

## A Unique Crystalline-State Reaction of an Overcrowded Distibene with Molecular Oxygen: The First Example of a Single Crystal to a Single Crystal Reaction with an External Reagent

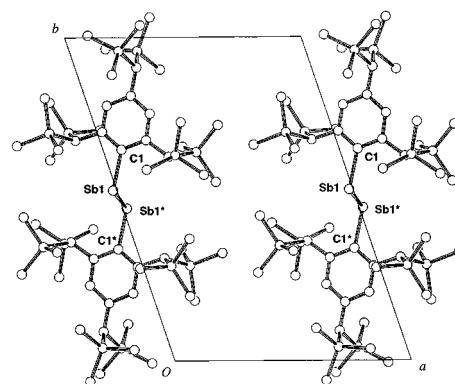
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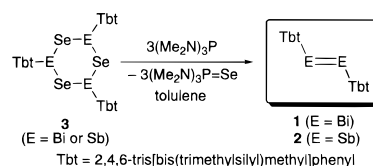
Since the first isolation of a stable diphosphene (ArP=PAR; Ar = 2,4,6-tri-*tert*-butylphenyl)<sup>1</sup> several examples of stable diphosphenes,<sup>2</sup> aza-<sup>3a</sup> and phospharsenes<sup>3b,c</sup> (RE=AsR; E = N, P), and diarsenes (RAs=AsR),<sup>3c,4</sup> i.e., the heavier congeners of an azo compound, have been synthesized by taking advantage of steric protection with bulky substituents. Although theoretical calculations predict that all the doubly bonded compounds between heavier group 15 elements can be isolated as stable species with appropriate steric protection groups,<sup>5</sup> no stable distibene (RSb=SbR) and dibismuthene (RBi=BiR) have been isolated so far. Very recently, however, we have succeeded in the synthesis and characterization of the first stable dibismuthene [TbtBi=BiTbt (**1**),<sup>6</sup> i.e., the ultimate doubly bonded compound consisting of the heaviest nonradioactive element, by utilizing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter).<sup>7</sup> The successful isolation of **1** prompted us to challenge the synthesis and characterization of the missing stable antimony–antimony double bond compound. Here, we present the first isolation of a stable distibene, TbtSb=SbTbt (**2**), and its unique reaction with molecular oxygen in the crystalline state.

Distibene **2** was synthesized by the same method as in the case of **1**, i.e., deselenation reaction of the 1,3,5,2,4,6-triselenatristibane **3** (E = Sb),<sup>8</sup> which was prepared by the reaction of TbtSbCl<sub>2</sub><sup>8</sup>



**Figure 1.** Perspective view of the crystal structure of distibene **2** along the *c* axis. Selected bond lengths (Å) and angles (deg): Sb(1)–Sb(1)\* 2.642(1), Sb(1)–C(1) 2.181(4), Sb(1)\*–Sb(1)–C(1) 101.4(1).

### Scheme 1



with Li<sub>2</sub>Se in THF, with excess amount of hexamethylphosphorous triamide in toluene at 100 °C in a sealed tube (Scheme 1). After heating for 12 h the solution turned green and the expected distibene **2**, which precipitated from the mixture on cooling, was isolated in 94% yield by filtration in a glovebox filled with argon as deep green single crystals.<sup>8</sup>

Distibene **2** is the first example of a stable antimony–antimony double bond, and the green solution of **2** in hexane showed two absorption maxima at  $\lambda_1 = 599$  nm ( $\epsilon$  170) and  $\lambda_2 = 466$  nm ( $\epsilon$  5200), which were assigned to the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions of the Sb=Sb chromophore, respectively. The absorption maxima thus obtained for **2** lie between those for the previously reported stable diarsenes<sup>4</sup> and those for the dibismuthene **1**,<sup>6</sup> and the experimentally observed red shifts for the double-bond systems of heavier group 15 elements on going from P to Bi agree with the changes in the  $n$ ,  $\pi$ , and  $\pi^*$  orbital levels calculated for HE=EH (E = P, As, Sb, and Bi).<sup>9</sup> Distibene **2** showed a strong Raman line at 207 cm<sup>-1</sup> (solid; excitation, He–Ne laser 632.8 nm) which is much higher than the frequencies observed for distibenes (e.g., Ph<sub>2</sub>Sb–SbPh<sub>2</sub> 141 cm<sup>-1</sup>).<sup>10</sup>

X-ray crystallographic analysis of the green crystal revealed the molecular geometry of distibene **2** as shown in Figure 1, which was found to be completely isomorphous with the dibismuthene **1**. Considerable bond shortening (7%) of the Sb–Sb bond length [2.642(1) Å] in **2** as compared with that reported for Ph<sub>2</sub>Sb–SbPh<sub>2</sub> [2.837 Å]<sup>10</sup> clearly indicates its double-bond character, while the observed Sb–Sb–C bond angle of 101.4(1)°, which deviates greatly from the ideal sp<sup>2</sup> hybridized bond angle (120°) and approaches 90°, suggests that **2** has a nonhybridized Sb–Sb double bond due to the 5s<sup>2</sup>5p<sup>3</sup> valence shell corelike nature of the Sb atom as in the case of dibismuthene **1**.

