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Structural and ^{31}P NMR Solution Studies on Some Cyclic Triphosphenium Ions and Their 2-Arsa-Analogues

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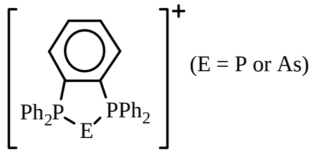
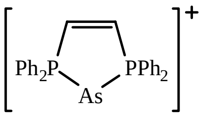
ABSTRACT: *Several new cyclic triphosphenium ions and their 2-arsa-analogues have been identified in solution by ^{31}P NMR spectroscopy. The crystal and molecular structures of the cations* **1a,b**, *as their hexachlorostannate (IV) salts have shown that the five-membered heterocyclic rings are planar, whereas the cation* **9b** *as its diphosphanedioxide-bis[pentachlorostannate(IV)] salt is nonplanar, like its saturated phosphorus counterpart.*



1a,b



9b

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INTRODUCTION

In a previous article [1], we summarized earlier work on cyclic triphosphenium ions, which commenced in 1982 with the synthesis and crystal structure determination by Schmidpeter and coworkers of a five-membered ring cation with an aliphatic carbon backbone, **6a**, (as its hexachlorostannate (IV) salt) [2]. This ring was nonplanar and readily identifiable in solution by its AB$_2$-type ^{31}P NMR spectrum, with characteristic shifts and coupling constant (δ P$_B$, 63.8; δ P$_A$, −231.6 ppm; $^1J_{P_AP_B}$, 448.9 Hz). Subsequently other triphosphenium cations with a five-membered ring, a six-membered ring or two linked six-membered rings have been described [3,4], as well as four- [5] and eight-membered ring neutral species with either one [6,7] or two [8,9] units of three linked phosphorus atoms. All of these species showed quite large (250–500 Hz) $^1J_{P_AP_B}$ coupling constants. The only arsenic analogues were reported by Gamper and Schmidbaur, who determined the crystal structure of a six-membered ring cationic species **10b** as its hexachlorostannate (IV) · 0.5 MeCN salt [4] and by Karsch and Witt, who determined the crystal structures of the four-membered ring neutral species **11a** and **11b** [7].

We have described the characterization in solution by ^{31}P NMR spectroscopy of several new cyclic triphosphenium ions with five-, six- or seven-membered rings present [1], and the crystal structure of the six-membered ring homologue **7a** of Schmidpeter's cation [2]. This work has now been extended to other P–P–P systems and to several P–As–P analogues. For the first time, the crystal structures of a related pair of P- and As-containing cations **1a** and **1b** have been determined, although the structures have been published previously of a corresponding pair of four-membered ring neutral

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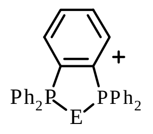

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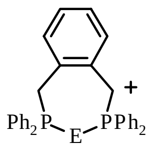

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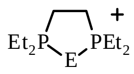

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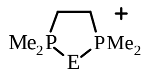

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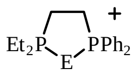

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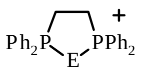

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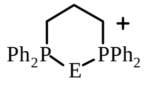

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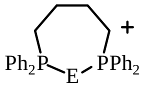

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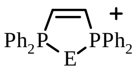

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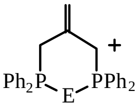
a: E = P
b: E = As



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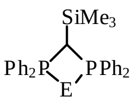

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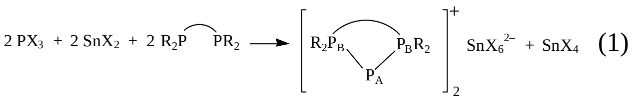
species, **11a** and **11b** [7]. These ions have an aromatic group attached to the carbon backbone, and in consequence, the five-membered heterocyclic rings are planar. The crystal structure has also been determined of a second arsenic-containing cation **9b**, which is closely related to Schmidpeter's cyclic triphosphenium ion **6a** [2], but with an unsaturated C=C backbone. As expected, the five-membered ring in this species is nonplanar.

RESULTS AND DISCUSSION

Cyclic Triphosphenium Ions

Reactions have been carried out between P(III) halides PX_3 (X = Cl, Br, or I) and the diphosphanes 1,2-bisdiphenylphosphinobenzene (dppben), α,α'-bisdiphenylphosphino-(*o*-xylene) (dppox), 1,2-bisdiethylphosphinoethane (bdpe), 1,2-bisdimethylphosphinoethane (dmpe), 1-diethylphosphino-2-diphenylphosphinoethane (depe), and 1,3-bisdiphenylphosphino-propane (dppp); some quantitative experiments were also performed with the reducing agents tin(II) chloride (for X = Cl) or tin(II) bromide (for X = Br) present, according to equation (1).



$$2\,PX_3 + 2\,SnX_2 + 2\,R_2P\frown PR_2 \longrightarrow \left[R_2P_B \frown P_BR_2 \; (P_A) \right]^{+}_{2} SnX_6^{2-} + SnX_4 \quad (1)$$

TABLE 1 $\delta\,^{31}P$ *and* $^1J_{P_AP_B}$ for Some Cyclic Triphosphenium Ions Formed by Symmetrical Diphosphanes (AB_2)

System		δP_B *(ppm)*	δP_A *(ppm)*	$^1J_{P_AP_B}$ *(Hz)*
PCl_3-dppben	**1a**	57.6	−212.8	453
PBr_3-dppben		57.6	−213.1	453
PI_3-dppben		57.6	−213.0	453
PCl_3-dppben-$SnCl_2$		57.6	−212.5	455
PBr_3-dppben-$SnBr_2$		57.5	−212.2	452
PCl_3-dppox	**2a**	25.1	−214.5	436
PBr_3-dppox		25.3	−214.5	436
PI_3-dppox		25.1	−217.4	439
PCl_3-dppox-$SnCl_2$		25.1	−216.9	438
PBr_3-dppox-$SnBr_2$		25.3	−214.9	435
PCl_3-bdpe	**3a**	81.5	−269.0	437
PCl_3-bdpe-$SnCl_2$		80.5	−264.1	444
PCl_3-dmpe	**4a**	60.4		433
PCl_3-dmpe-$SnCl_2$		59.9	−212.5	437
PCl_3-dppp	**7a**	23.3	−209.2	423

