

Synthesis and Structure of a Novel Bis(stibole)

Donald P. Hsu, Benjamin P. Warner, Richard A. Fisher, William M. Davis, and Stephen L. Buchwald*

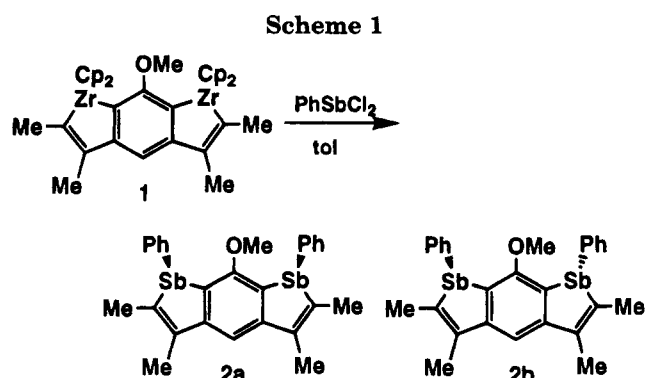
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Summary: The novel benzobis(stibole) **2a**, synthesized from bis(zirconacycle) **1**, crystallizes to place all three ring substituents in a *syn* orientation. Complex **2a** stacks in such a manner so that the central phenyl rings of two adjacent Sb_2C_{10} ring systems are nearly perfectly eclipsed.

For several years we have been interested in the use of zirconacycles for the synthesis of novel main group derivatives.¹ Our efforts have focused principally on developing synthetic routes to cyclic compounds of the heavier main group elements for which there are few reliable methods.² We have been particularly interested in synthetic routes to stiboles, certain derivatives of which are thermochromic.³ In this account, we report the synthesis and solid state structure of some unusual bis(stibole)benzene derivatives.

We have previously reported the synthesis, characterization, and reactivity of zirconocene complexes of certain benzdiynes, and these studies provide the starting point for the current investigation. We felt that bis(zirconacycle) **1**, prepared as previously described,⁴ would provide us with a ready entry for the synthesis of unique bis main group heterocycles by use of the procedure developed by Fagan and Nugent.⁵ Treatment of toluene solutions of **1** with 2 equiv of phenylantimony dichloride, gives the isomeric phenylstiboles **2** (Scheme



1).⁶ Filtration of the reaction mixture through alumina III provides **2** in 71% yield as a mixture of *syn* (**2a**) and *anti* (**2b**) isomers (**2a/2b** = 55/45). Isomer **2a** can be preferentially crystallized (rectangular prisms) from cold hexane/toluene solutions of the mixture of isomeric metallacycles. Recrystallization of **2** from ether generates two distinct crystal types, rectangular prisms of **2a** and small needles of **2b**. The crystal types may be physically separated to give small amounts of each isomer. Once purified, solutions of the isomers are stable with respect to interconversion at temperatures up to 150 °C, at which point the compounds begin to decompose. However, **2** is not configurationally stable if exposed to Lewis acids.⁷ When pure **2a** was adsorbed onto silica gel for 1 h, then eluted with ether, the recovered compound **2** was found to be a mixture of **2a:2b** in an 82:18 ratio.

The solid state structure of **2a** was determined by a single crystal X-ray diffraction study.⁸ The ORTEP and packing diagrams are shown in Figures 1 and 2. The bond distances and angles within the ring system are in the range found in stiboles which have been previously reported.^{1,3a-c} The Sb_2C_{10} ring system is virtually planar. The bond angles about the antimony atom are narrow, as might be expected from consideration of the hybridization of the antimony center in stibines.^{3a} Quite

(6) When **1** was treated with 2 equiv of $SbCl_3$ or $SbBr_3$, the analogous chloro- and bromostiboles were formed as quite insoluble powders, which we were unable to isolate in sufficient purity.

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(8) Crystals of **2a** are monoclinic; space group $P2_1/n$ (No. 14); $a = 12.284(2)$, $b = 14.281(3)$, $c = 13.898(3)$ Å; $\beta = 95.31(20)^\circ$; $Z = 4$; $r_{\text{calc}} = 1.669$ g/cm³. A total of 5790 unique reflections were collected using a Rigaku AFC6R diffractometer with graphite-monochromated Mo K α radiation and a 12 kW rotating anode generator. The structure was solved using a combination of the Patterson method and direct methods. The final cycle of full-matrix least-squares refinement was based on 2832 observed reflections for which $I > 3.00\sigma(I)$ and 271 variable parameters and converged with $R = 0.037$ and $R_w = 0.053$. Anisotropic thermal parameters were assigned to non-hydrogen atoms while hydrogen atoms were included as fixed contributions to the structure factors.

