

Compounds containing  $\lambda^3, \sigma^2$ -Sb=C bonds: synthesis and structural characterisation of the first stiba-enol, Mes\* $C(O)Sb=C(OH)Mes^*$  (Mes\* = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3-2,4,6</sub>) and a 2,3-distibabutadiene, {Mes(Me<sub>3</sub>SiO)C=Sb}<sub>2</sub> (Mes = C<sub>6</sub>H<sub>2</sub>Me<sub>3-2,4,6</sub>)<sup>†</sup>

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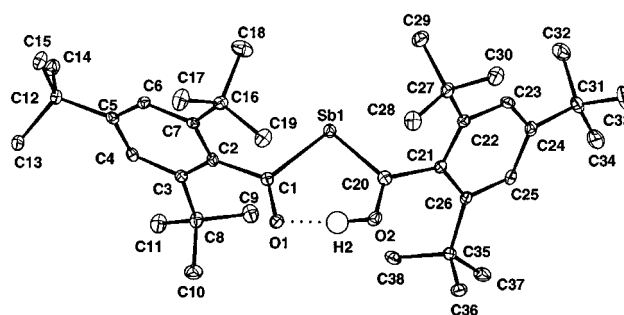
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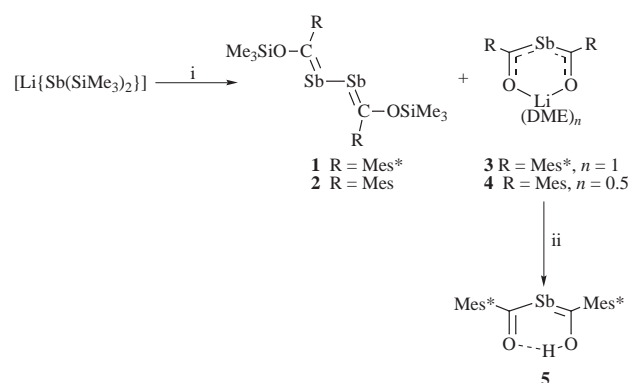
The reactions of [Li{Sb(SiMe<sub>3</sub>)<sub>2</sub>}] with RCOCl, R = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3-2,4,6</sub> (Mes\*) or C<sub>6</sub>H<sub>2</sub>Me<sub>3-2,4,6</sub> (Mes), afford mixtures of the 2,3-distibabutadienes, {R(Me<sub>3</sub>SiO)C=Sb}<sub>2</sub>, and the 2-stiba-1,3-dionatolithium complexes, [Li{OC(R)-SbC(R)O}(DME)<sub>n</sub>], *n* = 1 or 0.5, the latter of which (R = Mes\*) can be protonated to give the first stiba-enol, Mes\* $C(O)Sb=C(OH)Mes^*$ , which has been structurally characterised.

Since the preparation of the first thermally stable phosphalkyne, P≡CBu<sup>t</sup>, in 1981 the field of low coordination phosphorus chemistry has become well established.<sup>1</sup> Not surprisingly, the chemistry of compounds containing As–C multiple bonds was slower to develop but is now relatively well explored.<sup>2</sup> By contrast, there is a paucity of knowledge of analogous low coordination antimony compounds which probably results from their inherent thermal instability. In fact, to date there is only one structurally characterised example of a compound, {R(Me<sub>3</sub>SiO)C=Sb}<sub>2</sub> **1** [R = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup><sub>3-2,4,6</sub> (Mes\*)], that contains largely localised Sb–C double bonds,<sup>3</sup> though related compounds have recently been implicated as reactive intermediates in the formation of stibacycles.<sup>4</sup> This remarkably stable compound was prepared in low yield from the reaction of Mes\*COCl with [Li{Sb(SiMe<sub>3</sub>)<sub>2</sub>}], a surprising result considering that the analogous reaction of Bu<sup>t</sup>COCl with [Li{Sb(SiMe<sub>3</sub>)<sub>2</sub>}] affords a high yield of the delocalised 2-stiba-1,3-dionatolithium complex, [Li{OC(Bu<sup>t</sup>)SbC(Bu<sup>t</sup>)O}(DME)<sub>0.5</sub>]<sub>2</sub>,<sup>5</sup> the coordination chemistry of which we are currently investigating.<sup>6</sup> Herein we report that a stibadionatolithium complex is, indeed, the major reaction product in the preparation of **1** and that a similar product mixture is obtained in the reaction of the less hindered acyl chloride MesCOCl (Mes = C<sub>6</sub>H<sub>2</sub>Me<sub>3-2,4,6</sub>) with [Li{Sb(SiMe<sub>3</sub>)<sub>2</sub>}]. In addition, this work has led to the synthesis and structural characterisation of the first stiba-enol which, in the solid state, contains a rare example of a localised Sb–C double bond.

