= 74.7 Hz). ^{31}P NMR: δ 59.88 (d, P trans to H, $^2J_{PP} = 7.4$, $^1J_{PPt} = 1722$ Hz), 60.60 (d, P trans to carbene, $^2J_{PP} = 7.4$, $^1J_{PPt} = 2236$ Hz). IR (Nujol): ν(PtH) 2028 (s) cm^{-1}; ν(C=N) 1552 (s) cm^{-1}; ν(NH) 3297 (m) cm^{-1}.

X-ray Structure Analysis of $C_{31}H_{32}N_3OPPt$. Colorless transparent crystals were grown by slow diffusion of CH_2Cl_2 into an *n*-hexane solution at 0 °C. A crystal suitable for X-ray analysis was mounted on a Lindemann capillary in air and then transferred to a Philips PW1100 diffractometer. A summary of the data collection is given in Table III. The $\pm h,\pm k,+l$ reflections were collected. The intensity data were corrected for Lorentz–polarization effects and for absorption on the basis of ψ scans of four Bragg reflections by following the method of North et al.[36] The 4157 observed reflections with $I \geq 3\sigma(I)$ were used for the structure solution (Patterson and Fourier methods) and refinement. The hydrogen atom positions were derived from difference maps, except those of the CH_3 group, which were introduced at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement ($d_{C-H} = 1.08$ Å and $U_{iso} = 0.07$ Å^2). The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined isotropically. Final R values were $R = 0.022$ and $R_w = 0.022$. The largest peak in the final difference map (0.5 e/Å^3) was located near the Pt atom position. All calculations were done by using the SHELX 76[37] program package with the atomic scattering factors taken from ref 38.

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Registry No. 1, 126018-84-6; (Pt-D)**1**, 126019-00-9; **2**, 126018-85-7; (Pt-D)**2**, 126019-01-0; (N-D)**2**, 126019-04-3; **3**, 126018-86-8; (Pt-D)**3**, 126019-02-1; **4**, 126018-87-9; **5a**, 126018-88-0; **5b**, 126106-96-5; **5c**, 126107-91-3; **6**, 125956-34-5; (Pt-D)**6**, 126019-03-2; **7**, 126018-90-4; **8**, 126018-91-5; **9**, 126018-92-6; **10**, 126018-94-8; **11**, 126035-25-4; *trans*-$PtCl(CH_2CN)(PPh_3)_2$, 42481-62-9; *trans*-$PtD(CH_2CN)(PPh_3)_2$, 126018-95-9; *p*-$MeOC_6H_4NC$, 10349-38-9; *trans*-$(PPh_3)_2Pt(CF_3)Br$, 64933-32-0; *trans*-$PtD(CF_3)(PPh_3)_2$, 126018-96-0; *trans*-$[(PPh_3)_2Pt(CF_3)(CH_2Cl_2)]BF_4$, 87249-59-0; *cis*-$PtH(CH_2CF_3)(PPh_3)_2$, 85319-86-4; $PtH(CF_3)(CNC_6H_4$-*p*-OMe$)(PPh_3)$, 125949-93-1; $PtH(CH_2CN)(CNC_6H_4$-*p*-OMe$)(PPh_3)$, 63637-41-2; $PtH(CH_2CF_3)(CNC_6H_4$-*p*-OMe$)(PPh_3)$, 126106-97-6; $PtD(CH_2CN)(CNC_6H_4$-*p*-OMe$)(PPh_3)$, 126018-97-1; $PtD(CH_2CF_3)(CNC_6H_4$-*p*-OMe$)(PPh_3)$, 126018-98-2; $PtD(CF_3)(CNC_6H_4$-*p*-OMe$)(PPh_3)$, 126018-99-3; *trans*-$PtD(CH_2CF_3)(PPh_3)_2$, 126106-98-7; $PtH(CF_3)(Ph_2PCH_2CH_2PPh_2)$, 125892-79-7; $PtH(CF_3)(Ph_2PCH{=}CHPPh_2)$, 64933-31-9; $PtD(CF_3)(Ph_2PCH_2CH_2PPh_2)$, 126019-05-4; $NHEt_2$, 109-89-7; CD_2HCF_3, 558-53-2; $HC(\overline{NCH_2CH_2C}H_2){=}N(C_6H_4$-*p*-OMe), 126018-82-4; $DC(\overline{NCH_2CH_2C}H_2){=}N(C_6H_4$-*p*-OMe), 126018-83-5; $HC(\overline{NCH_2CH_2CH_2CH_2C}H_2){=}N(C_6H_4$-*p*-OMe), 74530-23-7; azetidine, 503-29-7; piperidine, 110-89-4.

