Inorg. Chem. **1996,** *35,* 6179−6183

Synthesis and Structures of Intramolecularly Base-Coordinated Aryl Group 15 Compounds

Smuruthi Kamepalli, Claire J. Carmalt, Robert D. Culp, Alan H. Cowley,* and Richard A. Jones

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas, 78712

Nicholas C. Norman

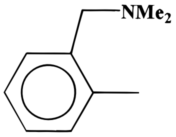
The University of Bristol, School of Chemistry, Cantock's Close, Bristol BS8 1TS, U.K.

Received May 9, 1996[⊗]

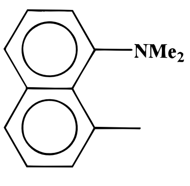
Several group 15 compounds of the type EAr_3 (Ar = 2-[(dimethylamino)methyl]phenyl; E = As (**4**), Sb (**5**), Bi (**6**)) have been prepared via salt elimination reactions of 2-$(Me_2NCH_2)C_6H_4Li$ and ECl_3. Treatment of the lithium salt of the 8-(dimethylamino)-1-naphthyl ligand (Ar′) with $AsCl_3$ afforded a triaryl derivative, $AsAr'_3$ (**7**). The X-ray crystal structures of **4**−**7** are described, and the observed trends in the degree of intramolecular coordination of the nitrogen atoms are discussed. Crystal data for **4**: monoclinic, space group $P2_1/c$, $a = 8.9336(6)$ Å, $b = 16.347(2)$ Å, $c = 17.875(2)$ Å, $\beta = 102.540(7)°$, $V = 2548.2(4)$ Å^3, $Z = 4$, $R = 0.0579$. Crystal data for **5**: monoclinic, space group $P2_1$, $a = 9.288(2)$ Å, $b = 18.356(4)$ Å, $c = 15.566(2)$ Å, $\beta = 90.28(2)°$, $V = 2654.1(8)$ Å^3, $Z = 4$, $R = 0.0520$. Crystal data for **6**: monoclinic, space group $P2_1$, $a = 9.2996(12)$ Å, $b = 18.445(3)$ Å, $c = 15.601(2)$ Å, $\beta = 90.076(11)°$, $V = 2676.1(7)$ Å^3, $Z = 4$, $R = 0.0783$. Crystal data for **7**: monoclinic, space group $P2_1/c$, $a = 9.5744(12)$ Å, $b = 16.273(2)$ Å, $c = 18.884(3)$ Å, $\beta = 100.708(11)°$, $V = 2890.9(7)$ Å^3, $Z = 4$, $R = 0.0495$.

Introduction

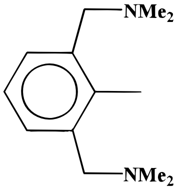
Ligands with the potential for supplemental Lewis base interactions such as **1**,[1] **2**,[2] and **3**[3] are finding increasing utility for the stabilization of electrophilic main group species such as group 13 hydrides[4] and intermetallics.[5] The use of ligands **1**−**3** has also permitted the isolation of several compounds with unusual geometries and/or solid state structures. A noteworthy development in this regard is the isolation of hypercoordinate main group compounds in which the customary coordination number is expanded by virtue of intramolecular dative interactions. In the context of group 15, for example, use of ligand **3** resulted in a series of trivalent compounds of general formula $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]ECl_2$ (E = P, As, Sb, Bi).[6] The antimony derivative was characterized structurally and found to possess an overall pentacoordinate arrangement in which the $(aryl)SbCl_2$ moiety adopts an unusual T-shaped geometry. In a more recent development[7] it has been shown that tris[8-(dimethylamino)-1-naphthyl]phosphine and tris[2-((dimethylamino)methyl)phenyl]phosphine feature hexacoordinate P(III) centers[8] in the solid state. The hypercoordinate behavior of these phosphines represents an interesting contrast to the observation that the structures of conventional triaryl pnictogen derivatives evince no short intermolecular interactions.[9] Ligand **1** has been also utilized in the synthesis of chiral chlorobismuthines[10] stabilized by the intramolecular coordination of the dimethylamino group. It should be noted, however, that when the Lewis acidity and size of the central atom increase, as in the case of Bi(III) halides, the coordination of additional halide ions or neutral two-electron-donor ligands is commonplace. A number of structural trends in these and related systems have become apparent.[11,12]



1



2



3

In this contribution, we describe the synthesis and X-ray structural assay of triaryl derivatives of As(III), Sb(III), and Bi-

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) (a) van Koten, G.; Noltes, J. C.; Spek, A. L. *J. Organomet. Chem.* **1976**, *118*, 183. (b) For a review see: Carmalt, C. J.; Cowley, A. H. *Main Group Chem. News,* in press.

(2) Jastrzebski, J. T. B. H.; Knaap, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287.

(3) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C. *J. Organomet. Chem.* **1978**, *148*, 233.

