Acyclic, Ring, and Cage As,C Compounds from Trimethylsilyl Ylides and $AsCl_3$

Florian Breitsameter, Alfred Schmidpeter,* and Heinrich Nöth[+][a]

Dedicated to Professor Gerhard Fritz on the occasion of his 80th birthday and to his former student Professor Gerd Becker on the occasion of his 60th birthday.

Abstract: From the reaction of trimethylsilyl ylides with $AsCl_3$ the dichloroarsanyl ylides **2b** and **5b** are obtained. As shown by X-ray structure determination, their $AsCl_2$ groups deviate systematically from the symmetric orientation. This conformation enables an effective charge transfer from the ylide moiety to one of the As–Cl bonds, which as a consequence is up to 15 pm longer than the other. At the same time the length of the As–C bonds in **2b** and **5b** indicates a partial double bond. The effects observed here are of the same type as those observed for the corresponding dichlorophosphanyl ylides; they are, however, more pronounced. The 1:1 condensation of the bis(trimethylsilyl) ylide **3** and $AsCl_3$ yields the oligomers $(Ph_3PCAsCl)_{2,3,4}$. The dimer **7b** has a diarsetane structure. HCl adds readily to one of its As–C bonds without opening it. The trimer and the tetramer are ionic. The cation of the trimer forms a six-membered ring with a delocalized arsenium/phosphonium charge, the cation of the tetramer forms a barrelane cage with a phosphonio substituent, and the anion is $AsCl_4^-$ in both cases (**10**, **13**). An arsa-phosphocyanine cation as in **10** is also part of the diphosphonio isoarsindolide tetrachloroarsenate(III) **12**. The structures of **7b**·HCl, **10**, and **13** reflect again an ylide to As–Cl charge transfer. The As–Cl bonds of **13** are by far the longest ones known for a chloroarsine (average 249 pm).

Keywords: arsenic · 1,3-diarsetane · phosphorus ylides · 1,3,5,7-tetraarsabarrelane · 1,3,5-triarsinane

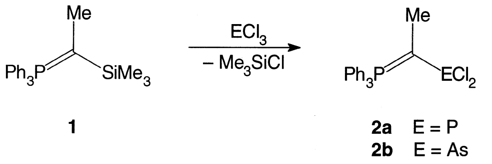
Introduction

The reaction of triphenylphosphonium trimethylsilyl ylides such as **1** and **3** with PCl_3 has proven effective and versatile.[1–10] It has gained particular interest because of two features of its products: 1) the PCl bonds of ylidyl chlorophosphines are elongated and those of bis(ylidyl)chlorophosphines eventually undergo heterolysis;[1–3, 7, 9] and 2) the ylidediyl chlorophosphine Ph_3PCPCl forms a dimer, trimer, and tetramer, the ionic character of which increases in this order.[4, 8–10] It seemed of interest to compare these results with those of analogous reactions with $AsCl_3$ instead of PCl_3.

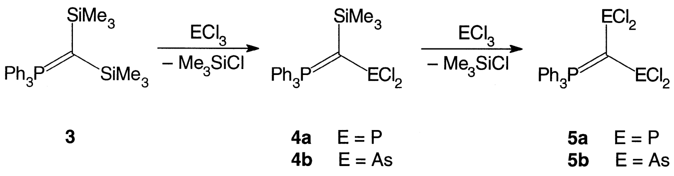
Results and Discussion

Ylidyl chloroarsanes (chloroarsanyl ylides): A number of phosphonium arsanylmethylides are known,[11–15] however, no haloarsanyl ylides. In a recent paper we reported the formation of ylide adducts of $AsCl_3$.[16]

The trimethylsilyl ylides **1** and **3** react smoothly with one and two equivalents of $AsCl_3$, respectively, to give the dichloroarsanyl ylide **2b** and bis(dichloroarsanyl) ylide **5b** as bright yellow and pale yellow crystals, respectively, (Schemes 1 and 2). If one equivalent of $AsCl_3$ is used, the substitution reaction at **3** stops at the dichloroarsanyl trimethylsilyl ylide **4b**, which is not stable in solution. Its decom-



Scheme 1.



Scheme 2.

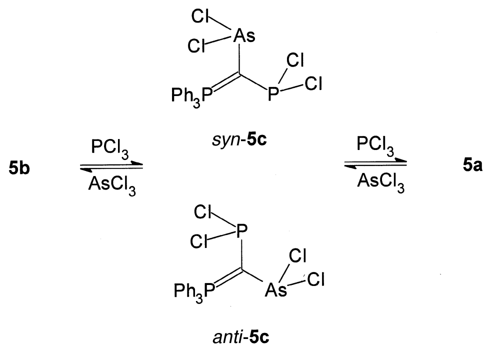
---

[a] Prof. Dr. A. Schmidpeter, Dr. F. Breitsameter, Prof. Dr. H. Nöth
Department Chemie der Universität München
Butenandtstraße 5-13, Haus D, 81377 München (Germany)
Fax: (+49) 89-2180-7866
E-mail: alfred@schmidpeter.de

[+] X-ray structure analysis.

position will be discussed in a later section. All reactions follow the formation of the respective phosphorus compounds **2a**, **4a**, and **5a**.

In solution compounds **5a** and **5b** enter in a slow exchange of ECl_2 (E = P, As) groups to give the mixed compound **5c** (Scheme 3). The respective equilibrium can be reached faster by adding PCl_3 to a solution of **5b**. Compound **5c** is favored over compounds **5a** and **5b** more than expected from statistics, presumably because it gives more structural opportunities. Like the two identical ECl_2 groups in **5a**[2] and in **5b** (see next section), the two different ECl_2 groups in **5c** will differ in orientation. This leads to two nonidentical conformers denoted as *syn*-**5c** and *anti*-**5c** (with regard to the synperiplanar and antiperiplanar orientation of the PCl_2 lone pair to the phosphonium group). Rotation interconverts the two conformers, however, as the ^{31}P NMR spectrum shows only averaged signals with $^2J_{PP} = 133.5$ Hz. If we assume that the individual coupling constants for **5c** are $^2J_{PP(syn)} \approx 210$ Hz and $^2J_{PP(anti)} \approx 0$ Hz as for **5a**[2], the averaged coupling constant found for **5c** suggests that *syn*-**5c** is significantly favored over *anti*-**5c**.