Formation of the five- or seven-membered ring cyclic triphosphenium ion **1a–5a** was observed in each case, as shown by the results in Table 1 for symmetrical diphosphanes. (For $Et_2P(CH_2)_2PEt_2$ and $Me_2P(CH_2)_2PMe_2$, reactions were only attempted with PCl_3, in the absence and presence of $SnCl_2$, because of shortage of material.) Results for the asymmetrical diphosphane $Et_2P(CH_2)_2PPh_2$ are listed in Table 2. The $^{31}P\{^1H\}$ spectra of **1a–4a** and of **7a** are of AB_2 type with $J/\nu_o\delta$ around 0.02 at $\nu_o = 80.96$ MHz, and they therefore deviate slightly, but observably, from the AX_2 case, showing four resonances for both the A- and the B-parts.

For ^{31}P NMR studies, a dppp-PCl_3 solution of **7a** (Table 1) was specially prepared (where the crystal structure is known) [1]. It was found that δP_A had an unusually large temperature coefficient of ca. 0.019 ppm/°C, moving to higher frequency with increasing T, and resulting in distortions of the signal due to small changes in the probe temperature. These changes were possibly related to heating caused by application of the decoupler. In order to obtain a reliable spectrum for similar systems, a small number of

TABLE 2 ^{31}P NMR Data for Cyclic Triphosphenium Ion **5a** Formed by $Et_2PCH_2CH_2PPh_2$ (ABC P_A: center P, P_B: PPh_2, P_C: PEt_2)

System	δP_B *(ppm)*	δP_C *(ppm)*	δP_A *(ppm)*	$^1J_{P_AP_B}$ *(Hz)*	$^1J_{P_AP_C}$ *(Hz)*	$^2J_{P_BP_C}$ *(Hz)*
PCl_3-depe	78.0	67.1	−251.0	431	460	10.4
PBr_3-depe	78.9	67.0	−251.0	433	461	10.4
PI_3-depe	78.2	66.7	−249.6	435	461	9.6
PCl_3-depe-$SnCl_2$	81.3	69.4	−251.0	434	466	9.6

TABLE 3 δ ^{31}P (ppm) for PX_3-$Cl_2P(CH_2)_2PCl_2$ Reaction Products

Species	*X = Br*	*X = I*
PCl_3	220.1	220.1
PCl_2X	225.4	228.7
$PClX_2$	228.6	214.3
PX_3	229.2	175.3
$Cl_2P(CH_2)_2PCl_2$	191.1	191.2
$XClP_A(CH_2)_2P_BCl_2$	P_A 190.3	173.6
	P_B 190.6	190.2
$XClP(CH_2)_2PClX$	189.7	174.6
$X_2P_A(CH_2)_2P_BCl_2$	P_A 186.7	132.1
	P_B190.1	189.2
$X_2P_A(CH_2)_2P_BClX$	P_A186.2	131.2
	P_B189.3	172.5
$X_2P(CH_2)_2PX_2$	185.7	130.7

transients should be used, and/or close temperature control of the sample should be employed.

Interestingly, the diphosphane $Cl_2P(CH_2)_2PCl_2$ did not react with PCl_3 to form a cyclic triphosphenium ion, even in the presence of tin(II) chloride, the ^{31}P spectrum showing only the signals from the starting materials at δ 191.3 and 220.4 ppm, respectively. Addition of PX_3 (X = Br or I) to a solution of $Cl_2P(CH_2)_2PCl_2$ in CH_2Cl_2 led to rapid halogen exchange and the formation of mixed halogeno species. These could be readily identified in solution by varying the proportions of the reagents and observing the relative signal intensities. In addition to the known trihalides PCl_nX_{3-n} (X = Br or I; $0 \leq n \leq 3$) [10], new derivatives of the diphosphane were formed. Their ^{31}P chemical shifts are listed in Table 3. No spin–spin coupling was detected in unsymmetrical species, even though both signals were clearly visible. This effect probably arises from rapid quadrupolar relaxation causing line broadening and implies that the J values are small. A small amount of P_2I_4 (δ 104.9 ppm) [11,12] was also detected in the PI_3 system.

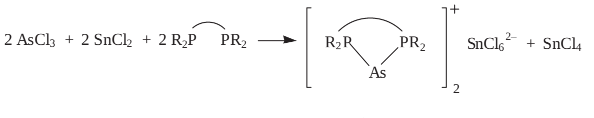
2-Arsa Analogues

TABLE 4 δ ^{31}P (ppm) for P_B in Corresponding Cyclic P_BAsP_B and $P_BP_AP_B$ Systems and Their Difference $\Delta = \delta^{31}P_B(P)$-$\delta$ $^{31}P_B(As)$

		δ^{31}P (P_B)			
System		*X = As* **a**	*X = P* **b**	*Ref.* *for X = P*	Δ
dppe[a]-XCl_3	**6**	62.6	64.4	[1]	1.8
dppp[b]-XCl_3	**7**	17.0	23.4	[1]	64
dppb[c]-XCl_3	**8**	29.0	34.3	[1]	5.3
dppE[d]-XCl_3-$SnCl_2$	**9**	68.4	71.2	[1]	2.8
dppben-XCl_3-$SnCl_2$	**1**	54.6	57.6	[f]	3.0
dppox-XCl_3-$SnCl_2$	**2**	23.6	25.1	[f]	1.5
bdpe-XCl_3-$SnCl_2$	**3**	75.5	80.5	[f]	5.0
depe[e]-XCl_3	**5**	P_B 75.3	78.0	[f]	2.7
		P_C 63.1	67.1	[f]	4.0
depe[e]-XCl_3-$SnCl_2$	**5**	P_B 74.5	81.3	[f]	6.8
		P_C 63.8	69.4	[f]	5.6

