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Antimony Compounds

Formation and Structure of the $[(1,2\text{-}C_6H_4P_2Sb)_2]^{4-}$ Ion: Implications for an Extended Family of Isoelectronic Main-Group Radicals**

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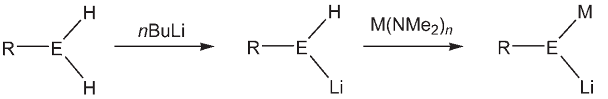
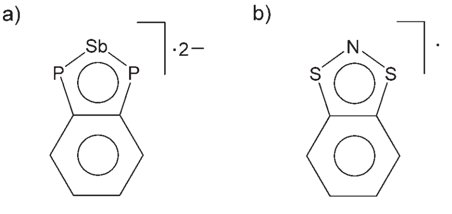
We have previously developed a strategy for the preparation of heterometallic main-group imido (RN^{2-}) and phosphinidene (RP^{2-}) compounds involving stepwise deprotonation of REH_2 (E = N,P) with alkali-metal organometallics (for example *n*BuLi), followed by reaction with $M(NMe_2)_n$ (M = As, Sb, Bi, *n* = 3; Sn *n* = 2; Scheme 1).[1] Recently, however, we have recognized the behavior of this type of mixed-metal system as superbases.[2] This effect was first apparent in the reaction of $MesPH_2$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) with $Sn(NMe_2)_2/PhCH_2Na$, which gives the unusual stannate ion $[Sn\{P(2\text{-}CH_2\text{-}4,6\text{-}Me_2C_6H_2)\}\{PMes\}]^{3-}$ [3] as a result of deprotonation of a PH_2 group and an *ortho*-CH_3 group. Remarkably, quadruple deprotonation of the PH_2 and NH_2 groups occurs in $1\text{-}NH_2\text{-}2\text{-}PH_2\text{-}C_6H_4$ (LH_4) using a similar $Sn(NMe_2)_2$/*n*BuLi mixture, giving the paramagnetic complex $[(\{(L)Sn(NMe_2)Li\cdot THF\}\{(L)SnLi\cdot 3\,THF\}Sn)_2]$ containing the L^{4-} tetraanion and $L^{\bullet 3-}$ radical.[4]



Scheme 1. Stepwise deprotonation of amines (E = N) and phosphines (E = P). M = As, Sb, Bi, *n* = 3; Sn *n* = 2; R = aliphatic or aromatic group.

Herein we report the reaction of $1,2\text{-}(PH_2)_2C_6H_4$ with $Sb(NMe_2)_3$/*n*BuLi, which results in the complete deprotonation of the PH_2 groups, giving the 6π-aromatic anion $[1,2\text{-}C_6H_4P_2Sb]^-$. Upon one-electron reduction, the $[1,2\text{-}C_6H_4P_2Sb]_2^{4-}$ tetraanion is formed. As established from DFT calculations, this highly charged, Sb–Sb-bonded distibane is best described as a dimer of two 7π-$[1,2\text{-}C_6H_4P_2Sb]^{\bullet 2-}$ radicals (Scheme 2 a) and is valence-isoelectronic with the important class of sulfur/nitrogen-based thiazolyl radicals (Scheme 2 b).[5]



Scheme 2. Comparison of a) the $[1,2\text{-}C_6H_4P_2Sb]^{\bullet 2-}$ radical and b) thiazolyl radical

Lithiation of $1,2\text{-}(PH_2)_2C_6H_4$ (1 equiv) with *n*BuLi (2 equiv) in tmeda (tmeda = $Me_2NCH_2CH_2NMe_2$) followed by reaction with $Sb(NMe_2)_3$ (0.67 equiv) gives $[Li(tmeda)_2]^+[1,2\text{-}C_6H_4P_2Sb]^-$ (**1**) after crystallization from THF/tmeda. However, black crystals of $[\{1,2\text{-}C_6H_4P_2Sb\}_2\{Li(tmeda)\}_4]$ (**2**)[6] are obtained if this reaction is undertaken in toluene and the product crystallized from toluene/tmeda. Compound **2** presumably arises from one-electron reduction of the 6π-aromatic anion of **1** (Scheme 3). The diamagnetic nature of **2** persists in the solid state and in dilute solutions in toluene as a result of spin-pairing of the electrons within the Sb–Sb-bonded dimer, as shown by the structural characterization (see below). This situation contrasts with the behavior of valence-isoelectronic dithiazolyl dimers, for which a dissociation energy of about 0 kJ mol^{-1} results in extensive dissociation in solution.[5]