(8) **2**: green crystals; mp > 300 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.128 (s, 36H), 0.132 (s, 36H), 0.15 (s, 36H), 1.44 (s, 2H), 2.75 (s, 2H), 2.94 (s, 2H), 6.54 (s, 2H), 6.64 (s, 2H); UV (hexane)  $\lambda_{\text{max}}$  599 nm ( $\epsilon$  170), 466 nm ( $\epsilon$  5200); FT-Raman (solid; excitation, He–Ne laser 632.8 nm) 207 cm<sup>-1</sup> ( $\nu_{\text{Sb=Sb}}$ ). Anal. Calcd for C<sub>54</sub>H<sub>118</sub>Sb<sub>2</sub>Si<sub>12</sub>: C, 48.11; H, 8.82. Found: C, 47.50; H, 8.70. All the other new compounds here obtained showed satisfactory spectral and analytical data, which are detailed in the Supporting Information together with their synthetic procedures.

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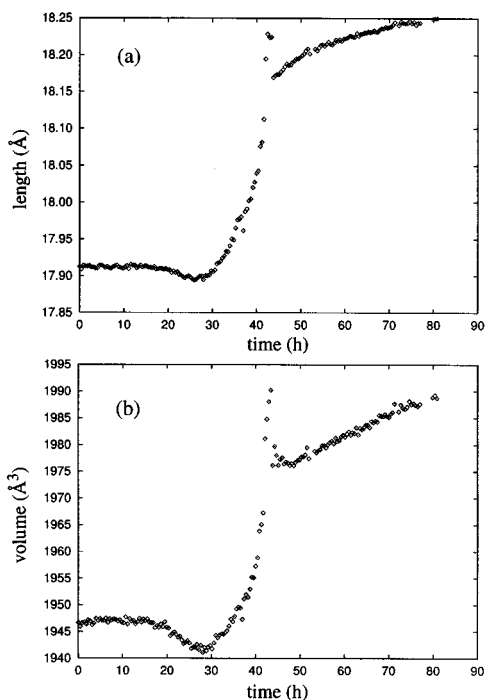
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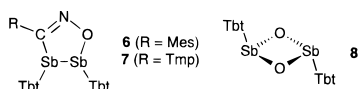
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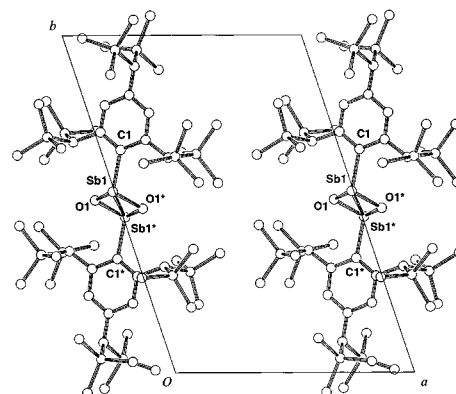
**Figure 2.** Monitored changes of the cell parameters from **2** to **8**: (a) change of *b* axis length; (b) change of unit cell volume.

With the stable distibene **2** in hand, we have examined the reactivity of the Sb–Sb double bond toward several reagents. Treatment of **2** with bromine and iodine in carbon tetrachloride at room temperature resulted in the cleavage of the Sb–Sb bond to give the corresponding dihalostibines TbtSbBr<sub>2</sub> (**4**) and TbtSbI<sub>2</sub> (**5**) in quantitative yields, respectively,<sup>8</sup> while the reaction of **2** with elemental selenium in tetrahydrofuran at 70 °C gave the precursor **3** (E = Sb; 23%) together with a triselenide TbtSe<sub>3</sub>Tbt (16%).<sup>8</sup> On the other hand, distibene **2** underwent a [2+3]-cycloaddition reaction with bulky aryl-substituted nitrile oxides ArCNO [Ar = 2,4,6-trimethoxyphenyl (Tmp) or 2,4,6-trimethylphenyl (Mes)] to afford the corresponding adducts **6** and **7** in 59 and 58% yields, respectively.<sup>8</sup>



Furthermore, during the course of our investigation of the reactivity of **2** we have found a unique, interesting reactivity of distibene **2** with oxygen. Although distibene **2** reacts with oxygen in solution quite rapidly to give quantitatively the corresponding colorless 1,3,2,4-dioxadistibetane derivative **8**,<sup>8</sup> **2** is considerably stable in the solid state in the open air. The crystals of **2** remained dark green for several hours, but they slowly reacted with atmospheric oxygen to give **8** quantitatively. Of particular note is that in the crystalline state **2** reacts with molecular oxygen while retaining its crystallinity. Thus, the reaction proceeds from single crystals of **2** to single crystals of **8**.