[a] dppe = 1,2-bisdiphenylphosphinoethane.
[b] dppp = 1,3-bisdiphenylphosphinopropane.
[c] dppb = 1,4-bisdiphenylphosphinobutane.
[d] dppE = cis-1,2-bisdiphenylphosphinoethene.
[e] depe = 1-diethylphosphino-2- diphenylphosphinoethane.
[f] This work.

Several diphosphanes have been reacted with $AsCl_3$, in the absence or presence of $SnCl_2$. For quantitative reactions with $SnCl_2$ present, the stoichiometry is shown in equation (2), parallel to equation (1) for formation of triphosphenium ions. The ^{31}P NMR results are collected in Table 4. Apart from the unsymmetrical diphosphane $Et_2P(CH_2)_2PPh_2$, these ligands give rise to only a single ^{31}P resonance when the P–As–P ring is formed. In all instances there are small shifts to lower frequency compared with the corresponding phosphorus atoms in the analogous cyclic triphosphenium ions, as shown in Table 4. This is entirely in keeping with the results of Gamper and Schmidbaur, who obtained shifts of δ ^{31}P 23.0 ppm for P_B where $E = P_A$, and 18.3 ppm for P_B where E = As, in their six-membered cationic rings **10a** and **10b**, giving $\Delta = 4.7$ ppm [4]. A larger shift in the same direction was observed by Karsch and Witt for the four-membered ring uncharged compounds **11a** and **11b** (δ ^{31}P 20.2 and −0.5 ppm respectively) [7]. For the unsymmetrical diphosphane $Et_2P(CH_2)_2PPh_2$, both phosphorus resonances (P_B and P_C) are at lower frequency in the arsenic derivative **5b** than in the cyclic triphosphenium ion **5a**. A notable side-effect of the incorporation of arsenic into the ring is that the $^2J_{P_BP_C}$ spin–spin coupling is no longer observable, presumably because of rapid relaxation induced by the quadrupolar ^{75}As nucleus.



(2)

Other Reaction Products

^{31}P NMR signals were sometimes observed in the nonquantitative diphosphane-PCl_3 and diphosphane-$AsCl_3$ reactions for either the diphosphane dichloride (AB spectrum) or the diphosphane tetrachloride (one singlet for the derivative of a symmetrical diphosphane), depending on the proportions of reagents used. These arise because, in the absence of SnX_2, the diphosphane must act as a reducing agent as well as forming the new heterocycle. Of particular interest were the resonances for the dichloro derivative of $Et_2P(CH_2)_2PPh_2$; two doublets were seen at δ 110.5 and −12.4 ppm, $^3J_{PP}$ 45.9 Hz, from the depe-PCl_3 system, and two doublets at δ 110.8 and −12.0 ppm, $^3J_{PP}$ 45.9 Hz, from the depe-$AsCl_3$ system. These shifts show clearly that chlorination takes place preferentially at the P atom with ethyl substituents. The shift for the chlorinated P is in very good agreement with literature data for Et_3PCl^+ (δ 112.1–105.0 ppm) [13,14], while in contrast, the reported value for $Ph_2P(Et)Cl^+$ is 78.1 ppm [13]. The lower frequency signal also agrees closely in shift with that of P_A in the parent diphosphane ($Et_2P_B(CH_2)_2P_APh_2$, $\delta P_A - 20.7$, δP_B −14.4 ppm) [15]. Hence the structure of the product may be confidently assigned as $[Et_2P^+(Cl)(CH_2)_2PPh_2]Cl^-$. The symmetrical diphosphane $Et_2P(CH_2)_2PEt_2$ gave a pair of doublets at δ 112.3 and −15.5 ppm, $^3J_{PP}$ 34.7 Hz, for $[Et_2P^+(Cl)(CH_2)_2PEt_2]Cl^-$, and a singlet at δ 109.7 ppm for $[Et_2P^+(Cl)(CH_2)_2P^+(Cl)Et_2]2Cl^-$, from its reaction with PCl_3. Evidence was also found for the monophosphane oxides $R_2P(O)(CH_2)_2PR_2$ in reactions of $Me_2P(CH_2)_2PMe_2$ (doublets at δ 42.4 and −45.1 ppm, $^3J_{PP}$ 37.2 Hz) and $Et_2P(CH_2)_2PEt_2$ (doublets at δ 51.7 and −15.5 ppm, $^3J_{PP}$ 34.7 Hz). These species were not investigated further, however, since they were not the main focus of the research.

