Synthesis and First X-ray Structural Analysis of Monomeric Imino-λ^5-stibanes

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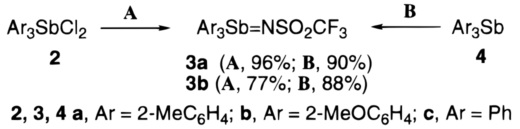
Iminopnictoranes of the general formula $R_3M{=}NR'$ ($M = P$, As, Sb, Bi)[1] are useful reagents in organic synthesis.[2] They are also versatile nitrene sources for transition-metal imido complexes.[3] The interesting structural feature of this class of compounds would be the formal double-bond character of the pnictogen−nitrogen bond. Recently, Koketsu et al. examined the structures of a series of imaginary iminopnictoranes, $H_3M{=}NH$ ($M = P$, As, Sb, Bi), by means of ab initio calculations (MP2-DZ-d level) and predicted that the double-bond character in the M═N bond would decrease in the order $P > As > Sb > Bi$.[4] Although the literature contains many reports for the crystal structures of lighter iminopnictoranes, very little information is available for imino-λ^5-stibanes ($R_3Sb{=}NR'$). In 1995, Wright et al. reported the X-ray crystal structure of $[Ph_3Sb(\mu\text{-}NCH_2CH_2Ph)]_2$ (**1**), which possesses the four-membered Sb_2N_2 core with two distorted trigonal bipyramidal antimony centers and, therefore, may be regarded as an imino-λ^5-stibane dimer.[5] To the best of our knowledge, however, there has been no report on the X-ray crystal structure of imino-λ^5-stibanes that exist in the monomeric form. Here we report the synthesis and first crystal structure determination of novel monomeric triaryl(imino)-λ^5-stibanes.

As shown in Scheme 1, triaryl(trifluoromethylsulfonylimino)-λ^5-stibanes **3a**,**b** ($Ar_3Sb{=}NSO_2CF_3$: **a**, Ar = 2-MeC_6H_4; **b**, Ar = 2-$MeOC_6H_4$) were prepared in good yield by the Kirsanov-type reaction[6] of triarylantimony dichlorides **2a**,**b** with $CF_3SO_2NH_2$ in the presence of KO-*t*-Bu and by the redox condensation[7] of triarylstibines **4a**,**b** with $CF_3SO_2NH_2$ in the presence of diethyl azodicarboxylate. These methods failed for the synthesis of **3c**.[8] Thus, ortho substituents are important for the stabilization of the Sb═N bond (see below).

The ortho substituted imino-λ^5-stibanes **3a**,**b** were characterized by ^1H NMR and IR spectroscopies as well as by X-ray diffraction analysis. Figures 1 and 2 show the ORTEP diagrams of **3a** and **3b**, respectively, with selected bond lengths and bond angles.[9] Both **3a** and **3b** have been found to exist in the monomeric form, and each antimony center possesses a distorted tetrahedral geometry. The Sb═N bond lengths, 1.958(4) and 1.962(2) Å, are shorter than the Sb−N bond lengths of compound **1**[5] [1.990(3)−2.122(3) Å] as well as those of antimony(III) amides[10] [2.041(6)−2.064(6) Å for $Sb(NHC_6H_2\text{-}t\text{-}Bu_3)_3$ and 2.074(7)−2.081(7) Å for $Sb(N{=}CPh_2)_3$]. However, the Sb═N bond lengths of **3a**,**b** are longer than the estimated value (1.91 Å) for the Sb═N double bond.[11] It is in contrast that the P═N bond length [1.579(4) Å] observed for $Ph_3P{=}NSO_2Tol$[12] is close to the estimated value

Scheme 1[a]



[a] Reagents and conditions: **A**, $H_2NSO_2CF_3$, KO-*t*-Bu (2.2 equiv), CH_2Cl_2, −50 °C to rt; **B**, $H_2NSO_2CF_3$, $EtO_2CN{=}NCO_2Et$, Et_2O, 0 °C to rt.