Scheme 3.

Structural comparisons: The results of the X-ray structure analysis of **2b** and **5b** (Figures 1 and 2) may be compared with each other as well as to the known structures of the corresponding phosphanyl compounds **2a**[2] (Table 1) and **5a**[2]. In case of the bis(phosphanyl) and bis(arsanyl) compounds the structure of the phenyl derivatives **6a**[17] and **6b**[13] (**5a**, **b** with Ph in place of Cl) are also known and may be included in the comparison (Table 2).

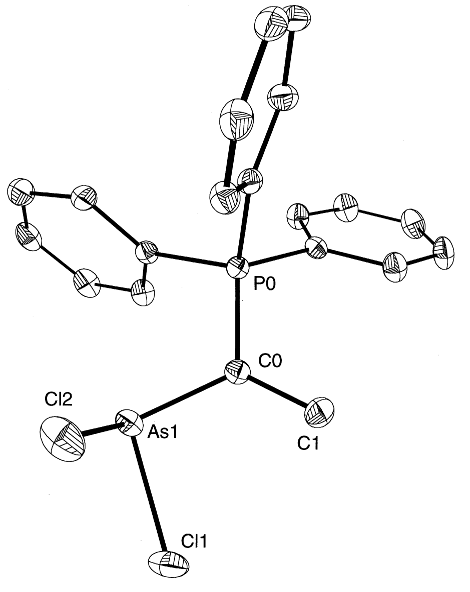


Figure 1. Molecular structure of **2b** in the crystal (thermal ellipsoids with 30% probability, hydrogen atoms omitted).

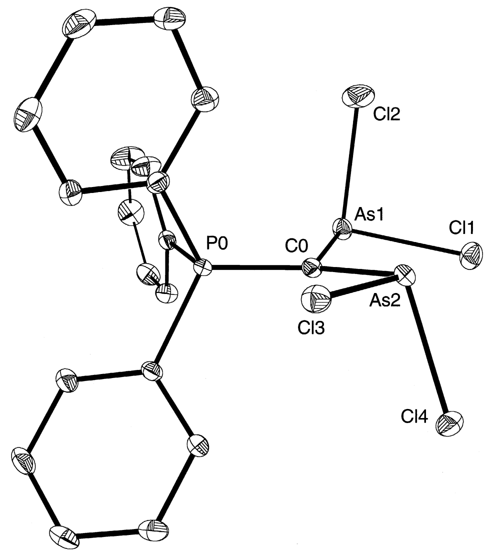


Figure 2. Molecular structure of **5b** in the crystal (thermal ellipsoids with 30% probability, hydrogen atoms omitted).

Table 1. Relevant bond lengths [pm], bond angles [°], and dihedral angles [°] of the dichlorophosphanyl ylide **2a**[2] and the dichloroarsanyl ylide **2b**. (The numbering refers to Figure 1; for **2a** E designates the P^{III} atom.)

	2a	**2b**
E	P	As
P0–C0	171.8(4)	172.3(2)
C0–E1	170.5(4)	183.1(2)
C0–C1	151.7(5)	151.3(3)
E1–Cl1	209.6(2)	221.6(1)
E1–Cl2	218.7(2)	237.0(1)
E1-C0-C1	125.2(3)	123.9(2)
P0-C0-E1	116.4(2)	113.9(1)
P0-C0-C1	117.7(3)	120.4(2)
sum	359.3	358.2
C0-E1-Cl1	102.8(1)	99.1(1)
C0-E1-Cl2	104.2(1)	105.0(1)
Cl1-E1-Cl2	92.2(1)	90.9(1)
sum	299.2	294.9
P0-C0-E1-Cl1	151.0	163.1
P0-C0-E1-Cl2	113.3	103.6
average	132.2	133.3

For a first approximation the orientation of the EX_2 groups is the same in all compounds. While the first EX_2 group stands with its vacant tetrahedral position (i.e., with its lone pair of electrons) roughly synperiplanar to the phosphonium group, the second one exhibits an antiperiplanar orientation.

The structure of the dichlorophosphanyl ylide **2a** (and that of related compounds) has been rationalized to reflect a charge transfer from the ylide moiety to one of the PCl bonds (negative hyperconjugation[2, 18]); the PCl group is rotated somewhat from the ideal synperiplanar orientation (with two equal dihedral P-C-P-Cl angles of approximately 130°). In this

Table 2. Relevant bond lengths [pm], bond angles [°], and dihedral angles [°] of the bis(phosphanyl) ylides **5a**[2], **6a**,[17] and bis(arsanyl) ylides **5b** and **6b**[13]. (The numbering refers to Figure 2; for **5a** and **6a** E1 and E2 mean the P^{III} atoms.)

	5a	**5b**	**6a**	**6b**
E	P	As	P	As
X	Cl	Cl	Ph	Ph
P0–C0	173.9(4)	173.2(3)	172.0(5)	169.8(4)
C0–E1	176.3(3)	189.2(2)	179.4(4)	193.6(4)
C0–E2	176.0(3)	189.1(3)	179.5(4)	193.8(4)
E1–X1	209.3(2)	221.3(1)	183.5(4)	197.0(4)
E1–X2	210.0(2)	227.4(1)	183.1(5)	195.9(5)
E2–X3	208.6(2)	222.2(1)	184.1(4)	197.4(5)
E2–X4	211.6(2)	225.2(1)	183.0(5)	197.0(5)
E1-C0-E2	116.3(2)	115.7(1)	119.4(2)	116.4(2)
P0-C0-E1	111.7(2)	114.6(1)	107.4(2)	108.4(2)
P0-C0-E2	131.9(2)	127.1(1)	179.5(4)	128.0(2)
sum	359.9	357.4	355.6	352.8
C0-E1-X1	102.9(1)	96.6(1)	107.6(2)	104.4(2)
C0-E1-X2	104.3(1)	103.2(1)	106.8(2)	103.6(2)
X1-E1-X2	96.0(1)	95.2(1)	101.6(2)	100.5(2)
sum	303.2	295.0	316.0	308.5
C0-E2-X3	105.0(1)	100.5(1)	109.5(2)	108.6(2)
C0-E2-X4	104.3(1)	102.5(1)	108.9(2)	104.6(2)
X3-E2-X4	97.4(1)	95.1(1)	102.6(2)	100.1(2)
sum	306.7	298.0	321.0	313.3
P0-C0-E1-X1	136.8	174.3	132.0	138.3
P0-C0-E1-X2	123.5	91.3	119.6	116.8
average	130.2	132.8	125.8	127.6
P0-C0-E2-X3	134.9	175.0	148.7	158.5
P0-C0-E2-X4	123.2	102.6	99.8	95.4
average	129.1	138.8	124.3	127.0