A few other related 6π-aromatic Group 15 anions have been reported; notably, the coordination chemistry of the 6π-benzatriazolyl ion, $[1,2\text{-}C_6H_4N_3]^-$, which is valence-isoelectronic with the $[1,2\text{-}C_6H_4P_2Sb]^-$ ion of **1**, has been investigated extensively.[7] However, the only representative of this type for the heavier Group 15 elements is the 6π-diaraarzoyl anion $[1,2\text{-}C_6H_4N_2As]^-$, which is obtained by the unusual reaction of the lithiate of $1,2\text{-}C_6H_4(NH_2)_2$ with $(Me_2N)_2AsCH_2As(NMe_2)_2$.[8] To our knowledge, however, one-electron reduction of this type of species has never been detected previously for Group 15 or elsewhere in the p block, except in sulfur/nitrogen chemistry.[5]

The low-temperature solid-state structures of **1** and **2** were both obtained.[9] After many attempts, only one very limited data set was obtained for **1**. Although the structural parameters involved should be treated with caution, the nature of the complex has been determined unequivocally, being composed of $[Li(tmeda)_2]^+$ and 6π-aromatic $[1,2\text{-}C_6H_4P_2Sb]^-$ ions (Figure 1). The atoms within each of the four independent C_2P_2Sb rings are almost exactly coplanar (maximum deviation 0.020 Å), as expected for the conjugation of all of the p orbitals throughout this ring. The small angle at antimony [mean 93.7°] is consistent with the lone pair on

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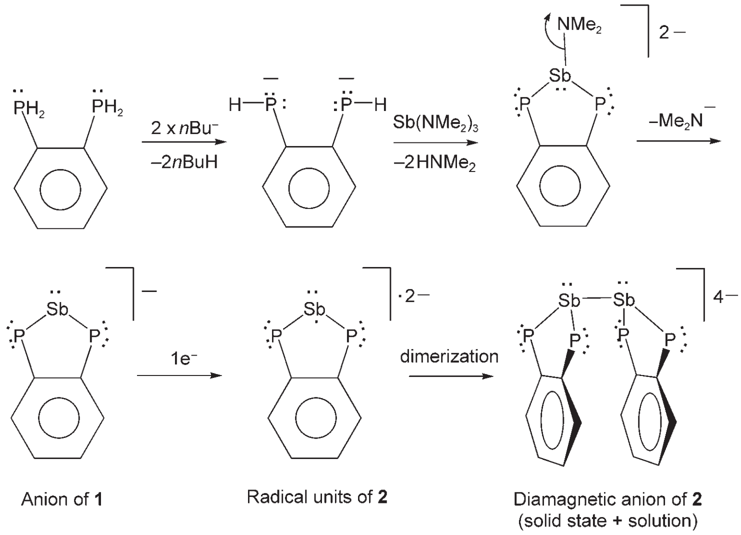

Scheme 3. Synthesis of **2**.

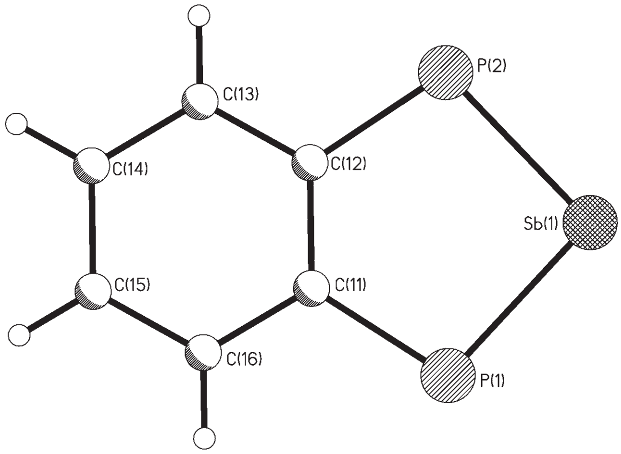

Figure 1. Structure of the $[C_6H_4P_2Sb]^-$ ion in the $[Li(tmeda)_2]^+$ salt of **1**. Only one of the four independent anions in the unit cell is shown.

