*Me$_3$), 128.9 (Sb*Ph*), 129.2 (129.3) (Sb*Ph*), 134.1 (135.2) (Sb*Ph*). Anal. calcd. for $C_{20}H_{28}N_2Sb_2$ (%): C 44.49, H 5.23, N 5.19; found: C 43.95, H 4.81, N 5.42.

Preparation of PhBi(μ-N-*t*-Bu)$_2$BiPh, 6

A slurry of LiHN-*t*-Bu (0.100 g, 1.27 mmol) in diethyl ether (5 mL) was added dropwise to a solution of [$PhBiCl_2$(thf)] (0.272 g, 0.633 mmol) in diethyl ether (5 mL) at 0°C to give a cloudy orange mixture, which was allowed to warm to 23°C. After 3 h, the solvent was removed under vacuum. After addition of hexane (5 mL), the mixture was centrifuged, and the supernatant was decanted and concentrated to 1 mL. After 2 days, red crystals of **6** were collected (0.040 g, 0.056 mmol, 18%). NMR data (thf-d_8): ^1H NMR δ: 0.66 (s, 18 H, N-*t-Bu*), 7.33 (m, 2 H, Bi*Ph-p*), 7.64 (m, 4 H, Bi*Ph-o*), 8.78 (m, 4 H, Bi*Ph-m*). ^{13}C NMR δ: 35.5 (NC*Me*$_3$), 55.1 (N*C*Me$_3$), 128.8 (Bi*Ph*), 131.3 (Bi*Ph*), 136.7 (Bi*Ph*). Anal. calcd. for $C_{20}H_{28}Bi_2N_2$ (%): C 33.62, H 3.95, N 3.92; found: C 33.84, H 4.03, N 4.17.

Preparation of Li_2[PhAs(N-*t*-Bu)$_2$], 7a

A solution of 2.5 M *n*-BuLi in hexanes (8.10 mL, 20.28 mmol) was added dropwise to a solution of PhAs(NH-*t*-Bu)$_2$ (3.003 g, 10.14 mmol) in diethyl ether (30 mL) at 0°C to give a cloudy yellow mixture, which was allowed to warm to 23°C. After 5 h, the solvent was removed under vacuum. The resulting product was washed with *n*-hexane (3 × 5 mL) to give **7a** as a white powder (2.002 g, 6.50 mmol, 64%). X-ray quality crystals were grown from diethyl ether – hexane at –15°C. NMR data (thf-d_8): ^1H NMR δ: 1.04 (s, 18 H, N-*t-Bu*), 6.95 (t, 1 H, As*Ph-p*), 7.06 (t, 2 H, As*Ph-o*), 7.60 (d, 2 H, As*Ph-m*). ^{13}C NMR δ: 38.2 (NC*Me*$_3$), 53.5 (N*C*Me$_3$), 126.0, (As*Ph*), 127.5 (As*Ph*), 131.1 (As*Ph*). ^7Li NMR δ: 1.92, 2.41. Anal. calcd. for $C_{14}H_{23}AsLi_2N_2$ (%): C 54.57, H 7.52, N 9.09; found: C 55.83, H 7.44, N 8.98.

X-ray structural analyses

Crystals of **5**, **6**, and **7a** were coated with oil (Paratone 8277, Exxon) and mounted on glass fibres. Measurements were made on a Nonius KappaCCD diffractometer using

Table 1. Crystallographic data for **5**, **6**, and **7a**.

	5	**6**	**7a**
Empirical formula	$C_{20}H_{28}N_2Sb_2$	$C_{20}H_{28}Bi_2N_2$	$C_{14}H_{23}AsLi_2N_2$
Formula mass	539.94	714.40	308.14
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	6.6067(2)	9.0544(3)	9.0354(1)
b (Å)	20.1293(6)	9.3725(2)	10.1088(2)
c (Å)	8.4739(3)	12.6567(5)	10.6036(3)
α (°)	90	90	87.9151(9)
β (°)	106.475(2)	92.641(1)	67.968(1)
γ (°)	90	90	64.324(1)
V (Å^3)	1080.66(6)	1072.94(6)	799.86(3)
Z	2	2	2
F(000)	528	656	320
D_{calcd}(g cm^{-3})	1.659	2.211	1.279
μ (mm^{-1})	2.50	16.4	2.11
T (K)	170(2)	170(2)	170(2)
λ (Å)	0.71069	0.71073	0.71073
R_1[a]	0.048	0.024	0.027
wR_2[a]	0.111	0.059	0.066

