SUPPORTING INFORMATION

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

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Contents of the Supporting Information:

1. Experimental Section.

General procedures. All experimental manipulations were performed using high-vacuum line techniques or in an argon atmosphere of an MBRAUN MB 150B-G glove box. All solvents were predried by conventional methods and finally dried and degassed over a potassium mirror in vacuo immediately prior to use. NMR spectra were recorded on AV-400FT NMR (^{1}H NMR at 400.1 MHz; ^{13}C NMR at 100.6 MHz; ^{29}Si NMR at 79.5 MHz) spectrometer. UV-Vis spectra were recorded on a Shimadzu UV-3150 UV-Vis spectrophotometer in hexane. High-resolution mass spectra were measured on a Bruker Daltonics micrOTOF-TU mass spectrometer with atmospheric pressure chemical ionization (APCI) method. The 1,1-dilithiosilane derivative (^{t}Bu$_2$MeSi)$_2$SiLi$_2$ was prepared from the 1,1-bis(di-*tert*-butylmethylsilyl)-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene by its reduction with metallic lithium according to a published procedure.[1] Mes*AsF$_2$ and Mes*SbF$_2$ (Mes* = 2,4,6-tri-*tert*-butylphenyl) were synthesized by the reaction of Mes*Li with either AsF$_3$ or SbF$_3$ in thf, as described before.[2,3] The synthesis and physico-chemical characteristics of the phosphasilene **1** were reported in the preceding publication.[4]

1.1. Experimental procedure and spectroscopic data for arsasilene 2.

A mixture of the bis(di-*tert*-butylmethylsilyl)dilithiosilane [prepared from 1,1-bis(di-*tert*-butylmethylsilyl)-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene (500 mg, 0.98 mmol) and Li (69.0 mg, 9.9 mmol) in THF (5 ml)] and (2,4,6-tri-*tert*-butylphenyl)difluoroarsine (340 mg, 0.98 mmol) was placed in a reaction tube with a magnetic stirring bar. Then dry oxygen-free THF (5 ml) was introduced into the reaction tube by vacuum transfer, and the reaction mixture was stirred at room temperature for 1 h to form a dark-red solution. Then the solvent was removed under vacuum, and dry hexane was introduced. After the inorganic salt was filtered off, the residue was recrystallized from hexane (1 ml) by slow evaporation of solvent to give **2** as orange crystals (140 mg, 22%). Mp 203–205 °C. ^{1}H NMR (C_6D_6, δ, ppm) –0.36 (s, 3 H, Me), 0.53 (s, 3 H, Me), 0.98 (s, 18 H, 2 CMe$_3$), 1.38 (s, 18 H, 2 CMe$_3$), 1.41 (s, 9 H, CMe$_3$), 1.69 (s, 18 H, 2 CMe$_3$), 7.54 (s, 2 H, H$_{meta}$); ^{13}C NMR (C_6D_6, δ, ppm) –6.30 (Me), –3.03 (Me), 22.21 (2 *C*Me$_3$), 22.24 (2 *C*Me$_3$), 30.37 (2 C*Me*$_3$), 30.55 (2 C*Me*$_3$), 31.86 (C*Me*$_3$), 34.24 (2 C*Me*$_3$), 34.90 (*C*Me$_3$), 39.14 (2 *C*Me$_3$), 122.14 (C$_{arom}$, *meta*),

141.67 (C_{arom}, *ipso*), 148.66 (C_{arom}, *para*), 153.77 (C_{arom}, *ortho*); ^{29}Si NMR (C_6D_6, δ, ppm) 16.79 (Si substituent), 23.83 (Si substituent), 214.11 (As=*Si*); UV-Vis (hexane) λ_{max}/nm (ε) 454 (240), 386 (4200); HRMS (APCI): *m/*z calcd. for $C_{36}H_{71}AsSi_3$ $[M]^+$ 662.4074, found: 662.4073. Anal. Calcd. for $C_{36}H_{71}AsSi_3$: C, 65.20; H, 10.79. Found: C, 65.49; H, 10.66.

The single crystals of **2** for X-ray diffraction analysis were grown from a hexane solution. Diffraction data were collected at 150 K on a MacScience DIP2030 image plate diffractometer with a rotating anode equipped with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by the direct method with the SIR-92[5] program, and refined by the full-matrix least-squares method by the SHELXL-97 program[6]. Crystal data for **2**: MF = $C_{36}H_{71}AsSi_3$, MW = 663.12, orthorhombic, $P2_12_12_1$, a = 11.8610(6), b = 17.6180(8), c = 19.3680(5) Å, V = 4047.3(3) Å^3, Z = 4, D_{calcd} = 1.088 g cm^{-3}. The final R factor was 0.0480 for 4585 reflections with $I_o > 2\sigma(I_o)$ (R_w = 0.1373 for all data, 5352 reflections), GOF = 1.085. The X-ray crystallographic data for **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition no. CCDC 960034. These data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif).

1.2. Experimental procedure and spectroscopic data for stibasilene 3.

A mixture of the bis(di-*tert*-butylmethylsilyl)dilithiosilane [prepared from 1,1-bis(di-*tert*-butylmethylsilyl)-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene (125 mg, 0.24 mmol) and Li (17.0 mg, 2.43 mmol) in THF (2 ml)] and (2,4,6-tri-*tert*-butylphenyl)difluorostibine (100 mg, 0.24 mmol) was placed in a reaction tube with a magnetic stirring bar.

Then dry oxygen-free THF (2 ml) was introduced into the reaction tube by vacuum transfer, and the reaction mixture was stirred at room temperature for 1 h to form a dark-red solution. Then the solvent was removed under vacuum, and dry hexane was introduced. After the inorganic salt was filtered off, the residue was subjected to dry silica gel column chromatography (eluent: hexane) in glove-box, followed by the recrystallization from hexane (1 ml) by slow evaporation of solvent to give **3** as orange-red crystals (20 mg, 12%). Mp 188–189 °C. ^{1}H NMR (C_6D_6, δ, ppm) –0.35 (s, 3

H, Me), 0.55 (s, 3 H, Me), 1.00 (s, 18 H, 2 CMe_3), 1.34 (s, 18 H, 2 CMe_3), 1.39 (s, 9 H, CMe_3), 1.65 (s, 18 H, 2 CMe_3), 7.60 (s, 2 H, H_{meta}); ^{13}C NMR (C_6D_6, δ, ppm) –5.85 (Me), –2.08 (Me), 21.03 (2 *C*Me_3), 22.48 (2 *C*Me_3), 30.25 (2 C*Me*$_3$), 30.65 (2 C*Me*$_3$), 31.76 (C*Me*$_3$), 34.88 (*C*Me_3), 35.13 (2 C*Me*$_3$), 39.22 (2 *C*Me_3), 122.66 (C_{arom}, *meta*), 137.87 (C_{arom}, *ipso*), 149.13 (C_{arom}, *para*), 157.03 (C_{arom}, *ortho*); ^{29}Si NMR (C_6D_6, δ, ppm) 21.91 (Si substituent), 31.21 (Si substituent), 215.22 (As=*Si*); UV-Vis (hexane) λ_{max}/nm (ε) 514 (500), 421 (7700). Anal. Calcd. for $C_{36}H_{71}SbSi_3$: C, 60.90; H, 10.08. Found: C, 61.02; H, 10.10.

The single crystals of **3** for X-ray diffraction analysis were grown from a pentane solution. Diffraction data were collected at 150 K on a Bruker AXS APEX II CCD X-ray diffractometer (Mo-Kα radiation, λ = 0.71073 Å, 50 kV/30 mA). The structure was solved by the direct method with the SHELXS-97 program[7] and refined by the full-matrix least-squares method with the SHELXL-97 program[6]. Crystal data for **3**: MF = $C_{36}H_{71}SbSi_3$, MW = 709.95, orthorhombic, $P2_12_12_1$, a = 12.0632(13), b = 17.6672(19), c = 19.301(2) Å, V = 4113.6(8) Å^3, Z = 4, D_{calcd} = 1.146 g cm^{-3}. The final R factor was 0.0286 for 8487 reflections with $I_o > 2\sigma(I_o)$ (R_w = 0.0650 for all data, 9229 reflections), GOF = 1.009. The X-ray crystallographic data for **3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition no. CCDC 960035. These data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif).

2. X-ray crystallography.

Table S1. Crystallographic data for compound **2**.

