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

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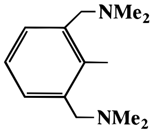
Four group 15 monochlorides of the type EAr_2Cl [Ar = 2-[(dimethylamino)methyl]phenyl, 2-$(Me_2NCH_2)C_6H_4$ ($C_9H_{12}N$), E = Sb (**4**), E = Bi (**5**); Ar = 8-(dimethylamino)-1-naphthyl, 8-$(Me_2N)C_{10}H_6$ ($C_{12}H_{12}N$), E = Sb (**6**), E = Bi (**7**)] have been prepared *via* the salt elimination reactions of 2 equiv of either 2-$(Me_2NCH_2)C_6H_4Li$ or 8-$(Me_2N)C_{10}H_6Li$ with ECl_3. Four related group 15 dihalides of the type $EArX_2$ [Ar = 8-$(Me_2N)C_{10}H_6$, X = Cl, E = As, (**8**), E = Sb (**9**); Ar = 2-$(Me_2NCH_2)C_6H_4$, X = Cl, E = Bi (**10**); X = I, E = Bi (**11**)] have been prepared *via* the salt elimination reactions of equimolar amounts of 8-$(Me_2N)C_{10}H_6Li$ or 2-$(Me_2NCH_2)C_6H_4Li$ with EX_3. The X-ray crystal structures of **4**−**6**, **8**, **9,** and **11** are described, and the observed trends in the degree of intramolecular coordination of the nitrogen atoms are consistent with the view that the Lewis acidity of these complexes is associated with the E−X σ* orbitals. Crystal data for **4**: triclinic, space group $P\bar{1}$, $a = 9.1483(1)$ Å, $b = 9.4868(1)$ Å, $c = 12.9776(2)$ Å, $\alpha = 70.614(8)°$, $\beta = 85.738(9)°$, $\gamma = 83.094(9)°$, $V = 1054.0(2)$ Å^3, $Z = 2$, $R = 0.0420$. Crystal data for **5**: monoclinic, space group $P2_1/c$, $a = 11.9498(1)$ Å, $b = 11.4695(1)$ Å, $c = 13.9456(8)$ Å, $\beta = 104.536(6)°$, $V = 1850.2(3)$ Å^3, $Z = 4$, $R = 0.0375$. Crystal data for **6**: monoclinic, space group $P2_1/n$, $a = 9.4991(8)$ Å, $b = 23.455(4)$ Å, $c = 9.726(1)$ Å, $\beta = 100.629(8)°$, $V = 2129.8(4)$ Å^3, $Z = 4$, $R = 0.0406$. Crystal data for **8**: orthorhombic, space group $P2_12_12_1$, $a = 9.713(3)$ Å, $b = 9.835(4)$ Å, $c = 13.310(3)$ Å, $V = 1273.8(5)$ Å^3, $Z = 4$, $R = 0.0695$. Crystal data for **9**: orthorhombic, space group $P2_12_12_1$, $a = 9.7140(3)$ Å, $b = 10.0196(1)$ Å, $c = 13.444(3)$ Å, $V = 1308.5(3)$ Å^3, $Z = 4$, $R = 0.0320$. Crystal data for **11**: monoclinic, space group $P2_1/c$, $a = 7.9455(7)$ Å, $b = 19.3949(3)$ Å, $c = 8.6226(9)$ Å, $\beta = 93.338(9)°$, $V = 1326.5(2)$ Å^3, $Z = 4$, $R = 0.0379$.

Introduction

Ligands with the capability of intramolecular coordination such as **1**[1] ("two-arm"), **2**[2] ("one-arm"), and **3**[3] ("stiff-arm") have been used extensively in the chemistry of both transition metal[4] and main group species.[5] In the context of main group chemistry, one of the principal points of interest in such ligands concerns the possibility of hypercoordination due to the proximity of additional donor sites which are constrained to lie close to or within the primary coordination sphere. Recently, we reported the preparation and characterization of several Ar_3E (where E = As, Sb, or Bi) compounds featuring ligands **2** and **3**.[6] In each case, it was found that the amine arms were weakly coordinated, thus representing an interesting contrast to the observation that the structures of conventional triarylpnictogen derivatives exhibit only weak Lewis acidity. Similar conclusions have been drawn for triarylphosphorus derivatives that employ ligands **2** and **3**.[7]



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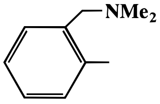

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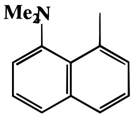

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In addition to the structural studies on Ar_3E compounds, we have also described the results of a number of crystal structure determinations for a range of aryl bismuth(III) halides and halo anions, and a number of structural trends in these and related compounds have become apparent.[8] In general, it is observed that diarylbismuth or -antimony monohalide compounds have a strong tendency to exhibit four-coordinate group 15 element centers in which an additional ligand or atom is coordinated *trans* to the E−X bond, thus resulting in an equatorially vacant, trigonal bipyramidal or disphenoidal coordination geometry. In contrast, monoarylbismuth and -antimony dihalide compounds tend to form two additional bonds *trans* to each of the two E−X bonds, thereby adopting square-based pyramidal five-coordination around the group 15 element. The coordination numbers and geometries observed for $EArX_2$ and EAr_2X (E = group 15 element, Ar = aryl, X = halide) compounds are thus consistent with the Lewis acidity of the E center being associated with the E−X σ* orbitals.[8] These observations have been summarized by means of the general formula $EAr_{3-n}X_n$ in which the generally observed coordination number of the E center is equal to $(3 + n)$.[8]

In the present contribution, we describe the synthesis and X-ray crystal structures of diaryl−Bi and −Sb monohalides and

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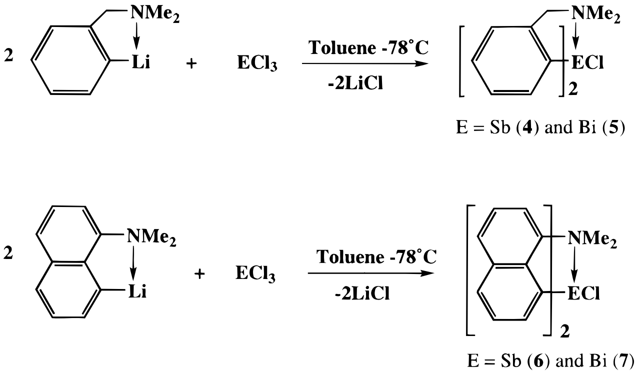
Scheme 1



monoaryl−Bi, −Sb, and −As dihalides that feature ligands **2** and **3**. Our motivation for the preparation and structural characterization of these aryl halides of the heavier group 15 elements stemmed from a number of considerations. First, we were interested in investigating the validity of the generalization $EAr_{3-n}X_n$ in the presence of potential supplemental coordination from an amine arm. Second, the prior use of ligands **1**−**3** has permitted the isolation of compounds which possess unusual geometries and/or solid state structures. Moreover arylelement(III) halides can exhibit solid state interactions such as halide bridges; hence potentially interesting coordination compounds could result. Third, higher coordination numbers are anticipated than in the case of the triaryl derivatives, Ar_3E (Ar = **2**, **3**).[6]