way one of the PCl bonds (dihedral angle 113°) approaches an orientation parallel to the carbon p_z orbital (corresponding to a dihedral angle of 90°) and becomes 9 pm longer than the other PCl bond (dihedral angle 151°). The same is now also found for the dichloroarsanyl ylide **2b**, but is distinctly more pronounced: The $AsCl_2$ group is rotated further towards the orientation of one AsCl bond (dihedral angle P-C-As-Cl = 104°) ecliptic to the ylidic lone pair. At the same time the second AsCl bond comes closer to the P-C-As plane (dihedral angle P-C-As-Cl = 163°). As a consequence, the first AsCl bond is 15 pm longer than the second one. With 237 pm it is the second longest AsCl bond in a ψ-tetrahedral structure known so far (see Table 6 later).The average dihedral angle is the same in **2a** and **2b**.

In the bis(dichlorophosphanyl)ylide **5a** two PCl_2 groups share the influence of one ylide unit, which consequently becomes less marked than in **2a**. The two PCl bond lengths of the same group differ by only 1 pm (in the *syn*-PCl_2 group) and 3 pm (in the *anti*-PCl_2 group). Again the effect is more pronounced in the corresponding dichloroarsanyl compound **5b**. In **5b** both $AsCl_2$ groups deviate more strongly from the symmetric situation than the PCl_2 groups in **5a**—the *syn*-$AsCl_2$ group more so than the *anti*-$AsCl_2$ group—and the AsCl bonds differ by 6 pm from each other in the *syn*-$AsCl_2$ group and by 3 pm in the *anti*-$AsCl_2$ group. In every case the longer AsCl bond comes along with the smaller dihedral angle.

This kind of charge transfer is also reflected in the length of the C–As bond,[19, 20] which becomes shorter in the expected order from **6b** (194 pm) to **5b** (189 pm) and **2b** (183 pm, which is shorter than the C–As bonds in arsabenzenes[20]). This is exactly the same trend as experienced for the corresponding phosphanyl ylides (Figure 3). The coordination of the ylidic carbon atom deviates only very little from planarity in all the ECl_2 compounds (sum of angles >357°); however, slightly more deviation is found in the EPh_2 compounds **6a** and **6b**. The bonding situation as deduced from the structures of **2b** and **5b** may be expressed by the resonance formulas shown in Scheme 4.

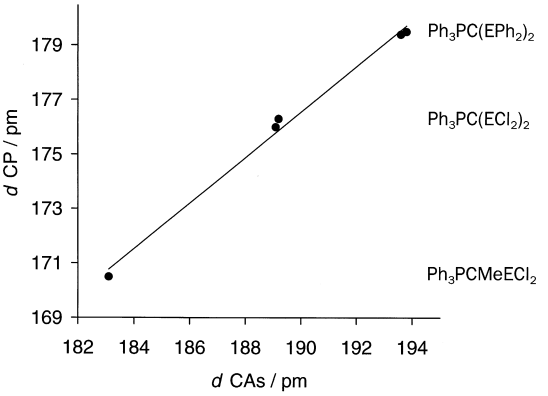
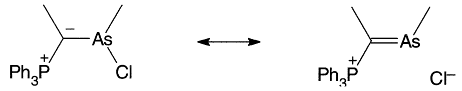
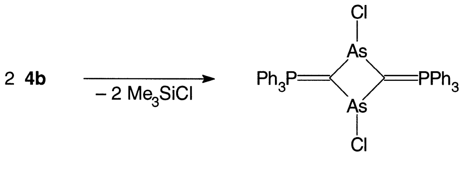


Figure 3. Correlation of CP and CAs bond lengths (Tables 1 and 2) in triphenylphosphonium phosphanyl and arsanyl ylides.



Scheme 4.

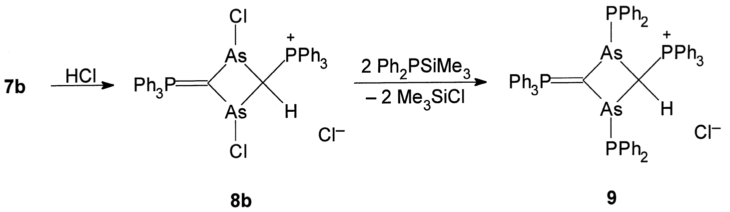
The Ph₃PCAsCl dimer, a 1,3-diarsetane: From the 1:1 mixture of **3** and PCl_3 eventually two moles of Me_3SiCl are lost and, consequently, Ph_3PCPCl can be anticipated as the product. As already mentioned in the introduction in fact a dimer (**7a**), a trimer, and a tetramer of this composition are obtained under somewhat different conditions.[4] The trimethylsilyl dichloroarsanyl ylide **4b**, which results as the primary product from the 1:1 reaction of **3** with $AsCl_3$ (see above), slowly loses a further molecule of Me_3SiCl leading to $Ph_3PCAsCl$ as the final product composition (Scheme 5). From its benzene solution yellow crystals of the dimer **7b** separate after two weeks.[21] In analogy to **7a** a 1,3-diarsetane structure is expected.



7b

Scheme 5.