Crystal and Molecular Structure of $(\mathbf{1a})_2\,SnCl_6^{2-}$, $(\mathbf{1b})_2\,SnCl_6^{2-}$, *and of* $(\mathbf{9b})_2\,[Cl_5SnOP(Ph_2)CH{=}CHP(Ph_2)OSnCl_5]^{2-}\cdot 2CH_2Cl_2$

One of the most interesting features of the cation structure of **1a** (Figure 1) is that the presence of the aromatic ring in the backbone forces the five-membered triphosphenium ring to be planar, in contrast with the dppe (5-membered ring) derivative

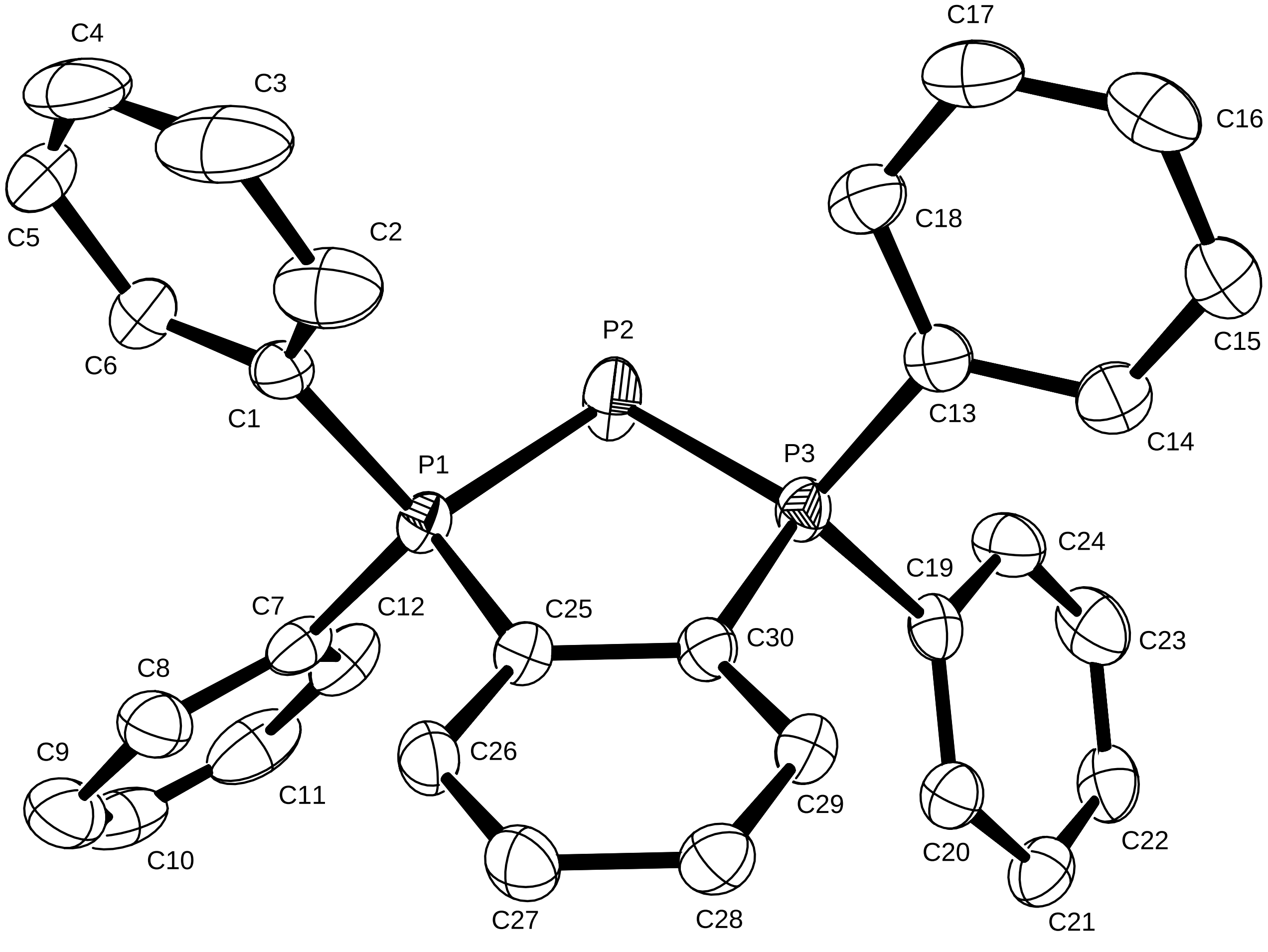


FIGURE 1 Thermal ellipsoid drawing of the cation **1a** showing 50% probability displacement ellipsoids for non-H atoms. All H atoms have been omitted for clarity.

TABLE 5 Selected Bond Lengths (Å) and Angles (°) in Cations **1a, 1b**, and **9b**

1a		**1b**		**9b**	
P1–P2	2.124(1)	P1–As	2.2517(8)	P1–As	2.254(2)
P2–P3	2.122(1)	P2–As	2.2468(9)	P2–As	2.252(1)
P1–C25	1.804(2)	P1–C1	1.808(2)	P1–C1	1.814(6)
P3–C30	1.803(2)	P2–C6	1.807(2)	P2–C2	1.823(6)
C25–C30	1.403(3)	C1–C6	1.401(3)	C1–C2	1.331(8)
				C3–C3#	1.32(1)
P1–P2–P3	90.67(4)	P1–As–P2	87.37(2)	P1–As–P2	84.57(5)
C25–P1–P2	108.10(8)	C1–P1–As	108.27(7)	C1–P1–As	106.7(2)
C30–P3–P3	107.98(9)	C6–P2–As	108.04(7)	C2–P2–As	106.3(2)
C1–P1–C7	106.3(1)	C11–P1–C21	106.6(1)	C10–P1–C20	106.8(3)
C13–P3–C19	107.1(1)	C31–P2–C41	107.1(1)	C30–P2–C40	107.9(3)

#Symmetry transformation used to generate equivalent atoms: $-x+1$, $-y+1$, $-z+2$. This bond length is in the anion.

6a described by Schmidpeter et al. [2], and the dppp (6-membered ring) analogue **7a** reported by us in a previous article [1]. Selected bond distances and angles are listed in Table 5. The phosphorus–phosphorus bond lengths of 2.124(1) and 2.122(1) Å are very similar to those in the dppe derivative (2.122(1) and 2.128(2) Å [2]) and are intermediate between normal P–P single (2.20–2.25 Å) and double (2.00–2.05 Å) bonds [16]. All of the C–C distances in the aromatic ring have normal values, between 1.382(4) and 1.403(3) Å. The angles C(30)–P(3)–P(2) and C(25)–P(1)–P(2) are 107.98 (9)° and 108.10 (8)°, respectively, close to the tetrahedral angle, while the P(3)–P(2)–P(1) angle of 90.67(4) ° is very slightly larger than in the saturated ring (88.9(1) ° [2]), although smaller than that in the less strained six-membered ring [1]. These results are all compatible with extensive charge delocalization over the system.