[a] $R_1 = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$ for $(F_o^2 > 2\sigma(F_o^2))$, $[I > 2\ \sigma(I)]$; $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ (all data).

monochromated Mo Kα radiation. Crystallographic data are summarized in Table 1.[2]

Data were measured using ω and φ scans. The crystals showed no sign of decay during data collection, and no decay correction was employed. Cell constants were obtained from the refinement (20) of 2330 (**5**), 2208 (**6**), or 3484 (**7a**) reflections in the range $1 < \phi < 27.5°$. The space groups for **5** and **6** were uniquely determined from the systematic absences. The data were corrected for Lorentz and polarization effects and for absorption using the multiscan method (20). The structures were solved using direct methods (21) and expanded using Fourier techniques (22) (SHELXL97) (23). The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined.

The Sb atom in **5** was disordered over two sites, Sb1 and Sb2, with occupancy factors 0.574(1) and 0.426(1), respectively. The *t*-Bu group exhibited rotational disorder wherein the methyl C atoms were located over two sites each with site occupancy factors 0.83(1) and 0.17(1). The disorder in the phenyl ring was also apparent from the large thermal displacement parameters of its carbon atoms.

Results and discussion

Synthetic and NMR studies

The treatment of $PhAsCl_2$ with 2 equiv of LiHN-*t*-Bu in diethyl ether yields $PhAs(NH\text{-}t\text{-}Bu)_2$ **4** in ca. 65% yield, as a colourless oil, after vacuum distillation. ^{1}H and ^{13}C NMR spectra of the unpurified material show that primarily one product is formed in this reaction with very minor amounts of impurities. The absence of the condensation product **3** (E = As, $R = R'$ = *t*-Bu) represents an improvement on the existing synthesis of **4** (15*a*). The identity of **4** was established by ^{1}H and ^{13}C NMR spectra and by metallation with 2 equiv of *n*-butyllithium to yield the dilithium salt $Li_2[PhAs(N\text{-}t\text{-}Bu)_2]$ **7a** (R = Ph), cf., the formation of $Li_2[PhP(N\text{-}t\text{-}Bu)_2]$ **7b** from $PhP(NH\text{-}t\text{-}Bu)_2$ (13*a*). The resulting colourless crystals were of sufficient quality to allow a definitive characterization via X-ray crystallographic analysis (vide infra). Wright and co-workers have recently described extensive studies of the formation of the $[As(N\text{-}t\text{-}Bu)_3]^{3-}$ trianion by the reaction of $As(NMe_2)_3$ (1 equiv) with a mixture of *t*-$BuNH_2$ and *t*-BuNHLi (3:3 equiv) (24). Although the formation of $As(NH\text{-}t\text{-}Bu)_3$ is implied in this synthesis, this intermediate was not isolated. The authors propose a facile condensation to produce the cyclodiars(III)azane, *t*-BuN(H)As(μ-N-*t*-Bu)$_2$AsN(H)-*t*-Bu (**3**, E = As, $R = R'$ = *t*-Bu) to explain this observation (24).

The reaction of $PhSbCl_2$ with 2 equiv of LiHN-*t*-Bu yields a yellow-orange oil after removal of the solvent. The oil crystallizes after 1 day at 23°C, and it was identified by CHN analyses and NMR spectra as the condensation product $PhSb(\mu\text{-}N\text{-}t\text{-}Bu)_2SbPh$ **5**. Compound **5** was obtained in 85% yield and the ^{1}H and ^{13}C NMR spectra of the unpurified material indicated a single product. For $PhBiCl_2$, the corresponding reaction proceeds in a similar manner but, in this case, the crude product was isolated as a solid. Crystals were obtained from *n*-hexane and characterized as $PhBi(\mu\text{-}N\text{-}t\text{-}Bu)_2BiPh$ **6**. The ^{1}H NMR spectrum of the reaction mixture exhibits three N-*t*-Bu resonances at δ 0.66, 1.01, and 1.07, with approximate relative intensities 1:2:1, in addition to a

[2] Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 188507(**7a**), 188508(**5**), and 188509(**6**) contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

complex set of overlapping Ph resonances. The *trans*-isomer of **6** was isolated in ca. 20% yield and shown to be attributable to the resonance at δ 0.66. It is tentatively proposed that one of the other products is the *cis*-isomer of **6**, but attempts to isolate this component by fractional crystallization were unsuccessful. A candidate for the second unidentified product is the monosubstituted derivative PhBi(Cl)(NH-*t*-Bu). However, when the reaction was carried out in a 1:1 stoichiometry, no resonances were observed at δ 0.66, 1.01, or 1.07 in the ^{1}H NMR spectrum. Resonances attributable to the N-*t*-Bu groups of an unidentified product appeared at δ 1.70 and 1.88.