(4) Cowley, A. H.; Gabbaï, F. P.; Atwood, D. A.; Carrano, C. J.; Mokry, L.; Bond, M. J. *J. Am. Chem. Soc.* **1994**, *116*, 1559. Contreras, L.; Cowley, A. H.; Gabbaï, F. P.; Jones, R. A.; Carrano, C. J.; Bond, M. R. *J. Organomet. Chem.* **1995**, *489*, C1. Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1995**, *14*, 2400. Cowley, A. H.; Gabbaï, F. P.; Isom, H. S.; Decken, A. *J. Organomet. Chem.* **1995**, *500*, 81

(5) Olazábal, C. A.; Gabbaï, F. P.; Cowley, A. H.; Carrano, C. J.; Mokry, L. M.; Bond, M. R. *Organometallics* **1994**, *13*, 421.

(6) Atwood, D. A.; Cowley, A. H.; Ruiz, J. *Inorg. Chim. Acta* **1992**, *198*, 271.

(7) Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reye, C.; Declereq, J P.; Dubourg, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1430. For related work, see: Carré, F.; Chuit, C.; Corriu, R. J. P.; Montforte, P.; Nayyar, N. K.; Reyé, C. *J. Organomet. Chem.* **1995**, *499*, 147.

(8) In ref 7, these are referred to as heptacoordinate species because of the inclusion of the phosphorus lone pair. We prefer to exclude the phosphorus lone pair from the coordination number count and refer to these as hexacoordinate.

(9) (a) Adams, E. A.; Kolis, J. W.; Pennigton, W. T. *Acta. Crystallogr.* **1990**, *C46*, 917. (b) Hawley, D. M.; Ferguson, G. *J. Chem. Soc. A* **1968**, 2059. (c) Trotter, J. *Can. J. Chem.* **1963**, *41*, 14. (d) Sobolew, A. N.; Romm, I. P.; Belskii, V. K.; Guryanova, E. N. *Koord. Khim.* **1980**, *6*, 945. (e) Whitmire, K. H.; Labahn, D.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *J. Organomet. Chem.* **1991** *402* 55.

(10) Suzuki, H.; Murafuji, T.; Matano, Y.; Azuma, N. *J. Chem. Soc., Perkin Trans.* **1993**, *1*, 2969.

(11) Clegg, W.; Errington, R. J.; Fisher, G. A.; Hockless, D. C. R.; Norman, N. C.; Orpen, A. G.; Stratford, S. E. *J. Chem. Soc., Dalton Trans.* **1992**, 1967.

S0020-1669(96)00516-2 CCC: $12.00

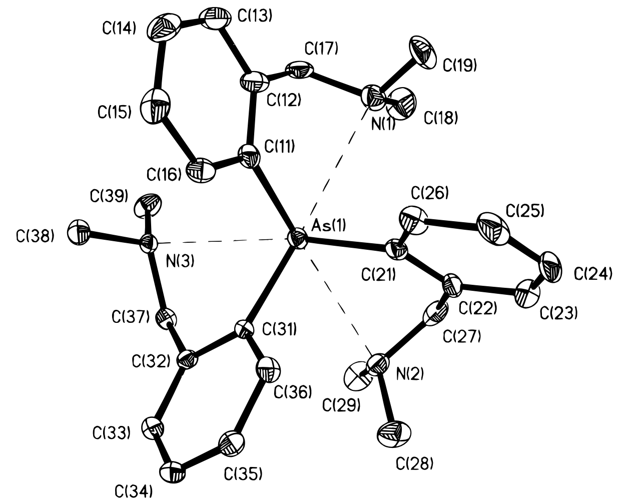
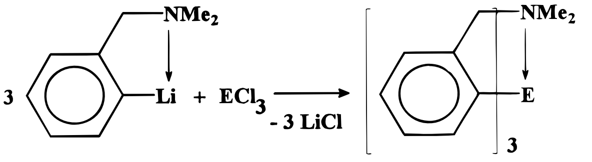


Figure 1. View of the molecular structure of **4** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

(III) that feature ligands **1** and **2**. Our interest in preparing intramolecularly base-coordinated compounds of the heavier group 15 elements was stimulated by two general considerations. First, we were interested to see to what extent triaryl species would coordinate additional ligands if the donor sites were constrained to lie close to or within the primary coordination sphere, with particular emphasis being placed on how this feature varied down group 15. Second, there existed the possibility that molecules of this type might serve as precursors for the deposition of inter-group 15 phases. Such materials have been shown to behave as semiconductors.[13]

Results and Discussion

The colorless crystalline compounds **4**−**6** were prepared via the salt elimination reaction of [2-((dimethylamino)methyl)-phenyl]lithium with the appropriate element trichloride in toluene or Et_2O solution at −78 °C as summarized in eq 1.



(1)

E = As (**4**), Sb (**5**), Bi (**6**)

Satisfactory elemental analytical data were obtained for each new compound. Moreover, the ^1H and ^{13}C NMR spectra of **4**−**6** are consistent with the anticipated formulas. However, in order to reveal the extent to which the NMe_2 groups are coordinated to the group 15 element centers, it was necessary to determine the structures of all three compounds by X-ray crystallography.

The structures of **4**−**6** are illustrated in Figures 1−3, respectively, and selected bond distance and angle data have been compiled in Table 1. The solid state structures of all three compounds comprise individual molecules, and there are no unusually short intermolecular contacts between the monomeric units.

