J|A|C|S
COMMUNICATIONS

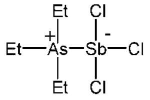
Coordination of Arsine Ligands as a General Synthetic Approach to Rare Examples of Arsenic−Antimony and Arsenic−Bismuth Bonds

Eamonn Conrad,[†] Neil Burford,[*,†] Robert McDonald,[‡] and Michael J. Ferguson[‡]

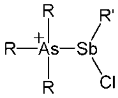
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3 Canada, and Department of Chemistry, University of Alberta, Edmonton AB, T6G 2G2, Canada

Received February 12, 2009; E-mail: neil.burford@dal.ca

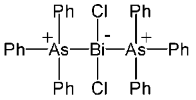
In spite of the similar electronegativities of the heavy pnictogen elements (As 2.18; Sb 2.05; Bi 2.02), examples of compounds containing As−Sb or As−Bi bonds are very rare. The limited data available for such compounds include Mössbauer[1] and ^{1}H NMR[2] spectroscopy for derivatives of $R_2Pn{-}Pn'R'_2$, vibrational spectroscopy[3,4] and mass spectrometry for Pn−Pn′ diatomics[5] and cyclo-pnictines,[6] XPS for binary arsenides,[7] melting points for a range of $R_3Pn{-}Pn'R'_3$ adducts,[8] and crystallographic data for two compounds containing an As−Sb bond[9,10] and for one compound containing an As−Bi bond.[10] We have now exploited the coordination chemistry of arsine ligands as a general approach to As−Pn bond formation using antimony or bismuth acceptor centers and report the preparation and the characterization of the first crystallographically characterized arsine−stibine adduct **1**, the first stibinoarsonium cations **2**, and the first bismuthidodiarsonium cation **3**.



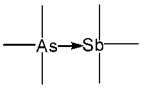
1a



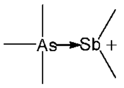
2a: R = Me, R = Cl
2b: R = R' = Ph



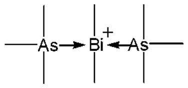
3a



1'



2'



3'

Phosphorus centers in phosphines (R_3P),[11] phosphenium cations (R_2P^+),[12] and phosphadiazonium cations ($P{\equiv}NR^+$)[13] can behave as Lewis acceptors, and the consequential coordination chemistry represents a versatile synthetic approach to new directions in phosphorus chemistry.[14] Moreover, the isolation of arsinophosphonium cations[15] and phosphinoarsonium[16] cations demonstrates that coordinative bonds between pnictogen centers can be "ambicoordinate". Extrapolation of this interpnictogen coordination chemistry offers a general synthetic approach to compounds containing As−Sb and As−Bi bonds with implications for systematic development of interpnictogen bonded compounds.

A crystalline sample obtained from a stoichiometric mixture of Et_3As and Cl_3Sb in CH_2Cl_2 has been characterized by X-ray crystallography as the neutral complex $Cl_3SbAsEt_3$ **1a**, containing an As−Sb bond, as shown in Figure 1. The arsenic center adopts a distorted tetrahedral geometry, and the antimony center occupies a disphenoidal environment with the arsenic center in an equatorial position, indicating that the arsenic center is the Lewis donor and the antimony center is the Lewis acceptor, as represented by the Lewis bonding model **1** and by the coordination chemistry model **1′**. Long range Sb···Cl [2.960(2), 2.918(2) Å] intermolecular contacts impose a distorted square pyramidal geometry at antimony and are responsible for the slightly longer Sb−Cl bonds involving bridging chlorine centers [2.791(2), 2.725(2) Å].