Supplementary Material Available: Listings of hydrogen atom coordinates, bond distances and angles, and thermal parameters (4 pages); a list of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Syntheses and X-ray Crystal Structures of the Compounds $[ArPAs]_2$ and $[ArPSb]_2$ (Ar = 2,4,6-(t-Bu)$_3C_6H_2$). P_2As_2- and P_2Sb_2-Substituted Analogues of Bicyclo[1.1.0]butane

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The syntheses and X-ray crystal structures of the new bicyclo compounds $[ArPAs]_2$, **1**, and $[ArPSb]_2$, **2** (Ar = 2,4,6-(t-Bu)$_3C_6H_2$) are reported. Both **1** and **2** represent the first well-characterized examples of their type to be described. They are analogues of the bicyclotetraphosphanes $[P_4\{N(SiMe_3)_2\}_2]$, **3**, and $[P_4Ar_2]$, **4**, which were recently reported. The P_2As_2 compound **1** adopts a structure similar to those of **3** and **4** with the aryl groups in the exo–exo orientation. In addition the bridgehead As–As bond is somewhat short averaging 2.383 (1) Å. In sharp contrast the P_2Sb_2 compound **2** adopts the exo,endo configuration with a significantly larger fold angle of 103.2° than those in **1**, **3**, and **4**, which average near 95°. The bridgehead Sb–Sb bond length is 2.723 (1) Å and is also significantly shorter than the sum of the covalent radii for antimony. Crystal data with Mo Kα ($\lambda = 0.71069$ Å) radiation at 130 K are as follows: **1**, $a = 20.777$ (5) Å, $b = 16.024$ (2) Å, $c = 25.958$ (4) Å, $\beta = 100.20$ (1)°, $Z = 8$, monoclinic, space group $P2_1/n$, $R_w = 0.063$; **2**, $a = 10.126$ (3) Å, $b = 13.770$ (3) Å, $c = 15.250$ (4) Å, $\alpha = 66.09$ (2)°, $\beta = 85.97$ (2)°, $\gamma = 77.71$ (2)°, $Z = 2$, triclinic, space group $P\bar{1}$, $R_w = 0.041$.

Introduction

The first heavier main group 5 analogue of bicyclo[1.1.0]butane was reported in 1982 by Niecke and coworkers.[1] This compound, $[P_4\{N(SiMe_3)_2\}_2]$, **3**, involved the $N(SiMe_3)_2$ substituents in a symmetric exo,exo configuration and a folded P_4 arrangement. Perhaps the most interesting feature of the structure was the short P–P bond, 2.129 Å, involving the bridgehead phosphorus atoms. These structural features were later confirmed in the compound $[P_4Ar_2]$,[2] which also had a short P–P bond of

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[1] Niecke, E.; Rüger, R.; Krebs, B. *Angew. Chem.* **1982**, *94*, 553; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 544.

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2.166 (2) Å. Calculations by Schoeller[3] have provided theoretical support of the observed P–P bond shortening and have accounted for this phenomenon in terms of olefinic character. The heavier analogues of these compounds have received much less attention. Thus, although the synthesis of the bicyclotetraarsane compound *exo*,-*exo*-[As_4(*t*-Bu)$_2$], **5**, has been published,[4] there are no structural data currently available.

Three isomeric forms are possible in this class of compounds: the exo,exo, exo,endo, and endo,endo isomer. Only solid-state structures of exo,exo species have been described so far, although the exo,endo isomers have been detected spectroscopically in the case of **3** and **4**.

In this paper, the synthesis and the spectroscopic and structural characterization of two novel bicyclic derivatives of the heavier main group 5 elements are described. These are the compounds *exo*,*exo*-[ArPAs]$_2$, **1**, and *exo*,*endo*-[ArPSb]$_2$, **2**. The structure of **1** features a shortened bridgehead As–As bond. The structure of **2** shows that the molecule is in the exo,endo configuration. In addition there are long Sb–Sb intermolecular contacts as well as a shortened bridgehead Sb–Sb bond.

Experimental Section

All manipulations were carried out under an N_2 or Ar atmosphere by using standard Schlenk techniques. All solvents were distilled from drying agents and degassed three times prior to use. Cp*H,[5] Cp*AsCl$_2$,[6] Cp*SbCl$_2$,[7] ArPH$_2$,[8] ArP(SiMe$_3$)Li,[9] and ArP=AsCp*[10] were synthesized according to literature procedures (Cp* refers to pentamethylcyclopentadienyl, Me_5C_5). NMR data were recorded on a Bruker AM 300 spectrometer.

[ArPAs]$_2$ (1). A solution of 2.14 g (4.40 mmol) of ArP=AsCp* in 150 mL of *n*-hexane was irradiated (Hg high-pressure lamp, Hanau/a TQ 150) for 2 h under stirring, which was continued for 4 h.[11] All volatiles were removed under reduced pressure. Addition of a 1:1 mixture of benzene and toluene (13 mL) to the residue and filtration followed by cooling in a refrigerator (–30 °C) gave pale-yellow crystals of the product **1**: yield 214 mg, 14%; mp 185 °C. Anal. Calcd for $C_{36}H_{58}As_2P_2$ (702.6): C, 61.54; H, 8.32. Found: C, 60.75; H, 8.21. ^{31}P NMR (C_6D_6) δ –98.4; ^{1}H NMR (C_6D_6) δ 1.15 (s, 9 H, *p*-*t*-Bu), 1.73 (s, 18 H, *o*-*t*-Bu), 7.51 (s br, 2 H, CH arom); ^{13}C NMR (C_6D_6) δ 31.2, 34.4, 35.3, 39.5 (CMe$_3$), 123.0, 148.7, 155.9 (C arom); MS 703 (M$^+$, 7.3%).