Compound **4** crystallizes in the space group $P2_1/c$ with four molecules per unit cell. Although not required crystallographically, individual molecules of **4** possess approximate C_3 symmetry. The primary coordination sphere consists of a trigonal pyramidal AsC_3 skeleton, and the average As−C bond length (1.982(2) Å) and C−As−C bond angle (98.5(9)°) do not differ greatly from those in triarylarsines such as $As(4\text{-}MeC_6H_4)_3$ (average As−C 1.96(5) Å and C−As−C 102°). However, weak secondary interactions between the pendant amines and the arsenic center are also evident. The orientations of these interactions are such that the formal lone pairs of the NMe_2 groups are directed toward the arsenic center and the As⋯N vectors lie approximately *trans* to the As−C bonds with N⋯As−C angles ranging from 167.5(3) to 168.5(2)°. Although the arsenic−nitrogen distances (average 2.97(4) Å) are less than the sum of van der Waals radii for arsenic and nitrogen (3.5 Å), they exceed typical N−As covalent bond distances (1.91 Å). If these subsidiary As⋯N interactions are included, the overall geometry at arsenic is that of a distorted octahedron in which the distortion is derived from an opening on the N_3As face as evidenced by the large N⋯As⋯N angles (range 108.1(2)−111.7(2)°). In terms of the stereochemical activity of the As(III) lone pair, this moiety may therefore be considered to point toward the N_3As face or, alternatively, to reside at the vertex of the AsC_3 pyramid. Such distortions have been observed previously in a number of group 15 compounds.[14,15] For comparison, the structure of the related germanium com-

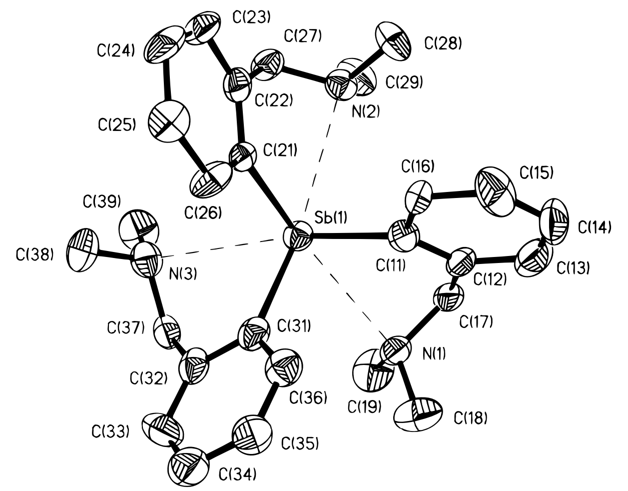


Figure 2. View of one of the independent molecules of **5** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

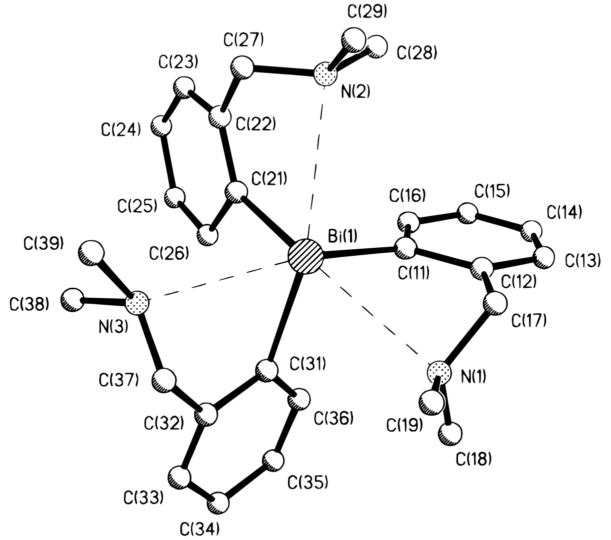


Figure 3. View of the structure of **6** showing the atom-numbering scheme. Atoms are drawn as spheres of arbitrary radius (note that **6** is isomorphous with **5**).

---

(12) Carmalt, C. J.; Cowley, A. H.; Decken, A.; Norman, N. C. *J. Organomet. Chem.* **1995**, *496*, 59.

(13) Carmalt, C. J.; Cowley, A. H.; Hector, A. L.; Norman, N. C.; Parkin, I. P. *J. Chem. Soc., Chem. Commun.* **1994**, 1987.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds **4**−**7**