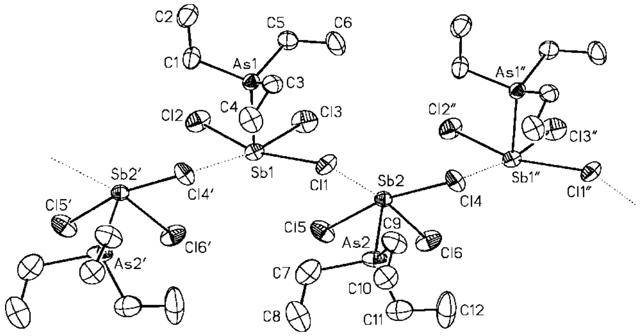


Figure 1. ORTEP representation of $Cl_3SbAsEt_3$ **1a** showing four molecular units with intermolecular Cl···Sb interactions. Dotted lines represent intermolecular interactions. Ellipsoids at 50% probability.

The imposition of coordinative unsaturation and a positive charge at a pnictogen center naturally enhances the Lewis acidity of the acceptor, and this enables a generalization of the As−Pn bond formation reaction. Reaction mixtures of an arsine (R_3As, R = Me, Ph) with a chlorostibine ($RSbCl_2$, R = Ph, Cl) or chlorobismuthine and a halide abstracting agent (Cl_3Al or $Me_3SiO_3SCF_3$), according to eqs 1, 2, and 3, give crystalline samples that have been isolated in high yield, independent of reaction stoichiometry, and characterized as $[Cl_2SbAsMe_3]$ **2a** $[O_3SCF_3]$, $[(Cl)PhSbAsPh_3]$ **2b** $[AlCl_4]$, and $[Cl_2Bi(AsPh_3)_2]$ **3a** $[O_3SCF_3]$, respectively, by crystallography, ^{1}H and ^{13}C[17] NMR spectroscopy (Supporting Information).

$$Me_3As + Cl_3Sb + Me_3SiO_3SCF_3 \longrightarrow [Cl_2SbAsMe_3]\ (\mathbf{2a})\ [O_3SCF_3] \qquad (1)$$

$$Ph_3As + Cl_2SbPh + AlCl_3 \longrightarrow [Ph(Cl)SbAsPh_3]\ (\mathbf{2b})\ [AlCl_4] \qquad (2)$$

$$2\ Ph_3As - Cl_3Bi + Me_3SiO_3SCF_3 \longrightarrow [Cl_2Bi(AsPh_3)_2]\ (\mathbf{3a})\ [O_3SCF_3] \qquad (3)$$

The solid state structures of **2a**$[O_3SCF_3]$, **2b**$[AlCl_4]$ and **3a**$[O_3SCF_3]$ are shown in Figures 2 and 3, respectively, with non-hydrogen atoms represented by ellipsoids at 50% probability and hydrogen atoms removed for clarity. A comparison of As−Pn distances and closest interion distances for all crystallographically characterized compounds containing As−Sb or As−Bi bonds is presented in Table 1.

Some of the structural features observed in the neutral complex **1a** are also evident in the ionic compounds **2a**$[O_3SCF_3]$ and **2b**$[AlCl_4]$, in which the cations are defined as complexes involving a donor arsenic center and an acceptor stibenium center, imposing a trigonal pyramidal geometry at the antimony center, as illustrated in **2′**. The closest anion−cation contacts in **2a**$[O_3SCF_3]$, **2b**$[AlCl_4]$, and **3a**$[O_3SCF_3]$ are significantly longer than those within the

---

[†] Dalhousie University.
[‡] University of Alberta.

10.1021/ja900968j CCC: $40.75

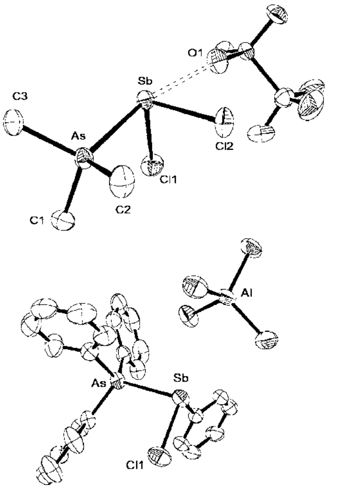


Figure 2. ORTEP representations of **2a** [O_3SCF_3] and **2b** [$AlCl_4$]. Ellipsoids at 50% probability.

