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Stibasilene Sb═Si and Its Lighter Homologues: A Comparative Study

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Supporting Information

ABSTRACT: The multiply bonded derivatives of the heavier main group elements are among the most challenging targets for synthetic pursuits. Those of them featuring a double bond between the silicon and group 15 element are represented mostly by the silaimines —*N*═Si< and phosphasilenes —P═Si< with a very few examples of arsasilenes —As═Si<. In this contribution, we report on the synthesis and structural elucidation of the first stable stibasilene and novel phosphasilene and arsasilene derivatives, featuring an identical substitution pattern. A systematic comparison within the series phosphasilene−arsasilene−stibasilene is made on the basis of their experimental and computational studies.

The topic of multiple bonding between the heavier main group elements is among the mainstreams in contemporary organometallic chemistry. A great variety of alkene analogues featuring a double bond between the identical heavier (of the third period and below) group 14−15 elements (homonuclear double bond) was synthesized following the original discovery of the first stable disilene >Si═Si<[1] and diphosphene —P═P—[2] derivatives. However, progress in the chemistry of the heteronuclear doubly bonded combinations between the different heavier main group elements lagged behind the spectacular achievements in the field of their homonuclear counterparts.[3] Thus, of the —E═Si< derivatives (E = heavier group 15 element), phosphasilenes —P═Si< are by far most comprehensively studied with many stable representatives reported to date.[4] For the —E═Si< combination of the third and fourth period elements, that is, arsasilenes —As═Si<, six isolable derivatives are known,[4r,5] of which only two were structurally characterized.[5] Doubly bonded combinations of the silicon with the heaviest group 15 element of the fifth and six periods, namely, stibasilenes —Sb═Si< and bismasilenes —Bi═Si<, have still eluded experimental realization.

Such lack of the isolable stibasilenes and bismasilenes prompted us to challenge preparation of a series of ArE═SiR_2 (E = P−Bi) doubly bonded derivatives, featuring identical substitution pattern allowing direct comparison of their structures and bonding nature. To fulfill this task, as a method of choice we employed a one-step procedure, based on the utilization of the highly reactive dianionic 1,1-dilithiosilane derivative $(^tBu_2MeSi)_2SiLi_2$, readily available in preparative scale.[6] This reagent was previously successfully used for the synthesis of a variety of compounds featuring double bonds to silicon, such as disilenes,[6a] silagermenes,[6a] silastannene,[7a] silaborene,[7b] tetrasilabuta-1,3-diene,[7c] hafnium silylidene,[7d] etc. We reasoned that the simple reaction of this 1,1-dilithiosilane with the pnictogen dihalides $ArEX_2$ (E = heavier group 15 element) bearing a sufficiently bulky Ar group required for kinetic stabilization of the otherwise highly reactive E═Si bond would result in the formation of the target ArE═$Si(SiMe^tBu_2)_2$ derivatives. It was expected that the particular substitution pattern in such compounds (electron donors on silicon and electron acceptor on pnictogen: "push−pull" substitution pattern) would lead to a relaxation of the natural polarity of the $E^{\delta-}$═$Si^{\delta+}$ bond (and accordingly its high reactivity), caused by the differing electronegativities of pnictogen and silicon atoms. In this communication, we report on the synthesis of a whole series of the E═Si (E = P−Sb) derivatives, novel phosphasilene[8] and arsasilene, and the first ever-reported stable stibasilene, prepared using the advantage of the above-described unified synthetic approach. A systematic comparison of the structural and bonding features along the series phosphasilene−arsasilene−stibasilene, made on the basis of experimental and computational data sets, is also discussed in this paper.