antimony having predominantly s character and with the antimony p orbitals being used in σ and π bonding. The presence of pπ–pπ bonding together with the low coordination number of the antimony center results in particularly short Sb–P bonds (mean 2.30 Å), which are considerably shorter than those detected in three-coordinate, σ-bonded Sb^{III} phosphinidenes [2.489(3)–2.593(1) Å].[10–12]

The solid-state structure of **2** is that of a dimer, formally composed of two $[1,2\text{-}C_6H_4P_2Sb]^{\bullet 2-}$ radicals which are associated in a *cisoid* (cofacial) arrangement (Figure 2). The two nearly coplanar phenyl rings are almost eclipsed with respect to each other, with their centroids separated by 3.72 Å. Valence-isoelectronic dithiazolyl radicals commonly dimerize by a similar *cisoid* mode,[13] involving 2e⁻ π–π interaction of the singly occupied molecular orbitals (SOMO) of each monomer between their S⩦N⩦S units.[14] In **2**, however, the build-up of negative charge on the phosphorus centers leads to the apparent predominance of Sb–Sb bonding. The P···P contacts in **2** (4.22–4.27 Å) are far longer than expected even for van der Waals interactions (3.8 Å),[15] whereas the Sb–Sb distance [2.9711(3) Å] is only slightly greater than the range of values reported for structurally authenticated single bonds.[16] In addition, the antimony atoms within the C_2P_2Sb heterocyclic rings bend towards each other (folding by 28.6° at the P···P vector) to promote metal–metal bonding. Bearing in mind the large electronic repulsion between the highly charged phosphorus centers, it is difficult to see why a *cisoid* structure should be preferred over an apparently sterically favored *trans* conformation.[17] A possible explanation for this result is the reinforcing effect of interdimer bridging by the tmeda-chelated Li^+ ions Li(3) and Li(4) [Li–P 2.525(6)–2.547(5) Å]. The other two Li^+ ions, Li(1) and Li(2), span the anionic phosphorus atoms within the monomer units of **2** [Li–P 2.580(6)–2.595(5) Å] and are involved in relatively short interactions with the two carbon atoms of the C_2P_2Sb unit [C···Li 2.650(6)–2.730(6) Å].

Model DFT calculations[18] show that addition of one electron to the HOMO of the 6π anion of **1** (Figure 3a) gives a SOMO in **2** (Figure 3b) in which 92% of the unpaired spin density is found on the phosphorus and antimony atoms. This result is accompanied by an increase in the Sb–P bond lengths and a reduction in the P-Sb-P angle,