The ^{31}P NMR spectrum of **7b** in pyridine shows only a singlet at $\delta = 11.6$ in accord with a symmetric structure. For the solution of **7b** in dichloromethane, however, an AB pattern is observed; this indicates that **7b** has been protonated to **8b** by this solvent (Scheme 6): $\delta_A = 19.7$ (Ph_3P), $\delta_B = 23.5$ (Ph_3P^+), $J_{AB} = 33.2$ Hz ($^4J_{PP}$).[23]



Scheme 6.

For a further structural proof **8b** was converted to its bis(diphenylphosphanyl) derivative **9**, which displays an ABC_2 spin system in the ^{31}P NMR spectrum (CH_2Cl_2): $\delta_A = 19.3$ (Ph_3P), $\delta_B = 24.4$ (Ph_3P^+), $\delta_C = -12.9$ (Ph_2P), $J_{AB} = 7.6$ Hz ($^4J_{PP}$), $J_{AC} = 3.0$ Hz ($^3J_{PP}$), $J_{BC} = 21.8$ Hz ($^3J_{PP}$).

The X-ray structure analysis of crystals grown from a 1:1 dichloromethane/benzene solution of **7b** also documents the ionic structure of **8b** for the solid state (Table 3). There are two independent molecules in the asymmetric unit of the unit cell. They have almost identical bonding parameters. Only one of the two molecules is depicted in Figure 4. The diarsetane ring of the cation is slightly folded with the substituents Cl1 and Cl2 at the same side. The three-coordinate carbon ring-member C1 deviates somewhat from planarity (sum of angles 356°). As the other carbon ring-member C2 is protonated, the structural effect of the ylide part can be read from the comparison of the two different halves of the cation. All the bonds of C1 are shorter than the corresponding ones of C2; in particular the C–As bonds are on the average 11 pm shorter. The dihedral angles P1-C1-As1-Cl1 and P1-C1-As2-Cl2 are small (95°) and promise long AsCl bonds (see above), which are indeed found: As1–Cl1 (average 233.5 pm) is similar in length to the AsCl bonds in **2b** and **10**; As2–Cl2 (average 241.4 pm) is further lengthened, however, by a contact of the anion Cl3 to As2 (average 278.4 pm). Including this contact, As2 approaches a ψ-trigonal-bipyramidal (ψ-tbp) coordination with Cl2 and Cl3 occupying the axial positions at rather different distances.[24] As a consequence of the higher coordination of As2, the two As2–C bonds are also somewhat longer than the corresponding As1–C bonds. As compared with **7b**, HCl has been added in **8b** to the bond As2–C2, which consequently has become the longest of the four ring bonds. The intramolecular contact of Cl3 to the other arsenic atom As1 (average 337.5 pm) is considerably longer than that to As2.[25] The crystal contains 2.5 molecules of benzene per molecule of **8b**.

Table 3. Selected bond lengths and distances [pm], bond angles [°], and dihedral angles [°] of the two symmetry-independent units of **8b**. (The numbering refers to Figure 4.)

P1–C1	173.2(10)	171.4(10)
P2–C2	180.5(9)	180.5(9)
C1–As1	186.2(9)	187.3(9)
C1–As2	188.7(10)	190.3(10)
C2–As1	197.5(11)	200.7(9)
C2–As2	200.5(9)	200.2(9)
As1–Cl1	233.6(3)	232.9(3)
As1–Cl3	339.3	335.7
As2–Cl2	241.6(3)	240.9(3)
As2–Cl3	277.7	279.1
P1-C1-As1	127.7(6)	126.8(6)
P1-C1-As2	128.7(5)	131.1(6)
As1-C1-As2	99.2(4)	98.0(4)
P2-C2-As1	122.0(5)	120.5(5)
P2-C2-As2	127.2(5)	127.9(4)
As1-C2-As2	91.6(4)	90.6(4)
C1-As1-C2	80.5(4)	81.3(4)
C1-As1-Cl1	105.2(3)	104.6(3)
C2-As1-Cl1	95.2(3)	95.1(3)
C1-As2-C2	79.1(4)	80.7(4)
C1-As2-Cl2	101.5(3)	102.3(3)
C2-As2-Cl2	94.4(3)	94.2(3)
C1-As2-Cl3	93.7	92.8
C2-As2-Cl3	84.6	84.0
Cl2-As2-Cl3	164.2	164.4
P1-C1-As1-Cl1	94.9	95.9
P1-C1-As2-Cl2	93.9	93.7

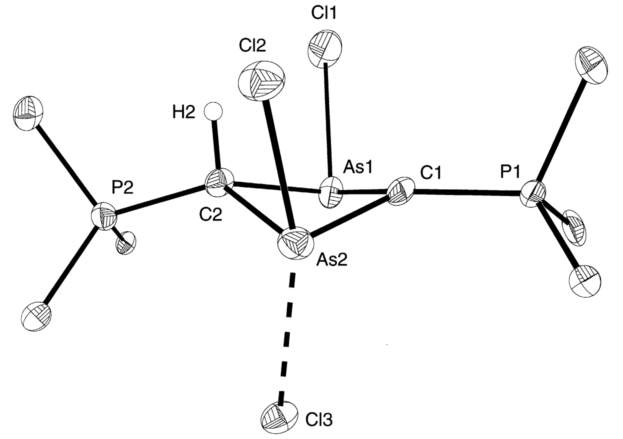
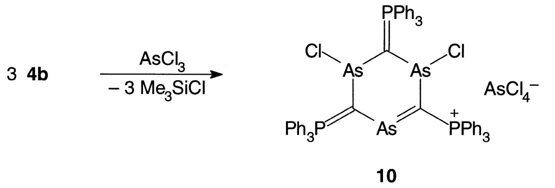


Figure 4. Molecular structure of one of the **8b** units (thermal ellipsoids with 30% probability, for clarity the phenyl groups are represented only by their ipso-carbon atoms).