[ArPSb]$_2$ (2). A solution of *n*-butyllithium in *n*-hexane (4.87 mL of 1.56 M solution, 7.60 mmol) was added at –78 °C to a solution of 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$PH$_2$ (2.10 g, 7.54 mmol) in 50 mL of THF. After the reaction mixture was stirred for 1 h at –78 °C and an additional hour at room temperature, a solution of Me$_3$SiCl (0.97 mL, 7.64 mmol) in 3 mL of THF was added at –78 °C. Stirring was continued for another hour at this temperature. After the reaction mixture was warmed to room temperature, the solvent was removed in vacuo. A solution of *n*-butyllithium in *n*-hexane (4.66 mL of a 1.56 M solution, 7.27 mmol) was added to the residue dissolved in 50 mL of diethyl ether. After being stirred for 1 h, this solution was added dropwise at –78 °C to a solution of Cp*SbCl$_2$ (2.27 g, 6.92 mmol) in 50 mL of *n*-hexane. The orange reaction mixture was warmed to room temperature, and the solvent removed in vacuo. The residue was dissolved in 50 mL of *n*-hexane. After filtration and centrifugation, crystallization at –30 °C afforded 2.13 g of orange crystals of the composition Cp*Ar(Me$_3$SiCl)PSb, mp 85 °C. The structure of this compound is still unknown [δ(^{31}P) –59 (s)]. A ^{31}P NMR spectrum of the remaining solution shows the presence of the exo,exo isomer of **2** [δ(^{31}P) –96 (s)] and to a smaller extent of the exo,endo isomer [δ(^{31}P) –17 (s), –77 (s, $^2J_{PP}$ unresolved)]. Crystallization at –40 °C afforded some crystals of the red exo,endo isomer suitable for X-ray crystal structure investigation.

Table I. Crystal Data,[a] Data Collection, and Structure Refinement Parameters for 1 and 2

	1	2
formula	$C_{36}H_{58}As_2P_2\cdot C_6H_6$	$C_{36}H_{58}Sb_2P_2$
fw	780.77	796.31
color and habit	yellow parallelepipeds	red parallelepipeds
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	20.777 (5)	10.126 (3)
b, Å	16.024 (2)	13.770 (3)
c, Å	25.958 (4)	15.250 (4)
α, deg		66.09 (2)
β, deg	100.20 (1)	85.97 (2)
γ, deg		77.71 (2)
V, Å^3	8506 (3)	1899.0 (9)
Z	8	2
cryst dimens, mm	0.15 × 0.38 × 0.48	0.25 × 0.37 × 0.50
d_{calcd}, g cm^{-3}	1.22	1.39
μ(Mo Kα),[a] cm^{-1}	16.7	15.4
range of trans fact	0.56–0.80	0.56–0.73
scan method	ω, 1.0° range, 1.0° offset for bkgnd	ω, 3.0° range, 2.0° offset for bkgnd
scan speed, deg min^{-1}	20	60
2θ range, deg	0–50	0–50
octants coll	$h,k,\pm l$	$h,\pm k,\pm l$
o. data coll	16062	6627
no. unique data	15026 [R(merge) = 0.012]	6627
no. data used in refnm	8354 [$I > 2\sigma(I)$]	5606 [$I > 2\sigma(I)$]
no. params refined	911	415
$R^{1\,b}$	0.070	0.036
$R_w{}^1$	0.063 [$w = (\sigma^2(F_o)^{-1}$]	0.041 [$w = (\sigma^2(F_o)^{-1}$]

[a] Data were collected at 130 K with Mo Kα radiation (λ = 0.71069 Å). [b] $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$.

X-ray Crystallographic Studies. Structure Determination and Refinement. Crystals of the title compounds were coated with hydrocarbon oil to retard decomposition, attached to a glass fiber with silicone grease, and mounted in the cold stream of a Syntex P2$_1$ diffractometer equipped with a locally modified LT-1 low-temperature device. Only random fluctuations of less than 2% occurred in the intensities of two standard reflections during the course of data collection. All computing was carried out by using SHELXTL version 5 programs installed on a Data General Eclipse computer. Atomic scattering factors and anomalous dispersion corrections were from common sources.[12]

The structure of the arsenic compound **1** was solved by direct methods.[13] There are two crystallographically independent "butterfly" and benzene molecules in the asymmetric unit. One of the *tert*-butyl groups of molecule **1** is disordered: there are two sets of three methyl groups bonded to C(11) with refined occupancies of 0.486 (7)/0.514 (7) for sets "A" and "B", respectively. Hydrogen atoms bonded to the carbon atoms were included at calculated positions by using a riding model, with C–H of 0.96 Å and $U_H = 1.2U_C$*. The hydrogen atoms bonded to the carbons

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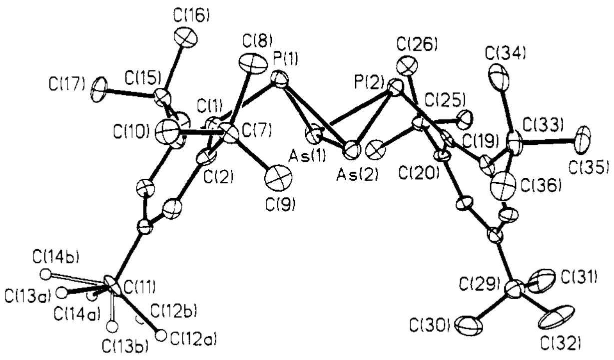

Figure 1. Crystal structure of 1 (molecule 1).

of the disordered *tert*-butyl groups and an additional arbitrarily chosen 15 methyl hydrogen atoms were omitted due to the SHELXTL restriction of 200 atoms. The data were corrected for absorption effects by use of the program XABS.[14] All non-hydrogen atoms were refined with anisotropic thermal parameters except for those having disorder. The largest feature on a final difference map was 0.81 e Å^{-3} in height and corresponds to one of the omitted hydrogen atoms.