In accord with our expectations, the reaction of 1,1-dilithiosilane $(^tBu_2MeSi)_2SiLi_2$ (generated by the reduction of 1,1-bis(di-*tert*-butylmethylsilyl)-2,3-bis(trimethylsilyl)-1-silacyclopro-2-ene with metallic lithium in THF)[6a] with an equimolar amount of Mes*EX_2 (E = P, As, Sb; X = F, Cl; Mes* = 2,4,6-$^tBu_3$-C_6H_2) in THF resulted in the formation of the alkene analogues featuring a double bond between the heavier group 14 and group 15 elements, phosphasilene **1**,[8] arsasilene **2** and stibasilene **3**, isolated as orange crystals in progressively lower yields of 34, 22, and 12%, in accord with the general trend of increasing difficulties in stabilization of the multiple bonds going down main groups of the periodic table (Scheme 1, Figure 1).[9] It should be noted that whereas **1** and **2** are new members of the stable phosphasilenes and arsasilenes family, the stibasilene **3** is the first compound featuring a Sb═Si bond and thus represents the "heaviest" doubly bonded combination between the group 14 and 15 elements.[10]

In accord with the presence of the stereochemically active lone pair on the pnictogen in **1**−**3**, the two $^tBu_2MeSi$ substituents are nonequivalent giving rise to two sets of signals in their ^1H, ^{13}C, and ^{29}Si NMR spectra. Interestingly, one of the Me groups of the two $^tBu_2MeSi$ substituents resonated in a quite distinct high-field area of −0.40 ppm (for **1**), −0.36 ppm (for **2**) and −0.35 ppm (for **3**), being ca. 0.90 ppm more shielded than the other Me group signal. This can be rationalized by taking into account the particular spatial arrangement of the former Me group directed toward the

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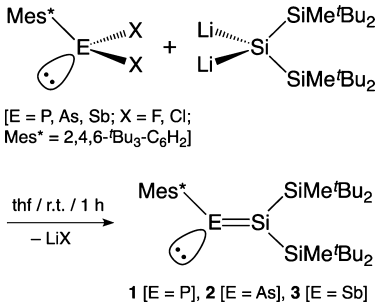
Scheme 1. General Approach for the Synthesis of the Stable Phosphasilene 1, Arsasilene 2, and Stibasilene 3



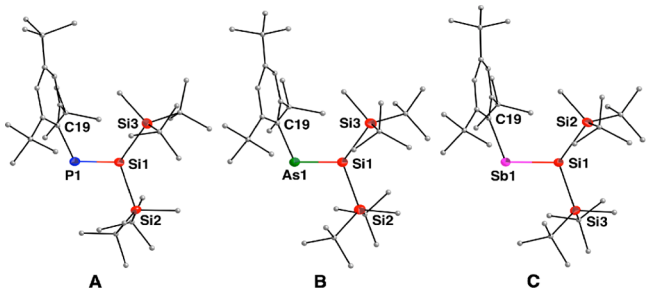


Figure 1. Molecular structures of the phosphasilene **1** (A), arsasilene **2** (B), and stibasilene **3** (C) [ORTEP, 50% probability level, hydrogen atoms omitted]. Selected bond lengths (Å) [calculated[9,13] values for the bond lengths of the model compounds **1**′, **2**′ and **3**′ are given in *italics* in square brackets]: **P1−Si1 = 2.1114(7)** [*2.1111*], P1−C19 = 1.863(2) [*1.885*], Si1−Si2 = 2.3855(8) [*2.3718*], Si1−Si3 = 2.4100(8) [*2.3803*] (A); **As1−Si1 = 2.2164(14)** [*2.1968*], As1−C19 = 2.004(4) [*1.987*], Si1−Si2 = 2.3864(17) [*2.3626*], Si1−Si3 = 2.4017(17) [*2.3727*] (B); **Sb1−Si1 = 2.4146(7)** [*2.4259*], Sb1−C19 = 2.200(2) [*2.245*], Si1−Si3 = 2.3748(10) [*2.3666*], Si1−Si2 = 2.3859(10) [*2.3687*] (C). Selected bond angles (deg): C19−P1−Si1 = 110.66(7), P1−Si1−Si2 = 104.83(3), P1−Si1−Si3 = 128.05(3) (A); C19−As1−Si1 = 108.97(12), As1−Si1−Si2 = 104.74(6), As1−Si1−Si3 = 127.94(7) (B); C19−Sb1−Si1 = 107.73(7), Sb1−Si1−Si3 = 106.54(3), Sb1−Si1−Si2 = 126.29(3) (C).

