

Synthesis and Structures of $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$ and $\text{Bi}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$: Implications for the Steric Limits of Supermesityl Substitution

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Syntheses and isolations of the tris(amino)stibine and tris(amino)bismuthine $\text{E}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$ ($\text{E} = \text{Sb}, \text{Bi}$) from ECl_3 and $\text{LiN}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)$ are described, together with spectroscopic and structural characterization [crystal data for $\text{C}_{54}\text{H}_{90}\text{N}_3\text{Sb}$, $M = 903.04$, space group $P\bar{1}$, $a = 11.491(5) \text{ \AA}$, $b = 24.652(7) \text{ \AA}$, $c = 10.002(5) \text{ \AA}$, $\alpha = 98.38(3)^\circ$, $\beta = 96.44(5)^\circ$, $\gamma = 77.25(3)^\circ$, $V = 2724(2) \text{ \AA}^3$, $D_c = 1.101 \text{ Mg/m}^3$, $Z = 2$, $R = 0.0547$; crystal data for $\text{C}_{54}\text{H}_{90}\text{BiN}_3$, $M = 990.27$, space group $P\bar{1}$, $a = 11.511(5) \text{ \AA}$, $b = 24.785(15) \text{ \AA}$, $c = 9.981(5) \text{ \AA}$, $\alpha = 98.06(5)^\circ$, $\beta = 96.50(4)^\circ$, $\gamma = 77.40(5)^\circ$, $V = 2742(2) \text{ \AA}^3$, $D_c = 1.200 \text{ Mg/m}^3$, $Z = 2$, $R = 0.0619$]. The compounds bear the “bulky” 2,4,6-tri-*tert*-butylphenyl substituent (known as supermesityl or Mes*), and their formation is considered in the context of the same reactions for PCl_3 and AsCl_3 , which have been previously shown to produce the aminoiminopnictine structures $[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]\text{P}=\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)$ and $[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]\text{As}=\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)$. The observations establish the limits of the steric control by the supermesityl substituent and provide qualitative support for the thermodynamic significance of substituent steric strain.

Introduction

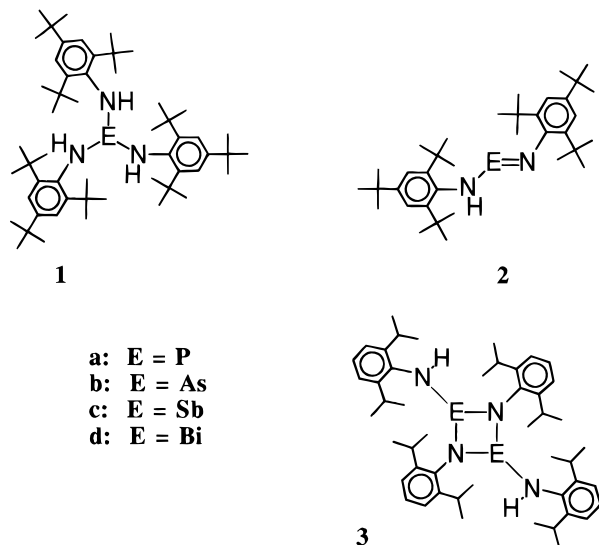
New structure and bonding imposed or stabilized by the presence of sterically “bulky” substituents have been a principal theme for 15 years. There are numerous designs of “bulky” substituents,¹ but 2,4,6-tri-*tert*-butylphenyl ($\text{C}_6\text{H}_2^t\text{Bu}_3$, known as supermesityl or Mes*) is perhaps the most common design and one of the largest and is responsible for the realization of stable compounds containing the heavier ($n > 2$) elements of groups 13,² 14,³ and 15⁴ in low-coordinate environments. The steric shield imposed by “bulky” substituents is frequently rationalized in terms of “kinetic stabilization”,^{5,6} where the substituents are envisaged as hindering the approach of molecules and preventing oligomerization and other types of reaction. However, substituent steric strain in these compounds provides an important thermodynamic contribution to their

stability. For example, there is experimental evidence indicating the preference of $\text{Se}(\text{C}_6\text{H}_2^t\text{Bu}_3)\text{I}$ over the diselenide $(\text{C}_6\text{H}_2^t\text{Bu}_3)_2\text{SeSe}(\text{C}_6\text{H}_2^t\text{Bu}_3)$ and elemental iodine,⁷ representing a unique example of a thermodynamically stable selenium–iodine bond.⁸ In addition, we recently reported the spontaneous elimination of secondary amines from a $\text{C}_6\text{H}_2^t\text{Bu}_3$ -substituted tris(amino)phosphine to give the corresponding iminophosphine containing a dicoordinate phosphorus center.⁹

