The First Chemical Trapping of Stibinidene, a Monovalent Antimony Compound

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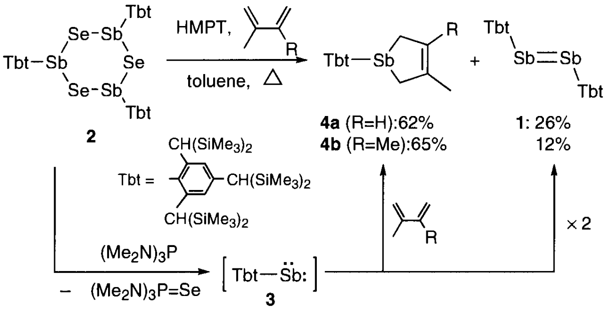
Deselenation of a 1,3,5-triselena-2,4,6-tristibane bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) groups in the presence of 1,3-butadienes resulted in the formation of the corresponding [1 + 4]-cycloadducts of a sterically hindered stibinidene (Tbt–$\ddot{\mathrm{Sb}}$:), a monovalent species of antimony. Thermal generation of the stibinidene from the stibolene derivatives via retro [1 + 4]-cycloaddition reaction was suggested by the diene-exchange reaction in thermolysis of the adducts in the presence of another butadiene derivative.

In recent decades, there has been much interest in the chemistry of low-coordinated species of heavier group 15 elements, namely doubly bonded systems and monovalent species. As for the double-bond compounds, several examples of stable diphosphenes (RP=PR), diarsenes (RAs=AsR), and related compounds have been synthesized and fully characterized[1–3] by utilizing kinetic stabilization since the first isolation of a stable diphosphene (Mes*P=PMes*; Mes*=2,4,6-tri-*t*-butylphenyl).[4] By contrast, phosphinidenes (R–$\ddot{\mathrm{P}}$:),[5] phosphorus analogues of nitrenes, have long been postulated as reactive intermediates. Stibinidenes (R–$\ddot{\mathrm{Sb}}$:) are also interesting monovalent species of group 15 elements, but no stibinidene has been detected or trapped so far probably due to its extremely high reactivity.

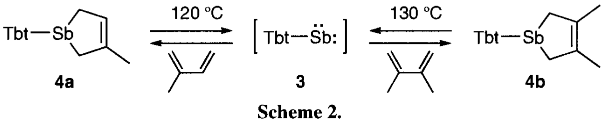
On the other hand, we have recently succeeded in the synthesis and characterization of the first stable distibene (TbtSb=SbTbt, **1**)[6] and dibismuthene (TbtBi=BiTbt),[7] novel doubly bonded systems between heavier group 15 elements, by taking advantage of an efficient steric protection group, Tbt. In the final step for the synthesis of distibene **1**, that is, deselenation reaction of $(\mathrm{TbtSbSe})_3$ (**2**) with hexamethylphosphorous triamide (HMPT), it is rational to postulate the initial formation of a stibinidene (Tbt–$\ddot{\mathrm{Sb}}$:, **3**) as an intermediate. In this paper, we wish to present the first successful trapping reaction of the intermediary stibinidene **3** with isoprene or 2,3-dimethyl-1,3-butadiene and also the re-generation of **3** by thermal retro [1 + 4]-cycloaddition of the diene adducts.

When **2** (217 mg, 0.10 mmol) was treated with HMPT (0.18 ml, 10 equiv) in the presence of isoprene (1.0 mL, 100 equiv) in toluene (4.5 mL) at 110 °C in a sealed tube for 22 h, a small amount of green crystals of distibene **1** (16 mg, 26%) were precipitated. Filtration of the reaction mixture followed by purification with gel permeation liquid chromatography afforded stibolene derivative **4a**[8] (133 mg, 62%), i.e., the [1 + 4]-cycloaddition product of the intermediary stibinidene **3** as colorless crystals. Stibolene **4b**[8] was also obtained (65%) in a similar treatment of **2** using 2,3-dimethyl-1,3-butadiene instead of isoprene. On the other hand, thermolysis of the isolated distibene **1** in the presence of 2,3-dimethyl-1,3-butadiene (in toluene, at 150 °C) did not give such a [1 + 4]-cycloadduct of stibinidene **3** but resulted in almost quantitative recovery of **1**.[9] These results suggest that distibene **1** is not thermally dissociated into stibinidene **3** which should be trapped as stibolene derivatives **4** if generated. Taking account of the above-mentioned results, the formation of **4a**,**b** as a main product in the deselenation reaction of **2** can be reasonably explained by the initial formation of a intermediary stibinidene **3** and the subsequent [1 + 4]-cycloaddition reaction of **3** with butadienes. It should be noted that the formation of stibolenes **4a,b** here described is the first example of the intermolecular chemical trapping of a stibinidene derivative.