This unique oxidation process of **2** in the crystalline phase was successfully monitored by repeated measurements of the cell dimensions using an X-ray diffraction technique with an imaging plate Weissenberg diffractometer.<sup>11</sup> In Figure 2 are shown the changes of the *b* axis length and unit cell volume. They clearly indicate that the crystal dimensions of **2** abruptly changed to those of **8** within 10 h after an induction period (ca. 30 h), and after completion of the transformation of the unit cell dimensions three-dimensional intensity data of **8** were collected using the identical crystal initially used for the structural analysis of **2**.<sup>12</sup>



**Figure 3.** Perspective view of the crystal structure of dioxadistibetane **8** along the *c* axis. Selected bond lengths (Å) and angles (deg): Sb(1)–O(1) 2.004(7), Sb(1)–O(1)\* 1.990(6), Sb(1)–Sb(1)\* 3.039(1), Sb(1)–C(1) 2.176(5), O(1)\*–Sb(1)–O(1) 80.9(3), O(1)\*–Sb(1)–C(1) 103.9(2), O(1)–Sb(1)–C(1) 102.8(2), Sb(1)\*–Sb(1)–C(1) 107.6(5).

In Figure 3 is shown the crystal structure of dioxadistibetane **8** viewed along the *c* axis together with selected intramolecular parameters. The insertion of two oxygen atoms into the Sb–Sb double bond effects only a slight change in the cell dimensions, but leads to the elongation of the Sb–Sb distance (ca. 0.4 Å) in **8** [3.040(1) Å] as compared to that of the starting distibene **2**. One can reasonably imagine that the extremely bulky Tbt group may provide molecular oxygen with enough space for the insertion against the packing force. The presence of the relatively long induction period is most likely interpreted in terms of a “domino” type reaction caused by the oxidation of the molecules of **2** lying on the exterior surface of the single crystal. The analysis of the detailed mechanism is now in progress.

In summary, we have succeeded in the synthesis and characterization of the first stable antimony–antimony double bond compound, distibene **2**, the structural and physical properties of which will be of great importance for the systematic elucidation of the intrinsic nature of the double bond systems between the heavier group 15 elements. To our best knowledge, the unique oxidation reaction of distibene **2** in the solid state is also the first example of an intermolecular chemical reaction with an external reagent in which the integrity of the crystal is fully preserved.<sup>13</sup>

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**Supporting Information Available:** Physical properties of compounds **3–8**, crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **2** and **8**, and figures for the monitored changes of all the cell parameters from **2** to **8** (29 pages). See any current masthead page for ordering and Internet access instructions.

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(12) The crystal data of **2** and **8** are as follows: (**2**) C<sub>54</sub>H<sub>118</sub>Sb<sub>2</sub>Si<sub>12</sub>, *M* = 1348.06, *a* = 12.863(2) Å, *b* = 17.866(3) Å, *c* = 9.2694(9) Å, α = 96.469(9)°, β = 107.036(11)°, γ = 105.404(6)°, *V* = 1921.3(5) Å<sup>3</sup>, triclinic, space group *P*1̄ (no. 2), *Z* = 1, final *R*1 = 0.0697, *w**R*2 = 0.1982 for 7907 [*I* > 2σ(*I*)] observed reflections, GOF (on *F*<sup>2</sup>) = 1.046; (**8**) C<sub>54</sub>H<sub>118</sub>O<sub>2</sub>Sb<sub>2</sub>Si<sub>12</sub>, *M* = 1380.06, *a* = 12.8965(13) Å, *b* = 18.1927(19) Å, *c* = 9.3392(11) Å, α = 93.964(7)°, β = 108.630(6)°, γ = 105.867(6)°, *V* = 1967.6(4) Å<sup>3</sup>, triclinic, space group *P*1̄ (no. 2), *Z* = 1, final *R*1 = 0.0842, *w**R*2 = 0.2556 for 7349 [*I* > 2σ(*I*)] observed reflections, GOF (on *F*<sup>2</sup>) = 1.086.

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