We now establish some guidelines for the limits of substituent steric strain by the $\text{C}_6\text{H}_2^t\text{Bu}_3$ substituent with the isolation and characterization of the tris(amino)stibine $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$, **1c**, and tris(amino)bismuthine $\text{Bi}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$, **1d**. In addition, we confirm that the phosphorus **1a** and arsenic **1b** analogues are inaccessible in favor of the unsaturated aminoiminopnictines **2** and the comparisons offer insight into the thermodynamic consequences of substituent steric strain.

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Experimental Section

General Procedures. 2,4,6-Tri-*tert*-butylaniline, bismuth(III) chloride, and *n*-butyllithium (1.6 M in hexane) were used as received (Aldrich). Antimony(III) chloride (Aldrich) was twice sublimed *in vacuo* prior to use. Diethyl ether was dried over sodium with benzophenone, hexane was dried over CaH₂, CD₂Cl₂ and CDCl₃ were dried over P₂O₅ and CaH₂, and all solvents were stored in evacuated bulbs. Solids were handled in a VAC Vacuum/Atmospheres nitrogen-filled glovebox, while liquids were manipulated in a nitrogen-filled glovebag. Reactions were performed in sealed reactors,¹⁰ which were flame-dried before use. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany. Infrared spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P FT-IR spectrometer. Raman spectra were recorded on powdered samples sealed under nitrogen in melting point tubes using a Bruker RFS 100 spectrometer. NMR spectra were recorded on a Bruker AC-250. NMR samples were flame-sealed in 5 mm Pyrex tubes. All chemical shifts are reported in ppm relative to an external standard (TMS for ¹H and ¹³C; 85% H₃PO₄ for ³¹P). Crystalline samples were obtained by slow removal of solvent from the reaction mixture within the reaction vessel by passing a cool stream of water over the empty adjacent compartment (or placing it over liquid nitrogen) and distilling the volatiles *in vacuo* (static). Crystals were washed with cool solvent by cold spot back-distillation.¹⁰

In a typical procedure, a solution of ⁿBuLi was slowly added through a rubber septum to a cooled (0 °C) solution of N(C₆H₂^tBu₃)₂ in diethyl ether (50 mL) under N₂ in one chamber of a two-chamber reactor.¹⁰ The resulting solution was warmed to room temperature and slowly (15 min) added to a stirred solution of ECl₃ [LiN(H)(C₆H₂^tBu₃): ECl₃ = 3:1] in diethyl ether (30 mL) in the second chamber. The reaction mixture was frozen and evacuated, and the septum chamber was replaced with a fritted receiver. The mixture was warmed to room temperature, stirred overnight (Sb, yellow; Bi, orange), and then filtered. Slow removal of solvent *in vacuo* gave crystalline solids, which were filtered off and washed four times with hexane (5 mL). ¹H NMR spectra of the reaction mixtures showed the presence of LiN(H)(C₆H₂^tBu₃) and the isolated product (Sb, ~20%; Bi, ~40%, by integration).

Characterization Data for Sb[N(H)(C₆H₂^tBu₃)]₃: Cube-shaped yellow crystals; yield 0.40 g, 0.44 mmol, 25%; dec pt 197–200 °C. Anal. Calcd: C, 71.82; H, 10.05; N, 4.65. Found: C, 72.00; H, 10.21; N, 4.65. IR (cm⁻¹): 3420 m, 3403 m, 3076 w, 1602 w, 1595 sh, 1421 s, 1390 sh, 1335 m, 1286 m, 1257 sh, 1239 sh, 1220 s, 1201 sh, 1170 m, 1141 w, 1113 m, 1019 w, 909 w, 877 m, 837 sh, 827 m, 810 m, 772 m, 749 w, 748 w, 730 w, 575 w, 482 sh, 460 m. Raman (cm⁻¹), 166 mW: 3421 w, 3405 w, 3087 w, 2963 s, 2904 s, 2776 w, 2707 w, 1603 m, 1463 sh, 1445 sh, 1426 w, 1290 m, 1264 w, 1240 sh, 1220