The arsenic analogue **1b** is isostructural, as illustrated in Figure 2, with the six-and five-membered rings again being coplanar. Selected bond distances and angles are included in Table 5. The P–As bond lengths of 2.2517(8) and 2.2468(9) Å are intermediate between the P=As double bond length of 2.124(2) Å in (Tms)$_2$HC–As=PMes* [17], and P–As single bond lengths of 2.316(8) Å in a molybdenum carbonyl heterocyclic complex [18], and of 2.350(3) and 2.361(2) Å for the independent P–As distances in ^{t}Bu$_6$As$_2$P$_6$ [19]. They are also in good agreement with the values of 2.250(1) and 2.244(1) Å obtained by Gamper and Schmidbaur for a six-membered (nonplanar) ring cation **10b** [4]. Very slightly longer P–As distances were found in the four-membered ring neutral compound **11b** (two independent molecules per unit cell; (a) P(1)As(1) 2.2710(7), P(2)As(1) 2.2692(7) Å; (b) P(1)As(1) 2.2729(7), P(2)As(1) 2.2681(7) Å) [7]. The P–As–P angle of 87.37(2)° is smaller than the P–P–P angle in its triphosphenium analogue, as expected for the large As atom. A similar effect is seen in six-membered rings, where the P–As–P angle of 93.0(1)° in the cation of **10b** [4] may be compared with the P–P–P angle of 96.44(6)° in a cyclic triphosphenium ion [1], and in the four-membered ring neutral species **11a** (two independent molecules, P–P–P angles 72.65(2) and 72.21(2)°) and **11b** (P–As–P angles 69.90(2) and 69.45(2)°) [7]. An angle of 84.57(5)° at As is found in the five-membered non-planar ring P–As–P cation described below (Figure 3 and Table 5).

The structure of the cation **9b** is shown in Figure 3, and that of the counterion is shown in Figure 4; selected bond distances and angles are listed in Table 5. The five-membered ring is nonplanar, as expected, although the P–As distances of 2.252(1) and 2.254(2) Å are very similar to those in the planar ring and clearly intermediate between expected values for P–As single and double bonds [17,18,19]. The interesting centrosymmetrical anion is derived by coordination of the diphosphane dioxide to two separate $SnCl_5^-$ moieties. The C=C bond in the backbone of the five-membered cationic ring has a normal length of 1.331(8) Å, which may be compared with the value of 1.32(1) Å for the corresponding C=C bond in the noncyclic anion. As mentioned previously, the P–As–P bond angle of 84.57(5)° is the smallest yet reported for a 5-membered ring, although only slightly smaller than that in the planar ring in **1b**. Naturally the P–As–P angle is smaller in the 4-membered ring compound **11b** [7].

EXPERIMENTAL

All manipulations, including NMR sample preparation, were carried out either under an inert