compound **4**		compound **5**		compound **6**		compound **7**	
As(1)−C(31)	1.989(5)	Sb(1)−C(31)	2.18(2)	Bi(1)−C(31)	2.28(2)	As−C(13)	1.989(3)
As(1)−C(11)	1.977(7)	Sb(1)−C(11)	2.19(2)	Bi(1)−C(11)	2.22(3)	As−C(1)	2.003(3)
As(1)−C(21)	1.980(7)	Sb(1)−C(21)	2.205(13)	Bi(1)−C(21)	2.30(2)	As−C(25)	1.994(3)
As(1)−N(3)	2.936(5)	Sb(1)−N(3)	3.03(2)	Bi(1)−N(3)	3.04(2)	As−N(3)	2.855(3)
As(1)−N(1)	2.961(5)	Sb(1)−N(1)	3.04(2)	Bi(1)−N(1)	3.08(2)	As−N(1)	2.813(3)
As(1)−N(2)	3.030(6)	Sb(1)−N(2)	3.041(11)	Bi(1)−N(2)	3.11(3)	As−N(2)	2.807(3)
		Sb(2)−C(51)	2.125(13)	Bi(2)−C(51)	2.26(3)		
		Sb(2)−C(61)	2.17(2)	Bi(2)−C(61)	2.26(3)		
		Sb(2)−C(41)	2.185(14)	Bi(2)−C(41)	2.32(2)		
		Sb(2)−N(5)	3.001(14)	Bi(2)−N(5)	2.97(2)		
		Sb(2)−N(6)	3.03(2)	Bi(2)−N(6)	2.99(3)		
		Sb(2)−N(4)	3.16(2)	Bi(2)−N(4)	3.15(2)		
C(11)−As(1)−C(21)	99.2(3)	C(11)−Sb(1)−C(21)	94.5(5)	C(11)−Bi(1)−C(21)	91.4(9)	C(13)−As−C(25)	99.42(14)
C(11)−As(1)−C(31)	98.9(3)	C(11)−Sb(1)−C(31)	95.0(5)	C(11)−Bi(1)−C(31)	95.1(10)	C(13)−As−C(1)	96.54(12)
C(21)−As(1)−C(31)	97.5(3)	C(21)−Sb(1)−C(31)	94.0(5)	C(21)−Bi(1)−C(31)	92.4(10)	C(25)−As−C(1)	96.31(13)
C(31)−As(1)−N(3)	71.0(2)	C(31)−Sb(1)−N(3)	68.3(5)	C(31)−Bi(1)−N(3)	67.2(9)	C(13)−As−N(2)	73.61(11)
C(11)−As(1)−N(1)	71.5(2)	C(11)−Sb(1)−N(1)	66.4(5)	C(11)−Bi(1)−N(1)	69.0(8)	C(25)−As−N(3)	71.62(11)
C(21)−As(1)−N(2)	71.5(2)	C(21)−Sb(1)−N(2)	68.5(4)	C(21)−Bi(1)−N(2)	64.9(9)	C(1)−As−N(1)	72.82(11)
N(3)−As(1)−N(1)	113.7(2)	N(3)−Sb(1)−N(1)	115.1(4)	N(3)−Bi(1)−N(1)	114.6(7)	N(3)−As−N(1)	108.09(8)
N(3)−As(1)−N(2)	108.1(2)	N(3)−Sb(1)−N(2)	111.0(4)	N(3)−Bi(1)−N(2)	109.1(7)	N(3)−As−N(2)	106.60(8)
N(1)−As(1)−N(2)	111.7(2)	N(1)−Sb(1)−N(2)	118.1(4)	N(1)−Bi(1)−N(2)	122.3(7)	N(1)−As−N(2)	106.32(9)
		C(51)−Sb(2)−C(61)	95.7(5)	C(51)−Bi(2)−C(61)	95.4(10)		
		C(51)−Sb(2)−C(41)	94.0(5)	C(51)−Bi(2)−C(41)	92.1(10)		
		C(61)−Sb(2)−C(41)	94.9(6)	C(61)−Bi(2)−C(41)	95.6(9)		
		C(41)−Sb(2)−N(4)	66.2(6)	C(41)−Bi(2)−N(4)	67.6(9)		
		C(51)−Sb(2)−N(5)	67.8(5)	C(51)−Bi(2)−N(5)	66.7(8)		
		C(61)−Sb(2)−N(6)	67.5(5)	C(61)−Bi(2)−N(6)	67.0(9)		
		N(5)−Sb(2)−N(6)	112.0(4)	N(5)−Bi(2)−N(6)	111.4(7)		
		N(5)−Sb(2)−N(4)	107.5(6)	N(5)−Bi(2)−N(4)	109.1(8)		
		N(6)−Sb(2)−N(4)	122.1(5)	N(6)−Bi(2)−N(4)	122.2(7)		

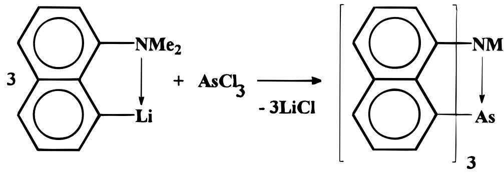
pound,[16] $(2\text{-}Me_2NCH_2C_6H_4)_3GeH$, is somewhat different in that the average C−Ge−C angle is 106.8°. The observation of a significantly larger angle than the corresponding angle in **4** indicates clearly the stereochemical consequences of exchanging a hydride ligand for a lone pair. The C−Ge···N angles in the germanium derivative range from 172.5 to 176.8(3)° (average 174.0°).