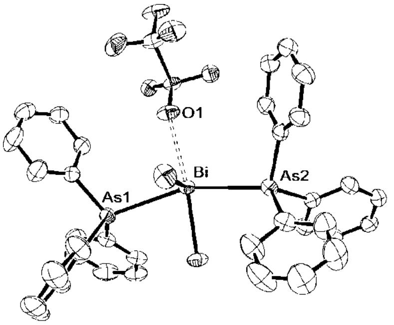


Figure 3. ORTEP representation of **3a** [O_3SCF_3]. Dashed lines represent interion contacts. Ellipsoids at 50% probability.

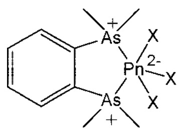
Table 1. Comparison of As−Pn Distances and Closest Interion Distances for Compounds Containing As−Sb or As−Bi Bonds

compd	As−Pn (Å) [Pn]	contact (Å)	ref
1a	[Sb] 2.6803(10)	Sb−Cl 2.960(2), 2.918(2)	*a*
2a[O_3SCF_3]	[Sb] 2.6676(4)	Sb−O 2.965(2)	*a*
2b[$AlCl_4$]	[Sb] 2.6991(3)	Sb−Cl 3.2503(9)	*a*
4a	[Sb] 2.663(1)−2.664(1)	N/A	10
5	[Sb] 2.601(2)−2.616(2)	N/A	9
3a[O_3SCF_3]	[Bi] 3.0159(5)−3.0214(5)	Bi−O 2.726 (3)	*a*
4b	[Bi] 2.801(2)−2.974(2)	N/A	10

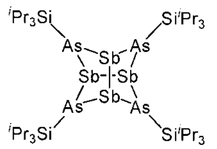
[a] This work.

covalent cations, consistent with observations for stibine−stibenium (stibinostibonium),[18] arsine−arsenium (arsinoarsonium) salts,[19] and phosphine−phosphenium (phosphinophosphonium) salts.[12] The As−Sb bond lengths in the neutral complex **1a** and in the cationic frameworks **2a** and **2b** are similar to those in the neutral compounds **4a** and **5** indicating that the As−Sb length is essentially independent of ring strain or molecular charge.

The structure of the cation in **3a**[O_3SCF_3] (Figure 3) can be described as a coordination complex **3′** composed of two arsine ligands interacting with a dichlorobismuthenium cation. The arsenic centers adopt a distorted tetrahedral geometry and are located in the axial positions of a distorted disphenoidal geometry for bismuth with an As−Bi−As angle of 157.852(12)°. The closest Bi−O cation−anion interaction is shorter than As−Bi but is substantially longer than the sum of the covalent radii for Bi−O (2.18 Å). The As−Bi bonds are slightly longer than those in the neutral cyclic frame of **4b**, possibly due to the axial (*trans*) configuration of the arsenic centers in **3a**, in contrast to the *cis* configuration of the arsenic centers enforced by the chelate structure of **4b**.



4a: Pn = Sb, X = Br
4b: Pn = Bi, X= I



5

In summary, a series of As−Sb and As−Bi bonded compounds have been isolated through the application of coordination chemistry involving arsine ligands. The observations have implications for general Pn−Pn′ bond formation leading to systematic development of interpnictogen compounds.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Canada Research Chairs Program, the Canada Foundation for Innovation, the Walter C. Sumner Foundation, and the Nova Scotia Research and Innovation Trust Fund for funding and the Atlantic Region Magnetic Resonance Centre for use of instrumentation.