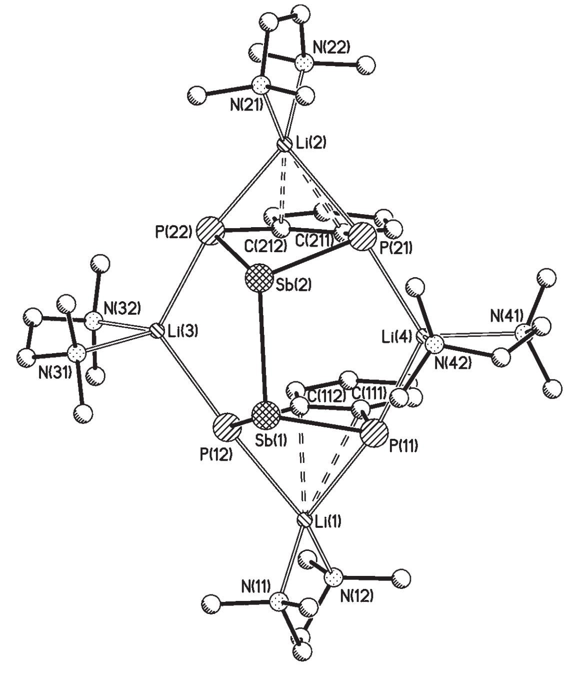

Figure 2. The dimeric structure of **2** in the toluene solvate (hydrogen atoms and toluene not shown for clarity). Selected bond lengths [Å] and angles [°]: Sb(1)-P(11) 2.4915(9), Sb(1)-P(12) 2.4932(8), Sb(1)-Sb(2) 2.9711(3), Sb(2)-P(21) 2.4962(9), Sb(2)-P(22) 2.4988(9), P(11)-Li(1) 2.595(5), P(12)-Li(1) 2.591(6), Li(1)-C(111) 2.717(6), Li(1)-C(112) 2.730(6), P(21)-Li(2) 2.582(6), P(22)-Li(2) 2.580(6), Li(2)-C(211) 2.690(6), Li(2)-C(212) 2.650(7), P(12)-Li(3) 2.540(6), P(22)-Li(3) 2.547(5), P(11)-Li(4) 2.538(5), P(21)-Li(4) 2.525(6); P-Sb-P mean 87.40, Sb-Sb-P mean 104.8, C-P-Sb mean 98.5, P-Li(1/2)-P 83.6, P-Li(3/4)-P 113.6, mean folding of C_2P_2Sb ring units about the P···P vectors, 28.6°.

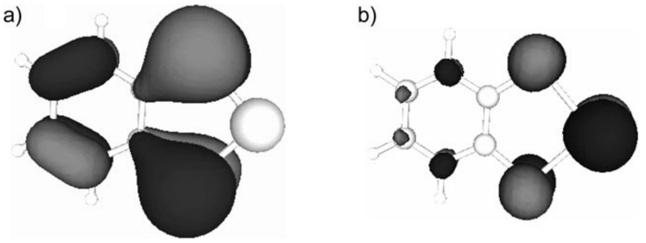

Figure 3. a) The HOMO of **1**; b) the SOMO of **2** (the LUMO of **1**).

both closely reflecting the experimental observations. The dimeric parent tetraanion $[(H_2C_2P_2Sb)_2]^{4-}$ was chosen for further study, for calculational simplicity. A stable C_{2v}-symmetric π^*–π^*-bonded $[(H_2C_2P_2Sb)_2]^{4-}$ dimer could not be found on the potential energy surface, and attempts at optimization resulted in the 7π-radical units moving apart because of substantial electrostatic repulsion. However, if the four Li^+ ions present in the structure of **2** are included the optimized structure is similar to the actual solid-state arrangement. The absence of Lewis base solvation of Li^+ ions results in shorter Sb···Li contacts and longer Sb–Sb bonds than found experimentally. Despite this result, however, the DFT calculations clearly reveal that association into a dimer is largely due to bonding to the Li^+ counterions rather than Sb–Sb bonding (that is, a dimer of two radicals associated mainly by electrostatic interactions). The large energy calculated for dimerization of the ion-paired monomer to the dimer ($[Li_2\{H_2C_2P_2Sb\}]^{\bullet} \rightarrow [Li_4\{H_2C_2P_2Sb\}_2]$, $-129.4\ \mathrm{kJ\,mol^{-1}}$) explains why, in contrast to the valence-isoelectronic dithiazolyl dimers, no observable 7π radical is found in solution or in the solid state for **2**.

In summary, this study has shown for the first time that one-electron reduction of 6π-aromatic anions, such as **1**, is possible, suggesting that this phenomenon might be a general for related main-group heterocycles. Although—as in **2**—the resulting species may not have fully developed radical character as a result of large (electrostatically induced) association energies, the results reported herein provide a key insight into the potential existence of an extensive family of materials that are valence-isoelectronic with well-known thiazolyl radicals.

Experimental Section

All manipulations were undertaken under dry O_2-free argon. **1**: *n*BuLi (1.6 M solution in hexanes, 0.61 mL, 0.97 mmol) was added dropwise to a solution of 1,2-$(PH_2)_2C_6H_4$ (69 mg, 0.49 mmol) in tmeda (5.0 mL) at 0 °C. The resulting yellow suspension was allowed to warm to room temperature and stirred for 30 min. The reaction mixture was cooled to 0 °C and a solution of $Sb(NMe_2)_3$ (2.0 M solution in toluene, 0.16 mL, 0.33 mmol) was added, giving an orange precipitate which was stirred for a further 30 min at room temperature. The precipitate was dissolved by the dropwise addition of THF, and the resulting deep red solution was cooled to 4 °C (12 h), giving orange crystalline blocks of **1**. These were isolated and dried under vacuum (30 min, 10^{-1} atm). Crystalline yield 40 mg, 36 %. ^1H NMR (+25 °C, $[D_8]THF$, 500.05 MHz): $\delta = 8.57$ (m, 2H, C(3,6)-H aromatic), 6.69 (m, 2H, C(4,5)-H aromatic), 2.27 (s, ca. 8H, $-CH_2-$tmeda), 2.12 ppm (s, ca. 24H, Me_2N tmeda). Elemental analysis (%) calcd for $C_6H_4LiP_2Sb\cdot 2\,C_6H_{16}N_2$: C 43.3, H 7.3, N 11.2, P 12.4; found: C 41.2, H 7.0, N 9.0, P 13.0. For **1**–0.5 tmeda: calcd C 40.8, H 6.4, N 9.5, P 14.0 (suggesting that some of the tmeda is liberated by placing **1** under vacuum during isolation).