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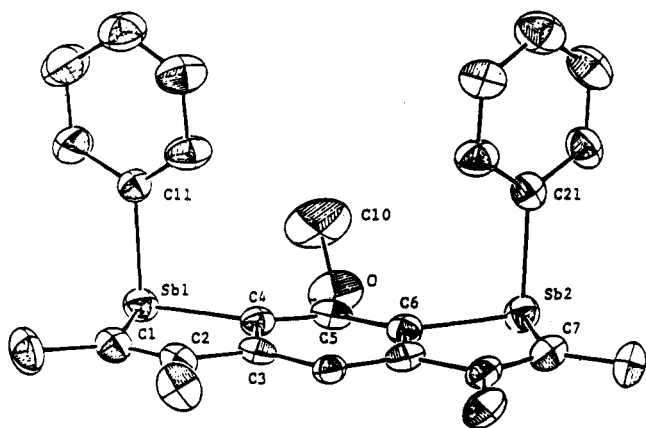


Figure 1. Molecular structure of compound **2a** with a partial listing of bond distances (Å) and angles (deg): C1-Sb1 2.148(8), C4-Sb1 2.114(7), C11-Sb1 2.165(7), C1-C2 1.31(1), C2-C3 1.48(1), C3-C4 1.42(1); C1-Sb1-C11 92.4(3), C4-Sb1-C11 96.3(3), C5-O-C10 120.0(9), C6-Sb2-C21 94.9(3), C7-Sb2-C21 98.0(3).

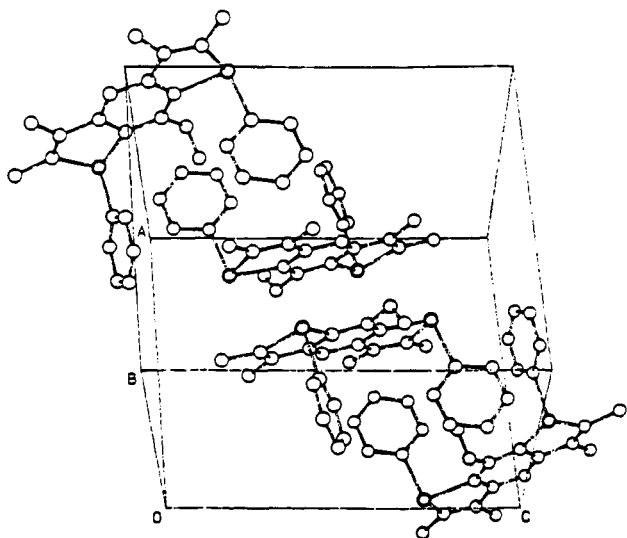


Figure 2. Packing diagram of compound **2a**.

unexpectedly, however, the methyl group of the ring methoxy substituent is oriented *syn* to the two phenyl groups located on the antimony centers. The likely reason for this structural feature is apparent from the examination of the packing diagram (Figure 2) and consideration of the close intermolecular contacts. Two Sb_2C_{10} ring systems lie parallel to each other, 3.6 Å apart. This proximity forces the methoxy carbon atoms to reside away from the neighboring Sb_2C_{10} ring system and toward the phenyl substituents. The interactions between the two Sb_2C_{10} rings are shown in Figure 3 in which the phenyl rings have been removed for clarity. Of particular interest is that the central six-membered rings of the two molecules, shown in Figure 3, are nearly perfectly eclipsed. This is in contrast to Jorgensen's recent theoretical results for the structure of the benzene-anthracene complex.⁹ This interesting difference may be due to crystal packing forces. The corresponding stibacyclopentadiene units are approximately anti with Sb_1 and Sb_2 lying between C1 and C2 and C7 and C8 of the opposite ring, respectively. This orientation mini-