Compound **5** crystallizes in the acentric space group $P2_1$ with two independent molecules per asymmetric unit. The metrical parameters and stereochemical features of the independent molecules are very similar. The structure of **5** (Figure 2) bears a very close resemblance to that of **4**. The pertinent bond distances and angles for **5** (averaged over both molecules) are Sb−C 2.17(2) Å, Sb···N 3.05(5) Å, C−Sb−C 94.6(6)°, N···Sb−C 160.23(2)°, and N···Sb···N 114.3(5)°. Given the similarities between **4** and **5**, all of the discussion for **4** presented above is therefore also valid for **5**. There are, however, some differences between **4** and **5** which are worth noting. First, the difference between the Sb−C and Sb···N average bond lengths (Δ) is 0.875 Å for **5** whereas the corresponding value of Δ for **4** (i.e. between the As−C and As···N bonds) is 0.993 Å. This reflects a stronger interaction with the nitrogen atom and, in the former case, is consistent with the antimony center being more Lewis acidic and also with the larger size of antimony which, in turn, renders it more able to support a larger coordination number. Second, the N_3C_3Sb octahedron is more distorted than that in **4** as a consequence of the constraints imposed by the [(dimethylamino)methyl]phenyl ligand. Third, the average C−Sb−C angle in **5** (94.6(6)°) is smaller than the corresponding C−As−C angle in **4** (98.5(9)°), consistent with generally observed group trends.

Compound **6** is isomorphous with **5** and crystallizes in the space group $P2_1$ with two independent molecules per asymmetric unit. Unfortunately, the structure of **6** is not of stellar quality due both to mediocre crystallinity and to high absorbance on the part of the bismuth atom. Thus, although the atom connectivity is undoubtedly correct (ball and stick diagram, Figure 3), the metrical parameters for **6** (Table 1) should be viewed with due caution. Nevertheless, it is clear (a) that the differences between **5** and **6** continue the trends described above for **4** and **5** and (b) that the C−Bi−C angles are smaller than those observed for **4** and **5**. Such a trend in C−E−C bond angles is common in group 15 and has been observed in e.g. the series $As(tolyl)_3$, $SbPh_3$, and $BiPh_3$.[9] One other noteworthy feature is that the N···Bi distances in **6** (average 3.07(3) Å) are appreciably longer than that in the related complex $(2\text{-}Me_2NCH_2C_6H_4)Bi(tolyl)Cl$[10] (2.52(6) Å). It is presumed that the stronger interaction in the latter stems from that *trans* disposition of the N···Bi−Cl bonds.

Comparison of the structures of **4**−**6** with that of the phosphorus analogue reveals that the trends discussed above are continued for the lighter congener: P···N 3.02(3) Å, C−P−C 100.7(5)°, and N···P−C 171.2(3)−173.1(3)°.[7]

The colorless crystalline compound **7** was prepared via the salt elimination reaction of [8-(dimethylamino)naphthyl]lithium with arsenic trichloride in toluene or Et_2O solution at −78 °C as shown in eq 2. Analytical and NMR data are consistent with the expected formula, and the structure was confirmed by X-ray crystallography, the results of which are shown in Figure 4; selected bond lengths and angles are given in Table 1.



(2)

7

---

(14) Clegg, W.; Elsegood, M. R. J.; Graham, V.; Norman, N. C.; Pickett, N. L. *J. Chem. Soc., Dalton Trans.* **1993**, 997.

(15) Clegg, W.; Elsegood, M. R. J.; Norman, N. C.; Pickett, N. L. *J. Chem. Soc., Dalton Trans.* **1994**, 1753.

(16) Brelière, C.; Carré, F.; Corriu, R. J. P.; Royo, G. *Organometallics* **1988**, *7*, 1006.

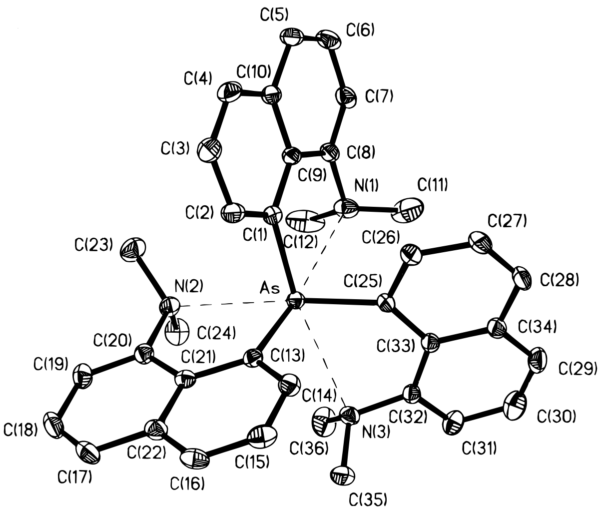


Figure 4. View of the molecular structure of **7** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

The structure of **7** is broadly similar to that of **4** with relevant average metrical parameters As−C 1.995(7) Å, As⋯N 2.82(2) Å, C−As−C 97.42(1)°, N⋯As−C 169.84(2)°, and N⋯As⋯N 107.11(4)°. One of the points to note in comparing **7** with **4** is that the As⋯N distances in **7** are somewhat shorter than those in **4**, and Δ (0.82 Å) is smaller, possibly as a consequence of the reduced flexibility of the aminonaphthyl group. This rigidity also explains the fact that the ^{1}H NMR spectrum of **7** comprises two singlets for the NMe$_2$ groups whereas the ^{1}H NMR spectrum of **4** exhibits a sharp singlet. As in the case of **4**, the formal lone pairs of the NMe$_2$ groups are directed toward the arsenic center and are disposed such that the As⋯N vectors lie approximately *trans* to the As−C bonds (average N⋯As−C 169.8(2)°).