The structure of the antimony derivative 2 was solved by Patterson methods. Location of all non-hydrogen atoms and most of the hydrogen atoms followed from successive least-squares refinement and calculation of difference maps. An absorption correction[14] was applied. In the final cycles of refinement, hydrogen atoms were included by using a riding model as above, and non-hydrogen atoms were assigned anisotropic thermal parameters. The largest feature of a final difference map was 1.2 e Å^{-3} in height., 0.9 Å from Sb(1). Further details are in Table I. Atom coordinates from 1 and 2 are given in Table II. Selected bond distance and angles are given in Tables III–VI.

Structural Description

$[ArPAs]_2$, 1. Compound 1 exists as discrete monomeric units. There are two crystallographically independent but chemically identical molecules in the unit cell. A benzene molecule was also observed for each molecule of 1. The P_2As_2 unit has a folded butterfly structure as illustrated in Figure 1 with a fold angle averaging 94.6°. A trans,trans or exo,exo configuration is observed, in which both of the Ar substituents are directed away from the open face of the butterfly. The phosphorus–arsenic distances average very near 2.35 Å. The bridgehead arsenic–arsenic distance, however, is only slightly longer with a value of 2.383 (1) Å. The sum of the angles at phosphorus averages 258° with an angle between the P–C bond and the PAs_2 plane that averages 100.6°.

$[ArPSb]_2$, 2. In contrast to 1, 2 exists in the cis,trans or endo,exo configuration as illustrated in Figure 2. In addition there are nonbonded contacts to other Sb atoms. Thus, the distances between Sb(1) and the Sb(2) and Sb(1) atoms in an adjacent molecule are 3.687 and 4.412 Å, respectively. The phosphorus–antimony bonds average 2.573 (2) Å. The bridgehead antimony–antimony distance is 2.723 (1) Å. The fold angle in the butterfly is 103.2°. The exo Ar group P(2)–C(19) bond makes an angle of 101.6° with the P(2)Sb(1)Sb(2) plane. The corresponding angle for P(1) C(1) and P(1)Sb(1)Sb(2) is 106.1°.

Discussion

Compounds 1 and 2 were synthesized in moderate (1) and low (2) yields via the route described by

$$2Cp^*ElCl_2 + 2ArP(SiMe_3)Li \rightarrow 2Cp^*El{=}PH \rightarrow$$

$$\overline{Cp^*ElPArElCp^*P}Ar \overset{h\nu\ (1)}{\xrightarrow{\Delta\ (2)}} [ArPEl]_2$$

1, El = As
2, El = Sb

$$Ar = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$$

Thus, reaction of pentamethylcyclopentadienyl dichloroarsane with lithium supermesityl(trimethylsilyl)phosphide yields the arsaphosphene Cp*El=PAr, which on irradiation is transferred in a [2 + 2] cycloaddition process to a 1,3-diphospha-2,4-diarsacyclobutane, which subsequently reacts under homolytic As–Cp* bond cleavage to the butterfly compound 1.[11] The reaction of pentamethylcyclopentadienyldichlorostibine with lithium supermesityl(trimethylsilyl)phosphide leads without further irradiation to the butterfly compound 2, passing through a complicated mixture of intermediates, which so far could not be characterized unambiguously.

The essential feature of these synthetic routes involves the exploration of the ready cleavage of the M–Cp* bond to give a radical intermediate that then reacts further under As–As or Sb–Sb bond formation to the compounds 1 or 2. Taking advantage of the weakness of El–Cp* bonds has also allowed the syntheses of other interesting species that have been documented elsewhere.[15,16]

Both 1 and 2 represent heavier element analogues of 3 and 4. In particular, compound 1 is very close to 4 in terms of both formula and structure. The stabilization of these butterfly compounds presumably is due to the large steric requirements of the substituents. This is reflected in the distortions within the P–Ar moiety. The P–C vector makes an average angle of 9° with the plane defined by the adjacent three carbon atoms. A similar effect is observed in the case of the two other *tert*-butyl groups. Such distortions, which were first described by Yoshifuji in the compound $P(O)Ar_2Cl$,[17] attest to the crowding within the molecule. The structure of the P_2As_2 core of the molecule 1 is notable primarily for the length of the As–As and P–As bonds. The latter, which are 2.35 Å long, are within the expected range for a normal P–As bond, and this value is very close to the sum of the atomic radii for phosphorus and arsenic, 2.34 Å. The observed As–As distance is 2.386 (1) Å, only 0.03 Å longer than the P–As distance. This short distance is indicative of significant multiple-bond character. A normal As–As single bond is about 2.44 Å, whereas an As–As double bond is about 2.25 Å. Thus, the shortening in 1 is between 0.06 and 0.07 Å. The amount of the contraction is thus as large in absolute terms as that seen in phosphorus analogue 4; however, in percentage terms, it is less. If it is assumed that the multiple character of the As–As bond in 1 and the P–P bond in 4 is due to olefinic character, the lower percentage of contraction is consistent with weaker multiple bonding for arsenic. The fold angle in 1 averages 94.6° and is practically identical with values of 95.2° and 95.5° seen in 3 and 4. This further underlines the very close similarity in the structure of these three compounds.