The $Ph_3PCAsCl$ trimer, a 1,3,5-triarsinane: Several months after the yellow crystals of **7b** had been obtained as described above, red crystals of compound **10** separated from the same solution (Scheme 7). They are much more soluble than those of **7b** and have the composition $(Ph_3PCAsCl)_3AsCl_3(C_6H_6)_{2/3}$. In contrast to **7b** the product **10** is not protonated in CH_2Cl_2. Its ^{31}P NMR spectrum represents an AB_2 spin system ($\delta_A = 28.0$, $\delta_B = 34.4$; $J_{AB} = 6.5$ Hz) and indicates a six-membered ring of alternating Ph_3PC and AsCl units; one AsCl unit is dissociated and its chloride ion is incorporated into an $AsCl_4^-$ anion.



Scheme 7.

While the chloride exchange in the analogous Ph_3PCPCl trimer is fast and leads to broad and averaged signals at room temperature,[4] the exchange in **10** is slow and leaves the signals sharp. However, this is not due to the $AsCl_4^-$ complex anion as the spectrum does not change when a soluble chloride such as $[Et_4N]Cl$ is added.

The structure as deduced from the ^{31}P NMR spectrum is confirmed also for the solid state by an X-ray structure analysis (Figure 5). One of the phenyl groups of the cation is rotationally disordered.

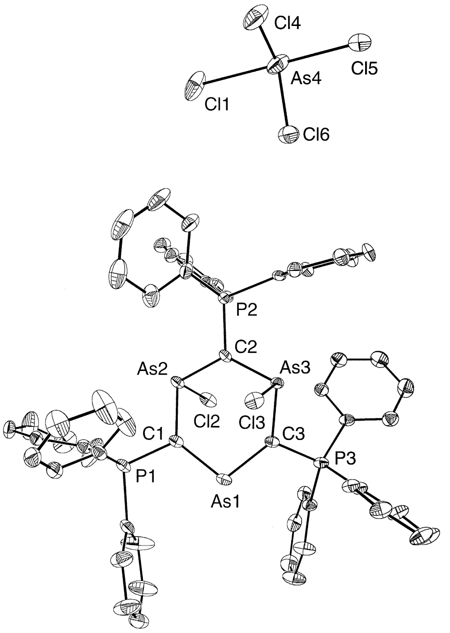


Figure 5. Molecular structure of the cation and anion of **10** (thermal ellipsoids with 30 % probability, hydrogen atoms omitted).

The triarsinane ring is present in a twist conformation with the three carbon atoms in planar coordination.[26] The two AsCl bonds are nearly perpendicular to the plane As2-C2-As3 (average dihedral angle P-C-As-Cl = 100°), see Figure 6.

All bond lengths and angles in the triarsinane ring (Table 4) are found in the expected range and order. The charge transfer of the type discussed above from the ylidic carbon atom C2 results in relatively short C2–As2 and C2–As3 bonds (188 pm) and in long As–Cl bonds (average 235 pm). In accordance with the dissociation the C-As-C angle at As1 is wider (104°) than those at atoms As2 and As3 (102°), and the adjacent CAs bonds (184 pm) are even shorter than C2–As2 and C2–As3. Evidently a good deal of the arsenium charge generated by the dissociation at As1 is delocalized over the phosphonium moieties P1 and P2. The C1–As2 and C3–As3 bonds (192 pm) on the other hand remain close to single bond length.[19] An analogous structure is to be assumed for the cation of the trimer $(Ph_3PCPCl)_3$, for which no structure determination is available. The anion of **10** has the ψ-tbp structure known from other salts.[27]

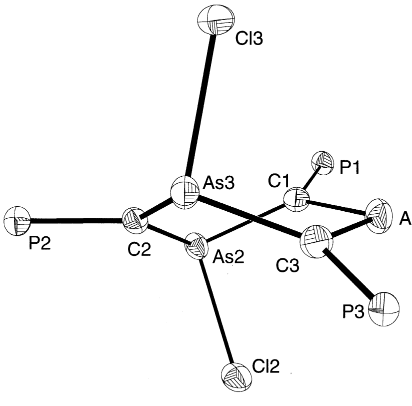
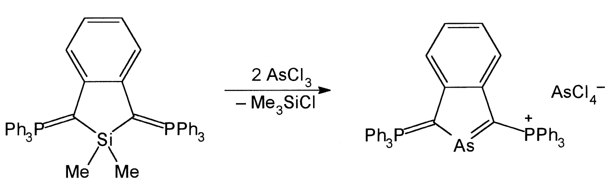


Figure 6. "Side view" of the cation of **10**.

Table 4. Selected bond lengths [pm], bond angles [°] and dihedral angles [°] of the cation and anion of **10**. (The numbering refers to Figure 5.)

P1–C1	174.2(5)	C1-As1-C3	103.7(2)
P2–C2	174.5(5)	C1-As2-Cl2	96.3(2)
P3–C3	174.7(5)	C2-As2-Cl2	100.9(2)
C1–As1	184.6(5)	C1-As2-C2	102.3(2)
C1–As2	192.1(5)	C3-As3-Cl3	99.1(2)
C2–As2	188.1(5)	C2-As3-Cl3	101.2(2)
C2–As3	188.0(5)	C3-As3-C2	101.1(2)
C3–As1	184.2(5)	P1-C1-As2-Cl2	117.1
C3–As3	192.4(5)	P2-C2-As2-Cl2	104.6
As2–Cl2	232.6(2)	P2-C2-As3-Cl3	94.9
As3–Cl3	236.7(1)	P3-C3-As3-Cl3	115.7
As1-C1-P1	116.4(3)		
As2-C1-P1	117.4(3)	As4–Cl4	219.6(2)
As1-C1-As2	124.9(3)	As4–Cl5	237.8(2)
sum	358.7	As4–Cl6	217.2(2)
As2-C2-P2	114.6(3)	As4–Cl1	251.1(2)
As3-C2-P2	116.0(2)	Cl4-As4-Cl5	90.8(2)
As2-C2-As3	129.4(3)	Cl4-As4-Cl6	100.7(1)
sum	360.0	Cl4-As4-Cl1	90.6(1)
As1-C3-P3	116.5(3)	Cl5-As4-Cl6	91.0(1)
As3-C3-P3	114.5(3)	Cl5-As4-Cl1	177.8(1)
As3-C3-As1	128.4(3)	Cl6-As4-Cl1	90.4(1)
sum	359.4		

As demonstrated by the discussed structural details, the cation of **10** consists of two rather independent parts, that is, the uncharged and the charged half of the ring. The latter represents the second example of an arsa-phosphocyanine.[28] As the first example we reported earlier a diphosphonio-isoarsindolide cation.[29] Its tetrachoroarsenate(III) **12** is readily obtained from the reaction of the dimethyl 2-silaindane **11** with arsenic trichloride (Scheme 8; see also Experimental Section).