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen or argon atmosphere using standard Schlenk techniques or a HE-493 Vacuum Atmospheres drybox. Unless otherwise stated, all solvents were dried over sodium and distilled from sodium benzophenone ketyl under argon prior to use. The reagents 2-(Me$_2$NCH$_2$)C$_6$H$_4$Li and 8-(Me$_2$N)C$_{10}$H$_6$Li were prepared according to literature methods.[1,2] All other reagents were purchased from Aldrich Chemicals and used without further purification. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Physical Measurements. Mass spectra (CIMS) were run on a MAT 4023 instrument, and NMR spectra were recorded on a GE QE-300 spectrometer (^{1}H, 300.19 MHz; ^{13}C, 75.48 MHz). NMR spectra were referenced to C$_6$D$_6$ which was dried over sodium−potassium alloy and distilled prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to Si(CH$_3$)$_4$ (0.00 ppm). Melting points were obtained in sealed glass capillaries under argon (1 atm) and are uncorrected.

Preparations. Compound 4. A solution of AsCl$_3$ (0.43 g, 2.37 mmol) in 20 mL of Et$_2$O was added via cannula to a stirred slurry of 2-(Me$_2$NCH$_2$)C$_6$H$_4$Li (1.00 g, 7.10 mmol) in 20 mL of Et$_2$O at −78 °C. The reaction temperature was maintained at −78 °C for 2 h, following which the reaction mixture was allowed to warm slowly to ambient temperature. After being stirred for an additional 12 h, the reaction mixture was filtered and the filtrate was warmed and concentrated to a total volume of 15 mL. Cooling of the resulting solution to −20 °C overnight afforded a 70% yield of colorless, crystalline **4** (mp 116 °C). Anal. Calcd for C$_{27}$H$_{36}$N$_3$As: C, 67.91; H, 7.59; N, 8.79. Found: C, 67.37; H, 7.81; N, 8.17. CIMS (CH$_4$): m/z = 477 (M$^+$ + H), 343 (M − ligand), 134 (ligand). ^{1}H NMR (C$_6$D$_6$): δ 1.92 (s, 18H, NMe$_2$), 3.61 (s, 6H, CH$_2$), 6.97 (t, 3H, C$_6$H$_4$), 7.09 (m, 6H, C$_6$H$_4$), 7.31 (t, 3H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 44.68 (CH$_3$), 64.46 (CH$_2$), 127.24 (CH, C$_6$H$_4$), 129.24 (CH, C$_6$H$_4$), 135.47 (CH, C$_6$H$_4$), 143.36 (C, C$_6$H$_4$), 143.76 (CH, C$_6$H$_4$), *ipso* carbon not detected.

Compound 5. A solution of SbCl$_3$ (0.54 g, 2.36 mmol) in 20 mL of Et$_2$O was added via cannula to a stirred slurry of 2-(Me$_2$NCH$_2$)C$_6$H$_4$-Li (1.00 g, 7.00 mmol) in 20 mL of Et$_2$O at −78 °C. The reaction temperature was maintained at −78 °C for 2 h, following which the reaction mixture was allowed to warm slowly to ambient temperature. After being stirred for an additional 12 h, the reaction mixture was filtered and the solvent was removed *in vacuo*. Slow (48 h) annealing of the residue (maximum temperature 70 °C) resulted in a 60% yield of colorless, crystalline **5** (mp 126−130 °C). Anal. Calcd for C$_{27}$H$_{36}$N$_3$-Sb: C, 61.84; H, 6.91; N, 8.01. Found: C, 60.33; H, 7.02; N, 7.73. CIMS (CH$_4$): m/z = 524 (M$^+$ + H), 389 (M − ligand), 136 (ligand + H). ^{1}H NMR (C$_6$D$_6$): δ 1.84 (s, 18H, NMe$_2$), 3.46 (s, 6H, CH$_2$), 6.95 (t, 3H, C$_6$H$_4$), 7.07 (m, 6H, C$_6$H$_4$), 7.53 (d, 3H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 44.27 (CH$_3$), 64.41 (CH$_2$), 126.77 (CH, C$_6$H$_4$), 128.87 (CH, C$_6$H$_4$), 137.66 (CH, C$_6$H$_4$), 138.74 (CH, C$_6$H$_4$), 144.93 (C, C$_6$H$_4$), 146.64 (C, C$_6$H$_4$).

Compound 6. A slurry of 2-(Me$_2$NCH$_2$)C$_6$H$_4$Li (2.72 g, 19.0 mmol) in 20 mL of toluene was added via cannula to a stirred solution of BiCl$_3$ (2.00 g, 6.34 mmol) in 20 mL of toluene at −78 °C. The reaction temperature was maintained at −78 °C for 2 h, following which the reaction mixture was allowed to warm slowly to ambient temperature. After being stirred for an additional 12 h, the reaction mixture was filtered and the filtrate was concentrated to a total volume of 15 mL. Cooling of the resulting solution to −20 °C overnight afforded an 81% yield of colorless, crystalline **6** (mp = 128−130 °C). Anal. Calcd for C$_{27}$H$_{36}$NBi: C, 53.08; H, 5.94; N, 6.88. Found: C, 52.97; H, 5.92; N, 6.85. CIMS (CH$_4$): m/z = 612 (M$^+$ + H), 478 (M − ligand), 343 (M − 2 ligand), 136 (ligand + H). ^{1}H NMR (C$_6$D$_6$): δ 1.93 (s, 18H, NMe$_2$), 3.44 (s, 6H, CH$_2$), 7.05 (t, 3H, C$_6$H$_4$), 7.15 (d, 3H, C$_6$H$_4$), 7.20 (t, 3H, C$_6$H$_4$), 8.10 (d, 3H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 44.69 (CH$_3$), 68.08 (CH$_2$), 127.00 (CH, C$_6$H$_4$), 129.20 (CH, C$_6$H$_4$), 129.68 (CH, C$_6$H$_4$), 140.70 (CH, C$_6$H$_4$), 145.27 (C, C$_6$H$_4$), 166.76 (C, C$_6$H$_4$).