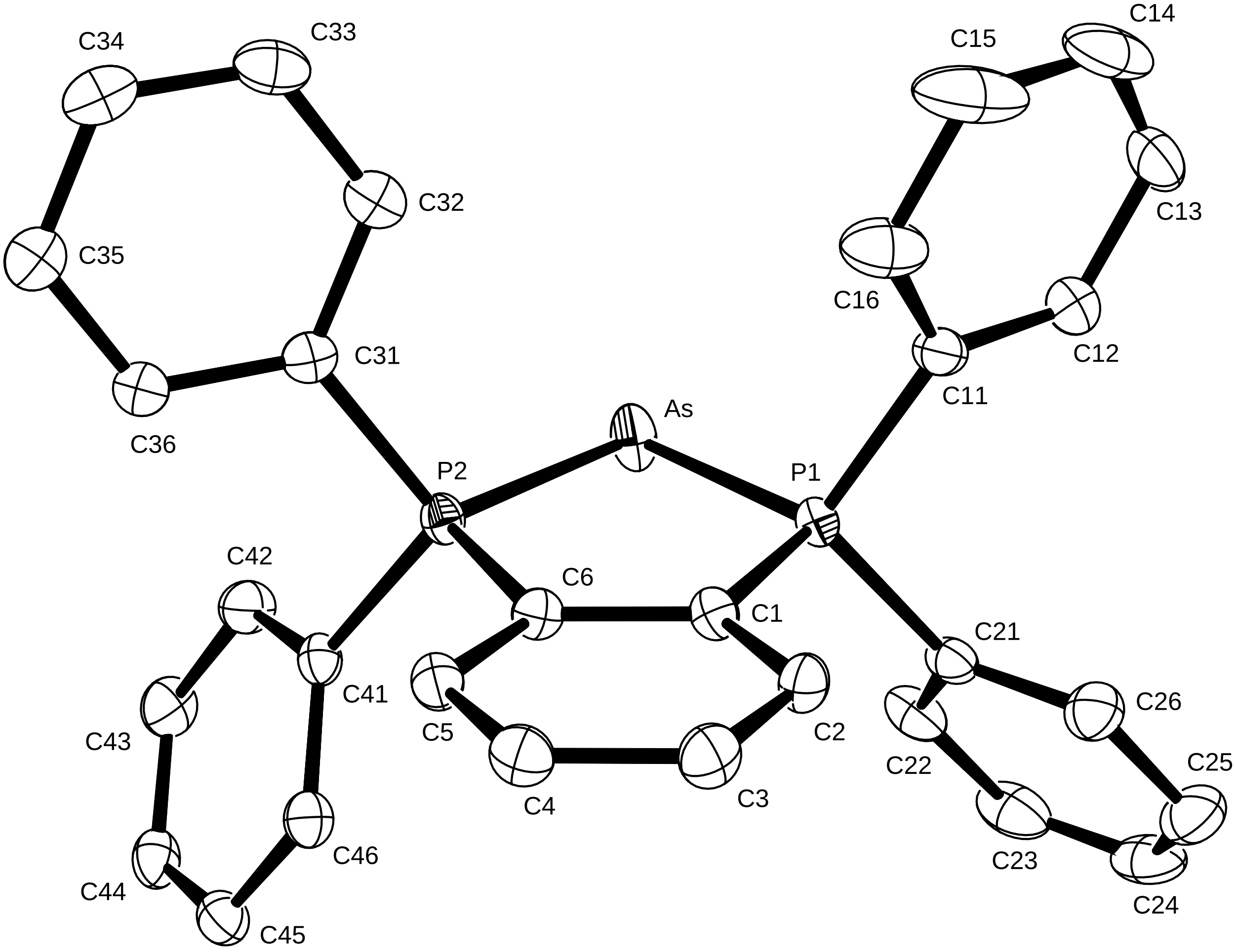


FIGURE 2 Thermal ellipsoid drawing of the cation **1b** showing 50% probability displacement ellipsoids for non-H atoms. All H atoms have been omitted for clarity.

atmosphere of dry nitrogen or in vacuo, using standard Schlenk procedures or a glovebox. Chemicals of the best available commercial grade were used, in general without further purification. ^{31}P NMR spectra were recorded on Varian Mercury 200, Varian VXR 400, or Varian Inova 500 Fourier-transform spectrometers, at 80.96, 161.91, and 202.32 MHz, respectively. Chemical shifts were measured relative to external 85% H_3PO_4, with the higher frequency direction taken as positive. The ^{31}P NMR spectra of all phosphorus-containing starting materials were recorded, to verify the absence of any major impurities; none was found. For PCl_3 or PBr_3, the calculated volumes were added by syringe to a solution of the requisite diphosphane in CH_2Cl_2. A standard solution of PI_3 in CH_2Cl_2 was prepared for PI_3 reactions, and the required volume of solution was added as described previously. $AsCl_3$ was transferred by syringe to a preweighed container in the glovebox, and the container was reweighed before addition of CH_2Cl_2. For reactions involving SnX_2 (X = Cl or Br), the solid materials were weighed separately, dissolved, or suspended in CH_2Cl_2 in the glovebox, and mixed together. The phosphorus or arsenic trihalide was then added by syringe, as previously.

*Preparation of (**1a**)$_2$ $SnCl_6^{2-}$*

1,2-Bisdiphenylphosphinobenzene (0.139 g, 0.291 mmol) was dissolved in CH_2Cl_2 (5 cm^3), then $SnCl_2$ (0.055 g, 0.290 mmol) was added, followed by more CH_2Cl_2 (5 cm^3). Finally, PCl_3 (0.030 cm^3, 0.344 mmol) was added. The mixture was left to stir. It was filtered by cannula after 10 days, and the ^{31}P NMR spectrum of the filtrate was recorded. After some time, colorless crystals suitable for X-ray diffraction were found growing in the NMR tube.