The product mixtures obtained from the treatment of [Li{Sb(SiMe<sub>3</sub>)<sub>2</sub>}] with 1 equivalent of either Mes\*COCl or MesCOCl were extracted with hexane to give the distibabutadienes, **1** and **2**, in low yield (18% and 5% respectively) after concentration of the extracts (Scheme 1). The hexane insoluble fractions of the reaction mixtures were further extracted with diethyl ether affording the 2-stiba-1,3-dionatolithium complexes, **3** and **4**, in moderate yields (38% and 45%) after recrystallisation. Treatment of a diethyl ether solution of **3** with 1 equivalent of anhydrous HCl, followed by recrystallisation from diethyl ether gave red crystals of the light sensitive stiba-enol, **5**, in high yield (97%).



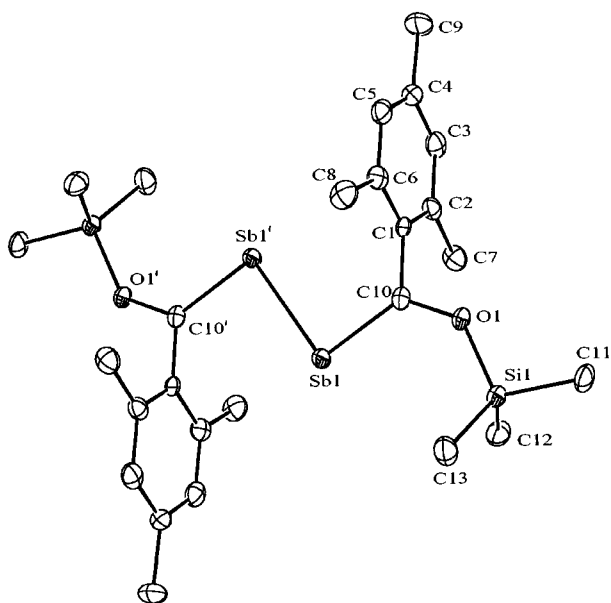
**Fig. 1** Molecular structure of Mes\* $C(O)Sb=C(OH)Mes^*$  **5**. Selected bond lengths (Å) and angles (°): Sb(1)–C(20) 2.078(3), Sb(1)–C(1) 2.192(3), O(1)–C(1) 1.248(4), O(2)–C(20) 1.319(4), O(2)–H(2) 0.96(5), O(1)⋯H(2) 1.61(5); C(20)–Sb(1)–C(1) 91.31(12), O(2)–H(2)–O(1) 172(5), O(1)–C(1)–C(2) 120.9(3), O(1)–C(1)–Sb(1) 121.2(2), C(2)–C(1)–Sb(1) 118.0(2), O(2)–C(20)–C(21) 117.9(3), O(2)–C(20)–Sb(1) 124.7(2), C(21)–C(20)–Sb(1) 117.2(2).



**Scheme 1** Reagents and conditions: i, RCOCl, DME, 18 h; ii, R = Mes\*, HCl, Et<sub>2</sub>O, 0 °C, 2 h.

Compound **5** is stable in toluene solutions for only 15 minutes at room temperature. As a result, spectroscopic data (see SUP 57542) for the compound were collected at 0 °C and are consistent with it existing predominantly in the enol form in this solvent (*cf.* its As analogue<sup>5</sup>). Evidence for this suggestion comes from its <sup>1</sup>H NMR spectrum which displays a low field resonance at  $\delta$  18.48 in the region normally associated with strongly hydrogen bonded alcoholic protons. The symmetry of this spectrum also suggests that **5** possesses a fully delocalised structure in solution in which the alcoholic proton is undergoing a rapid exchange between the two oxygen centres of the molecule. In the solid state **5** is more thermally stable (decomp. 103 °C) and its crystal structure<sup>‡</sup> (Fig. 1) confirms that it exists in the enol form but with localised Sb(1)–C(20) and C(1)–O(1) double bonds, the former of which compares well with those in **1** [2.056(10) Å]<sup>3</sup> and **2** [2.066(5) Å] (see below) but is considerably shorter than normal Sb–C single bonds {e.g. 2.225

<sup>†</sup> Supplementary data available: synthetic and spectroscopic details for compounds **2–5**. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/1541/>, otherwise available from BLDSC (No. SUP 57542, 4 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).



**Fig. 2** Molecular structure of  $\{\text{Mes}(\text{Me}_3\text{SiO})\text{C}=\text{Sb}\}_2$  **2**. Selected bond lengths (Å) and angles (°): Sb(1)–C(10) 2.066(5), Sb(1)–Sb(1)' 2.8018(8), O(1)–C(10) 1.377(5), Si(1)–O(1) 1.697(3); C(10)–Sb(1)–Sb(1)' 92.99(13), O(1)–C(10)–C(1) 110.6(4), O(1)–C(10)–Sb(1) 125.2(3), C(1)–C(10)–Sb(1) 124.3(3).