Table 1. Crystallographic Data for Sb[NH(C₆H₂^tBu₃)]₃, **1c**, and Bi[NH(C₆H₂^tBu₃)]₃, **1d**

	1c	1d
empirical formula	C ₅₄ H ₉₀ N ₃ Sb	C ₅₄ H ₉₀ BiN ₃
<i>a</i> (Å)	11.491(5)	11.511(5)
<i>b</i> (Å)	24.652(7)	24.785(15)
<i>c</i> (Å)	10.002(5)	9.981(5)
α (deg)	98.38(3)	98.06(5)
β (deg)	96.44(5)	96.50(4)
γ (deg)	77.25(3)	77.40(5)
<i>V</i> (Å ³)	2724(2)	2742(2)
<i>Z</i>	2	2
fw	903.04	990.27
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
temp (°C)	-20	-20
wavelength, λ (Å)	0.710 69	0.710 69
<i>D_c</i> (g/cm ³)	1.101	1.200
linear abs coeff (mm ⁻¹)	0.540	3.249
transm coeff	0.9087–0.9996	0.8149–1.0000
no. of reflns collected	8020	5660
no. of independent reflns	7577	5114
<i>R</i> (int) ^a	0.0397	0.1117
goodness of fit on <i>F</i> ² ^b	1.207	1.033
<i>R</i> (<i>F</i> _o), ^c > 2σ(<i>I</i>)	0.0547	0.0619
<i>R</i> _w (<i>F</i> _o ²), ^d > 2σ(<i>I</i>)	0.1603	0.1502

^a *R*(int) = $\sum \sum |F_o^2 - F_c^2| / \sum \sum F_o^2$. *n* = number of unique reflections measured more than once; *m* = number of times reflection observed; *F_i*² = average value of *F*² for unique reflection. ^b GOF = $\{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$. *n* = number of reflections; *p* = total number of parameters. ^c *R*(*F*_o) = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^d *R*_w(*F*_o²) = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_c^2)^2]\}^{1/2}$.

sh, 1201 w, 1176 w, 1141 w, 922 w, 814 w, 748 w, 569 w, 480 sh, 458 w, 254 w, 143 w, 105 sh, 85 sh. ¹H NMR: 1.26 (s, 9H), 1.31 (s, 18H), 5.07 (s, 1H), 7.11 (s, 2H). ¹³C NMR: 31.7, 32.9, 34.5, 35.8, 123.1, 138.0, 140.3, 144.3.

Characterization Data for Bi[N(H)(C₆H₂^tBu₃)]₃: Dark orange/red crystals recrystallized from hexane; decomposition occurs in ether and CH₂Cl₂ over a period of days; yield 0.18 g, 0.18 mmol, 11%; dec pt 144–147 °C. Anal. Calcd: C, 65.49; H, 9.16; N, 4.24%. Found: C, 65.76; H, 9.41; N, 4.13. IR (cm⁻¹): 3406 w, 3396 w, 3076 w, 1601 w, 1420 m, 1389 m, 1376 sh, 1285 m, 1220 s, 1200 sh, 1166 sh, 1113 m, 1020 w, 877 m, 825 w, 808 w, 774 m, 730 w, 588 w, 444 w, 393 w. Raman (cm⁻¹), 47 mW: 3405 w, 3390 w, 3086 w, 2958 s, 2904 s, 2777 w, 2705 w, 1601 s, 1463 sh, 1445 sh, 1421 m, 1287 sh, 1253 m, 1220 m, 1198 sh, 1175 sh, 1140 m, 810 m, 741 sh, 727 sh, 723 m, 527 s, 456 sh, 443 m, 393 sh, 343 w, 323 w, 252 w, 153 w, 93 s, decomposition at 166 mW. ¹H NMR: 1.27 (s, 9H), 1.31 (s, 18H), 5.86 (s, 1H), 7.18 (s, 2H). ¹³C NMR: 32.0, 33.0, 34.3, 35.5, 122.2, 139.2, 140.8, 145.9.