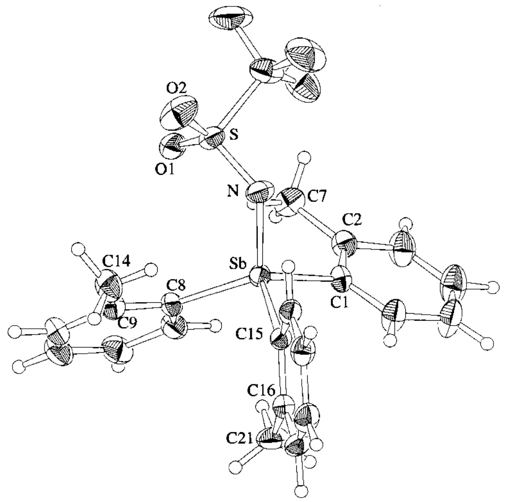


Figure 1. ORTEP diagram of **3a** (30% ellipsoids). Bond lengths (Å): Sb−C1, 2.112(4); Sb−C8, 2.103(4); Sb−C15, 2.107(4); Sb−N, 1.958(4); N−S, 1.536(4); S−O1, 1.441(3); S−O2, 1.428(4). Bond angles (deg): C1−Sb−C8, 113.2(2); C1−Sb−C15, 106.3(2); C8−Sb−C15, 108.9(2); C1−Sb−N, 109.5(2); C8−Sb−N, 117.2(2); C15−Sb−N, 100.5(2); C1−C2−C7, 123.9(4); C8−C9−C14, 123.2(4); C15−C16−C21, 123.0(4).

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(1) Regardless of the degree of double-bond character, the pnictogen−nitrogen bonds in iminopnictoranes are described as M═N for clarity.

(2) See, e.g.: (a) Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993. (b) Lloyd, D.; Gosney, I. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994; Chapter 16, pp 657−693. (c) Matano, Y.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2673.

(3) See, e.g.: (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186. (c) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420.

(4) Koketsu, J.; Ninomiya, Y.; Suzuki, Y.; Koga, N. *Inorg. Chem.* **1997**, *36*, 694. The predicted bond length and bond order of the M═N bond in $H_3M{=}NH$: P, 1.601 Å, 1.667; As, 1.715 Å, 1.537; Sb, 1.899 Å, 1.492; Bi, 1.977 Å, 1.315. The Sb−N bond length of $H_2Sb{-}NH_2$ was predicted to be 2.049 Å.

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(8) Radchenko et al. prepared $Ph_3Sb{=}NSO_2CF_3$ from Ph_3Sb and $N_3SO_2CF_3$. Radchenko, O. A.; Nazaretyan, V. P.; Yagupol'skii, L. M. *Zh. Obshch. Khim.* **1976**, *46*, 565.

(9) See Supporting Information.

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10.1021/ic991120e CCC: $19.00

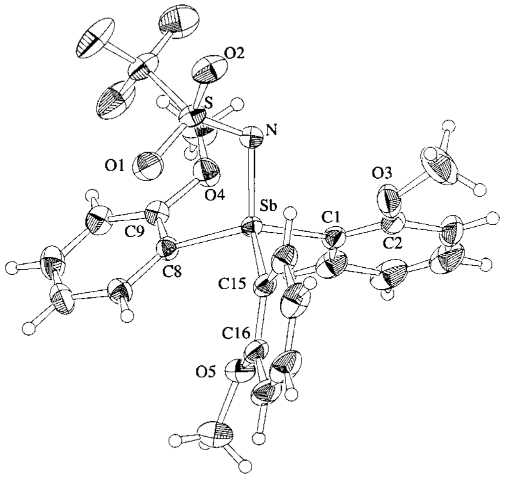
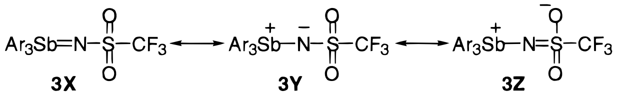


Figure 2. ORTEP diagram of **3b** (30% ellipsoids). Bond lengths (Å): Sb−C1, 2.096(2); Sb−C8, 2.089(2); Sb−C15, 2.096(2); Sb−N, 1.962(2); N−S, 1.536(2); S−O1, 1.444(2); S−O2, 1.434(2). Bond angles (deg): C1−Sb−C8, 110.45(10); C1−Sb−C15, 106.58(9); C8−Sb−C15, 113.23(9); C1−Sb−N, 107.58(9); C8−Sb−N, 111.42(8); C15−Sb−N, 107.29(9); C1−C2−O3, 114.8(2); C8−C9−O4, 114.8(2); C15−C16−O5, 115.1(2).