The P_2Sb_2 compound 2 is the first exo,endo isomer in group 5 butterfly chemistry crystallographically characterized. The fold angle of 103.2° is significantly larger than that in 1, 3, and 4. Simple molecular models indicate that

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 1 and 2[a]

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
1									
As(1)	2882 (1)	1854 (1)	1590 (1)	21 (1)*	C(37)	5570 (4)	8067 (5)	2524 (3)	16 (3)*
As(2)	2523 (1)	3083 (1)	1104 (1)	21 (1)*	C(38)	5161 (4)	8726 (5)	2651 (3)	17 (3)*
P(1)	2640 (1)	3086 (1)	2019 (1)	17 (1)*	C(39)	5438 (4)	9491 (5)	2805 (3)	20 (3)*
P(2)	1772 (1)	2036 (1)	1234 (1)	18 (1)*	C(40)	6104 (4)	9623 (5)	2903 (3)	22 (3)*
C(1)	3487 (4)	3516 (5)	2184 (3)	15 (3)*	C(41)	6498 (4)	8933 (5)	2864 (3)	25 (3)*
C(2)	3648 (4)	4288 (5)	1961 (3)	17 (3)*	C(42)	6257 (4)	8151 (5)	2695 (3)	20 (3)*
C(3)	4294 (4)	4408 (5)	1893 (3)	21 (3)*	C(43)	4425 (4)	8665 (5)	2675 (3)	19 (3)*
C(4)	4793 (4)	3836 (5)	2061 (3)	14 (3)*	C(44)	4119 (4)	7774 (5)	2596 (4)	29 (3)*
C(5)	4641 (4)	3179 (5)	2367 (3)	17 (3)*	C(45)	4007 (4)	9249 (5)	2282 (4)	30 (3)*
C(6)	4002 (4)	3029 (5)	2452 (3)	21 (3)*	C(46)	4342 (4)	8912 (6)	3230 (3)	27 (3)*
C(7)	3180 (4)	5056 (5)	1835 (3)	17 (3)*	C(47)	6393 (4)	10497 (6)	3021 (4)	35 (4)*
C(8)	2533 (4)	4980 (5)	2036 (4)	24 (3)*	C(48)	6193 (6)	11065 (8)	2548 (5)	76 (6)*
C(9)	3052 (4)	5258 (5)	1248 (3)	26 (3)*	C(49)	6079 (7)	10904 (8)	3463 (5)	87 (7)*
C(10)	3532 (4)	5820 (5)	2133 (3)	25 (3)*	C(50)	7113 (5)	10523 (7)	3206 (6)	72 (6)*
C(11)	5485 (4)	3958 (5)	1947 (3)	18 (3)*	C(51)	6778 (4)	7441 (6)	2757 (3)	25 (3)*
C(12A)	5406 (8)	3960 (11)	1327 (7)	20 (4)	C(52)	7126 (5)	7446 (7)	3334 (4)	44 (4)*
C(13A)	5758 (9)	4799 (11)	2152 (7)	28 (5)	C(53)	7294 (4)	7625 (7)	2406 (4)	45 (4)*
C(14A)	5934 (9)	3242 (11)	2137 (7)	30 (5)	C(54)	6520 (4)	6554 (5)	2648 (4)	30 (3)*
C(12B)	5667 (9)	3168 (12)	1647 (7)	37 (5)	C(55)	4936 (4)	7141 (5)	265 (3)	18 (3)*
C(13B)	5575 (9)	4729 (12)	1633 (7)	39 (5)	C(56)	5525 (4)	7144 (5)	49 (3)	22 (3)*
C(14B)	5993 (9)	4025 (12)	2487 (7)	39 (5)	C(57)	5587 (4)	7758 (5)	−313 (3)	28 (3)*
C(15)	3937 (4)	2381 (5)	2898 (3)	19 (3)*	C(58)	5111 (4)	8347 (5)	−496 (3)	24 (3)*
C(16)	3265 (4)	2365 (5)	3074 (3)	24 (3)*	C(59)	4499 (4)	8211 (5)	−355 (3)	24 (3)*
C(17)	4422 (4)	2654 (5)	3391 (3)	26 (3)*	C(60)	4392 (4)	7604 (5)	10 (3)	21 (3)*
C(18)	4110 (4)	1490 (5)	2748 (3)	25 (3)*	C(61)	6072 (4)	6485 (6)	146 (4)	33 (4)*
C(19)	1725 (4)	1486 (5)	589 (3)	14 (3)*	C(62)	5947 (5)	5733 (6)	490 (4)	41 (4)*
C(20)	1967 (4)	661 (5)	568 (3)	16 (3)*	C(63)	6740 (4)	6867 (7)	360 (4)	45 (4)*
C(21)	2165 (4)	409 (5)	102 (3)	17 (3)*	C(64)	6095 (5)	6076 (7)	−392 (4)	50 (5)*
C(22)	2096 (4)	902 (5)	−343 (3)	20 (3)*	C(65)	5227 (5)	9055 (6)	−874 (4)	39 (4)*
C(23)	1764 (4)	1636 (5)	−330 (3)	18 (3)*	C(66)	5834 (6)	9522 (8)	−652 (5)	91 (7)*
C(24)	1552 (4)	1939 (5)	119 (3)	18 (3)*	C(67)	5370 (6)	8641 (8)	−1404 (4)	67 (5)*
C(25)	1961 (4)	−39 (5)	978 (3)	18 (3)*	C(68)	4634 (5)	9600 (7)	−1039 (5)	67 (5)*