Results and Discussion

The colorless crystalline compounds **4** and **5** were prepared *via* the salt elimination reaction of [2-[(dimethylamino)methyl]phenyl]lithium ($2\text{-}(Me_2NCH_2)C_6H_4Li$) with the appropriate element trichloride in toluene solution at −78 °C (Scheme 1). The colorless crystalline compounds **6** and **7** were prepared in a similar manner *via* the salt elimination reaction of [8-(dimethylamino)-1-naphthyl]lithium ($8\text{-}(Me_2N)C_{10}H_6Li$) with the appropriate element trichloride in toluene solution at −78 °C (Scheme 1). Satisfactory elemental analytical data were obtained for each new compound. Moreover, the ^1H and ^{13}C NMR spectra of **4**−**7** 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 these compounds by X-ray crystallography.

The structures of **4**−**6** are illustrated in Figures 1, 3, and 4, respectively, and selected bond distance and angle data have been compiled in Table 1.

The molecular structure of **4** (Figure 1) reveals that the two amine groups differ in their extent of interaction with the Sb center, with N(1) being strongly coordinated [Sb(1)−N(1) 2.463(2) Å] and N(2) having only a weak interaction [Sb(1)−N(2) 3.216(3) Å]. The orientation of the interaction of N(1) is such that the formal lone pair of the NMe_2 group is directed toward the Sb center and the Sb−N(1) vector lies approximately *trans* to the Sb−Cl bond [N(1)−Sb−Cl(1) 165.58(6)°]. This deviation from the ideal angle of 180° is due to the constraints imposed by the coordinated amine arm. The overall geometry at the antimony center is best described as distorted equatorially vacant trigonal bipyramidal; the angles around the Sb center are C(1)−Sb(1)−Cl(1) 91.31(8)°, Cl(1)−Sb(1)−C(10) 85.50(7)°, C(10)−Sb(1)−N(1) 91.57(9)°, C(1)−Sb(1)−N(1) 75.1(1)°, and C(1)−Sb(1)−C(10) 97.74(1)°. Evidently, there are weak Sb···Sb interactions between centrosymmetrically related pairs of molecules of **4** since the observed Sb−Sb distance of 4.059(6) Å is slightly smaller than the sum of the van der Waals radii [4.3 Å] but considerably larger than the sum of the covalent radii [2.88 Å]. Moreover, there are also weak intermolecular interactions between the Cl atoms and a hydrogen of the CH_2 groups in these “dimer units” (Figure 2). Additional weak interactions are also present between the Cl atoms and a hydrogen atom from the CH_3 groups of neighboring dimers.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds **4**−**6**, **8**, **9**, and **11**

Compound **4**			
Sb(1)−C(1)	2.152(3)	Sb(1)−Cl(1)	2.579(9)
Sb(1)−C(10)	2.160(3)	Sb(1)−N(2)	3.216(3)
Sb(1)−N(1)	2.463(2)		
C(1)−Sb(1)−C(10)	97.7(1)	N(1)−Sb(1)−Cl(1)	165.58(6)
C(1)−Sb(1)−N(1)	75.1(1)	C(1)−Sb(1)−N(2)	152.37(9)
C(10)−Sb(1)−N(1)	91.57(9)	C(10)−Sb(1)−N(2)	66.48(9)
C(1)−Sb(1)−Cl(1)	91.31(8)	N(1)−Sb(1)−N(2)	82.58(8)
C(10)−Sb(1)−Cl(1)	85.50(7)	Cl(1)−Sb(1)−N(2)	108.97(5)
Compound **5**			
Bi(1)−C(1)	2.258(6)	Bi(1)−Cl(1)	2.667(2)
Bi(1)−C(10)	2.264(5)	Bi(1)−N(2)	3.047(5)
Bi(1)−N(1)	2.570(5)		
C(1)−Bi(1)−C(10)	95.1(2)	N(1)−Bi(1)−Cl(1)	165.1(1)
C(1)−Bi(1)−N(1)	72.7(2)	C(1)−Bi(1)−N(2)	159.0(2)
C(10)−Bi(1)−N(1)	89.0(2)	C(10)−Bi(1)−N(2)	68.1(2)
C(1)−Bi(1)−Cl(1)	92.8(1)	N(1)−Bi(1)−N(2)	93.7(1)
C(10)−Bi(1)−Cl(1)	89.0(1)	Cl(1)−Bi(1)−N(2)	99.2(1)
Compound **6**			
Sb(1)−C(1)	2.167(5)	Sb(1)−Cl(1)	2.559(1)
Sb(1)−C(13)	2.164(4)	Sb(1)−N(2)	2.903(4)
Sb(1)−N(1)	2.519(4)		
C(1)−Sb(1)−C(13)	96.5(2)	N(1)−Sb(1)−Cl(1)	164.9(1)
C(1)−Sb(1)−N(1)	74.3(2)	C(1)−Sb(1)−N(2)	163.6(1)
C(13)−Sb(1)−N(1)	86.5(1)	C(13)−Sb(1)−N(2)	68.25(2)
C(1)−Sb(1)−Cl(1)	91.6(2)	N(1)−Sb(1)−N(2)	98.01(2)
C(13)−Sb(1)−Cl(1)	89.8(1)	Cl(1)−Sb(1)−N(2)	94.20(8)
Compound **8**			
As(1)−C(1)	1.94(1)	As(1)−Cl(1)	2.340(3)
As(1)−Cl(1)	2.207(3)	As(1)−N(1)	2.351(9)
C(1)−As(1)−Cl(1)	96.1(3)	C(1)−As(1)−N(1)	79.9(4)
C(1)−As(1)−Cl(2)	94.9(3)	Cl(1)−As(1)−N(1)	88.6(2)
Cl(1)−As(1)−Cl(2)	91.3(2)	Cl(2)−As(1)−N(1)	174.8(2)
Compound **9**			
Sb(1)−C(1)	2.136(5)	Sb(1)−N(1)	2.460(4)
Sb(1)−Cl(2)	2.382(1)	Sb(1)−Cl(1)	2.500(1)
C(1)−Sb(1)−Cl(1)	92.84(3)	C(1)−Sb(1)−N(1)	75.3(2)
C(1)−Sb(1)−Cl(2)	94.87(2)	Cl(1)−Sb(1)−N(1)	167.2(1)
Cl(1)−Sb(1)−Cl(2)	88.98(6)	Cl(2)−Sb(1)−N(1)	87.39(1)
Compound **11**			
Bi(1)−C(1)	2.239(8)	Bi(1)−I(2)	3.1156(6)
Bi(1)−N(1)	2.503(6)	Bi(1)−I(2a)	3.2432(6)
Bi(1)−I(1)	2.9874(6)	Bi(1)−I(1a)	3.9823(7)
C(1)−Bi(1)−N(1)	73.2(2)	I(1)−Bi(1)−I(2a)	175.58(2)
C(1)−Bi(1)−I(1)	94.8(2)	I(2)−Bi(1)−I(2a)	88.52(2)
N(1)−Bi(1)−I(1)	87.9(2)	C(1)−Bi(1)−I(1a)	154.4(2)
C(1)−Bi(1)−I(2)	91.8(2)	N(1)−Bi(1)−I(1a)	86.7(2)
N(1)−Bi(1)−I(2)	163.9(2)	I(1)−Bi(1)−I(1a)	100.11(1)
N(1)−Bi(1)−C(1)	163.1(6)	I(2)−Bi(1)−I(1a)	109.34(2)
I(1)−Bi(1)−I(2)	87.89(2)	I(2a)−Bi(1)−I(1a)	78.674(4)
C(1)−Bi(1)−I(2a)	87.8(2)	Bi(1)−I(1)−Bi(1a)	79.887(4)
N(1)−Bi(1)−I(2a)	96.3(2)		