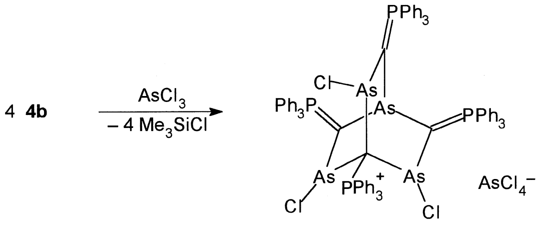


11 **12**

Scheme 8.

In more general terms arsacyanines are polyene cations with a central two-coordinate arsenic atom. Depending on the length of the chain and the nature of the terminal groups the center has arsenium or arsenide character. The cations of **10** and **12** naturally are of the arsenium type and correspond in this respect to the heterocyclic arsatrimethyne cyanines,[22, 30] while the heterocyclic arsamonomethyne cyanines[22, 31] represent the arsenide type.

The $Ph_3PCAsCl$ tetramer, a 1,3,5,7-tetraarsabarrelane: If performed in pyridine, the reaction of equimolar amounts of **3** and PCl_3 leads to a tetramer of the final condensation product.[4, 10] An analogous result is obtained with $AsCl_3$. Compound **4b** is monitored as an intermediate and survives longer than the corresponding phosphorus compound **4a**. Also observed are compounds **8b** and **10** as minor byproducts. As the main product the tetramer **13** is formed (Scheme 9), which starts to separate from the solution after two weeks in orange crystals of the composition $(Ph_3PCAsCl)_4AsCl_3(C_5H_5N)_5$.



13

Scheme 9.

The ^{31}P NMR spectrum (in CH_2Cl_2) demonstrates an A_3B spin system: $\delta_A = 27.9$, $\delta_B = 43.4$, $J_{AB} = 7.2$ Hz. This suggests an ionic structure for **13** and a barrelane structure for its cation in analogy to the structure found for the phosphorus-containing tetramer. The arsenium charge originating from the dissociation of an AsCl bond shows up as a phosphonium charge.

This structure is further confirmed by an X-ray investigation (Figures 7 and 8 and Table 5). The AsCl bond lengths in the cation (average 249 pm) are by far the longest observed at a three-coordinate, pyramidal arsenic atom (see Table 6). This result gains particular significance by the fact that the PCl bond in the analogous cation, which contains phosphorus in place of arsenic, are also the longest observed so far for three-coordinate phosphorus. These PCl and AsCl bond lengths in fact fit well into a more general correlation of PCl/AsCl bonds of chlorophosphines and chloroarsines (see below, Figure 9). The extreme bond lengths seem to result from two superimposed effects: 1) the ECl bonds stand almost exactly perpendicular to the ylide plane (dihedral angle P-C-P-Cl = 90.5°[10], average P-C-As-Cl = 90.1°, Table 5) and enable a

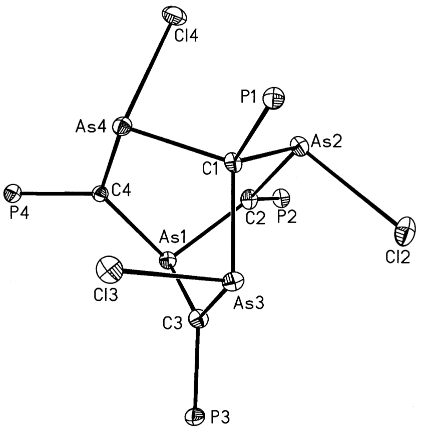


Figure 7. Molecular structure of the cation of **13** (thermal ellipsoids with 30% probability, for clarity the twelve phenyl groups at P1–P4 are omitted).

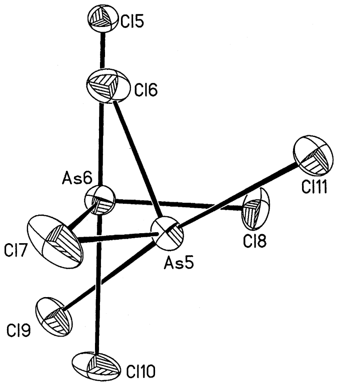


Figure 8. The $AsCl_4^-$ anion of **13** in two overlapping sites at Cl7 (thermal ellipsoides with 30% probability).

Table 5. Selected bond lengths [pm], bond angles [°], and dihedral angles [°] of the cation and anion of **13** (The numbering refers to Figures 7 and 8.)