C(26)	1616 (4)	193 (5)	1438 (3)	26 (3)*	C(69)	3656 (4)	7433 (6)	37 (3)	23 (3)*
C(27)	2652 (4)	−348 (5)	1199 (3)	23 (3)*	C(70)	3532 (4)	6667 (6)	365 (4)	31 (3)*
C(28)	1552 (4)	−784 (5)	695 (3)	24 (3)*	C(71)	3301 (4)	7245 (7)	−532 (3)	37 (4)*
C(29)	2365 (4)	606 (5)	−824 (3)	26 (3)*	C(72)	3339 (4)	8220 (6)	249 (4)	29 (3)*
C(30)	3102 (5)	602 (7)	−704 (4)	50 (4)*	C(73)	849 (5)	5606 (6)	87 (4)	54 (5)*
C(31)	2109 (5)	−264 (6)	−985 (4)	47 (4)*	C(74)	1192 (5)	6153 (7)	431 (4)	58 (5)*
C(32)	2148 (6)	1188 (7)	−1293 (4)	58 (5)*	C(75)	1464 (6)	6859 (8)	244 (5)	71 (5)*
C(33)	1109 (4)	2728 (5)	28 (3)	24 (3)*	C(76)	1400 (5)	7001 (7)	−291 (5)	64 (5)*
C(34)	769 (4)	3000 (6)	487 (3)	33 (3)*	C(77)	1048 (5)	6429 (7)	−641 (5)	56 (5)*
C(35)	525 (4)	2506 (6)	−421 (3)	32 (3)*	C(78)	766 (5)	5740 (7)	−438 (4)	55 (5)*
C(36)	1477 (5)	3475 (5)	−158 (4)	33 (4)*	C(79)	9902 (4)	835 (6)	1635 (4)	32 (3)*
As(3)	4724 (1)	7998 (1)	1341 (1)	20 (1)*	C(80)	9909 (4)	−17 (6)	1560 (4)	31 (3)*
As(4)	5817 (1)	7522 (1)	1380 (1)	23 (1)*	C(81)	9751 (4)	−341 (6)	1061 (4)	33 (3)*
P(3)	5245 (1)	7218 (1)	2062 (1)	17 (1)*	C(82)	9592 (4)	183 (7)	638 (4)	39 (4)*
P(4)	4937 (1)	6733 (1)	940 (1)	20 (1)*	C(83)	9586 (4)	1028 (6)	712 (4)	40 (4)*
					C(84)	9742 (5)	1352 (6)	1217 (4)	45 (4)*
2									
Sb(1)	524 (1)	4337 (1)	1562 (1)	22 (1)*	C(17)	−4858 (5)	6361 (4)	750 (4)	30 (2)*
Sb(2)	−1562 (1)	3920 (1)	828 (1)	21 (1)*	C(18)	−6371 (5)	5662 (4)	2091 (4)	29 (2)*
P(1)	−1768 (1)	5658 (1)	1114 (1)	20 (1)*	C(19)	90 (5)	1675 (4)	2627 (3)	18 (2)*
P(2)	−926 (1)	2977 (1)	2629 (1)	19 (1)*	C(20)	1499 (5)	1376 (3)	2804 (3)	20 (2)*
C(1)	−2656 (5)	5348 (4)	2295 (3)	19 (2)*	C(21)	2293 (5)	758 (4)	2347 (3)	24 (2)*
C(2)	−2026 (5)	5299 (4)	3113 (3)	20 (2)*	C(22)	1730 (5)	368 (4)	1781 (3)	23 (2)*
C(3)	−2359 (4)	4592 (4)	4010 (3)	20 (2)*	C(23)	339 (5)	478 (4)	1787 (3)	25 (2)*
C(4)	−3346 (5)	3983 (4)	4137 (3)	19 (2)*	C(24)	−506 (5)	1072 (4)	2246 (3)	21 (2)*
C(5)	−4161 (5)	4255 (4)	3346 (3)	19 (2)*	C(25)	2262 (5)	1576 (4)	3548 (4)	25 (2)*
C(6)	−3878 (4)	4966 (4)	2428 (3)	18 (2)*	C(26)	1346 (6)	2040 (5)	4183 (4)	32 (2)*
C(7)	−1067 (5)	6043 (4)	3119 (3)	23 (2)*	C(27)	3283 (5)	2297 (4)	3062 (4)	33 (2)*
C(8)	−857 (6)	6934 (4)	2150 (4)	32 (2)*	C(28)	3044 (6)	461 (4)	4232 (4)	37 (2)*
C(9)	−1742 (6)	6647 (4)	3741 (4)	30 (2)*	C(29)	2586 (5)	−162 (4)	1160 (4)	30 (2)*
C(10)	334 (5)	5377 (4)	3563 (4)	32 (2)*	C(30)	2329 (7)	646 (5)	97 (4)	47 (3)*
C(11)	−3521 (5)	3102 (4)	5133 (3)	20 (2)*	C(31)	2167 (7)	−1214 (5)	1295 (4)	42 (3)*
C(12)	−3955 (6)	3603 (4)	5860 (4)	31 (2)*	C(32)	4098 (6)	−428 (6)	1403 (5)	54 (3)*
C(13)	−2185 (5)	2298 (4)	5461 (4)	29 (2)*	C(33)	−1992 (5)	913 (4)	2381 (4)	26 (2)*
C(14)	−4592 (5)	2463 (4)	5118 (4)	29 (2)*	C(34)	−2803 (5)	1394 (5)	3049 (4)	33 (2)*
C(15)	−5020 (5)	5338 (4)	1647 (3)	21 (2)*	C(35)	−2770 (6)	1350 (5)	1421 (4)	35 (2)*
C(16)	−5150 (5)	4428 (4)	1349 (4)	24 (2)*	C(36)	−1921 (6)	−321 (4)	2887 (4)	37 (2)*