The solid state structure of **5** comprises individual molecules with no unusually short intermolecular contacts. The structure of **5** (Figure 3) bears a very close resemblance to that of **4** (although they are not isomorphous) such that the geometry at the bismuth center is best described as distorted equatorially vacant trigonal bipyramidal. Only one of the amine groups is

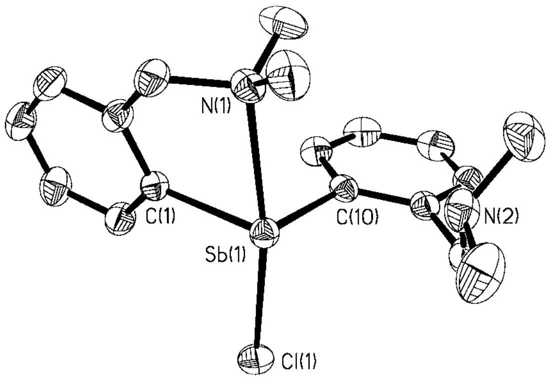


Figure 1. View of the molecular structure of **4** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

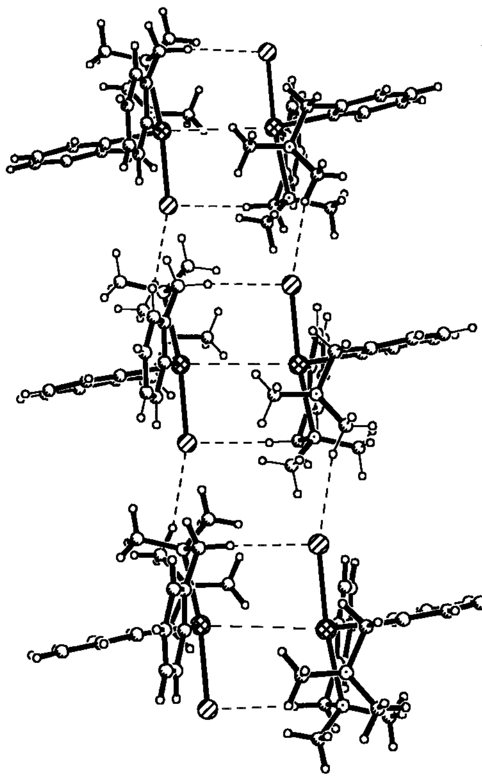


Figure 2. View of the "dimer units" of **4** showing the intermolecular interactions.

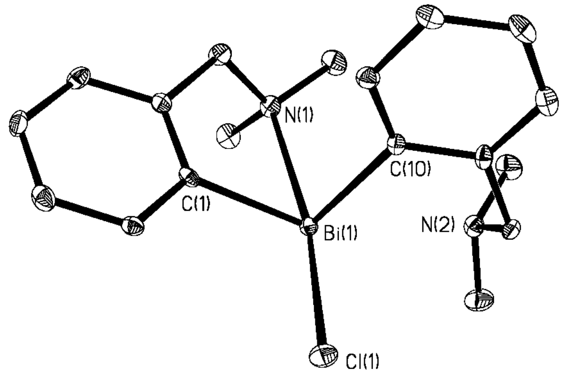


Figure 3. View of the molecular structure of **5** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

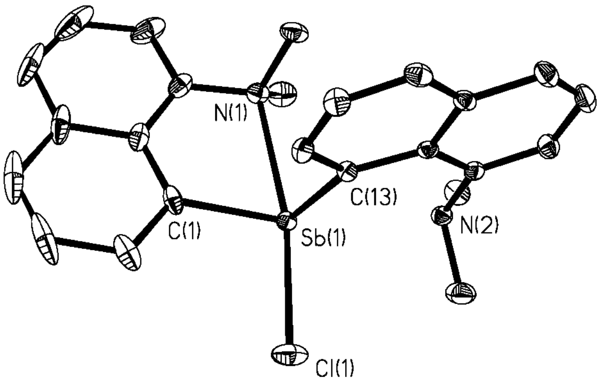


Figure 4. View of the molecular structure of **6** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