[1] $$PhECl_2 \xrightarrow[-2LiCl]{+2\ LiNH\text{-}t\text{-}Bu} PhE(NH\text{-}t\text{-}Bu)_2$$
$$(E = Sb, Bi)$$
$$\xrightarrow{-\ t\text{-}BuNH_2} 1/2\ PhE(\mu\text{-}N\text{-}t\text{-}Bu)_2EPh$$
$$\mathbf{5}, E = Sb$$
$$\mathbf{6}, E = Bi$$

For both **5** and **6**, the ^{1}H NMR spectra of the pure products show resonances for N-*t*-Bu and Ph groups in the ratio 1:1, suggesting that a condensation reaction has occurred (eq. [1]). Previous routes to bis(organyl)cyclodistib(III)azanes **3** (*E* = Sb; *R* = Me, *t*-Bu) involve metathesis reactions between the organolithium reagents and ClSb(μ-N-*t*-Bu)$_2$SbCl (**2**, *E* = Sb, *R* = *t*-Bu), which is prepared from $SbCl_3$ and Li(Me$_3$Si)N-*t*-Bu (24*a*, 24*b*). Bismuth analogues of **3** (*E* = Bi) have not been reported, nor have the dichloro derivatives **2** (*E* = Bi). The reaction of organyldihalopnictines and lithiated primary amides thus represents a novel synthetic route to these cyclodipnict(III)azanes.

X-ray structural analyses

ORTEP diagrams of **5** and **6** are shown in Figs. 1 and 2, respectively. The X-ray structure analyses of **5** and **6** confirm the formation of condensation products. In both structures, the exocyclic Ph groups are in a *trans* arrangement with respect to the E_2N_2 ring. In the case of **5**, there is a static disorder in the Sb atom over two positions, giving two unique molecules (Fig. 1). In one molecule, Sb(1) is bound to C(5) of the phenyl ring and N(1) of the N-*t*-Bu group, giving a *trans*-PhSb(μ-N-*t*-Bu)$_2$SbPh structure, as a result of inversion symmetry. The second molecule shows Sb(2) bound to C(6) of the phenyl ring, as well as N(1) of the N-*t*-Bu group, giving an Sb_2N_2 ring that also has a *trans*-PhSb(μ-N-*t*-Bu)$_2$SbPh structure. The Sb—N and Sb—N* interactions are quite different in one molecule, but not in the other (Sb(1)—N(1) = 1.988(4) Å, Sb(1)—N(1*) = 2.063(4) Å; Sb(2)—N(1) = 2.019(4) Å, Sb(2)—N(1*) = 2.034(4) Å). However, the average Sb—N bond distances are similar for the two molecules (|Sb(1)—N| = 2.02(4) Å; |Sb(2)—N| = 2.027(8) Å), while the Sb—C_{phenyl} bond distances are significantly different (Sb(1)—C(5) = 2.169(5) Å; Sb(2)—C(6) = 2.234(7) Å). The structural parameters for **5** and **6** are compared in Table 2. As expected, bond lengths to the bismuth centre in **6** are longer than those to the antimony centres (Bi—C = 2.285(4) Å vs. Sb—C = 2.169(5) and 2.234(7) Å; Bi—N = 2.163(3) and 2.167(3) Å vs. Sb—N = 1.988(4)–2.063(4) Å), and the bond angles at the bismuth centre are considerably smaller than those at antimony. These observations can be attributed to the larger covalent radius of Bi(III) vs. Sb(III).

Fig. 1. ORTEP diagram of **5** showing the two disordered molecules (30% probability ellipsoids). Symmetry transformations used to generate equivalent atoms: –*x* + 1, –*y*, –*z* + 1.