Empirical formula	C36 H71 As Si3
Formula weight	663.12
Temperature	150 K
Wavelength	0.71070 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 11.8610(6) A alpha = 90 deg.
	b = 17.6180(8) A beta = 90 deg.
	c = 19.3680(5) A gamma = 90 deg.
Volume	4047.3(3) A^3
Z, Calculated density	4, 1.088 Mg/m^3
Absorption coefficient	0.950 mm^-1
F(000)	1448
Crystal size	0.50 x 0.30 x 0.30 mm
Theta range for data collection	2.07 to 27.91 deg.
Limiting indices	0<=h<=15, 0<=k<=23, 0<=l<=25
Reflections collected / unique	5352 / 5352 [R(int) = 0.086]
Completeness to theta = 27.91	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5352 / 0 / 362
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1234
R indices (all data)	R1 = 0.0610, wR2 = 0.1373
Absolute structure parameter	0.351(12)
Extinction coefficient	0.0308(18)
Largest diff. peak and hole	0.806 and -0.657 e.A^-3

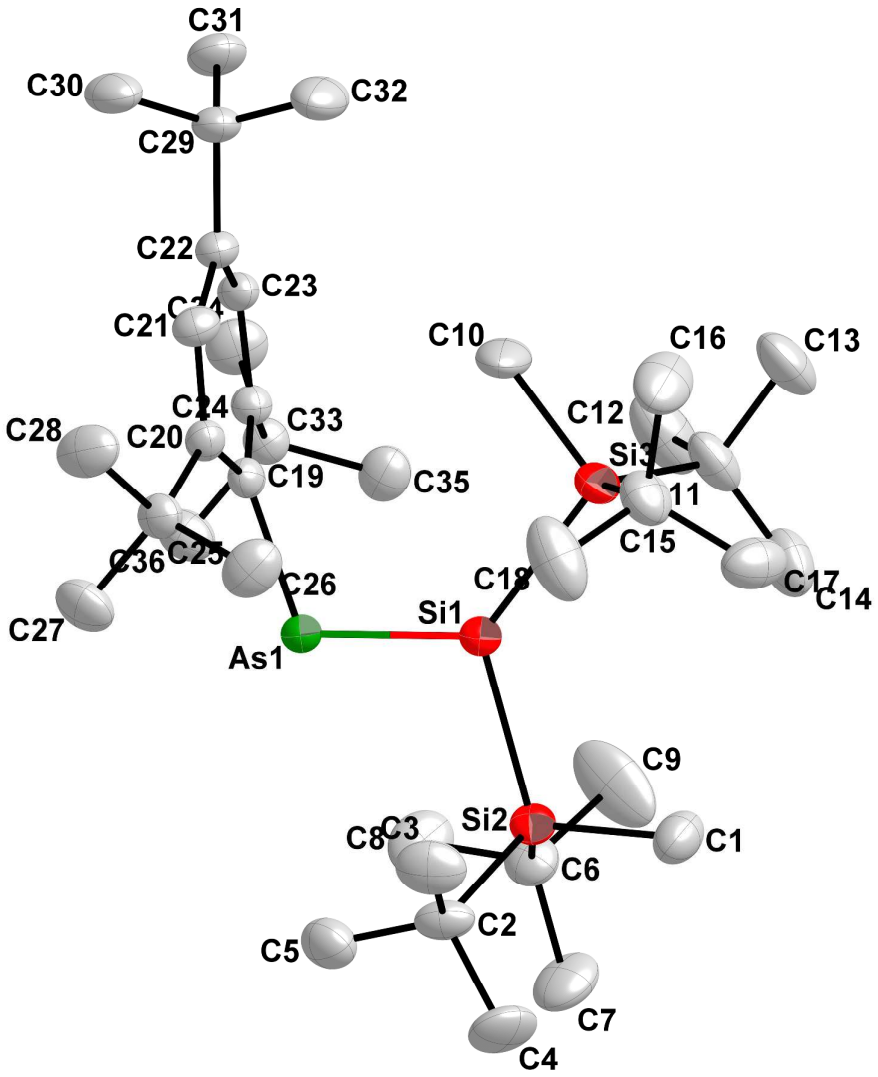


Figure S1. Molecular structure of the arsasilene **2** (ORTEP plot with the thermal ellipsoids drawn at the 50% probability level), hydrogen atoms are not shown.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
As(1)	2905(1)	366(1)	9778(1)	28(1)
Si(1)	4137(1)	-116(1)	9037(1)	29(1)
Si(2)	5177(1)	-1026(1)	9691(1)	28(1)
Si(3)	4379(1)	200(1)	7840(1)	37(1)
C(1)	6408(5)	-1337(3)	9142(3)	47(1)
C(2)	5828(5)	-580(3)	10511(3)	37(1)
C(3)	6337(6)	200(3)	10330(3)	52(2)
C(4)	6781(6)	-1078(4)	10778(3)	60(2)
C(5)	4984(6)	-464(3)	11103(3)	48(1)
C(6)	4223(5)	-1890(3)	9857(3)	41(1)
C(7)	4851(7)	-2509(3)	10276(4)	62(2)
C(8)	3137(5)	-1702(3)	10238(4)	54(2)
C(9)	3890(9)	-2211(4)	9150(4)	89(3)
C(10)	3221(7)	913(5)	7654(3)	71(2)
C(11)	4142(5)	-658(4)	7242(3)	50(2)
C(12)	2932(7)	-928(5)	7317(3)	78(3)
C(13)	4333(6)	-413(5)	6488(3)	63(2)
C(14)	4910(7)	-1335(4)	7399(3)	58(2)
C(15)	5803(6)	705(3)	7712(3)	45(1)
C(16)	5708(7)	1264(4)	7109(3)	65(2)
C(17)	6784(5)	161(4)	7560(3)	54(2)
C(18)	6120(7)	1159(4)	8370(4)	71(2)
C(19)	1955(4)	1138(3)	9289(2)	26(1)
C(20)	2307(4)	1914(3)	9294(2)	27(1)
C(21)	1818(4)	2392(3)	8804(2)	30(1)
C(22)	959(4)	2167(3)	8356(2)	29(1)

C(23)	519(4)	1449(3)	8458(2)	29(1)
C(24)	977(4)	921(3)	8926(2)	27(1)
C(25)	3111(4)	2283(3)	9839(2)	32(1)
C(26)	4365(5)	2121(3)	9696(3)	48(1)
C(27)	2790(6)	2029(4)	10566(3)	49(1)
C(28)	3005(6)	3152(3)	9845(3)	51(2)
C(29)	543(5)	2706(3)	7783(2)	36(1)
C(30)	317(6)	3500(3)	8073(3)	48(2)
C(31)	−554(5)	2427(3)	7451(3)	49(1)
C(32)	1462(6)	2748(4)	7228(3)	57(2)
C(33)	341(4)	159(3)	9025(2)	31(1)
C(34)	−859(5)	183(3)	8706(3)	47(1)
C(35)	921(5)	−519(3)	8675(3)	42(1)
C(36)	152(5)	−6(3)	9795(3)	43(1)

Table S3. Bond lengths [A] and angles [deg] for **2**.

As(1)-C(19)	2.004(4)
As(1)-Si(1)	2.2164(14)
Si(1)-Si(2)	2.3864(17)
Si(1)-Si(3)	2.4017(17)
Si(2)-C(1)	1.888(6)
Si(2)-C(6)	1.924(5)
Si(2)-C(2)	1.932(5)
Si(3)-C(10)	1.897(6)
Si(3)-C(11)	1.924(6)
Si(3)-C(15)	1.926(6)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-C(4)	1.523(7)
C(2)-C(5)	1.534(8)
C(2)-C(3)	1.541(7)
C(3)-H(3A)	0.9600
C(3)-H(3B)	0.9600
C(3)-H(3C)	0.9600
C(4)-H(4A)	0.9600
C(4)-H(4B)	0.9600
C(4)-H(4C)	0.9600
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(6)-C(8)	1.521(8)
C(6)-C(9)	1.533(8)
C(6)-C(7)	1.550(8)
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600

C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(12)	1.519(10)
C(11)-C(14)	1.533(10)
C(11)-C(13)	1.538(7)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.531(8)
C(15)-C(17)	1.537(8)
C(15)-C(18)	1.551(8)
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9600

C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-C(24)	1.410(6)
C(19)-C(20)	1.429(6)
C(20)-C(21)	1.395(6)
C(20)-C(25)	1.565(6)
C(21)-C(22)	1.395(6)
C(21)-H(21)	0.9300
C(22)-C(23)	1.382(7)
C(22)-C(29)	1.543(6)
C(23)-C(24)	1.409(6)
C(23)-H(23)	0.9300
C(24)-C(33)	1.552(6)
C(25)-C(27)	1.524(7)
C(25)-C(28)	1.536(7)
C(25)-C(26)	1.540(8)
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-C(30)	1.530(7)
C(29)-C(32)	1.532(8)
C(29)-C(31)	1.533(7)
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600
C(31)-H(31A)	0.9600