shielding area of the aromatic ring of the Mes* substituent, which was also observed in the crystal structures of **1**−**3**. One can notice that this shielding effect (and, accordingly, the extent of the high-field shift of the Me group in —E═Si< (E = P, As, Sb) derivatives) steadily drops from **1** to **2** to **3**, given the greater atomic radius of E and longer E−Si bond distance. The resonances of the sp^2-Si atoms were particularly important for the structural assignment in solution. Thus, a very characteristic low-field resonance of the doubly bonded Si atom was observed at 201.2 ppm (for **1**: doublet with the $^1J(^{29}Si-^{31}P)$ = 171.3 Hz), 214.1 ppm (for **2**) and 215.2 ppm (for **3**). The diagnostic deshielding of the sp^2-Si atom in phosphasilene **1**, well-documented in our previous study, was explained by its small HOMO−LUMO energy gap and, accordingly, important paramagnetic contribution.[4i] Given a further progressive decrease in the HOMO−LUMO gap on going from **1** to **2** to **3** (3.52 vs 3.42 vs 3.08 eV, respectively; see Figure 2 below), one can expect a notable low-field shift on going from arsasilene **2** to stibasilene **3**. However, in reality the resonances of the sp^2-Si atoms in **2** and **3** are only marginally different ($\Delta\delta$ = 0.9 ppm). This can be rationalized by the remarkable difference in the electronegativity (EN) of the As and Sb atoms (2.18 vs 2.05: Pauling scale),[11] which opposes and counteracts the influence of the above-described paramagnetic effect.

For the first-ever reported stibasilene **3**, there are no literature precedents available for the structural comparison. However, the Sb1═Si1 bond distance of 2.4146(7) Å is notably shorter than the sum of the single-bond covalent radii of the Sb and Si atoms of 2.56 Å[12] by 6%, thus suggesting the double bond character of the antimony−silicon bond [Wiberg bond index (WBI) was calculated as 1.85] (Figure 1).[13] The As1═Si1 bond in the novel arsasilene **2** of 2.2164(14) Å can be compared with those of only a couple of the structurally characterized arsasilenes: it is very close to that reported for the intramolecularly N-donor-stabilized arsasilene (2.2178(1) Å),[5b,14] however being longer (presumably due to the greater steric congestions around the double bond in **2**) than that in the arsasilene lacking intramolecular coordination (2.164(1) Å) (Figure 1).[5a] On the other hand, the arsenic−silicon interatomic distance in **2** (2.2164(14) Å) is markedly smaller (by 6.5%) than the sum of the single-bond covalent radii of the As and Si atoms of 2.37 Å[12] (WBI = 1.84).[13] Although the P1═Si1 bond in the previously reported phosphasilene **1** of 2.1114(7) Å[4i] is longer than the majority of others reported for the stable phosphasilenes (2.062(1)−2.0980(9) Å),[4] it is shorter than those of the heterocyclic zwitterionic phosphasilenes (2.1701(12)−2.2012(7)),[4l,m,14] being also shorter (by 7%) than the sum of the single bond covalent radii of the P and Si atoms (2.27 Å)[12] (WBI = 1.83) (Figure 1).[13] One can notice a steady decrease in the shortening of the double bonds (comparing with the single bonds) descending group 15: that is, on going from P═Si (7%) to As═Si (6.5%) to Sb═Si (6%) bonds.[14] In all Mes*E═Si(SiMe^{t}Bu$_2$)$_2$ (E = P, As, Sb) derivatives **1**−**3**, the E═Si double bond is practically undistorted, featuring nearly ideal trigonal-planar geometry at the sp^2-Si (with the sum of the bond angles around it totaling 360°, for **1**−**3**) and nontwisted E═Si bonds (torsional angles: C19−P1−Si1−Si2 = 178.81(7)° in **1**, C19−As1−Si1−Si2 = 179.4(2)° in **2**, C19−Sb1−Si1−Si3 = 177.72(7)° in **3**). Overall, all these structural features, manifested in the planar geometry of the E═Si bond (see above), allow for the effective np_π(E)−$3p_\pi$(Si) (n = 3 for P in **1**, 4 for As in **2** and 5 for Sb in **3**) orbital overlap to form rather strong double bonds that are indefinitely stable both in the solid state and in solution (even in the stibasilene **3** with the greatest mismatch in the energy and size of the interacting $5p_\pi$ (Sb) and $3p_\pi$ (Si) orbitals). Interestingly, although the drop in the C19−E1−Si1 bond angle on going from **1** to **3** is rather marginal (110.66(7)° for **1**, 108.97(12)° for **2** and 107.73(7)° for **3**), the trend itself is quite diagnostic. It reflects a well-documented tendency of the increase in the *s*-character of the lone pair nonbonding orbital (and, accordingly, increase in the *p*-character of the bonding orbitals) descending the main groups of the periodic table, caused by the inherent reluctance of the heavier elements to hybridize.[15] On the other hand, the trend of the decreasing C19−E1−Si1 angle may also be a manifestation of the more diffused nature of the lone pair orbital on the E center on going from P to As to Sb atoms.