Compound 7. A slurry of 8-(Me$_2$N)C$_{10}$H$_6$Li (0.99 g, 5.61 mmol) in 20 mL of toluene was added via cannula to a stirred solution of AsCl$_3$ (0.34 g, 1.87 mmol) in 20 mL of toluene at −78 °C. The reaction temperature was maintained at −78 °C for 2 h, following which the reaction mixture was allowed to warm slowly to ambient temperature. After being stirred for an additional 12 h, the reaction mixture was filtered and the solution was concentrated to a total volume of 15 mL. Cooling of the resulting solution to −20 °C overnight afforded an 80% yield of colorless, crystalline **7** (mp 270 °C dec). Anal. Calcd for C$_{36}$H$_{36}$N$_3$As: C, 73.83; H, 6.19; N, 7.17. Found: C, 73.69; H, 6.22; N, 7.11. ^{1}H NMR (C$_6$D$_6$): δ 1.60 (s, 9H, NMe), 2.62 (s, 9H, NMe), 6.81 (t, 3H, C$_6$H$_4$), 7.25 (m, 9H, C$_6$H$_4$), 7.37 (d, 3H, C$_6$H$_4$), 7.49 (t, 3H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 45.80 (CH$_3$), 48.91 (CH$_3$), 120.07 (CH, C$_8$H$_6$), 125.17 (CH, C$_8$H$_6$), 126.03 (CH, C$_8$H$_6$), 126.76 (CH, C$_8$H$_6$), 127 (CH, C$_8$H$_6$), 135.25 (C, C$_8$H$_6$), 135.84 (CH, C$_8$H$_6$), 136.13 (C, C$_8$H$_6$), 145.43 (C, C$_8$H$_6$), 153.98 (C, C$_8$H$_6$).

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **4**−**7** are given in Table 2. Crystals of **4** were grown from diethyl ether solution at −20 °C whereas **6** and **7** were grown from toluene solutions stored at −20 °C. Crystals of **5** were grown by annealing powdered **5** at 70 °C for 48 h. Crystals of **4** and **7** were mounted on glass fibers, and crystals of **5** and **6** were mounted in thin-walled glass capillaries and sealed under argon (1 atm). Data sets for **4** and **7** were collected on a Siemens P4 diffractometer at −100 °C, and an Enraf-Nonius CAD4 diffractometer was used for the collection of data for compounds **5** and **6** at 25 °C. Graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used for all structures. The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using the Siemens SHELXTL PLUS 5.0 (PC) software package.[17] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. As a result of the low quality of the crystal of **6** and the presence of a highly absorbing bismuth atom, problems were encountered with some thermal and atomic parameters. Hence, in order to prevent several atoms from going "non-positive definite", all carbon and nitrogen atoms of **6** were subjected to rigid bond restraints; i.e., the components of the anisotropic displacement parameters in the direction of the bond

---

(17) Sheldrick, G. M. *SHELXTL PC Version 5.0*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.

Table 2. Crystal Data and Details of Intensity Measurement and Structure Refinement for **4**−**7**

	4	**5**	**6**	**7**
formula	$C_{27}H_{36}N_3As$	$C_{27}H_{36}N_3Sb$	$C_{27}H_{36}N_3Bi$	$C_{36}H_{36}N_3As$
fw	477.51	524.34	611.57	585.60
temp, K	173(2)	293(2)	293(2)	193(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$	$P2_1$	$P2_1/c$
a, Å	8.9336(6)	9.288(2)	9.2996(12)	9.5744(12)
b, Å	16.347(2)	18.356(4)	18.445(3)	16.273(2)
c, Å	17.875(2)	15.566(2)	15.601(2)	18.884(3)
β, deg	102.540(7)	90.28(2)	90.076(11)	100.708(11)
V, Å^3	2548.2(4)	2654.1(8)	2676.1(7)	2890.9(7)
Z	4	4	4	4
d(calc), g/cm^3	1.245	1.312	1.518	1.345
abs coeff, cm^{-1}	13.52	10.57	66.05	12.06
cryst size, mm	0.45 × 0.18 × 0.11	0.56 × 0.25 × 0.13	0.48 × 0.47 × 0.19	0.50 × 0.38 × 0.14
θ range, deg	2.33−22.50	2.19−24.97	2.55−24.97	2.16−27.50
abs cor	SHELXA	SHELXA	SHELXA	SHELXA
max/min T_0	0.90406/0.57501	0.92428/0.53565	0.61909/0.13519	0.91417/0.53076
GOF on F^2	1.019	1.033	1.080	1.004
wR2/R1[a]	0.1177/0.0579	0.1171/0.0520	0.2130/0.0783	0.0980/0.0495

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\mathrm{Max}(0,F_o^2)/3 + 2F_c^2/3]$.