C(31)-H(31B)	0.9600
C(31)-H(31C)	0.9600
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600
C(33)-C(36)	1.535(7)
C(33)-C(35)	1.536(7)
C(33)-C(34)	1.552(7)
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600
C(35)-H(35A)	0.9600
C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600

C(19)-As(1)-Si(1)	108.97(12)
As(1)-Si(1)-Si(2)	104.74(6)
As(1)-Si(1)-Si(3)	127.94(7)
Si(2)-Si(1)-Si(3)	127.31(7)
C(1)-Si(2)-C(6)	108.6(3)
C(1)-Si(2)-C(2)	105.8(3)
C(6)-Si(2)-C(2)	114.8(2)
C(1)-Si(2)-Si(1)	107.18(18)
C(6)-Si(2)-Si(1)	108.40(18)
C(2)-Si(2)-Si(1)	111.69(16)
C(10)-Si(3)-C(11)	107.5(3)
C(10)-Si(3)-C(15)	107.7(3)
C(11)-Si(3)-C(15)	114.5(3)
C(10)-Si(3)-Si(1)	104.52(19)

C(11)-Si(3)-Si(1)	112.46(19)
C(15)-Si(3)-Si(1)	109.63(18)
Si(2)-C(1)-H(1A)	109.5
Si(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
Si(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(4)-C(2)-C(5)	107.9(5)
C(4)-C(2)-C(3)	107.5(5)
C(5)-C(2)-C(3)	107.9(5)
C(4)-C(2)-Si(2)	110.0(4)
C(5)-C(2)-Si(2)	114.0(4)
C(3)-C(2)-Si(2)	109.4(3)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5

C(8)-C(6)-C(9)	107.2(6)
C(8)-C(6)-C(7)	107.8(5)
C(9)-C(6)-C(7)	109.3(6)
C(8)-C(6)-Si(2)	114.0(4)
C(9)-C(6)-Si(2)	107.2(4)
C(7)-C(6)-Si(2)	111.2(4)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(6)-C(9)-H(9A)	109.5
C(6)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(6)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
Si(3)-C(10)-H(10A)	109.5
Si(3)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
Si(3)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(14)	107.4(6)
C(12)-C(11)-C(13)	108.5(5)

C(14)-C(11)-C(13)	108.6(5)
C(12)-C(11)-Si(3)	109.1(5)
C(14)-C(11)-Si(3)	113.9(4)
C(13)-C(11)-Si(3)	109.2(5)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(17)	108.0(5)
C(16)-C(15)-C(18)	108.3(5)
C(17)-C(15)-C(18)	107.2(6)
C(16)-C(15)-Si(3)	109.3(5)
C(17)-C(15)-Si(3)	113.6(4)
C(18)-C(15)-Si(3)	110.2(4)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(24)-C(19)-C(20)	120.1(4)
C(24)-C(19)-As(1)	120.9(3)
C(20)-C(19)-As(1)	118.9(3)
C(21)-C(20)-C(19)	116.9(4)
C(21)-C(20)-C(25)	117.5(4)
C(19)-C(20)-C(25)	125.4(4)
C(20)-C(21)-C(22)	123.7(4)
C(20)-C(21)-H(21)	118.1
C(22)-C(21)-H(21)	118.1
C(23)-C(22)-C(21)	116.6(4)
C(23)-C(22)-C(29)	123.1(4)
C(21)-C(22)-C(29)	120.4(4)
C(22)-C(23)-C(24)	123.4(4)
C(22)-C(23)-H(23)	118.3
C(24)-C(23)-H(23)	118.3
C(23)-C(24)-C(19)	117.4(4)
C(23)-C(24)-C(33)	117.6(4)
C(19)-C(24)-C(33)	125.0(4)

C(27)-C(25)-C(28)	105.4(4)
C(27)-C(25)-C(26)	110.6(5)
C(28)-C(25)-C(26)	105.4(5)
C(27)-C(25)-C(20)	110.4(4)
C(28)-C(25)-C(20)	111.7(4)
C(26)-C(25)-C(20)	113.0(4)
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(25)-C(28)-H(28A)	109.5
C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(30)-C(29)-C(32)	109.8(5)
C(30)-C(29)-C(31)	107.4(5)
C(32)-C(29)-C(31)	109.0(5)
C(30)-C(29)-C(22)	110.7(4)
C(32)-C(29)-C(22)	107.9(4)
C(31)-C(29)-C(22)	112.1(5)
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5

H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(29)-C(32)-H(32A)	109.5
C(29)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(29)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(36)-C(33)-C(35)	110.3(4)
C(36)-C(33)-C(24)	110.8(4)
C(35)-C(33)-C(24)	113.7(4)
C(36)-C(33)-C(34)	104.9(4)
C(35)-C(33)-C(34)	104.8(4)
C(24)-C(33)-C(34)	111.9(4)
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(33)-C(35)-H(35A)	109.5
C(33)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(33)-C(35)-H(35C)	109.5

H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(33)-C(36)-H(36A)	109.5
C(33)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(33)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for **2**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
As(1)	31(1)	29(1)	25(1)	2(1)	0(1)	6(1)
Si(1)	30(1)	30(1)	26(1)	2(1)	0(1)	3(1)
Si(2)	30(1)	23(1)	31(1)	4(1)	-2(1)	0(1)
Si(3)	36(1)	50(1)	26(1)	6(1)	3(1)	9(1)
C(1)	43(3)	44(3)	52(3)	7(3)	8(3)	11(3)
C(2)	40(3)	31(2)	42(2)	8(2)	-17(2)	-2(2)
C(3)	57(4)	43(3)	57(3)	1(3)	-21(3)	-15(3)
C(4)	56(4)	55(4)	67(4)	11(3)	-29(3)	12(3)
C(5)	61(4)	46(3)	38(3)	-5(2)	-10(2)	4(3)
C(6)	50(3)	27(2)	46(3)	3(2)	-1(2)	-4(2)
C(7)	71(4)	32(3)	82(4)	19(3)	6(4)	2(3)
C(8)	43(3)	42(3)	76(4)	11(3)	7(3)	-14(2)
C(9)	151(9)	59(4)	58(4)	-16(3)	1(5)	-64(5)
C(10)	78(5)	98(6)	36(3)	30(3)	12(3)	45(5)
C(11)	49(3)	75(4)	26(2)	-10(3)	2(2)	-10(3)
C(12)	64(5)	123(7)	47(3)	-15(4)	8(4)	-37(5)
C(13)	66(4)	96(5)	28(2)	-8(3)	0(2)	-7(4)
C(14)	79(5)	50(4)	46(3)	-14(3)	10(3)	-9(4)
C(15)	55(4)	45(3)	36(3)	4(2)	9(2)	-3(3)
C(16)	70(5)	61(4)	65(4)	27(3)	29(4)	12(4)
C(17)	38(3)	67(4)	58(3)	20(3)	1(3)	3(3)
C(18)	84(6)	71(5)	57(4)	-20(3)	22(4)	-36(4)
C(19)	24(2)	30(2)	24(2)	-1(2)	2(2)	2(2)
C(20)	24(2)	31(2)	26(2)	-4(2)	-2(2)	1(2)
C(21)	29(3)	27(2)	34(2)	5(2)	-4(2)	1(2)
C(22)	32(3)	29(2)	27(2)	3(2)	-2(2)	6(2)

C(23)	30(3)	31(2)	26(2)	-5(2)	-7(2)	5(2)
C(24)	29(2)	26(2)	26(2)	0(2)	-1(2)	1(2)
C(25)	37(3)	27(2)	31(2)	-6(2)	-5(2)	2(2)
C(26)	37(3)	40(3)	66(4)	-8(3)	-11(3)	-6(2)
C(27)	60(4)	53(3)	33(2)	-7(2)	-12(3)	-5(3)
C(28)	63(4)	32(2)	57(3)	-10(2)	-22(3)	4(3)
C(29)	43(3)	36(2)	29(2)	5(2)	-9(2)	10(2)
C(30)	70(4)	34(3)	40(3)	5(2)	-15(3)	10(3)
C(31)	51(4)	48(3)	46(3)	3(2)	-19(3)	12(3)
C(32)	55(4)	75(4)	40(3)	24(3)	7(3)	14(3)
C(33)	29(2)	31(2)	33(2)	-2(2)	-2(2)	-5(2)
C(34)	34(3)	50(3)	58(3)	0(3)	-9(2)	-9(3)
C(35)	38(3)	39(3)	49(3)	-10(2)	-6(2)	-4(2)
C(36)	52(3)	41(3)	37(2)	1(2)	-4(3)	-10(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **2**.