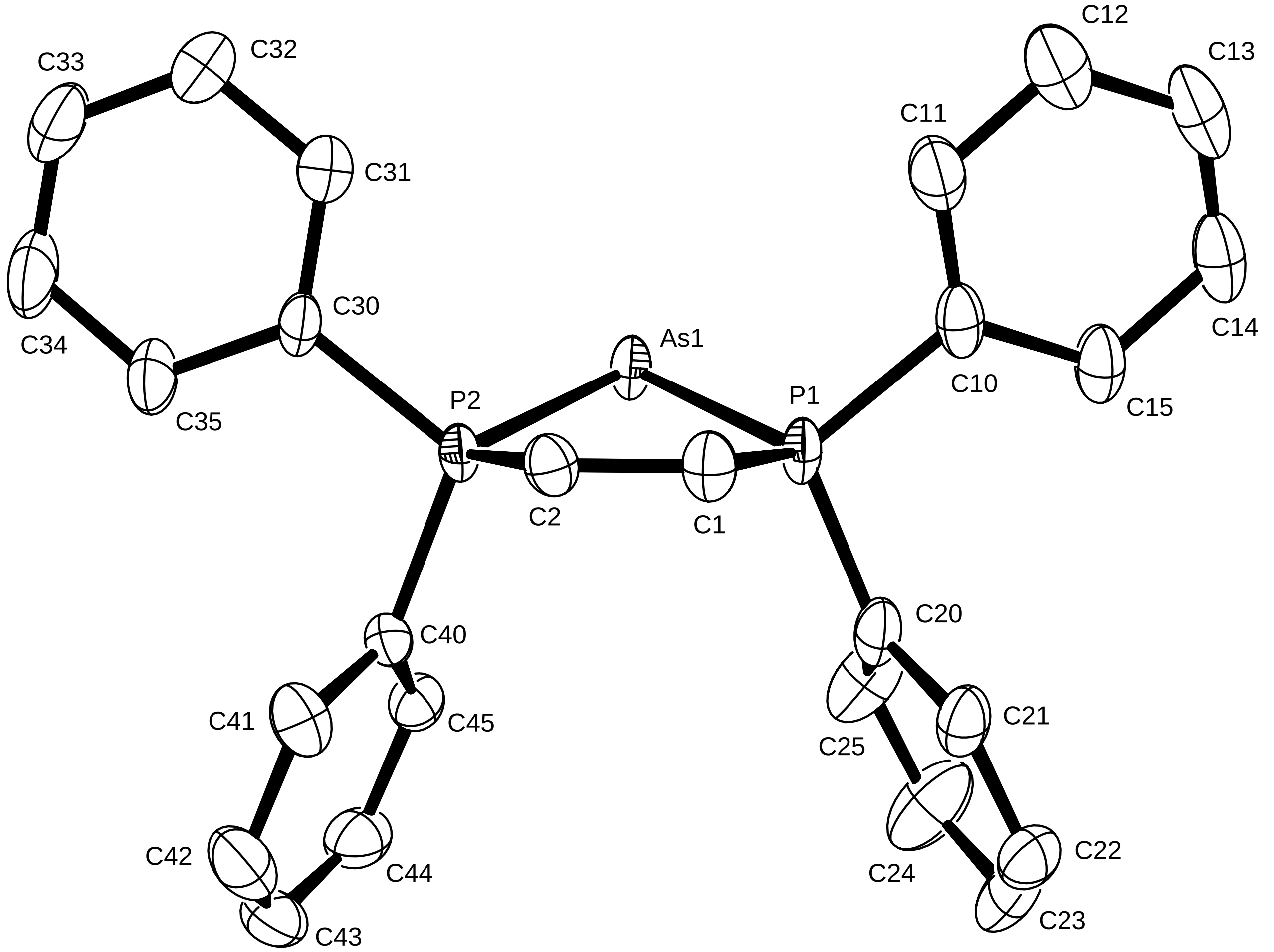


FIGURE 3 Thermal ellipsoid drawing of the cation **9b** showing 50% probability displacement ellipsoids for non-H atoms. All H atoms have been omitted for clarity.

*Preparation of (**1b**)$_2$ SnCl$_6$$^{2-}$*

1,2-Bisdiphenylphosphinobenzene (0.228 g, 0.511 mmol) was dissolved in CH_2Cl_2. $SnCl_2$ (0.100 g, 0.527 mmol) was added, and the mixture was stirred. A solution of $AsCl_3$ (0.092 g, 0.508 mmol) in CH_2Cl_2 was added. The solution immediately turned yellow and was allowed to stir for 4 days before filtration. The filtrate was placed in a refrigerator, and fine yellow crystals formed, which were characterized by X-ray crystallography.

*Preparation of (**9b**)$_2$ C$_2$H$_2$(Ph$_2$POSnCl$_5$)$_2$$^{2-}$*

cis-1,2-Bisdiphenylphosphinoethene (dppE) (0.185 g, 0.466 mmol) and $SnCl_2$ (0.098 g, 0.517 mmol) were dissolved in CH_2Cl_2 and stirred for 2 h. $AsCl_3$ (0.092 g, 0.508 mmol) was added, with stirring, resulting in a yellow solution. After the ^{31}P NMR spectrum of a small sample had been recorded, the solution was placed in a refrigerator. After some days the solution had turned slightly brown, and a small amount of brown fine solid had been deposited at the bottom of the Schenk tube. The solution was filtered, and the filtrate was layered with diethyl ether. Yellow crystals suitable for X-ray diffraction formed at the interface after cooling.

X-ray Crystallography

Single crystal structure determinations were carried out from data collected using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$) on a Bruker SMART-CCD detector diffractometer equipped with a Cryostream N2 flow cooling device [20]. Series of narrow ω-scans (0.3°) were performed at several ϕ-settings in such a way as to cover a hemisphere (for **1a**) or sphere (for **1b** and **9b**) of data to a maximum