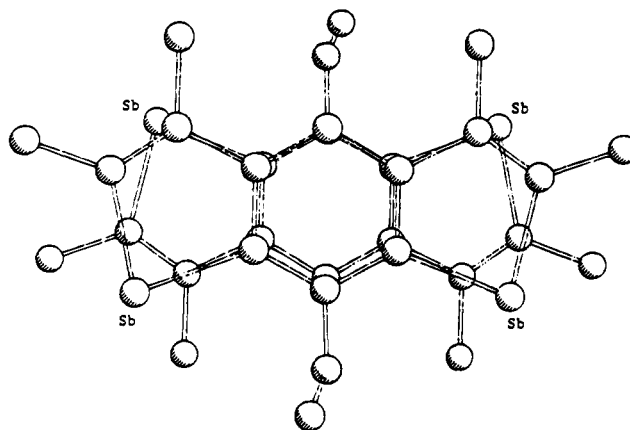


Figure 3. Orientation of the symmetry related Sb_2C_{10} rings. The phenyl rings have been omitted.

mizes the unfavorable Coulombic interactions between the lone pairs of related antimony centers of the two units.

In summary, we have prepared the first example, to our knowledge, of bis(metallacyclopentadienes) of a main group element. Investigations are underway in our laboratory to further explore the use of zirconacyclic intermediates as vehicles for the preparation of new and interesting main group compounds.

Experimental Section

Diphenyldistibolobenzenes 2a and 2b. Two dry Schlenk flasks were charged with **1** (0.400 g, 0.61 mmol) and phenylantimony dichloride (0.329 g, 1.22 mmol) separately, in a nitrogen-filled glovebox. The flasks were removed from the glovebox and attached to a Schlenk line under argon, and toluene (10 mL) was added to each. The solution of **1** was added to the phenylantimony dichloride solution *via* cannula at room temperature. The color of the reaction mixture quickly changed from red to pale yellow. The reaction mixture was stirred for 2 h, then a sample was removed by pipet. At this point, the reaction was judged to be complete (¹H NMR), with the product being a 55:45 ratio of **2a**:**2b**. The reaction solution was then filtered through a plug of alumina III with an additional 50 mL of toluene used to wash the material through the column. The solvent was removed *in vacuo* to leave a yellow solid (0.265 g, 0.434 mmol, 71%). This material was dissolved in approximately 0.5 mL of toluene and 2.5 mL of hexane (with gentle heating to 50 °C to dissolve) and allowed to crystallize, under argon, at -20 °C to yield several large, blocky, yellow crystals (0.062 g, 0.102 mmol, 17%). Further attempts to separate the diastereomers from the remaining material by fractional crystallization were unsuccessful. In a separate experiment, a mixture of **2a** and **2b** was crystallized from ether to yield two distinct forms of crystals: rectangular (**2a**) and needle-type crystals (**2b**). A small amount of the each isomer (**2b**) was physically separated and used for full characterization. **2a**: ¹H NMR (300 MHz, C₆D₆) δ 7.5–7.4 (m, 4H), 7.32 (s, 1 H), 7.0–6.9 (m, 6 H), 3.45 (s, 3 H), 2.05 (s, 6 H), 2.03 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 166.3, 158.3, 147.1, 145.6, 137.5, 135.6, 131.0, 128.7, 128.4, 116.8, 60.7, 18.6, 14.8; IR (KBr) 3059, 2987, 2907, 2848, 1563, 1510, 1475, 1430, 1364, 1350, 1317, 1193, 1063, 1035, 1018, 998, 855, 730, 695, 450 cm⁻¹; Anal. Calcd for C₂₇H₂₆OSb₂: C, 53.16; H, 4.3. Found: C, 53.05; H, 4.36. **2b**: ¹H NMR (300 MHz, CDCl₃) δ 7.46–7.42 (m, 4 H), 7.26–7.18 (m, >6 H solvent included), 3.61 (s, 3 H), 2.21 (s, 6 H), 2.19 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 166.3, 158.3, 147.1, 145.6, 137.3, 135.6, 130.7, 128.8, 128.5,

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116.8, 60.5, 18.5, 14.8; IR (KBr) 3060, 2986, 2929, 2908, 2842, 1565, 1512, 1476, 1430, 1354, 1318, 1063, 1036, 1019, 998, 855, 729, 695, 450 cm^{-1} ; Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{OSb}_2$: C, 53.16; H, 4.3. Found: C, 53.37; H, 4.36.

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Supplementary Material Available: An ORTEP diagram of **3a**, tables of crystal data, bond distances and angles, least squares planes, and final positional and thermal parameters for **3a**, and a textual presentation of crystallographic data and procedures (28 pages). Ordering information is given on any current masthead page.

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