(1.60 Å) for the P═N double bond.[11] Thus, the Sb(V)═N bond of monomeric imino-λ^5-stibanes **3a**,**b** possesses moderate single-bond character, whereas the P(V)═N bond of $Ph_3P{=}NSO_2Tol$ has a significant double-bond character. On the other hand, the N−S bond lengths [1.536(4) and 1.536(2) Å] are much shorter than the N−S single-bond length (1.76 Å) of sulfamic acid[13] and fall in the range of the N═S double bonds.[11] Moreover, the S═O bond lengths [1.428(4)−1.444(2) Å] are longer than a typical S═O double-bond length (1.40 Å).[14] The observed N−S and S═O bond lengths of **3a**,**b** are close to those of chloramine-T hydrate [1.590(2) and 1.439(2)−1.455(2) Å], which are considered to possess an N═S double bond as well as an S−O single bond.[15] It appears therefore that the canonical forms **3Y** and **3Z** contribute considerably to the actual bond state in **3**.[16] This is also consistent with the low-frequency appearance of an asymmetric SO_2 stretching band of **3a**,**b** (1287 cm^{-1} for **3a**; 1279 cm^{-1} for **3b**) compared with that of $CF_3SO_2NH_2$ (1360 cm^{-1}) in the IR spectra. One of the sulfonyl oxygen atoms, O1, was found to coordinate weakly to the antimony center with Sb···O1 distances of 3.261(3) and 3.110(2) Å, which are shorter than the sum of their van der Waals radii (ca. 3.6 Å).[11] Due to the intramolecular coordination, the Sb, N, S, and O1 atoms in **3a**,**b** are almost in the same plane with a small torsion angle (10.0(4)° for **3a**; 9.5(2)° for **3b**).



$$\mathrm{Ar_3Sb{=}N{-}\overset{O}{\underset{O}{S}}{-}CF_3} \longleftrightarrow \mathrm{Ar_3\overset{+}{Sb}{-}\overset{-}{N}{-}\overset{O}{\underset{O}{S}}{-}CF_3} \longleftrightarrow \mathrm{Ar_3\overset{+}{Sb}{-}N{=}\overset{\overset{-}{O}}{\underset{O}{S}}{-}CF_3}$$

The ortho substituents are likely to contribute to kinetic and thermodynamic stabilization[17] of the Sb═N bond. The *o*-methyl groups in **3a** lean ca. 3° away from the antimony center, indicating the steric congestion around the Sb═N bond. On the other hand, the *o*-methoxy groups in **3b** lean ca. 5° closer toward the antimony, indicating the attractive interaction between the methoxy oxygen and antimony atoms.[18] Thus, the Sb═N bond may be sterically protected in **3a**, while it may be stabilized both electronically and sterically in **3b**.

The reason why compound **1** exists in the dimeric form and compounds **3** exist in the monomeric form may be largely attributed to the electronic and steric influences from the N- as well as Sb-substituents. When we consider the monomeric form of **1**, the negative charge arising from the bond polarization $Sb^{\delta+}-N^{\delta-}$ should be mostly localized on the nitrogen and the steric environment around the Sb═N bond seems to be less congested. By contrast, the negative charge in **3** can be delocalized through the sulfonyl group, and the steric congestion around the Sb═N bond should be much larger. As a result, the Sb═N bond in monomeric **1** would readily dimerize, whereas that in **3** would remain unchanged.

In summary, we have determined the crystal structure of the monomeric imino-λ^5-stibanes **3a**,**b** for the first time and revealed that the Sb═N bond possesses moderate single-bond character owing to the resonance hybridization with the electron-withdrawing *N*-sulfonyl group. It appears that the ortho substituents as well as the *N*-sulfonyl group stabilize the Sb═N bond and prevent it from dimerization.

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Supporting Information Available: Experimental procedures for the synthesis of **3** and spectroscopic, analytical, and X-ray diffraction data for **3a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The relatively short Sb═N bond lengths compared with the known Sb−N single-bond distances may suggest that **3X** contributes, to some extent, to the actual bond state. However, the electrostatic attraction force between the polarized $Sb^{\delta+}$ and $N^{\delta-}$ atoms in **3Y** would also cause the Sb−N bond shortening.

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(18) The Sb···O(methoxy) distances in **3b** are 2.951(2)−3.018(2) Å.