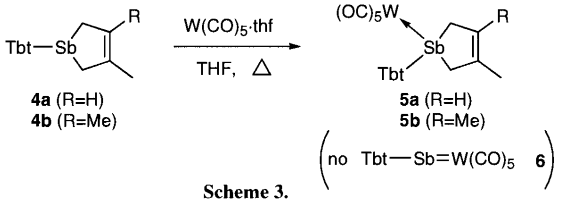
Scheme 1.

Since the stibinidene adducts **4a**,**b** thus obtained are expected to be good precursors of stibinidene **3**, the isolated cycloadduct **4a** (22.3 mg, 0.03 mmol) was heated in the presence of 2,3-dimethyl-1,3-butadiene (34 μL, 10 equiv) in toluene-d_8 (120 °C for 20 h, in a sealed tube) to give the diene-exchanged adduct **4b** in 74% yield. Thermolysis of **4a** in the absence of such a trapping reagent resulted in the formation of distibene **1** in 55% yield, suggesting the dimerization of the initially formed stibinidene intermediate **3**. Also, thermolysis of **4b** in toluene-d_8 in the presence of an excess amount of isoprene (120 °C for 23 h and then 130 °C for 12 h, in a sealed tube) afforded the corresponding diene-exchanged product **4a** in 78% yield. These results indicate that the stibinidene **3** was re-generated by the thermal retrocycloaddition of stibolenes **4a**,**b**. The formation of distibene **1** by the thermolysis of **4a** in the absence of excess dienes is reasonably interpreted in terms of the irreversible dimerization of the stibinidene intermediate **3** leading to the formation of extremely stable Sb=Sb double-bond species from the equilibrated mixture of stibolene **4a** and **3**.



Scheme 2.

Previous studies on phosphinidenes and arsinidenes, i.e., the lighter congeners of stibinidenes, have shown that they readily undergo coordination towards some transition metals to give stable terminal pnictogenidene complexes.[10] These reports prompted us to examine the thermodynamic stabilization of stibinidene **3** by the complexation with a transition metal. However, thermal reactions of the stibinidene precursors **4a** (at 100 °C for 20 h) and **4b** (at 120 °C for 18 h) with $W(CO)_5$·thf in THF in a sealed tube afforded no expected terminal stibinidene complex **6** but the corresponding η^1-tungsten complexes **5a**[11] and **5b**[8] in 75 and 65% yields, respectively.



Scheme 3.

The molecular structure of complex **5a** was determined unambiguously by X-ray crystallographic analysis (Figure 1),[12] which is the first structural analysis of the compound having stibolene framework. Of particular note among the structural features of **5a** is the quite small C(28)–Sb–C(31) angle [83.3(5)°], which might promote the elimination of isoprene via thermal retrocycloaddition to give terminal stibinidene complex **6**. The other bond lengths and angles are not significantly different from those of reported stibine–tungsten complexes,[13] except for the large C(1)–Sb–W angle [130.2(2)°] which might be caused by steric repulsion between the extremely bulky Tbt group and $W(CO)_5$ moiety.

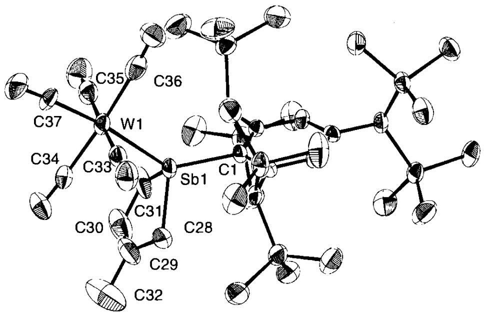


Figure 1. ORTEP drawing of **5a** with thermal ellipsoids (50% probability). Selected bond distances (Å) and bond angles (°): Sb–W 2.7908(6), Sb–C(1) 2.177(7), Sb–C(28) 2.139(10), Sb–C(30) 2.149(9), W–C(33) 2.012(10), W–C(34) 2.034(10), W–C(35) 2.000(10), W–C(36) 2.048(12), W–C(37) 1.985(8), W–Sb–C(1) 130.2(2), W–Sb–C(28) 109.2(3), W–Sb–C(31) 106.4(3), C(28)–Sb–C(31) 83.3(5), Sb–W–C(33) 91.2(2), Sb–W–C(34) 84.4(2), Sb–W–C(35) 87.1(3), Sb–W–C(36) 99.8(2), Sb–W–C(37) 172.1(3) .