[a] Asterisks indicate equivalent isotropic *U* defined as one-third of the trace of the orthogonalised $\mathbf{U}_{ij}$ tensor.

in a exo,exo isomer with a fold angle of about 103° the Ar ligands would interfere sterically. The same would be true for a exo,endo isomer with a fold angle of about 95°. The P–Sb bonds, which are 2.573 (2) Å in length, are within the expected range for a normal P–Sb bond. The observed Sb–Sb distance is 2.723 (1) Å. A normal Sb–Sb single bond

Table III. Selected Bond Distances (Å) for 1

As(1)-As(2)	2.386 (1)	As(1)-P(1)	2.363 (2)
As(1)-P(2)	2.346 (2)	As(2)-P(1)	2.344 (2)
As(2)-P(2)	2.356 (2)	P(1)-C(1)	1.869 (8)
P(2)-C(19)	1.881 (8)	C(1)-C(2)	1.431 (11)
C(1)-C(6)	1.403 (11)	C(2)-C(3)	1.398 (12)
		C(3)-C(4)	1.394 (11)
C(4)-C(5)	1.388 (11)	C(4)-C(11)	1.531 (11)
C(5)-C(6)	1.405 (12)	C(6)-C(15)	1.579 (12)
C(7)-C(8)	1.531 (12)	C(7)-C(9)	1.536 (11)
As(3)-As(4)	2.380 (1)	As(3)-P(3)	2.349 (2)
As(3)-P(4)	2.355 (2)	As(4)-P(3)	2.351 (3)
As(4)-P(4)	2.345 (2)	P(3)-C(37)	1.858 (8)
P(4)-C(55)	1.871 (8)	C(37)-C(38)	1.430 (12)
C(37)-C(42)	1.425 (11)	C(38)-C(39)	1.383 (11)
C(38)-C(43)	1.543 (12)	C(39)-C(40)	1.378 (12)
C(40)-C(41)	1.390 (12)	C(40)-C(47)	1.534 (12)
C(41)-C(42)	1.390 (12)	C(42)-C(51)	1.558 (12)

Table IV. Selected Bond Angles (deg) for 1

As(2)-As(1)-P(1)	59.2 (1)	As(2)-As(1)-P(2)	59.7 (1)
P(1)-As(1)-P(2)	78.8 (1)	As(1)-As(2)-P(1)	59.9 (1)
As(1)-As(2)-P(2)	59.3 (1)	P(1)-As(2)-P(2)	79.0 (1)
As(1)-P(1)-As(2)	60.9 (1)	As(1)-P(1)-C(1)	98.4 (3)
As(2)-P(1)-C(1)	99.1 (3)	As(1)-P(2)-As(2)	61.0 (1)
As(1)-P(2)-C(19)	100.6 (2)	As(2)-P(2)-C(19)	97.8 (3)
P(1)-C(1)-C(2)	120.3 (5)	P(1)-C(1)-C(6)	120.8 (6)
C(2)-C(1)-C(6)	118.0 (7)	C(1)-C(2)-C(3)	117.9 (7)
C(1)-C(2)-C(7)	125.7 (7)	C(3)-C(2)-C(7)	116.1 (7)
C(2)-C(3)-C(4)	123.2 (8)	C(3)-C(4)-C(5)	116.5 (7)
C(4)-C(5)-C(6)	122.4 (7)	C(1)-C(6)-C(5)	119.0 (7)
As(4)-As(3)-P(3)	59.6 (1)	As(4)-As(3)-P(4)	59.4 (1)
P(3)-As(3)-P(4)	78.3 (1)	As(3)-As(4)-P(3)	59.5 (1)
As(3)-As(4)-P(4)	59.8 (1)	P(3)-As(4)-P(4)	78.5 (1)
As(3)-P(3)-As(4)	60.9 (1)	As(3)-P(3)-C(37)	100.8 (2)
As(4)-P(3)-C(37)	99.3 (3)	As(3)-P(4)-As(4)	60.8 (1)
As(3)-P(4)-C(55)	98.3 (3)	As(4)-P(4)-C(55)	98.0 (3)
P(3)-C(37)-C(38)	121.8 (5)	P(3)-C(37)-C(42)	120.0 (6)
C(38)-C(37)-C(42)	117.5 (7)	C(37)-C(38)-C(39)	119.1 (7)
C(37)-C(38)-C(43)	126.6 (7)	C(39)-C(38)-C(43)	114.1 (7)
C(38)-C(39)-C(40)	122.9 (8)	C(39)-C(40)-C(41)	116.7 (8)
C(40)-C(41)-C(42)	123.8 (8)	C(37)-C(42)-C(41)	117.9 (7)