	x	y	z	U(eq)
H(1A)	6894	-911	9058	70
H(1B)	6135	-1531	8710	70
H(1C)	6822	-1726	9378	70
H(3A)	5755	527	10156	79
H(3B)	6909	137	9984	79
H(3C)	6664	421	10736	79
H(4A)	6492	-1571	10891	89
H(4B)	7103	-851	11184	89
H(4C)	7351	-1126	10429	89
H(5A)	4661	-944	11228	73
H(5B)	4398	-125	10956	73
H(5C)	5367	-251	11494	73
H(7A)	5082	-2304	10713	92
H(7B)	5503	-2674	10023	92
H(7C)	4358	-2933	10351	92
H(8A)	3314	-1500	10685	81
H(8B)	2694	-2155	10289	81
H(8C)	2717	-1333	9979	81
H(9A)	4558	-2336	8894	134
H(9B)	3461	-1839	8901	134
H(9C)	3443	-2660	9213	134
H(10A)	3315	1349	7946	106
H(10B)	2500	685	7742	106
H(10C)	3262	1068	7179	106
H(12A)	2800	-1085	7785	117
H(12B)	2803	-1349	7012	117
H(12C)	2427	-522	7201	117

H(13A)	5094	−238	6434	95
H(13B)	3819	−11	6373	95
H(13C)	4204	−838	6188	95
H(14A)	4796	−1496	7867	87
H(14B)	5683	−1189	7337	87
H(14C)	4733	−1746	7091	87
H(16A)	5101	1611	7194	98
H(16B)	5564	989	6690	98
H(16C)	6401	1541	7064	98
H(17A)	6619	−127	7151	81
H(17B)	6885	−178	7943	81
H(17C)	7463	448	7489	81
H(18A)	5523	1506	8481	106
H(18B)	6803	1438	8289	106
H(18C)	6230	815	8748	106
H(21)	2079	2888	8774	36
H(23)	−113	1308	8204	35
H(26A)	4551	2281	9236	71
H(26B)	4506	1586	9741	71
H(26C)	4822	2393	10022	71
H(27A)	2837	1486	10595	73
H(27B)	2033	2188	10665	73
H(27C)	3298	2253	10894	73
H(28A)	3203	3348	9399	76
H(28B)	3503	3359	10187	76
H(28C)	2242	3291	9953	76
H(30A)	−263	3471	8418	72
H(30B)	79	3830	7707	72
H(30C)	995	3696	8278	72
H(31A)	−442	1928	7265	73
H(31B)	−769	2767	7086	73
H(31C)	−1140	2412	7793	73

H(32A)	1598	2249	7046	85
H(32B)	2143	2943	7428	85
H(32C)	1219	3077	6862	85
H(34A)	−1278	592	8909	71
H(34B)	−1238	−288	8797	71
H(34C)	−803	259	8217	71
H(35A)	1029	−411	8194	63
H(35B)	458	−963	8724	63
H(35C)	1639	−608	8889	63
H(36A)	−213	421	10007	65
H(36B)	865	−93	10015	65
H(36C)	−314	−448	9844	65

Table S6. Crystallographic data for compound **3**.

Identification code	stibasilene_0m	
Empirical formula	C36 H71 Sb Si3	
Formula weight	709.95	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.0632(13) Å	□lpha = 90 deg.
	b = 17.6672(19) Å	□eta = 90 deg.
	c = 19.301(2) Å	□amma = 90 deg.
Volume	4113.6(8) $Å^3$	
Z	4	
Density (calculated)	1.146 Mg/m^3	
Absorption coefficient	0.779 mm^{-1}	
F(000)	1520	
Crystal size	0.26 x 0.25 x 0.15 mm^3	
Theta range for data collection	1.56 to 27.50°.	
Index ranges	-15<=h<=11, -22<=k<=22, -25<=l<=19	
Reflections collected	23270	
Independent reflections	9229 [R(int) = 0.0289]	
Completeness to theta = 27.50–	99.1 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8921 and 0.8232	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9229 / 0 / 384	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0286, wR2 = 0.0625	
R indices (all data)	R1 = 0.0341, wR2 = 0.0650	
Absolute structure parameter	0.535(12)	
Largest diff. peak and hole	0.277 and -0.319 e.$Å^{-3}$	

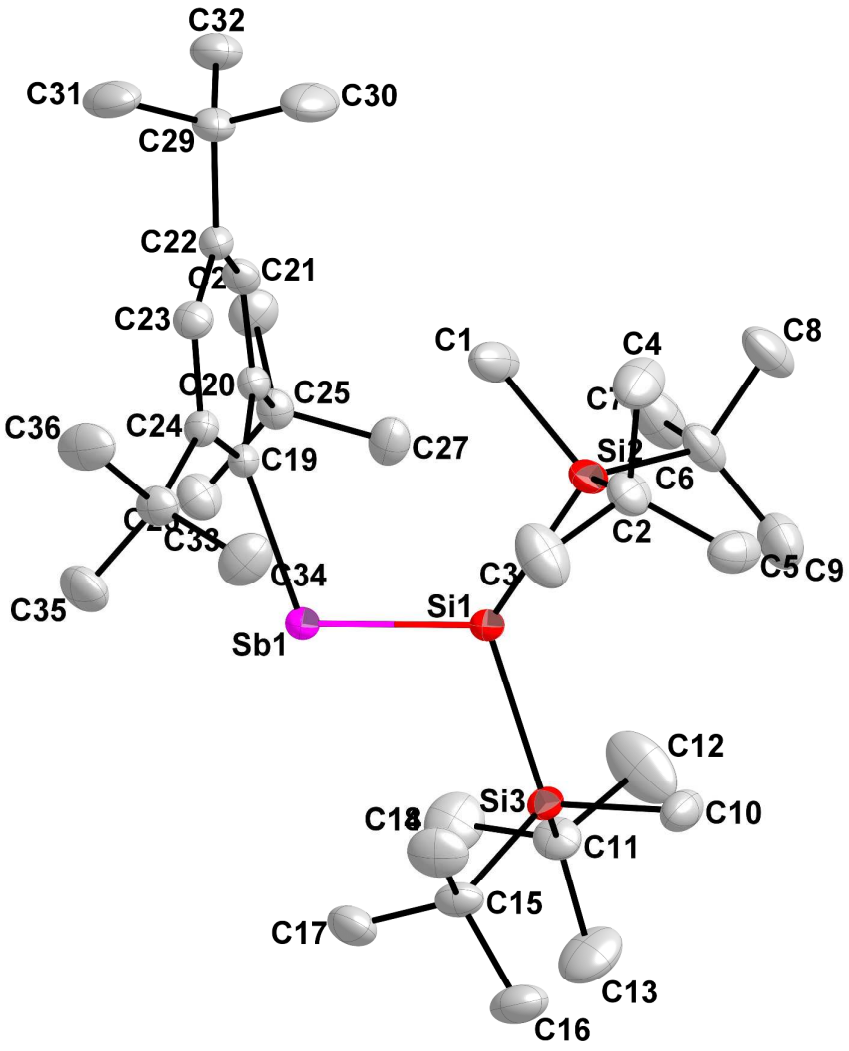


Figure S2. Molecular structure of the stibasilene **3** (ORTEP plot with the thermal ellipsoids drawn at the 50% probability level), hydrogen atoms are not shown.