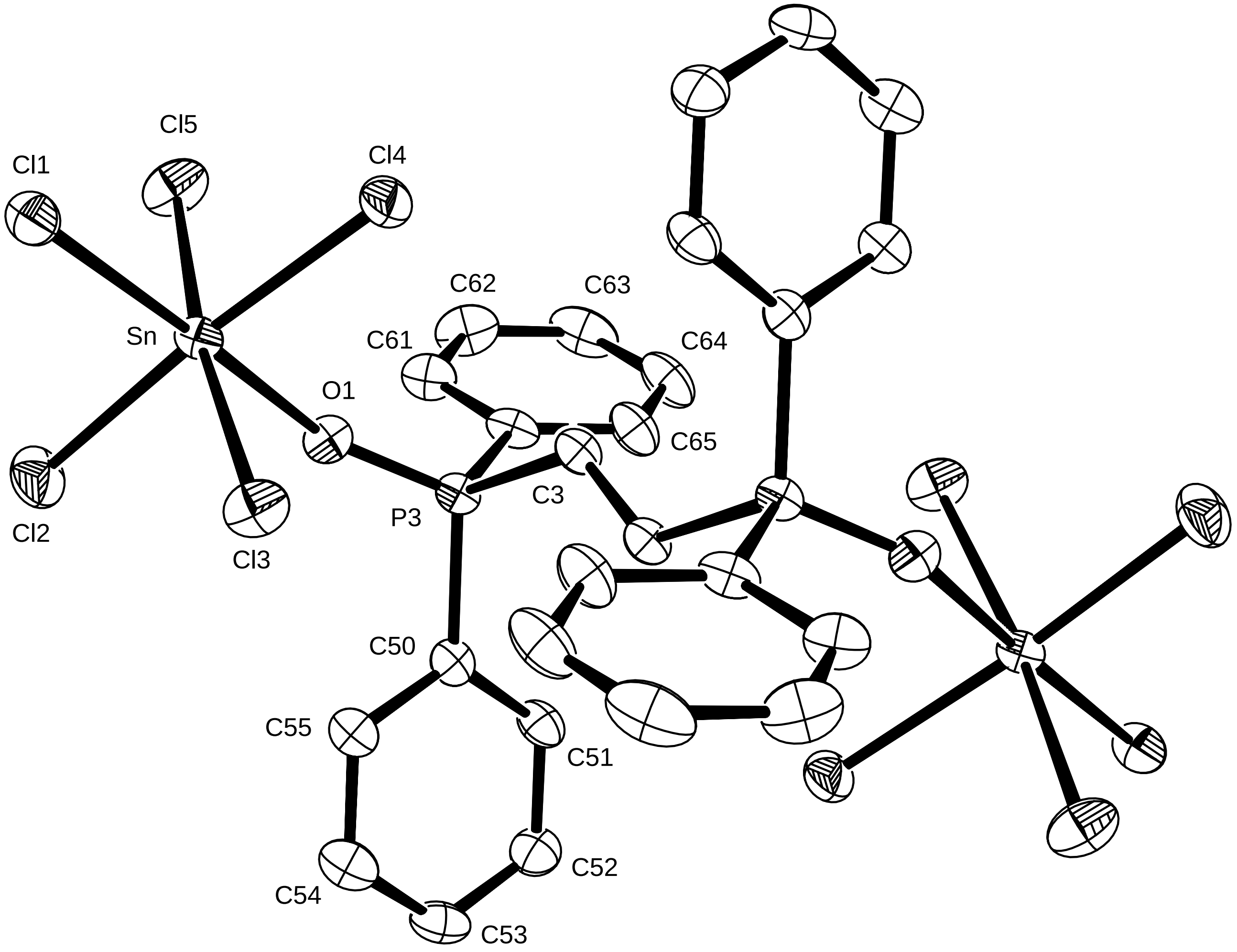


FIGURE 4 Thermal ellipsoid drawing of the anion to **9b** showing 50% probability displacement ellipsoids for non-H atoms. All H atoms have been omitted for clarity.

resolution between 0.70 and 0.77 Å. Data collections were carried out at 150K for **1a** and 100K for **1b** and **9b**. Cell parameters were determined and refined using the SMART software [21], and raw frame data were integrated using the SAINT program [22]. The structures were solved using Direct Methods and refined by full-matrix least squares on F^2 using SHELXTL [23]. Crystal data and structure refinement parameters are shown in Table 6, while selected bond distances and angles are given in Table 5. Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 154510, 154511, and 154512. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44 1223 336033 or E-mail: deposit@ccdc.cam.ac.uk).

No absorption correction was applied to data from **1a**. The $SnCl_6^{2-}$ anion in the **1a** salt is disordered over two positions around a Cl–Sn–Cl axis. The population of the major component is 0.929(2). Data from **1b** were corrected for absorption by numerical integration based on measurements and indexing of the crystal faces using SHELXTL software [23], $T_{min} = 0.499$, $T_{max} = 0.807$. For **1a** and **1b**, all nonhydrogen atoms were refined with anisotropic displacement parameters (adps). Hydrogen atoms were located from difference Fourier maps, and their coordinates and isotropic displacement parameters were refined. Data from **9b** were corrected for absorption by a semiempirical method from equivalent reflections [24], $T_{min} = 0.578$, $T_{max} = 0.746$. Disordered dichloromethane is also present in the structure of the **9b** salt. For **9b** all nonhydrogen atoms were refined with anisotropic displacement parameters

TABLE 6 Crystal Data and Structure Refinement Parameters

Compound	*(**1a**)$_2$ $SnCl_6{}^{2-}$*	*(**1b**)$_2$ $SnCl_6{}^{2-}$*	*(**9b**)$_2$ $C_2H_2(Ph_2PO\text{-}SnCl_5)_2{}^{2-}\cdot 2CH_2Cl_2$*
Empirical formula	$C_{60}H_{48}Cl_6P_6Sn$	$C_{60}H_{48}As_2Cl_6P_4Sn$	$C_{40}H_{35}AsCl_7OP_3Sn$
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P-1$
No. of reflections for cell determination	871	973	998
θ range (°)	12.02–24.06	12.10–24.11	4.39–22.70
Crystal size (mm)	0.30 × 0.22 × 0.10	0.50 × 0.14 × 0.12	0.36 × 0.30 × 0.20
a (Å)	11.974(1)	11.975(5)	10.777(2)
b (Å)	14.000(2)	13.968(5)	13.304(2)
c (Å)	17.227(2)	17.270(5)	16.925(3)
α (°)	90	90	88.724(7)
β (°)	90.593(3)	90.245(5)	76.733(6)
λ (°)	90	90	66.566(6)
Volume (Å^3)	2887.6(5)	2889(2)	2160.6(6)
Z	2	2	2
Formula mass (g mol^{-1})	1286.19	1374.09	1066.35
Density (g cm^{-3})	1.479	1.580	1.639
Reflections	20607	33293	23023
Unique	7945	7259	9850
μ (mm^{-1})	0.925	2.006	1.927
R_{int}	0.0432	0.0373	0.0387
Observed data [$I > 2\sigma(I)$]	5937	6499	7650
R Indices [$I > 2\sigma(I)$]	$R1 = 0.0376$ $wR2 = 0.0758$	$R1 = 0.0260$ $wR2 = 0.0695$	$R1 = 0.0552$ $wR2 = 0.1493$
R Indices (all data)	$R1 = 0.0611$ $wR2 = 0.0844$	$R1 = 0.0310$ $wR2 = 0.0737$	$R1 = 0.0758$ $wR2 = 0.1632$
Goodness of fit (s)	1.028	1.096	1.059
No. of variables	434	427	475

(adps) except those from the dichloromethane which were refined with isotropic displacement parameters. Hydrogen atoms were geometrically placed and allowed to ride on their parent C atom with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. Idealized C–H distances were fixed at 0.95 Å. Hydrogen atoms bound to dichloromethane carbon atoms were neither found nor geometrically placed.

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