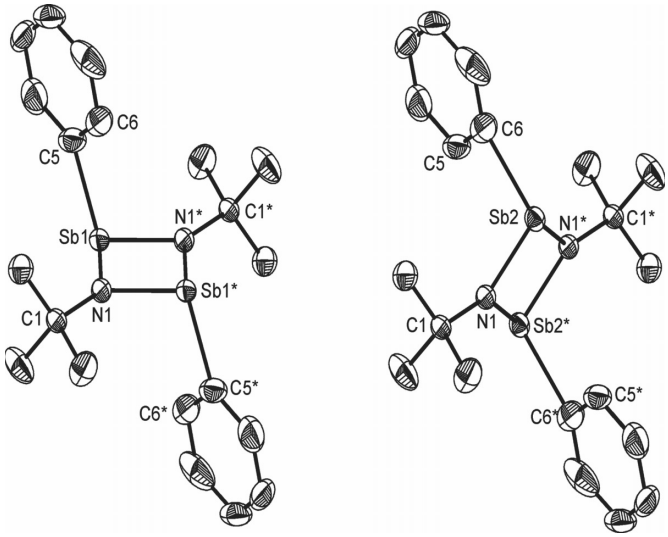
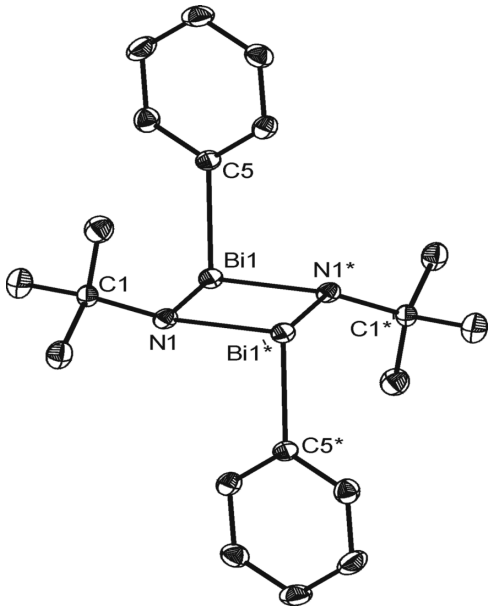


Fig. 2. ORTEP diagram of **6** (30% probability ellipsoids). Symmetry transformations used to generate equivalent atoms: –*x*, –*y*, –*z* + 1.

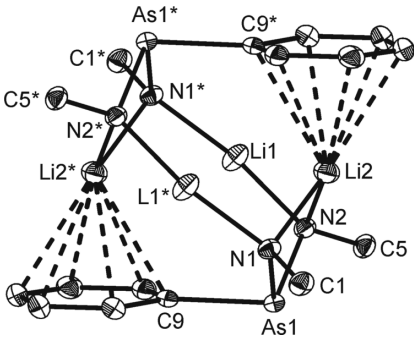


Only one example of a bis(organyl)cyclodistib(III)azane has been structurally characterized, i.e., *trans*-*t*-BuSb(μ-N-*t*-Bu)$_2$Sb-*t*-Bu **8** (25). Comparison of the bond angles and Sb—N_{ring} bond distances in **5** and **8** show all values to be in the same range. The Sb—C bond distances in **5** are shorter than those of **8** (2.252(6) Å), presumably as a result of sp^2 rather than sp^3 hybridization of carbon. Comparison with other analogues shows that the bond angles at antimony in **5** are greater than those in [(*R*HN)Sb(μ-N*R*)$_2$(NH*R*)] (*R* = 2,6-Me$_2$C$_6$H$_3$) **9** (8), while the Sb—N_{ring} bond distances are in

Table 2. Selected bond lengths (Å) and bond angles (°) for **5** and **6**.

	5	**6**
Bond lengths (Å)		
E(1)—C(5)	2.169(5)	2.285(4)
E(1)—N(1)	1.988(4)	2.167(3)
E(1)—N(1*)	2.063(4)	2.163(3)
E(2)—C(6)	2.234(7)	
E(2)—N(1)	2.019(4)	
E(2)—N(1*)	2.034(4)	
Bond angles (°)		
C(5)-*E*(1)-N(1)	103.7(2)	93.4(1)
C(5)-*E*(1)-N(1*)	103.3(2)	102.2(1)
N(1)-*E*(1)-N(1*)	77.7(2)	78.7(1)
E(1)-N(1)-*E*(1*)	102.3(2)	101.3(1)
C(6)-*E*(2)-N(1)	104.9(3)	
C(6)-*E*(2)-N(1*)	104.3(2)	
N(1)-*E*(2)-N(1*)	77.7(2)	
E(1)-N(1)-*E*(1*)	102.3(2)	