strongly coordinated [Bi(1)−N(1) 2.570(5) Å], and as in the case of **4**, the axial positions are occupied by the nitrogen and chlorine atoms; the N(1)−Bi(1)−Cl(1) angle is 165.1(1)°. The remaining angles around the Bi center, which are C(1)−Bi(1)−Cl(1) 92.8(1)°, Cl(1)−Bi(1)−C(10) 89.0(1)°, C(10)−Bi(1)−N(1) 89.0(2)°, C(1)−Bi(1)−N(1) 72.7(2)°, and C(1)−Bi(1)−C(10) 95.1(2)°, are similar to the corresponding angles in **4**. The Bi(1)−N(1) distance in **5** is longer than the sum of the covalent radii but much shorter than that of the sum of the van der Waals radii [3.66 Å] and compares favorably with the Bi−N distance of 2.525(6) Å observed in ArBi(tolyl)Cl (Ar = 2-(Me_2NCH_2)C_6H_4, $C_9H_{12}N$).[9] The Bi−Cl distance of 2.667(2) Å is similar to that observed in ArBi(tolyl)Cl [2.700(2) Å] but longer than those in chlorobis(2,4,6-tris(trifluoromethyl)phenyl)bismuthine [2.463(3) Å][10] and sulfonyl-stabilized chlorobismuthine, Ar′Bi(tolyl)Cl (Ar′ = 2-(*tert*-butylsulfonyl)phenyl) [2.556(2) Å],[11] in which there are no groups coordinated *trans* to the chlorine atom. The second amine arm, with a Bi(1)−N(2) distance of 3.047(5) Å, is very weakly bound and lies approximately *trans* to C(1) [C(1)−Bi(1)−N(2) 159.0(2)°].

The solid state structure of **6** consists of individual molecules, and there are no unusually short intermolecular contacts (Figure 4). As in the case of **4** and **5**, interactions with the amine arms are evident; however, the two arms interact with antimony to different extents. The stronger bound amine arm with an Sb(1)−N(1) distance of 2.519(4) Å lies *trans* to the Sb−Cl bond, and the Cl(1)−Sb(1)−N(1) angle is 164.9(1)°. The second amine arm, with an Sb(1)−N(2) distance of 2.903(4) Å, is more weakly bound and lies approximately *trans* to C(1) [C(1)−Sb(1)−N(2) 163.6(1)°]. The deviations from the idealized angles of 180° are due to the constraints of the ligand, and the effect of the reduced flexibility of the aminonaphthyl group becomes apparent on comparing the structures of **6** and **4**, the extent of interaction of the stronger bound amine arm with the Sb center being weaker in the case of **6** as indicated by a longer Sb−N distance. The overall coordination geometry at the antimony center [ignoring N(2)] can be described as distorted equatorially vacant trigonal bipyramidal with the angles around the Sb center being C(1)-Sb(1)−Cl(1) 91.6(1)°, Cl(1)−Sb(1)−C(13) 96.5(2)°, C(13)−Sb(1)−N(1) 86.5(1)°, and C(1)−Sb(1)−N(1) 74.3(2)°.

Crystals of **7** were examined by X-ray crystallography and found to be isomorphous with those of **6**, but problems during refinement prevented an accurate structure from being obtained.

It is worth noting that the solution phase ^1H NMR spectra of compounds **4**−**7** each exhibit a sharp singlet for the NMe_2

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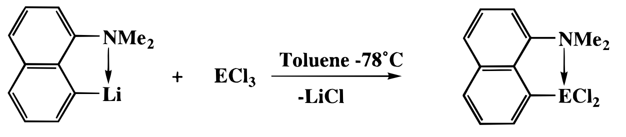
Scheme 2



E = As (**8**) and Sb (**9**)

protons at room temperature, thus suggesting rapid equilibrium between more strongly [N(1)] and more weakly [N(2)] bound arms.

In all cases, the structures of **4**−**6** are consistent with the σ^*-orbital bonding model in the sense that the more strongly bound amine arm is *trans* to the E−Cl bond. This is consistent with the view that the Lewis acidity of aryl-element(III) halide compounds is associated with the E−X σ^* orbitals as opposed to the E−C σ^* orbitals and is also in accord with previous observations on related structures.[8,12,13] As outlined in the Introduction, the structures of ligand adducts of diarylbismuth or -antimony monohalide compounds tend to exhibit four-coordinate group 15 element centers, examples of which include $[BiPh_2Br(thf)]$[12] (thf = tetrahydrofuran), $[Bi(mes)_2Br(OSPh_2)]$ (mes = $2,4,6\text{-}Me_3C_6H_2$), and $[Bi(mes)_2Br(hmpa)]$ (hmpa = hexamethylphosphoramide, $OP(NMe_2)_3$).[8] In all three compounds, the geometry about the bismuth center is best described as equatorially vacant trigonal bipyramidal, with the neutral donor ligand and the bromine occupying axial sites. This coordination geometry was also observed in the structures of **4**−**6** although the angles about the element centers deviate more substantially from the ideal values due to the constraints of the ligand. Four-coordination in diaryl complexes can also be satisfied by the addition of halide to give halo anions; examples include $[PPh_4][EPh_2X_2]$ (E = Bi, X = Br;[12] E = Sb, X = Cl, Br[14]), $[NEt_4][EPh_2X_2]$ (E = Bi, X = I;[15] E = Sb, X = Cl, I[16,17]), and $[Co(\eta\text{-}C_5H_5)_2][SbPh_2Cl_2]$.[18]

The colorless crystalline compounds **8** and **9** were prepared *via* the salt elimination reaction of $8\text{-}(Me_2N)C_{10}H_6Li$ with the appropriate element trichloride in toluene solution at −78 °C (Scheme 2). Satisfactory elemental analytical data were obtained for each new compound. Moreover, the ^1H and ^{13}C NMR spectra of **8** and **9** are consistent with the anticipated formulas. 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 both compounds by X-ray crystallography.

The structures of **8** and **9** are illustrated in Figures 5 and 6, respectively, and selected bond distance and angle data have been compiled in Table 1. In the solid state structure of **8** (Figure 5), the amine arm interacts strongly with the arsenic center and the As−N bond [2.351(9) Å] is located *trans* to the As(1)−Cl(2) bond [N(1)−As(1)−Cl(2) 174.8(2)°], thus explaining the fact that the As(1)−Cl(2) bond distance [2.340(3) Å] is slightly longer than that for As(1)−Cl(1) [2.207(3) Å]. The geometry at the arsenic center is equatorially vacant trigonal bipyramidal; the angles around the As center are C(1)−As(1)−Cl(1) 96.1(3)°, C(1)−As(1)−Cl(2) 94.9(3)°, Cl(1)−As(1)−Cl(2) 91.3(2)°, C(1)−As(1)−N(1) 79.9(4)°, Cl(1)−As(1)−N(1) 88.6(2)°, and Cl(2)−As(1)−N(1) 174.8(2)°. There are, however, additional intermolecular interactions between a chlorine atom on one molecule and the arsenic on another, resulting in the formation of infinite chains in the solid state. Note, however, that the ^1H NMR spectrum shows a singlet for the methyl groups, thus indicating an equilibrium between closed and open forms in the solution phase.