Table V. Selected Bond Distances (Å) for 2

Sb(1)-Sb(2)	2.723 (1)	Sb(1)-P(1)	2.565 (1)
Sb(1)-P(2)	2.583 (1)	Sb(2)-P(1)	2.566 (2)
Sb(2)-P(2)	2.578 (1)	P(1)-C(1)	1.885 (5)
P(2)-C(19)	1.869 (5)	C(1)-C(2)	1.412 (8)
C(1)-C(6)	1.416 (7)	C(2)-C(3)	1.388 (6)
C(2)-C(7)	1.557 (8)	C(3)-C(4)	1.391 (7)
C(4)-C(5)	1.385 (7)	C(5)-C(6)	1.397 (6)
C(19)-C(24)	1.430 (8)	C(19)-C(20)	1.412 (7)
C(20)-C(25)	1.558 (8)	C(20)-C(21)	1.402 (8)
C(22)-C(23)	1.384 (7)	C(21)-C(22)	1.391 (9)
C(23)-C(24)	1.405 (8)		

Table VI. Selected Bond Angles (deg) for 2

Sb(2)-Sb(1)-P(1)	58.0 (1)	Sb(2)-Sb(1)-P(2)	58.0 (1)
P(1)-Sb(1)-P(2)	83.3 (1)	Sb(1)-Sb(2)-P(1)	57.9 (1)
Sb(1)-Sb(2)-P(2)	58.3 (1)	P(1)-Sb(2)-P(2)	83.4 (1)
Sb(1)-P(1)-Sb(2)	64.1 (1)	Sb(1)-P(1)-C(1)	103.6 (1)
Sb(2)-P(1)-C(1)	103.5 (2)	Sb(1)-P(2)-Sb(2)	63.7 (1)
Sb(1)-P(2)-C(19)	101.1 (1)	Sb(2)-P(2)-C(19)	97.8 (1)
P(1)-C(1)-C(2)	121.6 (4)	P(1)-C(1)-C(6)	119.8 (4)
C(2)-C(1)-C(6)	117.6 (4)	C(1)-C(2)-C(3)	118.3 (5)
C(1)-C(2)-C(7)	126.0 (4)	C(3)-C(2)-C(7)	115.5 (5)
C(2)-C(3)-C(4)	122.7 (5)	C(3)-C(4)-C(5)	116.4 (4)
C(4)-C(5)-C(6)	122.3 (5)	C(1)-C(6)-C(5)	118.3 (4)

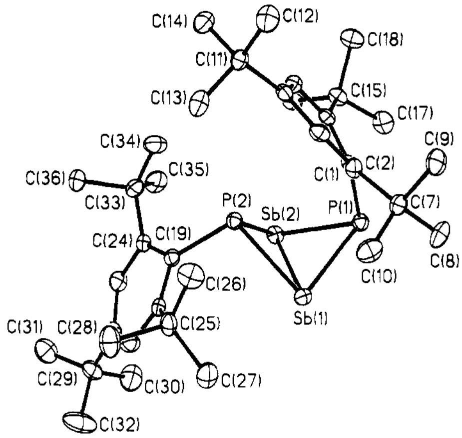

Figure 2. Crystal structure of 2.

is about 2.86 Å. Thus, the shortening in 2 is about 0.14 Å. Once more, the short distance is indicative of multiple-bond character. The amount of contraction is larger in absolute terms than that observed in the phosphorus and arsenic analogues, 4 and 1. In 2, the Sb–Sb distances of adjacent molecules are in the range 3.68–4.41 Å, thus indicating some degree of intermolecular contact. Similar Sb–Sb contacts have been described for the solid-state structures of $R_2Sb–SbR_2$[18] and of $M^+Sb_3Ph_4^-$.[19] A common feature of all these antimony compounds is their red color. There are no short intermolecular contacts in the structure of the arsenic compound 1.

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Registry No. 1, 115879-21-5; 2, 126017-40-1; ArP=AsCp*, 111398-02-8; 2,4,6-(t-Bu)$_3$C$_6$H$_2$PH$_2$, 83115-12-2; Cp*SbCl$_2$, 126017-41-2.

Supplementary Material Available: Full tables of bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (17 pages); listings of structure factor amplitudes (82 pages). Ordering information is given on any current masthead page.

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