Table 3. Selected Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(C_9H_{12}N)_3As$ (**4**)

atom	*x*	*y*	*z*	*U*(eq)[a]
As(1)	2507(1)	6272(1)	2767(1)	25(1)
N(1)	5143(6)	6779(4)	3989(3)	39(2)
N(2)	433(6)	5086(4)	3363(3)	33(2)
N(3)	3400(6)	5518(3)	1438(3)	22(1)
C(11)	3532(8)	7207(4)	2387(4)	29(2)
C(21)	1523(7)	6857(5)	3503(4)	30(2)
C(31)	669(6)	6191(5)	1913(3)	26(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(C_9H_{12}N)_3Sb$ (**5**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Sb(1)	26385(1)	7486(1)	6590(1)	54(1)
Sb(2)	21227(1)	7507(1)	11598(1)	57(1)
N(1)	27758(15)	8890(8)	5968(9)	8(4)
N(2)	23916(11)	6851(7)	5541(7)	62(3)
N(3)	28482(14)	6307(9)	7129(10)	73(4)
N(4)	23539(19)	8376(13)	10529(12)	120(7)
N(5)	18969(14)	8574(9)	12155(9)	69(4)
N(6)	19921(16)	6096(9)	10956(8)	79(2)
C(11)	24942(16)	8428(9)	6646(9)	58(4)
C(21)	24996(12)	6784(8)	7382(9)	46(3)
C(31)	27722(14)	7831(8)	7674(9)	62(4)
C(51)	20027(13)	7121(7)	12665(9)	52(3)
C(61)	22768(17)	6616(9)	11594(9)	66(4)
C(41)	22571(14)	8231(8)	12377(10)	62(4)

[a] See footnote *a* in Table 3.

Table 5. Selected Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(C_9H_{12}N)_3Bi$ (**6**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Bi(1)	−16405(1)	2511(1)	3447(1)	46(1)
Bi(2)	−11209(1)	2491(1)	−1563(1)	48(1)
N(1)	−17808(2)	1076(14)	4023(14)	61(6)
N(2)	−13899(24)	3232(15)	4463(17)	71(7)
N(3)	−18522(22)	3677(14)	2887(15)	55(6)
N(4)	−13525(25)	1634(18)	−497(19)	82(8)
N(5)	−8927(22)	1468(1)	−2119(16)	56(6)
N(6)	−9945(26)	3890(19)	−971(15)	84(10)
C(11)	−14861(24)	1597(16)	3351(20)	56(7)
C(21)	−14926(20)	3246(14)	2650(19)	43(6)
C(31)	−17713(27)	2182(15)	2276(16)	51(6)
C(41)	−12578(24)	1715(14)	−2406(20)	51(7)
C(51)	−9946(21)	2890(15)	−2711(20)	56(7)
C(61)	−12760(29)	3376(19)	−1580(19)	67(9)

[a] See footnote *a* in Table 3.

Table 6. Selected Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(C_{10}H_6NMe_2)_3As$ (**7**)

atom	*x*	*y*	*z*	*U*(eq)[a]
As	7651(1)	6379(1)	2032(1)	25(1)
N(1)	6152(3)	7793(2)	2310(2)	41(1)
N(2)	9716(3)	6906(2)	1254(1)	33(1)
N(3)	9149(3)	5762(2)	3376(1)	32(1)
C(1)	6261(3)	6640(2)	1129(2)	29(1)
C(13)	8443(3)	5369(2)	1664(2)	27(1)
C(25)	6249(3)	5865(2)	2556(2)	28(1)

[a] See footnote *a* in Table 3.

were restrained to be equal within an effective standard deviation of 0.01. All hydrogen atoms except those of the methyl groups in **4**, **5**, and **7** were placed in idealized positions and refined using the riding model with general isotropic temperature factors. The methyl hydrogens in **4**, **5**, and **7** were placed by using a difference electron density synthesis to set the initial torsion angle and then refined as a riding−rotating model with general isotropic temperature factors. The final values of atomic positional parameters for **4**−**7** are listed in Tables 3−6.

Acknowledgment. Dr. Vincent Lynch of the departmental crystallography laboratory at The University of Texas at Austin is thanked for the low-temperature data collection for **4** and **7**. We are grateful to the National Science Foundation (Grant CHE-9108228), the Science and Technology Center Program of the National Science Foundation (Grant CHE-08920120), and the Robert A. Welch Foundation for generous financial support. N.C.N. and A.H.C. also thank NATO for an international collaborative research grant. This material is based upon work supported under a National Science Foundation Graduate Research Fellowship (R.D.C.).

Supporting Information Available: Listings of X-ray experimental details, bond distances, bond angles, atomic coordinates, and thermal parameters for **4**−**7** (35 pages). Ordering information is given on any current masthead page.

IC960516C