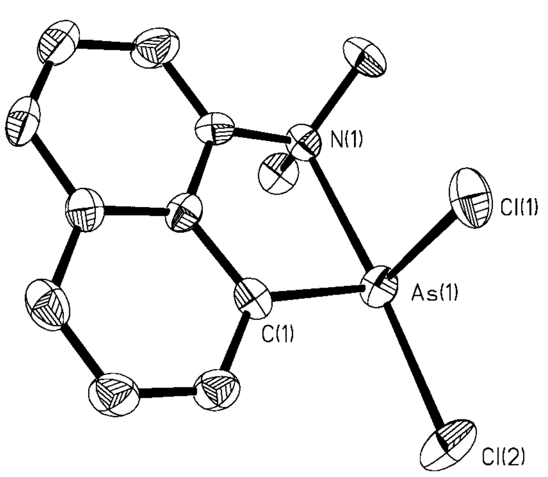


Figure 5. View of the molecular structure of **8** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

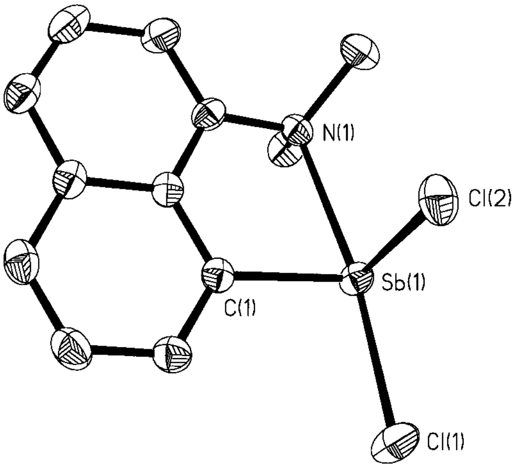


Figure 6. View of the molecular structure of **9** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Compound **9** (Figure 6) is isomorphous with **8**, and the structural description given for **8** is therefore appropriate here as well. The amine arm interacts strongly with the antimony center [Sb(1)−N(1) 2.460(4) Å] *trans* to Cl(1) [N(1)−Sb(1)−Cl(1) 167.2(1)°], and the Sb(1)−Cl(1) bond distance [2.500(1) Å] is slightly longer than that of the Sb(1)−Cl(2) bond [2.3821 Å] due to this *trans* effect. The angles around the Sb center are C(1)−Sb(1)−Cl(1) 92.84(3)°, C(1)−Sb(1)−Cl(2) 94.87(2)°, Cl(1)−Sb(1)−Cl(2) 88.98(6)°, C(1)−Sb(1)−N(1) 75.3(2)°, Cl(1)−Sb(1)−N(1) 167.28(1)°, and Cl(2)−Sb(1)−N(1) 87.39(1)°. As in the case of **8**, there are intermolecular interactions between a chlorine atom on one molecule and the antimony on another, resulting in the formation of infinite chains in the solid state.

Attempts to prepare monoarylbismuth or -antimony dichlorides by salt elimination reactions of $2\text{-}(Me_2NCH_2)C_6H_4Li$ with the appropriate element trichloride in toluene solution at −78 °C resulted only in the isolation of the diaryl derivatives **4** and **5**. Accordingly, it was necessary to prepare the bismuth

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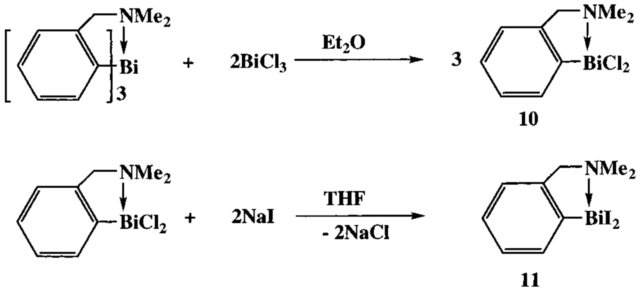
Scheme 3



dichloride $BiArCl_2$ (Ar = 2-(Me_2NCH_2)C_6H_4, $C_9H_{12}N$) (**10**) *via* the redistribution reaction of 2 equiv of $BiCl_3$ with $BiAr_3$ in diethyl ether solution. Satisfactory elemental data and mass spectral analyses were obtained for the product. However, **10** is insoluble in all common solvents; hence it was not possible to grow crystals suitable for X-ray diffraction experiments. It was therefore deemed appropriate to synthesize the corresponding iodide in an effort to obtain a more soluble compound. The yellow crystalline compound $BiArI_2$ (**11**) was prepared by treatment of **10** with 2 equiv of sodium iodide in thf solution (Scheme 3).

The structure of **11** is illustrated in Figures 7 and 8, and selected bond distance and angle data have been assembled in Table 1. The crystal structure of **11** established that the amine group is coordinated to the Bi center [Bi(1)−N(1) 2.503(6) Å] *trans* to I(2) [N(1)−Bi(1)−I(2) 163.9(2)°]. As expected, the Bi(1)−I(2) bond distance [3.1156(6) Å] is slightly longer than the Bi(1)−I(1) distance [2.9874(6) Å]. The crystal structure also revealed that the molecule is associated into centrosymmetric dimers *via* a bridging interaction involving I(2) [Bi(1)−I(2a) 3.2432(6)Å] (Figure 7) such that the overall geometry at bismuth is best described as distorted square-based pyramidal with the aryl group in the apical position and the three iodines and the nitrogen atom of the amine arm in the basal plane. In turn, these dimers interact further *via* a very symmetric interaction involving I(1) [Bi(1)−I(1a) 3.9823(7) Å] as shown in Figure 8; if these interactions are considered, the overall Bi coordination geometry is octahedral. Because **11** is a weakly bound polymer of more strongly bound dimers, its solid state structure resembles those of the phosphine oxide and phosphine complexes [BiI_3(hmpa)][19] and [SbI_3(PMe_3)],[20] respectively, in which similar iodide bridging interactions are present.