NMR Studies of [N(H)(C₆H₂^tBu₃)]E[N(C₆H₂^tBu₃)H₂ (E = P, As). Equimolar mixtures of [N(H)(C₆H₂^tBu₃)]PN(C₆H₂^tBu₃) with N(C₆H₂^tBu₃)H₂ in diethyl ether showed the presence of [N(H)(C₆H₂^tBu₃)]PN(C₆H₂^tBu₃) only by ³¹P NMR. ¹H NMR studies of equimolar mixtures of [N(H)(C₆H₂^tBu₃)]AsN(C₆H₂^tBu₃) with N(C₆H₂^tBu₃)H₂ in CD₂Cl₂ showed the presence of the starting materials only. In both cases, exposure of the samples to ultrasound had no measurable effect.

NMR Studies of Thermolyzed Samples of E[N(H)(C₆H₂^tBu₃)]₃ (E = Sb, Bi). Sealed samples of E[N(H)(C₆H₂^tBu₃)]₃ (E = Sb, Bi) in CD₂Cl₂ were heated (60 °C) with ultrasound for several hours and then examined by ¹H NMR spectroscopy. Sb[N(H)(C₆H₂^tBu₃)]₃ showed no change, while Bi[N(H)(C₆H₂^tBu₃)]₃ produced a white precipitate and signals corresponding to N(C₆H₂^tBu₃)H₂.

X-ray Crystallography. Crystals were selected and mounted in Pyrex capillaries in the drybox. A summary of the crystallographic data is given in Table 1. Structures were solved by Patterson methods which located the Sb and Bi atoms, respectively. The remaining non-hydrogen atoms were located through successive Fourier syntheses and were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions (C–H 1.08 Å, N–H 1.02 Å). Full-matrix least-squares refinement was carried out on *F*² data using

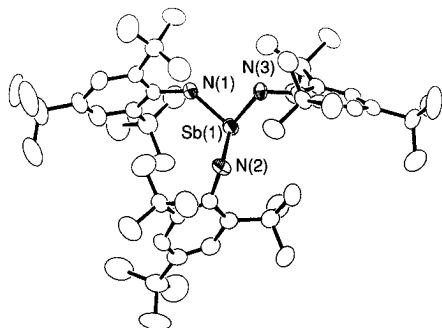


Figure 1. Crystallographic view of $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$, **1c**

Sb(1)–N(1)	2.041(6)	N(1)–Sb(1)–N(3)	85.6(2)
Sb(1)–N(3)	2.048(6)	N(1)–Sb(1)–N(2)	104.4(3)
Sb(1)–N(2)	2.064(6)	N(3)–Sb(1)–N(2)	99.9(2)
N(1)–C(1)	1.423(9)	C(1)–N(1)–Sb(1)	137.8(5)
N(2)–C(7)	1.421(9)	C(7)–N(2)–Sb(1)	117.4(5)
N(3)–C(13)	1.442(8)	C(13)–N(3)–Sb(1)	119.9(4)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\text{Bi}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$, **1d**

Bi(1)–N(1)	2.14(2)	N(1)–Bi(1)–N(3)	106.7(6)
Bi(1)–N(3)	2.179(14)	N(1)–Bi(1)–N(2)	82.7(6)
Bi(1)–N(2)	2.214(13)	N(3)–Bi(1)–N(2)	98.5(5)
N(1)–C(1)	1.47(2)	C(1)–N(1)–Bi(1)	136.6(11)
N(2)–C(7)	1.45(2)	C(7)–N(2)–Bi(1)	114.8(10)
N(3)–C(13)	1.49(2)	C(13)–N(3)–Bi(1)	113.2(10)

SHELXL-93.¹¹ The function minimized was $R_w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2]^{1/2}$. Bond lengths and angles for the *tert*-butyl groups of the $(\text{C}_6\text{H}_2^t\text{Bu}_3)$ units were constrained to 1.54 Å and 109.5°, respectively, and the aromatic moieties of $\text{Bi}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$ were also constrained.