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters († ^{2}x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8293(3)	885(2)	7741(2)	47(1)
C(2)	10827(3)	707(2)	7742(2)	34(1)
C(3)	11128(3)	1149(2)	8401(2)	52(1)
C(4)	10695(3)	1283(2)	7144(2)	50(1)
C(5)	11789(2)	181(2)	7563(2)	40(1)
C(6)	9194(3)	-657(2)	7272(2)	38(1)
C(7)	7994(3)	-934(2)	7363(2)	56(1)
C(8)	9341(3)	-401(2)	6514(2)	52(1)
C(9)	9969(3)	-1333(2)	7399(2)	47(1)
C(10)	11548(2)	-1324(2)	9109(2)	35(1)
C(11)	9499(2)	-1964(1)	9855(2)	32(1)
C(12)	9218(4)	-2315(2)	9158(2)	69(1)
C(13)	10163(3)	-2544(2)	10283(2)	58(1)
C(14)	8420(3)	-1820(2)	10248(2)	51(1)
C(15)	10994(2)	-620(2)	10504(2)	29(1)
C(16)	11987(3)	-1101(2)	10748(2)	48(1)
C(17)	10190(3)	-535(2)	11112(2)	40(1)
C(18)	11452(3)	169(2)	10328(2)	44(1)
C(19)	6890(2)	1156(1)	9336(1)	20(1)
C(20)	5941(2)	948(2)	8944(1)	22(1)
C(21)	5518(2)	1474(2)	8469(1)	24(1)
C(22)	5955(2)	2188(2)	8378(1)	25(1)
C(23)	6790(2)	2408(2)	8832(1)	26(1)
C(24)	7241(2)	1928(1)	9329(1)	23(1)
C(25)	5307(2)	184(2)	9015(1)	25(1)
C(26)	5073(2)	10(2)	9787(2)	33(1)

C(27)	5920(2)	−474(2)	8680(2)	33(1)
C(28)	4161(2)	213(2)	8666(2)	36(1)
C(29)	5557(3)	2730(2)	7802(2)	31(1)
C(30)	6457(3)	2769(2)	7251(2)	58(1)
C(31)	5342(3)	3520(2)	8100(2)	51(1)
C(32)	4475(3)	2466(2)	7467(2)	42(1)
C(33)	8049(2)	2286(1)	9867(2)	28(1)
C(34)	9274(2)	2102(2)	9725(2)	41(1)
C(35)	7715(3)	2057(2)	10607(2)	40(1)
C(36)	7963(3)	3158(2)	9864(2)	45(1)
Sb(1)	7892(1)	301(1)	9879(1)	23(1)
Si(1)	9241(1)	−182(1)	9068(1)	21(1)
Si(2)	9438(1)	184(1)	7884(1)	28(1)
Si(3)	10348(1)	−1065(1)	9687(1)	21(1)

Table S8. Bond lengths [A] and angles [deg] for **3**.

C(1)-Si(2)	1.875(3)
C(2)-C(5)	1.525(4)
C(2)-C(3)	1.536(5)
C(2)-C(4)	1.547(4)
C(2)-Si(2)	1.932(3)
C(6)-C(8)	1.541(4)
C(6)-C(7)	1.538(5)
C(6)-C(9)	1.536(5)
C(6)-Si(2)	1.923(3)
C(10)-Si(3)	1.884(3)
C(11)-C(12)	1.519(5)
C(11)-C(14)	1.527(4)
C(11)-C(13)	1.540(4)
C(11)-Si(3)	1.919(3)
C(15)-C(17)	1.530(4)
C(15)-C(18)	1.538(4)
C(15)-C(16)	1.543(4)
C(15)-Si(3)	1.926(3)
C(19)-C(20)	1.421(4)
C(19)-C(24)	1.427(4)
C(19)-Sb(1)	2.200(2)
C(20)-C(21)	1.401(4)
C(20)-C(25)	1.557(4)
C(21)-C(22)	1.378(4)
C(22)-C(23)	1.389(4)
C(22)-C(29)	1.545(4)
C(23)-C(24)	1.392(4)
C(24)-C(33)	1.559(4)
C(25)-C(27)	1.522(4)
C(25)-C(28)	1.539(4)

C(25)-C(26)	1.547(4)
C(29)-C(30)	1.522(5)
C(29)-C(31)	1.532(4)
C(29)-C(32)	1.529(4)
C(33)-C(34)	1.538(4)
C(33)-C(35)	1.539(4)
C(33)-C(36)	1.544(4)
Sb(1)-Si(1)	2.4146(7)
Si(1)-Si(3)	2.3748(10)
Si(1)-Si(2)	2.3859(10)

C(5)-C(2)-C(3)	108.5(3)
C(5)-C(2)-C(4)	108.0(3)
C(3)-C(2)-C(4)	107.9(3)
C(5)-C(2)-Si(2)	113.6(2)
C(3)-C(2)-Si(2)	109.3(2)
C(4)-C(2)-Si(2)	109.3(2)
C(8)-C(6)-C(7)	108.1(3)
C(8)-C(6)-C(9)	108.1(3)
C(7)-C(6)-C(9)	107.9(3)
C(8)-C(6)-Si(2)	109.8(2)
C(7)-C(6)-Si(2)	108.6(2)
C(9)-C(6)-Si(2)	114.1(2)
C(12)-C(11)-C(14)	108.5(3)
C(12)-C(11)-C(13)	108.6(3)
C(14)-C(11)-C(13)	106.8(3)
C(12)-C(11)-Si(3)	107.8(2)
C(14)-C(11)-Si(3)	113.7(2)
C(13)-C(11)-Si(3)	111.3(2)
C(17)-C(15)-C(18)	107.9(2)
C(17)-C(15)-C(16)	108.1(2)
C(18)-C(15)-C(16)	106.7(3)

C(17)-C(15)-Si(3)	114.3(2)
C(18)-C(15)-Si(3)	109.6(2)
C(16)-C(15)-Si(3)	109.9(2)
C(20)-C(19)-C(24)	118.7(2)
C(20)-C(19)-Sb(1)	121.23(18)
C(24)-C(19)-Sb(1)	119.83(18)
C(21)-C(20)-C(19)	118.1(2)
C(21)-C(20)-C(25)	117.0(2)
C(19)-C(20)-C(25)	124.9(2)
C(22)-C(21)-C(20)	123.4(3)
C(21)-C(22)-C(23)	116.9(2)
C(21)-C(22)-C(29)	122.7(3)
C(23)-C(22)-C(29)	120.4(3)
C(22)-C(23)-C(24)	123.2(3)
C(23)-C(24)-C(19)	118.2(2)
C(23)-C(24)-C(33)	117.2(2)
C(19)-C(24)-C(33)	124.6(2)
C(27)-C(25)-C(28)	106.0(2)
C(27)-C(25)-C(26)	110.2(2)
C(28)-C(25)-C(26)	105.3(2)
C(27)-C(25)-C(20)	112.8(2)
C(28)-C(25)-C(20)	111.9(2)
C(26)-C(25)-C(20)	110.3(2)
C(30)-C(29)-C(31)	110.0(3)
C(30)-C(29)-C(32)	109.1(3)
C(31)-C(29)-C(32)	107.0(3)
C(30)-C(29)-C(22)	108.0(2)
C(31)-C(29)-C(22)	110.4(2)
C(32)-C(29)-C(22)	112.3(3)
C(34)-C(33)-C(35)	111.2(3)
C(34)-C(33)-C(36)	105.9(2)
C(35)-C(33)-C(36)	104.4(2)

C(34)-C(33)-C(24)	113.3(2)
C(35)-C(33)-C(24)	110.3(2)
C(36)-C(33)-C(24)	111.2(2)
C(19)-Sb(1)-Si(1)	107.73(7)
Si(3)-Si(1)-Si(2)	127.15(4)
Si(3)-Si(1)-Sb(1)	106.54(3)
Si(2)-Si(1)-Sb(1)	126.29(3)
C(1)-Si(2)-C(6)	107.84(17)
C(1)-Si(2)-C(2)	107.59(15)
C(6)-Si(2)-C(2)	114.51(14)
C(1)-Si(2)-Si(1)	104.33(11)
C(6)-Si(2)-Si(1)	111.31(11)
C(2)-Si(2)-Si(1)	110.65(10)
C(10)-Si(3)-C(11)	108.02(14)
C(10)-Si(3)-C(15)	105.85(14)
C(11)-Si(3)-C(15)	114.51(14)
C(10)-Si(3)-Si(1)	107.07(10)
C(11)-Si(3)-Si(1)	109.19(10)
C(15)-Si(3)-Si(1)	111.83(9)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters († $2x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	43(2)	68(2)	30(2)	18(2)	7(1)	22(2)
C(2)	38(2)	36(2)	28(2)	5(1)	7(1)	-2(1)
C(3)	64(2)	51(2)	42(2)	-4(2)	13(2)	-22(2)
C(4)	51(2)	48(2)	50(2)	21(2)	18(2)	10(2)
C(5)	28(2)	52(2)	40(2)	13(2)	1(1)	0(1)
C(6)	33(2)	61(2)	21(2)	-6(1)	2(1)	-5(2)
C(7)	41(2)	91(3)	37(2)	-13(2)	3(2)	-20(2)
C(8)	45(2)	87(3)	23(2)	-4(2)	0(1)	-1(2)
C(9)	61(2)	46(2)	35(2)	-8(2)	5(2)	-3(2)
C(10)	31(2)	38(2)	36(2)	8(1)	6(1)	10(1)
C(11)	42(2)	19(1)	35(1)	5(1)	-2(2)	-7(1)
C(12)	107(4)	47(2)	52(2)	-7(2)	-1(2)	-47(2)
C(13)	64(3)	30(2)	81(3)	19(2)	4(2)	1(2)
C(14)	48(2)	37(2)	68(3)	12(2)	11(2)	-16(2)
C(15)	30(2)	26(1)	31(2)	4(1)	-12(1)	0(1)
C(16)	47(2)	49(2)	49(2)	2(2)	-22(2)	11(2)
C(17)	53(2)	41(2)	26(2)	-2(1)	-11(1)	3(2)
C(18)	47(2)	33(2)	50(2)	-3(1)	-16(2)	-14(2)
C(19)	22(1)	22(1)	18(1)	-1(1)	0(1)	4(1)
C(20)	22(1)	24(1)	19(1)	0(1)	2(1)	2(1)
C(21)	22(1)	28(1)	22(1)	-4(1)	-4(1)	1(1)
C(22)	30(2)	25(1)	20(1)	0(1)	0(1)	7(1)
C(23)	30(2)	20(1)	26(1)	1(1)	-2(1)	-1(1)
C(24)	24(1)	22(1)	23(1)	-2(1)	-1(1)	3(1)
C(25)	24(1)	25(1)	26(1)	-3(1)	0(1)	-3(1)
C(26)	36(2)	33(1)	31(2)	1(1)	4(1)	-6(1)