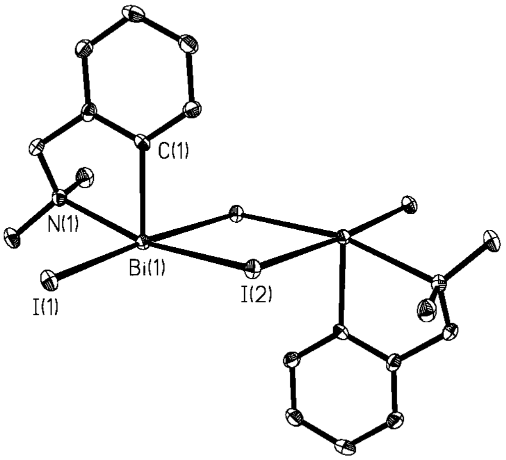


Figure 7. View of the molecular structure of **11** showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

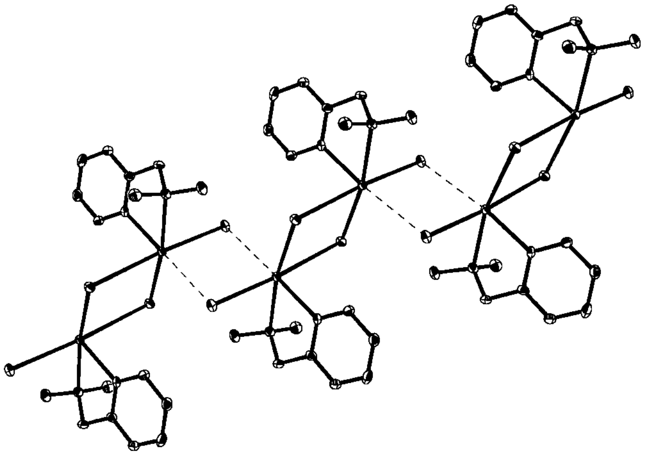


Figure 8. View of the molecular structure of **11** showing the "polymer of dimers".

As described in the Introduction, monoaryl−Bi, and −Sb dihalides generally exhibit square-based pyramidal pentacoordinate structures with apical aryl groups. Thus, the previously reported structures of [$BiPhBr_2$($OPPh_3$)]$_2$, [$BiPhBr_2$(dmpu)]$_2$ (dmpu = *N,N′*-dimethyl-1,3-propanediylurea), and [$BiPhBr_2$(dmpu)$_2$] feature apical aryl groups and a basal plane of bromines and ligand oxygen atoms.[8] This geometry is also observed in the structure of **11** if the weak interaction with I(1a) is ignored. Note, however, that **8** and **9** do not follow this general trend in the sense that only four-coordinate structures are observed. These differences arise as a consequence of the size and rigid nature of ligand **3** which does not allow for the coordination of other halides. It is also of interest to compare these structures with that of [$SbAr'Cl_2$] (Ar′ = 2,6-(Me_2NCH_2)$_2C_6H_3$) (**12**).[21] In this case, the Sb center possesses an overall pentacoordinate arrangement and the nitrogen atoms of the pendant arms are not coordinated *trans* to the chloride ligands. This departure from the general trend is obviously a result of the constraints imposed by the "two-arm" ligand.

In conclusion, several aryl group 15 halide compounds featuring ligands capable of intramolecular base coordination have been synthesized and structurally characterized. The extent of the interaction between the metal center and nitrogen atom of the pendant arm is dependent on the nature of the substituents and the particular group 15 element. Thus, it was noted that the Sb(1)−N(1) distance in **4** is shorter than that in **6**, suggesting that the constraints of the naphthyl group in ligand **3** may hinder coordination. However, it should be noted that the Sb(1)−N(1) bond distance in **9** is essentially identical to that in **4**. It was also observed that the nitrogen/group 15 element interaction is stronger in the halide derivatives Ar_2EX and $ArEX_2$ than in the previously reported trisubstituted derivatives Ar_3E.[6] Such a trend is consistent with the view that the Lewis acidity of these complexes is associated with the E−X σ^* orbitals[13] through which the amine arms can coordinate *trans* to the E−X bonds and that E−X σ^* orbitals are better acceptors than E−C σ^* orbitals.

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

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sodium benzophenone ketyl under argon prior to use. The reagents 2-(Me_2NCH_2)C_6H_4Li and 8-(Me_2N)$C_{10}H_6Li$ were prepared according to literature methods.[1,2] All other reagents were procured commercially 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 (^1H, 300.19 MHz; ^{13}C, 75.48 MHz). NMR spectra are referenced to C_6D_6 which was dried over sodium−potassium alloy and distilled prior to use; ^1H 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.

Compound 4. A slurry of 2-(Me_2NCH_2)C_6H_4Li (1.00 g, 7 mmol) in 20 mL of toluene was added *via* cannula to a stirred solution of $SbCl_3$ (0.798 g, 3.5 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 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 118 °C). Anal. Calcd for $C_{18}H_{24}N_2SbCl$: C, 50.79; H, 5.68; N, 6.58; Cl, 8.32. Found: C, 50.86; H, 5.69; N, 6.52; Cl, 8.40. CIMS (CH_4): $m/z = 425$ ($M^+ + H$), 389 ($M - Cl^-$), 136 (ligand + H). ^1H NMR (C_6D_6): δ 1.83 (s, 12H, NMe_2), 3.24 (s, 4H, CH_2), 6.80 (t, 2H, C_6H_4), 7.07 (m, 6H, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 45.0 (s, CH_3), 65.9 (s, CH_2), 129.1 (s, CH, C_6H_4), 136.2 (s, CH, C_6H_4), 143.7 (s, CH, C_6H_4), 148.1 (s, CH, C_6H_4), *ipso* carbons not detected.

Compound 5. A solution of 2-(Me_2NCH_2)C_6H_4Li (0.453 g, 3.17 mmol) in 20 mL of toluene was added *via* cannula to a stirred slurry of $BiCl_3$ (1 g, 3.15 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 warmed and concentrated to a total volume of 15 mL. Cooling of the resulting solution to −20 °C overnight afforded a 50% yield of colorless, crystalline **5** (mp 150−152 °C) Anal. Calcd for $C_{18}H_{24}N_2BiCl$: C, 42.16; H, 4.72; N, 5.46; Cl, 6.80. Found: C, 42.20; H, 4.68; N, 5.37; Cl, 6.89. CIMS (CH_4): $m/z = 513$ ($M^+ + H$), 477 ($M-Cl^-$), 136 (ligand + H^+). ^1H NMR (C_6D_6): δ 1.86 (s, 12H, NMe_2), 3.29 (s, 4H, CH_2), 7.23 (m, 6H, C_6H_4), 8.97 (d, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 45.4 (s, CH_3), 67.8 (s, CH_2), 129.6 (s, CH, C_6H_4), 131.3 (s, CH, C_6H_4), 140.5 (s, CH, C_6H_4), 146.1 (s, CH, C_6H_4), *ipso* carbons not detected.