Results and Discussion

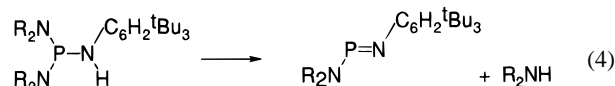
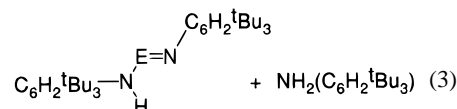
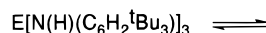
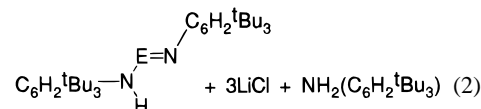
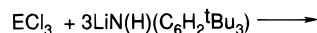
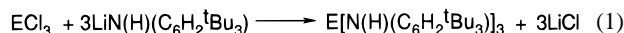
Syntheses and Structures of $\text{E}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$ (E = Sb, Bi). Mixtures of SbCl_3 and BiCl_3 each with 3 equiv of $\text{LiN}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)$ in ether at room temperature undergo incomplete reaction to give $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$, **1c**, and $\text{Bi}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$, **1d**, respectively, as the only identifiable products [^1H NMR spectra of the reaction mixtures show the presence of the product and $\text{LiN}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)$ only]. The new tris(amino) compounds have been isolated and comprehensively characterized, and the solid state structures are isomorphous. A representative view of $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$ is shown in Figure 1, illustrating the substantial steric crowding imposed by the $\text{C}_6\text{H}_2^t\text{Bu}_3$ substituents, which effects a severe distortion from a pyramidal geometry at the pnictogen center in both structures with N–E–N bond angles ranging over 19°. Selected bond lengths and angles are presented in Tables 2 and 3.

To our knowledge, there are no structural reports for tris(amino)stibines. The closest example is the trisaminostibine $\text{Sb}(\text{NPh}_2)_3$ [$\text{Sb}–\text{N}$ 2.081(7), 2.074(7), 2.077(7) Å],¹² with $\text{Sb}–\text{N}$ bond lengths slightly longer than those of $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$ [$\text{Sb}–\text{N}$ 2.041(6), 2.048(6), 2.064(6) Å], which are typical for amido–antimony covalent bonds.¹³ Structural studies on homoleptic tris(amino)bismuthines are rare¹⁴ but reveal consistent $\text{Bi}–\text{N}$ bond lengths [$\text{Bi}(\text{NMe}_2)_3$: 2.189(18), 2.180(21) Å. $\text{Bi}(\text{NPh}_2)_3$: 2.17(2), 2.16(3), 2.26(3), 2.28(2), 2.12(2), 2.21(4) Å] with which the bonds in $\text{Bi}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)_3]$ are comparable

[2.14(2), 2.179(14), 2.214(13) Å] and are significantly shorter than examples of coordinate $\text{N} \rightarrow \text{Bi}$ bonds.¹⁵

Structure Defined by Steric Strain for Aminopnictines.

Although the yields of **1c** and **1d** do not correlate with stoichiometry and the poor progress of the reactions is likely a manifestation of the kinetic consequences of the sterically imposing substituents, we envisage the reactions to proceed according to eq 1. These observations are in contrast to those



for the analogous reactions of PCl_3 and AsCl_3 with $\text{LiN}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)$, which are reported to give the aminoiminopnictines $[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]\text{P}=\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)$, **2a**, and $[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]\text{As}=\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)$, **2b** [the first example of a stable aminoiminoarsine (arsazene)],¹⁶ independent of stoichiometry. To our knowledge, the tris(amino)pnictines **1a** and **1b** have not been observed; nevertheless, the formation of **2a** and **2b** can be viewed in terms of eqs 1 and 2 with the consequential elimination of $\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)_2\text{H}_2$. Consistently, ^{31}P NMR spectra of mixtures of **2a** with excess $\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)_2\text{H}_2$ show no indication

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of reaction. Together, these observations imply that the tris(amino)phosphine **1a** and tris(amino)arsine **1b** are thermodynamically unstable with respect to $\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)_2$ and **2a** or **2b**, respectively (eq 3). Indeed, the spontaneous elimination of secondary amines from tris(amino)phosphines possessing a single $\text{C}_6\text{H}_2^t\text{Bu}_3$ substituent (eq 4)⁹ clearly demonstrates the thermodynamic consequences of substituent steric strain.