P1−C1	185.4(6)	P1-C1-As2	108.6(3)
P2−C2	173.3(6)	P1-C1-As3	109.8(3)
P3−C3	174.3(6)	P1-C1-As4	108.6(3)
P4−C4	171.8(7)	C1-As2-Cl2	90.6(2)
C1−As2	202.6(6)	C2-As2-Cl2	107.6(2)
C1−As3	203.8(6)	C1-As2-C2	100.8(3)
C1−As4	205.8(6)	C1-As3-Cl3	92.2(2)
C2−As1	192.6(7)	C3-As3-Cl3	107.7(2)
C2−As2	183.7(7)	C1-As3-C3	101.6(3)
C3−As1	193.8(6)	C1-As4-Cl4	91.1(2)
C3−As3	182.6(7)	C4-As4-Cl4	105.9(2)
C4−As1	193.6(6)	C1-As4-C1	102.0(3)
C4−As4	185.0(6)		
As2−Cl2	251.6(2)	As1-C2-P2	115.0(4)
As3−Cl3	247.8(2)	As2-C2-P2	117.5(4)
As4−Cl4	247.4(2)	As1-C2-As2	127.4(3)
		sum	359.9
P2-C2-As2-Cl2	92.7		
P3-C3-As3-Cl3	92.3	As1-C3-P3	116.6(4)
P4-C4-As4-Cl4	85.4	As3-C3-P3	116.8(3)
		As1-C3-As3	126.6(3)
		sum	360
As1-C4-P4	117.0(4)		
		As4-C4-P4	118.0(3)
		As1-C4-As4	124.9(3)
		sum	359.9
C2-As1-C3	98.1(3)		
		C2-As1-C4	99.4(3)
		C3-As1-C4	97.9(3)
As5−Cl6	224.4(5)	Cl6-As5-Cl7	88.2(2)
As5−Cl7	215.0(3)	Cl6-As5-Cl9	94.0(2)
As5−Cl9	246.4(5)	Cl6-As5-Cl11	92.2(2)
As5−Cl11	245.1(5)	Cl7-As5-Cl9	88.1(1)
		Cl7-As5-Cl11	97.2(1)
As6−Cl7	235.5(3)	Cl9-As5-Cl11	172.0(2)
As6−Cl8	222.8(5)		
As6−Cl5	249.1(4)	Cl7-As6-Cl8	88.8(2)
As6−Cl10	243.8(5)	Cl7-As6-Cl5	96.8(1)
		Cl7-As6-Cl10	91.4(2)
		Cl8-As6-Cl5	90.5(2)
		Cl8-As6-Cl10	91.7(2)
		Cl5-As6-Cl10	171.6(2)

Table 6. *d*ECl bond lengths in corresponding chlorophosphines and chloroarsines.

	*d*ECl [pm]	
	P	As
ECl_3	204.3(3)[39]	216.1(4)[40]
$(tBuNECl)_2$	209.6(7)[41]	224.9(3)[42]
	211.4(7)	225.2(2)
$Ph_3PC(ECl_2)_2$	208.6(2)[2]	221.3(1)
	209.3(2)	222.2(1)
	210.0(2)	225.2(1)
	211.6(2)	227.4(1)
$(CH_2)_3(MeN)_2ECl$	–	235.7(2)[43]
$Ph_3PMeCECl_2$	209.6(2)[2]	221.6(1)
	218.7(2)	237.0(1)
$(CH_2)_2(tBuN)_2ECl$	231.4(1)[44]	237.5(2)[45]
$(CH_2)_2(MeN)_2ECl$	–	239.0(5)[43]
$E(Ph_3PCECl)_3CPPh_3^+$	235.3(2)[4]	247.4(2)
		247.8(2)
		251.6(2)

most effective charge transfer, and 2) each ECl bond has an intramolecular *trans* contact to the chlorine atom of a neighboring ECl group. These contacts (dP$\cdots$Cl = 319.0 pm,[10] average dAs$\cdots$Cl = 329.0 pm) are far beyond normal bond lengths[32], but they are shorter than the respective van der Waals distances (dP$\cdots$Cl = 370 pm, dAs$\cdots$Cl = 380 pm). The $AsCl_4^-$ anion of **13** has a *ψ*-tbp structure as in **10**. It occupies, however, to an equal extent two different sites that share the position of one equatorial chlorine atom (Cl7, Figure 8).

The structural data of the new ylide derivatives **2b**, **5b**, **8b**, **10**, and **13** extend the range of known AsCl bond lengths in chloroarsines considerably, and the same applies to the data of the corresponding chlorophosphines and to the PCl bond lengths. In order to compare the impact of a certain molecular situation on the PCl and AsCl bond, we collected the available pairs of molecular structures in Table 6 and correlated their PCl and AsCl bond lengths in Figure 9. As can be seen, the two sorts of bonds are influenced in the same manner and to quite the same extent.

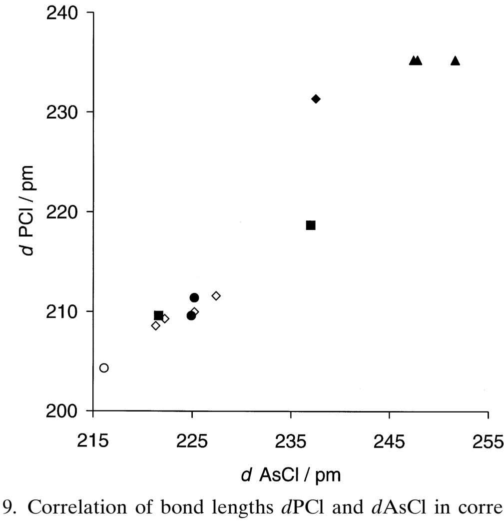


Figure 9. Correlation of bond lengths *d*PCl and *d*AsCl in corresponding compounds (from Table 6). ○ ECl_3, ■ $Ph_3PMeCECl_2$, ◇ $Ph_3PC(ECl_2)_2$, ● $(tBuNECl)_2$, ◆ $(CH_2)_2(tBuN)_2ECl$, ▲ $E(Ph_3PCECl)_3CPPh_3^+$.

Experimental Section

All manipulations were carried out in flame-dried glassware under argon with Schlenk tube techniques. Dry dichloromethane, benzene ,and pyridine were used as obtained (Fluka). Cyclohexane and heptane were dried over molecular sieves (4 Å). $AsCl_3$, PCl_3, and dimethylchlorosilane were distilled prior to use. Melting points were measured in sealed capillaries and are uncorrected. NMR: Jeol EX400 (^{1}H, ^{13}C), Jeol GSX270 (^{31}P) with Me_4Si (internal) and 85% H_3PO_4 as standards. Trimethylsilylethylidene triphenylphosphorane **1**,[34] bis(trimethylsilyl)methylidene triphenylphosphorane **3**,[35] and *o*-xylylene bis(triphenylphosphonium) dibromide[36] were prepared as described.