(average) in  $[\text{Bu}^t_3\text{Sb}\cdot\text{Fe}(\text{CO})_4]^7$ . The acute nature of the C–Sb–C angle in **5** [ $91.31(12)^\circ$ ] probably results from a significant degree of s-character for the hetero-atom lone pair. This is a common feature of other low coordinate Group 15 systems (e.g. RE=ER, E = N, P, As, Sb, Bi) and has been found to be augmented with increasing molecular weight of the Group 15 element.<sup>8</sup> The alcoholic proton H(2) was located from difference maps and refined isotropically. It is bonded to O(2) and appears to have a strong H-bonded interaction with O(1), the angle O(1)–H(2)–O(2) being  $172(5)^\circ$ . As has been suggested for **1**<sup>3</sup> the unusual stability of **5** can probably be attributed to a combination of the steric protection afforded by its bulky aryl substituents and the conjugated nature of the system.

The distibabutadiene **2** (decomp.  $105^\circ\text{C}$ ) is not as thermally stable as its more sterically protected counterpart **1** (decomp.  $213^\circ\text{C}$ ) but is nevertheless stable in air at ambient temperature for days. Its molecular structure ‡ (Fig. 2) is similar to that of **1** and shows it to exist in the *trans*- form with the atoms C(10), Sb(1), Sb(1)' and C(10)' being necessarily co-planar. The Sb–C bond length is close to those in **1** and **5** (see above) and as with the C–Sb–C angle in **5** the sharp Sb–Sb–C angles in **2** [ $92.99(13)$ , cf.  $94.7(3)^\circ$  in **1**<sup>3</sup>] can be explained by a high degree of s-character for the Sb lone pairs.

The 2-stibadionato lithium complexes, **3** and **4**, are considerably more stable (**3** decomp.  $170^\circ\text{C}$ , **4** decomp.  $103^\circ\text{C}$ ) than the only other example of such a compound,  $[\{\text{Li}\{\text{OC}(\text{Bu}^t)\text{SbC}(\text{Bu}^t)\text{O}\}(\text{DME})_{0.5}\}_2]_z$  **6** (decomp.  $65^\circ\text{C}$ ).<sup>5</sup> No crystallographic data were obtained for **4** but in the solid state it probably consists of oxygen and lithium bridged dimeric units linked by non-chelating, bridging DME molecules, as has been found for **6** and a number of related 2-arsa- and 2-phospha-dionatolithium complexes.<sup>5</sup> Compound **3** on the other hand is probably monomeric in the solid state and has its Li centre chelated by a

DME molecule, as is the case for its As counterpart.<sup>9</sup> These differences in the degree of association between **3** and **4** would be expected considering the bulk of the aryl substituent in **3**. As is the case for **6**, the symmetry of the solution state <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** and **4** suggest that the ligand backbones of these complexes are delocalised.

We are currently exploring the use of **2** and **5** as ligands in inorganic synthesis and the utility of **3** and **4** as reagents for the transfer of the 2-stiba-1,3-dionate fragments onto other metal centres. We are also investigating the mechanisms of formation of **1**–**4**. The results of these investigations will form the basis of forthcoming publications.

## Acknowledgements

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## Notes and references

‡ Crystal data for **5**:  $\text{C}_{38}\text{H}_{59}\text{O}_2\text{Sb}$ ,  $M = 669.60$ , orthorhombic, space group  $Pcab$ ,  $a = 11.4906(2)$ ,  $b = 20.0826(4)$ ,  $c = 31.2742(5)$  Å,  $V = 7216.9(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.233$  g cm<sup>-3</sup>,  $F(000) = 2832$ ,  $\mu = 7.94$  cm<sup>-1</sup>, crystal  $0.20 \times 0.20 \times 0.10$  mm, radiation Mo-K $\alpha$  ( $\lambda = 0.71070$  Å),  $T = 100(2)$  K, 50378 reflections collected. For **2**:  $\text{C}_{26}\text{H}_{40}\text{O}_2\text{Sb}_2\text{Si}_2$ ,  $M = 684.26$ , monoclinic, space group  $P2_1/c$ ,  $a = 10.704(2)$ ,  $b = 14.043(3)$ ,  $c = 10.889(2)$  Å,  $\beta = 109.57(3)^\circ$ ,  $V = 1542.2(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.473$  g cm<sup>-3</sup>,  $F(000) = 1368$ ,  $\mu = 18.48$  cm<sup>-1</sup>, crystal  $0.20 \times 0.20 \times 0.10$  mm, radiation Mo-K $\alpha$  ( $\lambda = 0.71070$  Å),  $T = 100(2)$  K, 13007 reflections collected. All crystallographic measurements were made using an Enraf-Nonius Kappa-CCD diffractometer. Both structures were solved by direct methods and refined on  $F^2$  by full matrix least squares (SHELX97)<sup>10</sup> using all unique data. All non-hydrogen atoms are anisotropic with H-atoms [except H(2) in **5**] included in calculated positions (riding model). Absorption corrections were carried out using Scalepack.<sup>11</sup> Final  $R$  (on  $F$ ) were 0.0426 (**5**) and 0.0331 (**2**) and  $wR$  (on  $F^2$ ) were 0.0838 (**5**) and 0.0940 (**2**) for  $I > 2\sigma(I)$ . CCDC reference number 186/1431. See <http://www.rsc.org/suppdata/dt/1999/1541/> for crystallographic files in .cif format.

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