C(27)	29(2)	31(2)	39(2)	-11(1)	-2(1)	-3(1)
C(28)	28(2)	37(2)	44(2)	-1(2)	-4(1)	-4(1)
C(29)	39(2)	31(2)	23(1)	5(1)	-4(1)	8(1)
C(30)	57(2)	80(3)	39(2)	29(2)	5(2)	15(2)
C(31)	76(3)	30(2)	46(2)	6(2)	-22(2)	11(2)
C(32)	51(2)	41(2)	33(2)	5(1)	-13(2)	6(2)
C(33)	33(2)	24(1)	29(1)	-4(1)	-7(1)	0(1)
C(34)	28(2)	35(2)	60(2)	-5(2)	-8(2)	-6(1)
C(35)	51(2)	42(2)	28(2)	-9(1)	-9(2)	0(2)
C(36)	60(2)	27(1)	49(2)	-10(1)	-23(2)	1(2)
Sb(1)	24(1)	25(1)	18(1)	2(1)	1(1)	5(1)
Si(1)	20(1)	24(1)	18(1)	2(1)	0(1)	3(1)
Si(2)	25(1)	40(1)	18(1)	5(1)	2(1)	6(1)
Si(3)	23(1)	18(1)	23(1)	3(1)	-1(1)	0(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters († ^{2}x 10 ^{3}) for **3**. Hydrogen coordinates (x 10^4) and isotropic displacement parameters

	x	y	z	U(eq)
H(1A)	8257	1013	7258	71
H(1B)	8436	1334	8007	71
H(1C)	7601	667	7884	71
H(3A)	11241	801	8776	78
H(3B)	10536	1490	8515	78
H(3C)	11796	1432	8322	78
H(4A)	11368	1568	7093	74
H(4B)	10094	1621	7246	74
H(4C)	10541	1017	6721	74
H(5A)	12465	467	7547	60
H(5B)	11657	-47	7119	60
H(5C)	11848	-206	7909	60
H(7A)	7866	-1363	7069	85
H(7B)	7490	-535	7241	85
H(7C)	7875	-1077	7838	85
H(8A)	10098	-256	6438	77
H(8B)	8865	24	6424	77
H(8C)	9150	-810	6209	77
H(9A)	9802	-1728	7074	71
H(9B)	9866	-1517	7862	71
H(9C)	10725	-1175	7339	71
H(10A)	11947	-1740	9309	53
H(10B)	12034	-896	9063	53
H(10C)	11274	-1467	8661	53
H(12A)	9890	-2430	8914	103
H(12B)	8785	-1964	8891	103
H(12C)	8802	-2771	9229	103

H(13A)	9753	−3008	10314	88
H(13B)	10289	−2347	10740	88
H(13C)	10863	−2637	10061	88
H(14A)	7963	−1479	9986	76
H(14B)	8584	−1602	10691	76
H(14C)	8034	−2290	10312	76
H(16A)	12533	−1124	10387	73
H(16B)	11738	−1604	10857	73
H(16C)	12308	−875	11154	73
H(17A)	10574	−319	11501	60
H(17B)	9904	−1023	11238	60
H(17C)	9589	−210	10980	60
H(18A)	10848	506	10228	65
H(18B)	11929	134	9932	65
H(18C)	11864	360	10716	65
H(21)	4912	1333	8200	29
H(23)	7060	2899	8801	31
H(26A)	4639	−443	9822	50
H(26B)	4673	425	9990	50
H(26C)	5762	−58	10028	50
H(27A)	6005	−378	8193	49
H(27B)	5503	−931	8746	49
H(27C)	6637	−527	8890	49
H(28A)	4252	282	8176	54
H(28B)	3743	628	8852	54
H(28C)	3774	−252	8751	54
H(30A)	7119	2979	7449	87
H(30B)	6211	3084	6876	87
H(30C)	6608	2269	7080	87
H(31A)	6029	3737	8254	76
H(31B)	4840	3483	8484	76
H(31C)	5022	3837	7748	76

H(32A)	4254	2822	7118	62
H(32B)	3907	2432	7814	62
H(32C)	4585	1978	7259	62
H(34A)	9470	2275	9270	62
H(34B)	9386	1565	9754	62
H(34C)	9731	2352	10062	62
H(35A)	7803	1520	10662	60
H(35B)	6954	2192	10687	60
H(35C)	8178	2316	10935	60
H(36A)	8394	3361	10238	68
H(36B)	7202	3305	9919	68
H(36C)	8240	3350	9432	68

3. Computations.

All of the calculations of the model compounds **1′**, **2′** and **3′** (with the Me_3Si groups replacing $^tBu_2MeSi$ substituents on the silicon) were carried out using the Gaussian 03 (Revision D.01) suite of programs.[8] Geometry optimization, frequency analysis calculations and NBO calculations were performed with hybrid density functional theory (DFT) at the B3LYP level using the 6-31G(d) basis set for all atoms except Sb [3-21G(d) basis set for the Sb atom].

Table S11. Optimized geometric parameters for the model phosphasilene (2,4,6-$^tBu_3$-C_6H_2)P=Si($SiMe_3$)$_2$ **1′** and its total energy.

Energy = –2152.75475443 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-1.006349	0.317899	-1.574241
2	14	0	-2.194452	-0.047399	0.132072
3	14	0	-4.502619	0.119266	-0.387404
4	14	0	-1.577320	-0.568899	2.370994
5	6	0	-5.446853	-1.344462	0.378045
6	1	0	-5.339509	-1.376367	1.468787
7	1	0	-5.099677	-2.304574	-0.020568
8	1	0	-6.518618	-1.260557	0.155354
9	6	0	-5.196529	1.732369	0.343034
10	6	0	0.254910	-0.244092	2.713002
11	1	0	0.901809	-0.830684	2.053102
12	1	0	0.491612	-0.510201	3.751757
13	1	0	0.509806	0.810295	2.566745
14	6	0	-1.975498	-2.400338	2.687386

15	6	0	-2.635001	0.495120	3.540867
16	6	0	0.796122	0.222816	-1.031673
17	6	0	1.483253	1.399064	-0.590455
18	6	0	2.726450	1.240307	0.044621
19	1	0	3.222197	2.118258	0.426987
20	6	0	3.354657	0.010119	0.208588
21	6	0	2.740773	-1.089052	-0.393651
22	1	0	3.259724	-2.036366	-0.357289
23	6	0	1.502242	-1.027762	-1.044734
24	6	0	0.998348	2.874599	-0.799858
25	6	0	-0.094453	3.283441	0.216456
26	1	0	-1.012052	2.708495	0.090528
27	1	0	-0.341897	4.345530	0.092159
28	1	0	0.261847	3.141687	1.244345
29	6	0	0.500411	3.100746	-2.247961
30	1	0	1.288105	2.855317	-2.969890
31	1	0	0.231159	4.155122	-2.385725
32	1	0	-0.380363	2.504534	-2.496103
33	6	0	2.156172	3.890029	-0.611234
34	1	0	3.020392	3.652645	-1.241264
35	1	0	2.494006	3.963587	0.428060
36	1	0	1.798080	4.885020	-0.897233
37	6	0	4.693622	-0.159433	0.950135
38	6	0	5.190487	1.158424	1.574823
39	1	0	6.127126	0.980562	2.115509
40	1	0	4.467354	1.568266	2.289276
41	1	0	5.390746	1.922086	0.814791
42	6	0	5.774883	-0.660555	-0.037094
43	1	0	6.733819	-0.793091	0.479442
44	1	0	5.923877	0.058158	-0.851082
45	1	0	5.502754	-1.621570	-0.486208
46	6	0	4.523623	-1.193176	2.088675