Compound 6. A solution of 8-(Me_2N)$C_{10}H_6Li$ (0.5 g, 2.82 mmol) in 20 mL of toluene was added *via* cannula to a stirred slurry of $SbCl_3$ (0.32 g, 2.82 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 warmed and concentrated to a total volume of 15 mL. Cooling of the resulting solution to −20 °C overnight afforded a 60% yield of colorless, crystalline **6** (mp 210 °C). Anal. Calcd for $C_{24}H_{24}N_2SbCl$: C, 59.92; H, 4.86; N, 5.62;. Found: C, 57.65; H, 4.84; N, 5.62. CIMS (CH_4): $m/z = 499$ ($M^+ + H$), 463 ($M-Cl^-$), 170 (ligand$^+$). ^1H NMR (C_6D_6): δ 2.64 (s, 6H, NMe_2), 7.22 (t, 1H, $C_{10}H_6$), 7.52 (m, 5H, $C_{10}H_6$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.1 (s, CH_3), 118.9 (s, CH, $C_{10}H_6$), 125.6 (s, CH, $C_{10}H_6$), 128.8 (s, CH, $C_{10}H_6$), 130.6 (s, CH, $C_{10}H_6$), 135.5 (s, CH, $C_{10}H_6$), 136.2 (s, CH, $C_{10}H_6$), *ipso* carbons not detected.

Compound 7. A slurry of 8-(Me_2N)$C_{10}H_6Li$ (1.0 g, 5.64 mmol) in 20 mL of toluene was added *via* cannula to a stirred solution of $BiCl_3$ (0.89 g, 2.82 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 warmed and concentrated to a total volume of 15 mL. Cooling of the resulting solution to −20 °C overnight afforded a 50% yield of colorless, crystalline **7** (mp 254°). CIMS (CH_4): $m/z = 585$ ($M^+ + H$), 550 ($M-Cl^-$). ^1H NMR (C_6D_6): δ 2.52 (s, 12H, NMe_2), 6.86 (t, 4H, $C_{10}H_6$), 7.24 (d, 2H, $C_{10}H_6$), 7.58 (d, 2H, $C_{10}H_6$), 7.98 (d, 2H, $C_{10}H_6$), 9.12 (d, 2H, $C_{10}H_6$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.0 (s, CH_3), 118.3 (s, CH, $C_{10}H_6$), 124.9 (s, CH, $C_{10}H_6$), 127.0 (s, CH, $C_{10}H_6$), 129.5 (s, CH, $C_{10}H_6$), 130.8 (s, CH, $C_{10}H_6$), 139.8 (s, CH, $C_{10}H_6$), 136.0 (s, C, $C_{10}H_6$), 154.0 (s, C, $C_{10}H_6$), other *ipso* carbons not detected.

Table 2. Crystal Data and Details of Intensity Measurement and Structure Refinement for **4**−**6**, **8**, **9**, and **11**

	4	**5**	**6**
formula	$C_{21}H_{27}CN_2Sb$	$C_{18}H_{24}ClN_2Bi$	$C_{24}H_{24}ClN_2Sb$
fw	464.65	512.82	497.65
temp, K	293(2)	173(2)	293(2)
λ, Å	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	9.1483(1)	11.9498(1)	9.4991(8)
b, Å	9.4868(1)	11.4695(1)	23.455(4)
c, Å	12.9776(2)	13.9456(8)	9.726(1)
α, deg	70.614(8)	90	90
β, deg	85.738(9)	104.536(6)	100.629(8)
γ, deg	83.094(9)	90	90
V, Å^3	1054.0(2)	1850.2(3)	2129.8(4)
Z	2	4	4
d(calc), g/cm^3	1.464	1.841	1.552
abs coeff, cm^{-1}	14.41	96.72	14.33
crystal size, mm	0.50 × 0.27 × 0.24	0.51 × 0.38 × 0.34	0.78 × 0.27 × 0.13
θ range, deg	2.74−34.95	2.33−30.00	2.30−27.47
total no. of rflns	9852	11673	5942
no. of obsd rflns	8497	5393	4798
no. of ref params	250	206	259
GOF on F^2	1.044	1.078	1.051
wR2/R1[a] [$I > 2\sigma(I)$]	0.0839/0.0420	0.0906/0.0375	0.1038/0.0406

	8	**9**	**11**
formula	$C_{12}H_{12}C_{12}NAs$	$C_{12}H_{12}C_{12}NSb$	$C_9H_{12}I_2NBi$
fw	316.05	362.88	596.98
temp, K	293(2)	293(2)	173(2)
λ, Å	0.710 73	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a, Å	9.7140(3)	9.7140(13)	7.9455(7)
b, Å	9.8535(4)	10.0196(1)	19.3949(3)
c, Å	13.310(3)	13.444(3)	8.6226(9)
α, deg	90	90	90
β, deg	90	90	93.338(9)
γ, deg	90	90	90
V, Å^3	1273.8(5)	1308.5(3)	1326.5(2)
Z	4	4	4
d(calc), g/cm^3	1.648	1.842	2.989
abs coeff, cm^{-1}	30.59	24.89	179.09
crystal size, mm	0.69 × 0.34 × 0.30	0.53 × 0.31 × 0.25	0.34 × 0.21 × 0.17
θ range, deg	2.57−26.95	2.54−34.22	2.10−30.00
total no. of rflns	2975	3531	8096
no. of obsd rflns	1837	3382	3860
no. of ref params	149	149	123
GOF on F^2	1.013	1.074	1.065
wR2/R1[a] [$I > 2\sigma(I)$]	0.1775/0.0695	0.0726/0.0320	0.0854/0.0379

[a] $R1 = \Sigma||F_o - F_c||/\Sigma|F_o|$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $1/[\sigma^2(F_o^2) + (a*P)^2 + b*P]$ where $P = [\mathrm{Max}(0,F_o^2)/3 + 2F_c^2/3]$.