Supporting Information Available: Experimental details for preparations and full characterization for **1a**, **2a**[O_3SCF_3], **2b**[$AlCl_4$], and **3a**[O_3SCF_3]. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Stevens, J. G.; Trooster, J. M.; Mertens, H. F.; Meinema, H. A. *Inorg. Chim. Acta* **1986**, *115*, 197–201.
(2) Ashe, A. J., III; Ludwig, E. G. *J. Organomet. Chem.* **1986**, *303*, 197–204.
(3) Yee, K. K.; Jones, W. E. *Chem. Commun.* **1969**, 752–753.
(4) Breidohr, R.; Shestakov, O.; Fink, E. H. *J. Mol. Spectrosc.* **1994**, *168*, 126–135.
(5) Kohl, F. J.; Prusaczyk, J. E.; Carlson, K. D. *J. Am. Chem. Soc.* **1967**, *89*, 5501–5502.
(6) Althaus, H.; Breunig, H. J.; Probst, R.; Rösler, R.; Lork, E. *J. Organomet. Chem.* **1999**, *585*, 285–289.
(7) Allen, G. C.; Carmalt, C. J.; Cowley, A. H.; Hector, A. L.; Kamepalli, S.; Lawson, Y. G.; Norman, N. C.; Parkin, I. P.; Pickard, L. K. *Chem. Mater.* **1997**, *9*, 1385–1392.
(8) Holmes, R. R.; Bertaut, E. F. *J. Am. Chem. Soc.* **1958**, *80*, 2980–2983, and 2983−2985.
(9) Nikolova, D.; von Haenisch, C. *Eur. J. Inorg. Chem.* **2005**, *2*, 378–382.
(10) Genge, A. R. J.; Hill, T. G.; Levason, W.; Reid, G. *Dalton Trans.* **2001**, 1007–1012.
(11) Muller, G.; Brand, J.; Jetter, S. E. *Z. Naturforsch.* **2001**, *56b*, 1163–1171. Muller, G.; Hans-Joachim, M.; Winkler, M. *Z. Naturforsch.* **2001**, *56b*, 1155–1162.
(12) Burford, N.; Ragogna, P. J. *Dalton Trans.* **2002**, 4307–4315. Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. *J. Am. Chem. Soc.* **2003**, *125*, 14404–14410. Burford, N.; Herbert, D. E.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 17067–17073.
(13) Burford, N.; Phillips, A. D.; Spinney, H. A.; Robertson, K. N.; Cameron, T. S.; McDonald, R. *Inorg. Chem.* **2003**, *42*, 4949–4954. Burford, N.; Spinney, H. A.; Ferguson, M. J.; McDonald, R. *Chem. Commun.* **2004**, 2696–2697. Burford, N.; Phillips, A. D.; Spinney, H. A.; Lumsden, M. D.; Werner-Zwanziger, U.; Ferguson, M. J.; McDonald, R. *J. Am. Chem. Soc.* **2005**, *127*, 3921–3927.
(14) Dyker, C. A.; Burford, N. *Chem. Asian J.* **2008**, *3*, 28–36.
(15) Kilah, N. L.; Petrie, S.; Stranger, R.; Wielandt, J. W.; Willis, A. C.; Wild, S. B. *Organometallics* **2007**, *26*, 6106–6113. Porter, K. A.; Willis, A. C.; Zank, J.; Wild, S. B. *Inorg. Chem.* **2002**, *41*, 6380–6386. Burford, N.; Ragogna, P. J.; Sharp, K.; McDonald, R.; Ferguson, M. J. *Inorg. Chem.* **2005**, *44*, 9453–9460.
(16) Conrad, E.; Burford, N.; McDonald, R.; Ferguson, M. J. *Inorg. Chem.* **2008**, *47*, 2952–2954.
(17) Olah, G. A.; McFarland, C. W. *J. Org. Chem.* **1969**, *34*, 1832–1834.
(18) Althaus, H.; Breunig, H. J.; Lotk, E. *Chem. Commun.* **1999**, 1971–1972.
(19) Kilah, N. L.; Weir, M. L.; Wild, S. B. *Dalton Trans.* **2008**, 2480–2486.

JA900968J