It comes as no surprise that, reflecting higher EN of pnictogens,[11] the σ- and the π-components of the E═Si (E = P, As, Sb) double bond are consistently polarized toward the pnictogen E.[16] However, the E═Si bonding situation in the pnictasilenes **1**−**3** is still better described by the covalent rather than the ionic (or donor−acceptor) interactions, given notably low values for the natural ionicity of their double bonds $I_{E=Si}$:[17] for phosphasilene **1**′ I = 0.14 (σ-bond) and 0.18 (π-bond), for arsasilene **2**′ I = 0.11 (σ-bond) and 0.14 (π-bond), for stibasilene **3**′ I = 0.07 (σ-bond) and 0.06 (π-bond). This

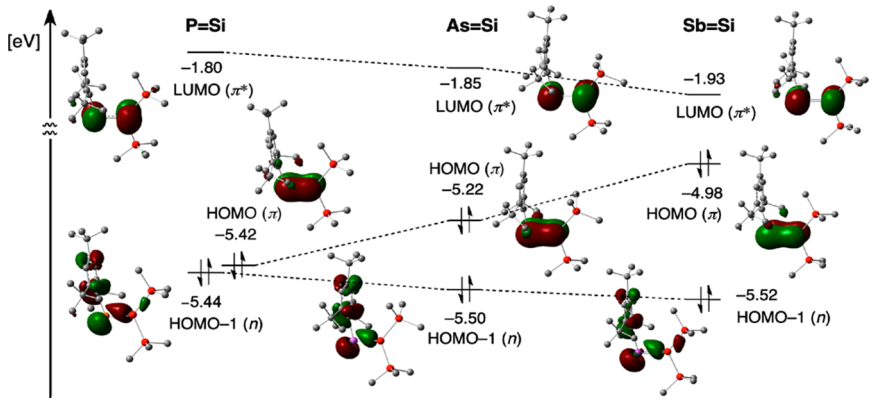


Figure 2. Frontier molecular orbitals (HOMO−1, HOMO, and LUMO, calculated at the DFT B3LYP level with the 6-31G(d) basis set [3-21G(d) for Sb] for the model compounds Mes*E═Si($SiMe_3$)$_2$ (Mes* = 2,4,6-^{t}Bu$_3$-C_6H_2) **1′** (E = P), **2′** (E = As) and **3′** (E = Sb): phosphasilene **1′** (left), arsasilene **2′** (center), and stibasilene **3′** (right).

hypothesis well agrees with the experimentally observed undistorted geometry (see above) around the E═Si bonds: planar skeleton with no signs of either *trans*-bending at Si or twisting around the E═Si bond.