Compound 8. A solution of 8-$(Me_2N)C_{10}H_6Li$ (0.50 g, 2.82 mmol) in 20 mL of toluene was added *via* cannula to a stirred solution of $AsCl_3$ (0.51 g, 2.82 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 warmed and concentrated to a total volume of 15 mL. Cooling of the resulting solution to −20 °C overnight afforded a 50% yield of colorless, crystalline **8** (mp 128°). Anal. Calcd for $C_{12}H_{12}NAsCl_2$: C, 45.60; H, 3.82; N, 4.43; Cl, 22.43. Found: C, 45.72; H, 3.86; N, 4.37; Cl, 22.60. CIMS (CH_4): $m/z = 315$ ($M^+ + H$), 280 ($M-Cl^-$). ^1H NMR (C_6D_6): δ 2.22 (s, 6H, NMe_2), 6.89 (d, 1H, $C_{10}H_6$), 7.14 (t, 1H, $C_{10}H_6$), 7.32 (t, 1H, $C_{10}H_6$), 7.43 (d, 1H, $C_{10}H_6$), 7.57 (d, 1H, $C_{10}H_6$), 9.13 (d, 1H, $C_{10}H_6$), $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.5 (s, CH_3), 110.1 (s, C, $C_{10}H_6$), 119.1 (s, CH, $C_{10}H_6$), 126.4 (s, CH, $C_{10}H_6$), 127.7 (s, CH, $C_{10}H_6$), 129.2 (s, CH, $C_{10}H_6$), 131.1 (s, CH, $C_{10}H_6$), 131.7 (s, C, $C_{10}H_6$), 133.5 (s, CH, $C_{10}H_6$), 134.9 (s, C, $C_{10}H_6$), 148.7 (s, C, $C_{10}H_6$).

Compound 9. A solution of 8-$(Me_2N)C_{10}H_6Li$ (0.50 g, 2.82 mmol) in 20 mL of toluene was added *via* cannula to a stirred slurry of $SbCl_3$ (0.643 g, 2.82 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 warmed and concentrated to a total volume of 15 mL. Cooling of the resulting solution to −20 °C overnight afforded a 50% yield of colorless, crystalline **9** (mp 172−176°). Anal. Calcd for $C_{12}H_{12}NAsCl_2$: C, 45.60; H, 3.82; N, 4.43; Cl, 22.43. Found: C, 45.72; H, 3.86; N, 4.37; Cl, 22.60. CIMS (CH_4): $m/z =$ 315 ($M^+ + H$), 280 ($M-Cl^-$). ^1H NMR (C_6D_6): δ 2.99 (s, 6H, NMe_2), 7.58 (t, 1H, $C_{10}H_6$), 7.70 (t, 1H, $C_{10}H_6$), 7.77 (d, 1H, $C_{10}H_6$), 7.90 (d, 1H, $C_{10}H_6$), 8.05 (d, 1H, $C_{10}H_6$), 8.86 (d, 1H, $C_{10}H_6$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 47.1 (s, CH_3), 119.0 (s, C, $C_{10}H_6$), 126.0 (s, CH, $C_{10}H_6$), 130.0 (s, CH, $C_{10}H_6$), 130.0 (s, CH, $C_{10}H_6$), 134.0 (s, CH, $C_{10}H_6$), 134.1 (s, CH, $C_{10}H_6$), 135.4 (s, C, $C_{10}H_6$), 147.7 (s, CH, $C_{10}H_6$), 145.0 (s, C, $C_{10}H_6$), other *ipso* carbon not detected.

Compound 10. A solution of $Bi(C_9H_{12}N)_3$[6] (1.00 g, 3.26 mmol) in 20 mL of Et_2O was added *via* cannula to a stirred solution of $BiCl_3$ (1.03 g, 1.64 mmol) in 20 mL of Et_2O at room temperature, resulting in the formation of a white precipitate. The solution was stirred for 30 min and pumped to dryness to yield 1.87 g of **10** (mp 228−230 °C). Anal. Calcd for $C_9H_{12}NBiCl_2$: C, 26.11; H, 2.92; N, 3.38; Cl, 17.12. Found: C, 25.84; H, 2.99; N, 3.25; Cl, 16.97. CIMS (CH_4): $m/z = 413$ ($M^+ + H$). No NMR data were obtained due to the insolubility of compound **10** in all common solvents.

Compound 11. To a stirred solution of $Bi(C_9H_{12}N)Cl_2$ (0.50 g, 1.21 mmol) in 30 mL of toluene was added NaI (0.363 g, 2.42 mmol) at room temperature. The reaction mixture was stirred for 5 h, after which a dark yellow solution formed. The solution was filtered, and the filtrate was transferred *via* cannula into a Schlenk flask. Hexane (20 mL) was cannulated onto the solution very slowly. Solvent diffusion at −20 °C resulted in the formation of a 71% yield of yellow X-ray-quality crystals. Anal. Calcd for $C_9H_{12}NBiI_2$: C, 18.11; H, 2.03; N, 2.36. Found: C, 19.68; H, 2.40; N, 1.56. CIMS (CH_4): $m/z = 598$ ($M^+ + H$), 470 ($M - I^-$). ^1H NMR (C_6D_6): δ 1.92 (s, 6H, NMe_2), 3.40 (s, 2H, CH_2), 7.42 (m, 3H, C_6H_4), 8.99 (d, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.3 (s, CH_3), 68.9 (s, CH_2), 130.0 (s, CH, C_6H_4), 131.3 (s, CH, C_6H_4), 141.5 (s, CH, C_6H_4), 147.6 (s, CH, C_6H_4), *ipso* carbons not detected.

X-ray Crystallography. Crystallographic data and details of the data collection procedures and structure refinement for **4**−**6**, **8**, **9**, and **11** are presented in Table 2. Crystals of **11** were grown from solvent diffusion of thf and hexanes at −20 °C whereas **4**−**6**, **8**, and **9** were grown from toluene solutions stored at −20 °C. Crystals of **5** and **11** were mounted on glass fibers, and crystals of **4**, **6**, **8**, and **9** were mounted in thin-walled glass capillaries and sealed under argon (1 atm). Data sets for **4**, **6**, **8,** and **9** were collected on an Enraf-Nonius CAD4 diffractometer at 25 °C, and a Siemens P4 diffractometer was used for the collection of data for compounds **5** and **11** at −100 °C. Graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) was used for all structures. Accurate unit cell parameters were determined by recentering 25 optimal high-angle reflections. Three standard reflections were measured every 1800 s during data collection, and no decrease in intensities was noted. Corrections were applied for Lorentz−polarization and absorption (SHELXA for **4**−**6**, **8,** and **9**, face-indexed for **11**) effects. The structures were solved for the heavy atoms by a Patterson map. Subsequent difference syntheses gave all other non-hydrogen atomic positions, and these were refined by full-matrix least squares on F^2 using the Siemens SHELXL PLUS 5.0 (PC) software package.[22] All non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were included at calculated positions (C−H 0.96 Å) and were refined using a riding model and a general isotropic thermal parameter.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **4**−**6**, **8**, **9**, and **11** are available on the Internet only. Ordering and/or Access information is given on any current masthead page.

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[22] Sheldrick, G. M. *SHELXTL PC Version 5.0*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.