47	1	0	5.470780	-1.331165	2.624891
48	1	0	4.211512	-2.171368	1.708016
49	1	0	3.769084	-0.859308	2.810172
50	6	0	1.038072	-2.330107	-1.781149
51	6	0	2.212592	-3.323159	-1.983238
52	1	0	3.067406	-2.855960	-2.484397
53	1	0	1.866848	-4.149604	-2.613691
54	1	0	2.560770	-3.767349	-1.044461
55	6	0	-0.037670	-3.101722	-0.980766
56	1	0	0.329484	-3.340896	0.025012
57	1	0	-0.273602	-4.047645	-1.484900
58	1	0	-0.963278	-2.534245	-0.882263
59	6	0	0.527172	-2.015554	-3.207690
60	1	0	1.304097	-1.511084	-3.793978
61	1	0	-0.362440	-1.381727	-3.213794
62	1	0	0.266903	-2.948930	-3.721638
63	6	0	-4.759739	0.116340	-2.265665
64	1	0	-4.420051	-0.822998	-2.715020
65	1	0	-4.210941	0.931294	-2.749427
66	1	0	-5.825025	0.238648	-2.501124
67	1	0	-4.703360	2.609658	-0.090437
68	1	0	-6.271326	1.814634	0.134826
69	1	0	-5.063405	1.778346	1.430108
70	1	0	-3.033179	-2.622828	2.506500
71	1	0	-1.380670	-3.057930	2.044188
72	1	0	-1.752231	-2.659675	3.730536
73	1	0	-2.449964	1.565143	3.393295
74	1	0	-2.393296	0.257284	4.585168
75	1	0	-3.707963	0.317736	3.402485

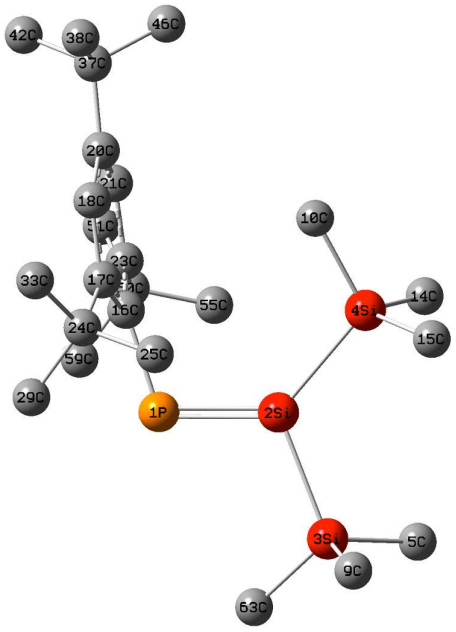


Figure S3. Optimized geometry of **1′** (P1–Si2 bond length = 2.1111 Å).

Table S12. Optimized geometric parameters for the model arsasilene (2,4,6-^{t}Bu$_3$-C$_6$H$_2$)As=Si(SiMe$_3$)$_2$ **2′** and its total energy.

Energy = –4045.19839426 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	33	0	1.082690	-1.543009	0.132686
2	14	0	2.125836	0.380782	-0.059422
3	14	0	4.457780	0.008520	0.012701
4	14	0	1.254770	2.577193	-0.275428
5	6	0	5.221342	0.891505	1.514405

6	1	0	4.767356	0.552182	2.452228
7	1	0	5.094096	1.978601	1.453775
8	1	0	6.298538	0.687009	1.570798
9	6	0	4.753091	-1.860599	0.161329
10	6	0	5.307638	0.665180	-1.556324
11	6	0	0.176140	2.720080	-1.828235
12	1	0	-0.690778	2.054206	-1.763190
13	1	0	0.731575	2.465904	-2.737897
14	1	0	-0.192018	3.748769	-1.937743
15	6	0	2.717473	3.783876	-0.414407
16	6	0	0.215190	3.036198	1.242911
17	6	0	-0.825963	-0.992937	0.084786
18	6	0	-1.504206	-0.643214	1.290435
19	6	0	-2.708600	0.063901	1.177157
20	1	0	-3.211087	0.388056	2.078245
21	6	0	-3.307227	0.365654	-0.050224
22	6	0	-2.727575	-0.195731	-1.186787
23	1	0	-3.233588	-0.074508	-2.132376
24	6	0	-1.518941	-0.913705	-1.154958
25	6	0	-1.078730	-1.150403	2.707536
26	6	0	0.256590	-0.571886	3.237961
27	1	0	0.308538	0.513504	3.097647
28	1	0	1.118707	-1.015194	2.740923
29	1	0	0.345163	-0.780176	4.311572
30	6	0	-0.973330	-2.696752	2.654697
31	1	0	-0.215561	-3.028416	1.938848
32	1	0	-1.931464	-3.143789	2.365951
33	1	0	-0.695965	-3.090821	3.640342
34	6	0	-2.147992	-0.821293	3.775839
35	1	0	-2.242007	0.256409	3.953042
36	1	0	-1.851580	-1.280617	4.725104
37	1	0	-3.134843	-1.217380	3.513858

38	6	0	-4.596100	1.207040	-0.095804
39	6	0	-5.722842	0.479906	0.676668
40	1	0	-5.932171	-0.499723	0.231972
41	1	0	-6.647563	1.069886	0.650551
42	1	0	-5.459990	0.320249	1.727623
43	6	0	-5.086722	1.453253	-1.535620
44	1	0	-4.329925	1.964442	-2.141642
45	1	0	-5.981467	2.085988	-1.518292
46	1	0	-5.356271	0.519542	-2.042308
47	6	0	-4.334379	2.583406	0.560882
48	1	0	-3.550818	3.130515	0.024012
49	1	0	-4.016470	2.484255	1.604083
50	1	0	-5.245817	3.193902	0.547075
51	6	0	-1.103455	-1.705304	-2.438574
52	6	0	-2.186390	-1.618557	-3.539342
53	1	0	-3.167805	-1.951662	-3.185590
54	1	0	-1.897652	-2.271146	-4.370568
55	1	0	-2.289344	-0.605154	-3.944535
56	6	0	0.217933	-1.233329	-3.092570
57	1	0	0.249426	-0.141980	-3.186200
58	1	0	0.304704	-1.663535	-4.098260
59	1	0	1.089751	-1.546821	-2.519485
60	6	0	-0.979121	-3.205645	-2.066113
61	1	0	-1.929955	-3.592304	-1.681730
62	1	0	-0.212265	-3.375339	-1.304746
63	1	0	-0.704782	-3.793381	-2.951008
64	1	0	5.828450	-2.075830	0.201313
65	1	0	4.289762	-2.267666	1.066737
66	1	0	4.328384	-2.401030	-0.691709
67	1	0	6.383929	0.451024	-1.522356
68	1	0	4.903800	0.199131	-2.462085
69	1	0	5.190226	1.750558	-1.654755

70	1	0	3.368344	3.738467	0.466217
71	1	0	3.333709	3.581072	-1.297892
72	1	0	2.347774	4.814139	-0.498860
73	1	0	0.802984	2.999901	2.167108
74	1	0	-0.176744	4.056448	1.136618
75	1	0	-0.636404	2.356818	1.355172

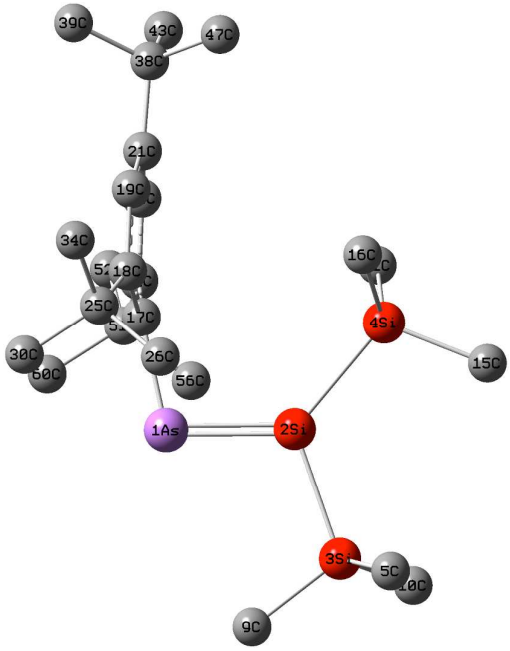


Figure S4. Optimized geometry of **2′** (As1–Si2 bond length = 2.1968 Å).