In expectation of trapping the terminal stibinidene complex **6**, thermolysis of complex **5a** was carried out in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene (130 °C for 5 h, toluene-d_8, in a sealed tube) to give a tungsten complex **5b** (58%) together with the demetallated stibolene **4b** (42%). Formation of the diene-exchanged product **5b** implies the generation of an expected complex **6**, but the formation of **4b** suggests another complicated pathway, that is, the initial elimination of $W(CO)_5$ moiety from **5a** prior to the diene-exchange reaction via intermediary stibinidene **3** as mentioned above. Then, a part of **4b** thus generated may undergo recombination with $W(CO)_5$ moiety to give **5b**.

Further investigation on the chemistry of low-coordinated species of heavier group 15 elements is currently in progress.

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References and Notes

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8 All the new products here obtained showed satisfactory spectral and analytical data. The spectral data for **4a** are shown as the representative as follows. **4a**: colorless powder, mp 123–125 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 0.31 (s, 54H), 1.27 (s, 1H), 1.81 (s, 3H), 1.97 (s, 1H), 2.03 (s, 1H), 2.34–1.47 (m, 2H), 3.05–3.10 (m, 2H), 5.89 (br s, 1H), 6.26 (s, 1H), 6.40 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.74 (q), 1.02 (q), 21.4 (q), 23.6 (t), 28.6 (t), 29.9(q), 30.8 (d), 31.0 (d), 121.8 (d), 126.7 (d), 127.4 (d), 133.3 (s), 142.0 (s), 142.7 (s), 150.5 (s), 150.7 (s). Anal. Calcd for $C_{32}H_{67}SbSi_6{\cdot}H_2O$: C, 50.56; H, 9.14%. Found: C, 50.61; H, 8.72%.

9 Distibene **1** is not photochemically dissociated to give stibinidene **3** (a medium pressure 400-W mercury lamp, Pyrex filter, in C_6D_6, at 70 °C). By contrast, diphosphene (Mes*P=PMes*) is known to be photochemically labile to generate the corresponding phosphinidene; M. Yoshifuji, T. Sato, and N. Inamoto, *Chem. Lett.*, **1988**, 1735.

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11 Spectral data for **5a**: pale yellow crystals; mp 200–205 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 18H), 0.11 (s, 18H), 0.12 (s, 18H), 1.22 (s, 1H), 1.28 (s, 1H), 1.34 (s, 1H), 1.79 (s, 3H), 2.57–2.76 (m, 2H), 3.51–3.56 (m, 2H), 5.77 (s, 1H), 6.35 (s, 1H), 6.48 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.79 (q), 1.14 (q), 1.45 (q), 20.9 (d), 29.5 (t), 30.4 (q), 33.3 (d), 33.8 (d), 34.1 (t), 122.4 (d), 124.3 (d), 126.6 (s), 127.6 (d), 139.5 (s), 145.2 (s), 150.0 (s), 150.1 (s), 198.0 (s, $^1J_{CW}$=126.2 Hz), 199.3 (s, $^1J_{CW}$=161.4 Hz). IR ($CHCl_3$) 2066, 1936 cm^{-1} (ν_{CO}). HRMS (FAB) *m/z* Obsd 1065.1753 ($[M+H]^+$), Calcd for $C_{37}H_{68}O_5SbSi_6W$: 1065.2230.

12 The intensity data for **5a** were collected on a Rigaku/MSC Mercury CCD diffractometer. Crystallographic data for **5a**: $C_{37}H_{67}O_5SbSi_6W$, fw = 1066.05, T = 173(2) K, triclinic, $P1$, a = 9.6414(6) Å, b = 14.8719(14) Å, c = 17.376(3) Å, α = 90.199(4)°, β = 93.007(4)°, γ = 97.7124(19)°, V = 2465.4(5) $Å^3$, Z = 2, D_{calc} = 1.436 g cm^{-3}, R_1 = 0.065, wR_2 = 0.171

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