The favorable formation of **1c** and **1d** rather than **2c** and **2d** can be superficially understood in terms of the more spacious tris(amino)stibine and -bismuthine environment in comparison with that of the tris(amino)phosphine or -arsine. The E–N bond lengths offer the most obvious comparison. The Sb–N bonds in $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$ [2.041(6), 2.048(6), 2.064(6) Å] and the Bi–N bonds in $\text{Bi}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$ [2.14(2), 2.179(14), 2.214(13) Å] are all in excess of 2 Å, while examples of tris(amino)phosphines^{17,18} [including $\{\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)\}\text{P}\{\text{NCPH}_2\}_2$ ¹⁹ containing the $\text{C}_6\text{H}_2^t\text{Bu}_3$ substituent] and tris(amino)arsines²⁰ reveal a substantially more restricted pnictogen environment (P–N 1.68–1.73 Å; As–N 1.79–1.89 Å). We therefore expect eq 3 for **1a** and **1b** to be exothermic due to the release of substituent strain energy upon elimination of $\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)_2$, consistent with previous experimental observations.⁹ The absence or relatively reduced substituent steric strain in **1c** and **1d** is presumably principally responsible for their relative stability and consequential isolation. In addition, these observations are consistent with recent structural reports for the sterically encumbered homoleptic trithiolates $\text{Sb}[\text{SC}_6\text{H}_3^i\text{Pr}_2]_3$ ²¹ ($\text{C}_6\text{H}_3^i\text{Pr}_2 = 2,6\text{-diisopropylphenyl}$) and $\text{Bi}[\text{S}(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$,²² although the presence of steric strain is indicated by the thermal instability of **1d** with respect to release of elemental bismuth.

Recent reports of the novel heterocyclic structures **3b** (E = As)²³ and **3d** (E = Bi)²⁴ introduce another interesting comparison. Compounds **3** can be considered dimers of the

“arsazene” $[\text{N}(\text{H})(\text{C}_6\text{H}_3^i\text{Pr}_2)]\text{As}=\text{N}(\text{C}_6\text{H}_3^i\text{Pr}_2)$ and “bismazene” $[\text{N}(\text{H})(\text{C}_6\text{H}_3^i\text{Pr}_2)]\text{Bi}=\text{N}(\text{C}_6\text{H}_3^i\text{Pr}_2)$ ($\text{C}_6\text{H}_3^i\text{Pr}_2 = 2,6\text{-diisopropylphenyl}$), respectively. Their formation from ECl_3 and $\text{LiN}(\text{H})(\text{C}_6\text{H}_3^i\text{Pr}_2)$ is independent of reaction stoichiometry, implying thermodynamic preference over the tris(amino)pnictine $\text{E}[\text{N}(\text{H})(\text{C}_6\text{H}_3^i\text{Pr}_2)]_3$ and illustrating the delicate energetic distinction among frameworks **1–3**. We conclude that the replacement of a methyl group from each ortho *tert*-butyl group of the $\text{C}_6\text{H}_2^t\text{Bu}_3$ substituent offers enough steric relief to allow for the association of the “-azene” units, as is clearly evident in the crystal structure of **3d**.²⁴ Arrangement **3** represents a structural alternative to the “-azene”, allowing for a tricoordinate pnictogen center, avoidance of $\text{E}=\text{N}$ π -interactions, and less steric strain than is present in a tris(amino) framework, $\text{E}[\text{N}(\text{H})(\text{C}_6\text{H}_3^i\text{Pr}_2)]_3$. Such a structure is precluded by the extra methyl group (*tert*-butyl rather than isopropyl) in the $\text{C}_6\text{H}_2^t\text{Bu}_3$ substituent, and the tris(amino) **1** framework therefore becomes the most thermodynamically favorable arrangement. The data do not preclude the elimination of $\text{N}(\text{C}_6\text{H}_2^t\text{Bu}_3)_2$ from **1c** or **1d** but indicate that such a process is part of equilibrium **3** rather than dimerization to give **3**.

Conclusions

The isolation of sterically burdened $\text{Sb}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$ and $\text{Bi}[\text{N}(\text{H})(\text{C}_6\text{H}_2^t\text{Bu}_3)]_3$ offer useful comparisons with the unstable phosphorus and arsenic analogues and provide guidelines for the limits of substituent steric strain imposed by the $\text{C}_6\text{H}_2^t\text{Bu}_3$ substituent.

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Supporting Information Available: Listings of crystal data, positional parameters, bond lengths and angles, and anisotropic thermal parameters for **1c** and **1d** (40 pages). Ordering information is given on any current masthead page.

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