Table S13. Optimized geometric parameters for the model stibasilene (2,4,6-$^{t}Bu_3$-C_6H_2)Sb=Si($SiMe_3$)$_2$ **3′** and its total energy.

Energy = –8100.24784661 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.356813	2.744133	-0.662749
2	1	0	-0.666428	3.784949	-0.826776
3	1	0	-0.895670	2.362122	0.210265
4	1	0	-0.680349	2.154649	-1.526608
5	6	0	1.996102	3.720281	1.090948
6	6	0	2.382839	3.378224	-1.955918
7	6	0	5.313532	0.166439	-1.799508
8	1	0	6.396839	-0.011125	-1.789766
9	1	0	5.140902	1.153106	-2.244699
10	1	0	4.856773	-0.579690	-2.459527
11	6	0	4.979871	-1.662625	0.671544
12	6	0	5.476888	1.367617	1.036153
13	6	0	-1.115869	-0.952867	0.156951
14	6	0	-1.787171	-0.925781	-1.102130
15	6	0	-2.991789	-0.207182	-1.202736
16	1	0	-3.475931	-0.144018	-2.164276
17	6	0	-3.594171	0.430377	-0.123606
18	6	0	-3.005719	0.231614	1.125607
19	1	0	-3.511349	0.639863	1.989486
20	6	0	-1.805501	-0.467289	1.313555
21	6	0	-1.336488	-1.692814	-2.392595
22	6	0	-0.942135	-3.152177	-2.059628
23	1	0	-0.719897	-3.699349	-2.983544
24	1	0	-1.759601	-3.668921	-1.544127

25	1	0	-0.051545	-3.225882	-1.430366
26	6	0	-0.182486	-0.974604	-3.129344
27	1	0	-0.473519	0.049051	-3.395120
28	1	0	0.060940	-1.507069	-4.057747
29	1	0	0.725598	-0.919305	-2.527739
30	6	0	-2.489457	-1.818244	-3.422821
31	1	0	-2.763443	-0.858071	-3.872391
32	1	0	-3.388580	-2.265721	-2.985120
33	1	0	-2.158757	-2.466674	-4.241501
34	6	0	-4.882733	1.263864	-0.250137
35	6	0	-4.631472	2.684785	0.308666
36	1	0	-4.337870	2.661925	1.363330
37	1	0	-5.541104	3.292911	0.228981
38	1	0	-3.833906	3.189112	-0.248801
39	6	0	-6.019181	0.591977	0.557010
40	1	0	-5.766170	0.500765	1.618511
41	1	0	-6.227845	-0.414266	0.175774
42	1	0	-6.941469	1.181703	0.483235
43	6	0	-5.351140	1.403144	-1.711206
44	1	0	-6.249850	2.029132	-1.752928
45	1	0	-5.605675	0.433453	-2.153812
46	1	0	-4.587584	1.875926	-2.339534
47	6	0	-1.374334	-0.711628	2.799391
48	6	0	-0.226912	0.227552	3.236959
49	1	0	-0.521569	1.277117	3.114042
50	1	0	0.684623	0.064816	2.660819
51	1	0	0.010456	0.065638	4.296205
52	6	0	-0.979683	-2.191345	3.024171
53	1	0	-0.079659	-2.484874	2.477817
54	1	0	-1.790653	-2.861927	2.718131
55	1	0	-0.773609	-2.365993	4.086903
56	6	0	-2.539859	-0.455511	3.789409

57	1	0	−2.221629	−0.759475	4.792671
58	1	0	−3.434353	−1.033975	3.533449
59	1	0	−2.817221	0.602016	3.853997
60	51	0	1.028680	−1.603123	0.291654
61	14	0	2.272735	0.448030	−0.069040
62	14	0	1.518657	2.666218	−0.418087
63	14	0	4.606932	0.059442	−0.036275
64	1	0	2.133455	2.808666	−2.858252
65	1	0	3.473745	3.375826	−1.849658
66	1	0	2.068008	4.417374	−2.119274
67	1	0	3.079498	3.730081	1.255132
68	1	0	1.669683	4.758665	0.946026
69	1	0	1.523371	3.346102	2.005881
70	1	0	6.063389	−1.840429	0.678267
71	1	0	4.516395	−2.456338	0.074893
72	1	0	4.616455	−1.764081	1.699985
73	1	0	5.114575	1.350372	2.070229
74	1	0	6.558891	1.181569	1.057863
75	1	0	5.324516	2.380268	0.645045

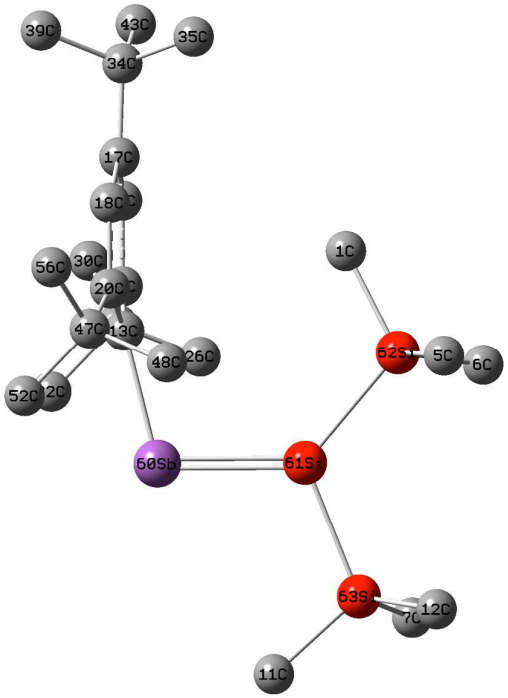
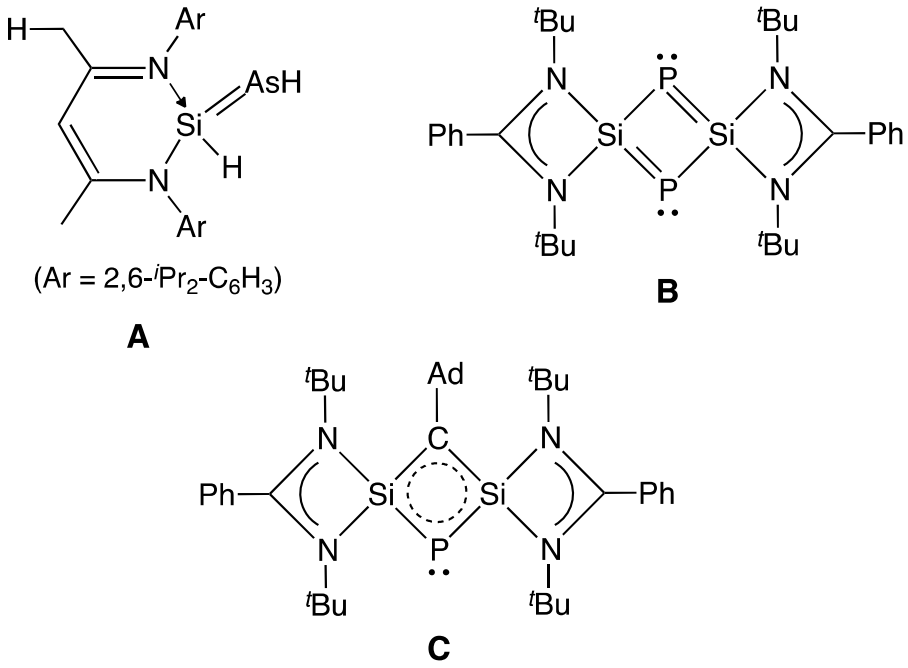


Figure S5. Optimized geometry of **3′** (Sb60–Si61 bond length = 2.4259 Å).



Scheme S1. Structural formulas of the N-donor-stabilized arsasilene (**A**)[9] and heterocyclic zwitterionic phosphasilenes (**B**)[10,11] and (**C**)[11].

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