Fig. 3. ORTEP diagram of **7a** (*R* = Ph; methyl carbon atoms of *t*-Bu groups are removed for clarity; 30% probability ellipsoids). Symmetry transformations used to generate equivalent atoms: $-x + 1, -y, -z + 2$.



same range. As **6** is the first structurally characterized example of a bis(organyl)cyclodibism(III)azane, *R*Bi(μ-N*R*′)$_2$Bi*R*, no direct structural comparisons can be made. However, comparison with [(*R*HN)Bi(μ-N*R*)$_2$(NH*R*)] (*R* = 2,6-*i*-Pr$_2$C$_6$H$_3$) **10**, the only reported analogue (9), shows the bond angles in **6** to be larger, while the Bi—N$_{ring}$ bond distances are similar. The larger bond angles for **5** and **6** are counterintuitive given the steric bulk of the substituted phenyl substituents in **9** and **10**, respectively.

An ORTEP diagram of **7a** is depicted in Fig. 3. The complex **7a** is isostructural with **7b**, reported previously (13*a*), and the metrical parameters are compared in Table 3. The structure shows the pnicogen atom bound to a phenyl carbon atom and two *tert*-butylamido nitrogen atoms in a pyramidal arrangement. One of the lithium atoms (Li(2)) is symmetrically chelated by the ligand in an *N*,*N*′ manner (Li(2)—N(1) = 2.015(4) Å; Li(2)—N(1) = 2.011(4) Å), while the second lithium atom (Li(1)) is bound to one nitrogen atom (N(1)) only (1.916(4) Å). The resulting moiety dimerizes via a short Li(1)—N(2*) interaction (1.920(4) Å) and an η^6-Li···Ph* interaction (Li(2)—C$^*_{phenyl}$ = 2.624(4)–2.752(4) Å) to the second molecule. The most significant differences in

Table 3. Selected bond lengths (Å) and bond angles (°) for **7a** (*E* = As) and **7b** (*E* = P).

	7a	**7b**[a]
Bond lengths (Å)		
E(1)—C(9)	2.004(2)	1.867(3)
E(1)—N(1)	1.853(2)	1.693(2)
E(1)—N(2)	1.850(2)	1.686(3)
Li(1)—N(1)	1.916(4)	1.918(5)
Li(1)—N(2*)	1.920(4)	1.928(6)
Li(2)—N(1)	2.015(4)	2.027(6)
Li(2)—N(2)	2.011(4)	2.017(5)
Li(2)—C$_{phenyl}$	2.624(4)–2.752(4)	2.618(6)–2.750(6)
Bond angles (°)		
C(9)-*E*(1)-N(1)	97.21(7)	99.8(1)
C(9)-*E*(1)-N(2)	97.32(7)	100.8(1)
N(1)-*E*(1)-N(2)	97.15(7)	102.8(1)

[a]Values for one of two unique molecules (13*a*).

the structures of **7a** and **7b** involve the longer *E*—C and (or) *E*—N bond distances and the smaller bond angles at the pnicogen center in **7a** (see Table 3), both of which are a result of the larger covalent radius of As(III) vs. P(III). For comparison with the unsolvated structure of **7a**, crystallization of **7a** from THF produces the trisolvated monomer {(THF)$_3$Li$_2$[PhAs(N-*t*-Bu)$_3$]} in which the [PhAs(N-*t*-Bu)$_2$]$^{2-}$ ligand is *N*,*N*′ chelated to both Li$^+$ ions. Each Li$^+$ ion is further coordinated by one terminal and one bridging THF molecule (26).

Conclusions

The reaction of Ph*E*Cl$_2$ with 2 equiv of LiHN-*t*-Bu has been studied for comparison with previous work on the analogous phosphorus systems, which yield bis(amido)organylphosphines. These reactions result in the formation of PhAs(NH-*t*-Bu)$_2$ in the case of arsenic, while a subsequent condensation reaction to afford the *trans*-cyclodipnict(III)azanes Ph*E*(μ-N-*t*-Bu)$_2$*E*Ph is observed for both the antimony and bismuth systems. This synthetic route represents a novel pathway to *RE*(μ-N*R*′)$_2$*ER* (*E* = Sb, Bi) species, including the first example of a bismuth analogue. The metallation of PhAs(NH-*t*-Bu)$_2$ with Li-*n*-Bu produces a dimeric dilithiated derivative that is isostructural with the phosphorus analogue.

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