2: The same quantities and molar equivalents of reagents were used as for **1**, except that toluene (5.0 mL) was used in place of tmeda. The reaction of the lithiated phosphine with $Sb(NMe_2)_3$ gave a dark brown solution and precipitate, which dissolved on addition of tmeda (0.32 mL, 2.14 mmol). The solution was stored at 4 °C overnight to yield black, block-shaped crystals of **2**. The crystals were isolated and dried under vacuum (30 min, 10^{-1} atm). Crystalline yield 60 mg, 28 %. Elemental analysis (%) calcd for $C_{12}H_4P_4Sb_2\cdot 4C_4H_{12}N_2\cdot 3\,C_7H_8$: C 53.1, H 7.5, N 8.7, P 9.6; found: C 50.5, H 7.2, N 8.5, P 11.3. For **2**·3 toluene: calcd C 53.2, H 7.2, N 8.7, P 9.6 (for **2**·2.5 toluene: calcd C 51.8, H 7.1, N 9.0, P 10.0, suggesting that about half of the toluene is lost during isolation of **2** under vacuum).

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[9] **1**: $C_{18}H_{36}LiN_4P_2Sb$, $M_r = 499.14$, orthorhombic, space group *Pmn*2(1), $Z = 4$, $a = 37.4633(12)$, $b = 21.3225(7)$, $c = 9.4221(3)$ Å, $V = 7526.5(4)$ Å^3, $\mu(Mo_{K\alpha}) = 1.236\ \mathrm{mm^{-1}}$, $\rho_{calcd} = 1.321\ \mathrm{Mg\,m^{-3}}$, $T = 180(2)$ K. Total reflections 9525, unique 4357 ($R_{int} = 0.033$). The only crystal that could be obtained diffracted poorly and data in the limited θ-range $< 21°$ were used in refinement. Satisfactory refinement was also hampered by parameter correlations between the four independent ion pairs, and considerable disorder of two of the $[Li(tmeda)_2]^+$ counterions which had C_s symmetry. To prevent a non-positive-definite displacement parameter, the carbon atoms of the counterions were refined with isotropic ADP. $R_1 = 0.088$ $[I > 2\sigma(I)]$ and $wR_2 = 0.224$ (all data). **2**·3 toluene: $C_{57}H_{96}Li_4N_8P_4Sb_2$, $M_r = 1288.55$, triclinic, space group $P\bar{1}$, $Z = 4$, $a = 15.0756(2)$, $b = 16.1753(3)$, $c = 17.2153(3)$ Å, $\alpha = 89.7980(10)$, $\beta = 68.4000(10)$, $\gamma = 64.0050(10)°$, $V = 3445.19(10$ Å^3, $\mu(Mo_{K\alpha}) = 0.915\ \mathrm{mm^{-1}}$, $\rho_{calcd} = 1.241\ \mathrm{Mg\,m^{-3}}$, $T = 180(2)$ K. Total reflections 39499, unique 14955 ($R_{int} = 0.039$). Two of the three toluene solvate molecules were disordered. One showed about 70:30 % overlap of two components and one showed a ca. 50:50 % rotational disorder (the two components differing in the position of the CH_3 substituent). There was also evidence of some disorder of the tmeda ligands but only one CH_2 group was resolved. $R_1 =$

0.043 [$I > 2\sigma(I)$] and $wR_2 = 0.110$ (all data). Data were collected on a Nonius KappaCCD diffractometer and solved by direct methods and refined by full-matrix least squares on F^2 (G. M. Sheldrick, *SHELX-97*, Göttingen, Germany, **1997**). CCDC-650551 (**1**) and CCDC-650552 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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