Inspection of the frontier molecular orbitals (FMO) revealed that all model compounds, phosphasilene **1′**, arsasilene **2′**, and stibasilene **3′**, uniformly exhibited identical FMO patterns: HOMO−1 is mostly represented by the pnictogen lone pair *n*-orbital (with the admixture of the conjugated aryl group *π*-orbital), whereas HOMO and LUMO are almost pure *π*- and *π**-orbitals of the E═Si bond (Figure 2).[13] Diagnostically, on going from phosphasilene to arsasilene to stibasilene the HOMO energy levels remarkably increase from −5.42 eV (in **1′**) to −5.22 eV (in **2′**) to −4.98 eV (in **3′**), whereas the HOMO−1 energy levels progressively decreased from −5.44 eV (in **1′**) to −5.50 eV (in **2′**) to −5.52 eV (in **3′**). Such trend can be well rationalized given the greater *s*-character of the lone pair MO (62% for **1′**, 69% for **2′** and 75% for **3′**) and notably weaker *π*-bonds descending group 15, resulting in the lowering of nonbonding *n*-orbital and a substantial rise of the bonding *π*-orbital energy levels on going from **1′** to **2′** to **3′**. Again, this is a clear manifestation of the general tendency of the reluctance of the heavier main group elements to hybridize and form multiple bonds.[10,15] Given the progressive lowering of the LUMO energy levels from −1.80 eV (in **1′**) to −1.85 eV (in **2′**) to −1.93 eV (in **3′**), one can notice quite remarkable, albeit expectable, drop in the HOMO−LUMO energy gap: from 3.62 eV (in **1′**) to 3.37 eV (in **2′**) to 3.05 eV (in **3′**).

In conclusion, a complete series of the stable pnictasilenes (2,4,6-^{t}Bu$_3$-C_6H_2)E═Si(SiMe^{t}Bu$_2$)$_2$ (E = P, As, Sb) was prepared and unambiguously characterized. A structural comparison, based on the NMR spectroscopy, X-ray crystallography, and computational studies, revealed principal similarities and differences between —E═Si< derivatives, depending on the nature of pnictogen E (lighter vs heavier group 15 element).

■ ASSOCIATED CONTENT

Supporting Information

Experimental Section (including synthetic procedures, spectral and crystallographic data for **2** and **3**), computational data for the model compounds **1′**, **2′**, and **3′**, and crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) Although the phosphasilene Mes*P═Si(SiMe^{t}Bu$_2$)$_2$ (Mes* = 2,4,6-^{t}Bu$_3$-C$_6$H$_2$) was preliminary reported [see ref 4i], for the sake of systematic comparison with the newly synthesized arsasilene and stibasilene, its spectroscopic and structural characteristics are briefly discussed in this paper.

(9) Details of experimental procedures, spectroscopic and crystallographic data for arsasilene **2** and stibasilene **3**, as well as computational data for the model compounds **1′**, **2′** and **3′** with the Me$_3$Si groups replacing ^{t}Bu$_2$MeSi substituents (including their optimized geometries and total energies) are given in the Supporting Information.

(10) Our attempts to synthesize the bismasilene —Bi═Si< featuring a double bond between the silicon and the heaviest group 15 element (Bi) failed, even utilizing much more sterically demanding (Mes*) terphenyl group Ar [Ar = 2,6-(2,4,6-Me$_3$-C$_6$H$_2$)$_2$-C$_6$H$_3$] on bismuth. Thus, the reaction of ArBiCl$_2$ with (^{t}Bu$_2$MeSi)$_2$SiLi$_2$ in different solvents (THF, Et$_2$O, toluene) resulted in the formation of complicated products mixture, of which only ArH and known dibismuthene ArBi═BiAr [(a) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357] could be identified. This manifests a particular reluctance of the heaviest elements of the main groups (i.e., those of the sixth period: Tl, Pb, *Bi*) to hybridize, caused by relativistic effects responsible for a particular stabilization of *s*-electrons [*inert pair effect*]: (b) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271. (c) Pyykkö, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276. (d) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.

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(13) All of the computations were carried out with the Gaussian 03 (Revision D.01) suite of programs at the DFT B3LYP level with the 6-31/G(d) basis set for all atoms except for Sb (3-21G(d) basis set for Sb) [for the computational details and complete Gaussian 03 (Revision D.01) reference, see the Supporting Information].

(14) For the structural formulas of the N-donor-stabilized arsasilene and heterocyclic zwitterionic phosphasilenes, see the Supporting Information, Scheme S1.

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(16) Polarization coefficients for the E and Si hybrids: **1′** [*s*-bond: 0.7558(P)/0.6548(Si), π-bond: 0.7690(P)/0.6392(Si)], **2′** [σ-bond: 0.7458(As)/0.6662(Si), π-bond: 0.7560(As)/0.6546(Si)] and **3′** [σ-bond: 0.6821(Sb)/0.7313(Si), π-bond: 0.7279(Sb)/0.6857(Si)].

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