Dichloroarsanylethylidene triphenylphosphorane (2b): $AsCl_3$ (2.71 mL, 31.4 mmol) was added dropwise at 0°C over a period of 5 min to a stirred solution of **1** (10.3 g, 28.5 mmol) in benzene (25 mL). The yellow solution was stirred for 4 h at RT, after which cyclohexane (6 mL) was added. After standing at room temperature for 12 h, bright yellow crystals of **2b** were filtered off, washed twice with benzene/cyclohexane (1:1), and dried in vacuo. After concentration of the filtrate to about 20% of its original volume a second crop could be obtained. Yield 10.3 g (83%) of **2b**; m.p. 153–155°C; ^{1}H NMR (C_6D_6): $\delta = 2.54$ (d, $^3J_{PH} = 15.7$ Hz, 3H, CH_3), 6.94–7.02 (m, 6H, *m*-H), 7.07–7.15 (m, 3H, *p*-H), 7.40–7.49 (m, 6H, *o*-H); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 16.0$ (d, $^2J_{PC} = 3.8$ Hz, CH_3), 63.7 (d, $^1J_{PC} = 91.5$ Hz, C=PPh_3), 125.0 (d, $^1J_{PC} = 88.4$ Hz, *i*-C), 129.4 (d, $^3J_{PC} = 12.3$ Hz, *m*-C), 133.3 (s, *p*-C), 133.9 (d, $^2J_{PC} = 10.0$ Hz, *o*-C); elemental analysis calcd (%) for $C_{20}H_{18}PAsCl_2$ (435.16): C 55.20, H 4.17; found C 54.87, H 4.26.

Bis(dichloroarsanyl)methylidene triphenylphosphorane (5b): Compound 5b was prepared from **3** (2.4 g, 5.8 mmol) and $AsCl_3$ (1.1 mL, 17.7 mmol) in benzene (15 mL) with the procedure described for **2b** above. Yield 2.8 g (86%) of **5b**; m.p. >93°C (decomp); ^{1}H NMR (CD_2Cl_2): $\delta = 7.60$–7.65 (m, 6H, *m*-H), 7.71–7.76 (m, 3H, *p*-H), 7.84–7.90 (m, 6H, *o*-H); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 68.0$ (d, $^1J_{PC} = 71.5$ Hz, C=PPh_3), 124.7 (d, $^1J_{PC} = 91.5$ Hz, *i*-C), 129.3 (d, $^3J_{PC} = 13.1$ Hz, *m*-C), 133.6 (d, $^4J_{PC} = 3.1$ Hz, *p*-C), 134.5 (d, $^2J_{PC} = 10.8$ Hz, *o*-C); elemental analysis calcd (%) for $C_{19}H_{15}PAs_2Cl_4$ (565.96): C 40.32, H 2.67; found C 40.68, H 2.79.

Reaction of 5b with PCl_3: PCl_3 (0.014 mL, 0.16 mmol) was added to a solution of **5b** (88 mg, 0.16 mmol) in dichloromethane (0.5 mL) in an NMR tube. After 45 min, a ^{31}P NMR spectrum of the pale yellow solution was recorded and showed the signals of **5c** (38%), **5a** (10%), and **5b** (31%). Another ^{31}P NMR spectrum was recorded after 3 d and showed the following intensities of the signals of **5c** (73%), **5a** (12%), and **5b** (15%).

Reaction of 5b with 5a: In an NMR tube **5b** (0.06 g, 0.11 mol) and **5a** (0.05 g, 0.10 mmol) were dissolved in dichloromethane (0.5 mL). After 2 h the ^{31}P NMR spectrum showed only the signals of **5a** and **5b**; after 3 d also the signals of **5c** (4%) were also observed.

1,3-Dichloro-2,4-bis(triphenylphosphoranediyl)-1,3-diarsetane (7b), 1,3-dichloro-2-triphenylphosphonio-4-triphenylphosphoranediyl-1,3-diarsetane chloride (8b), and 3,5-dichloro-2,4,6-tris(triphenylphosphoranediyl)-1,3,5-triarsinenium tetrachloroarsenate(III) (10): $AsCl_3$ (1.16 mL, 13.4 mmol) was added dropwise at RT over a period of 30 min to a stirred solution of **3** (6.07 g, 14.4 mmol) in benzene (200 mL). The yellow solution was stirred for additional 3 h. After 3 weeks yellow crystals of **7b** were filtered off, washed twice with cyclohexane/benzene (2:1), and dried in vacuo. In the next 3 months four crops of **7b** were obtained. Yield 0.91 g (18%), m.p. >103°C (decomp); elemental analysis calcd (%) for $C_{38}H_{30}As_2Cl_2P_2$ (769.35): C 59.32, H 3.93; found C 59.65, H 4.01. From the mother liquor, after 4 months, some pale yellow crystals of **8b** were filtered off and used for a crystal structure determination. After 11 months red crystals of **10**$\cdot$2/3C_6H_6 were filtered off, washed with cyclohexane/benzene (3:1), and dried in vacuo. Yield 0.51 g (3%); m.p. >141°C (decomp); ^{1}H NMR (CD_2Cl_2): $\delta = 7.36$ (s, 4H, C_6H_6), 7.43–7.56 (m, 18H, *m*-H), 7.63–7.77 (m, 27H, *o*-H/*p*-H); elemental analysis calcd (%) for $C_{61}H_{49}As_4Cl_6P_3$ (1387.39): C 52.86, H 3.56; found C 52.02, H 3.66.

Reaction of 7b with Ph_2PSiMe_3: In an NMR tube **7b** (180 mg, 0.2 mmol) was dissolved in dichloromethane (0.5 mL) and Ph_2PSiMe_3 (0.13 g, 0.5 mmol) was added. After 45 min a ^{31}P NMR spectrum of the orange solution was recorded and showed the signals of **9**.

3,5,7-Trichloro-2,6,8-tris(triphenylphosphoranediyl)-4-triphenylphosphonio-1,3,5,7-tetraarsabarrelane tetrachloroarsenate(III) (13): $AsCl_3$ (0.25 mL, 2.90 mmol) was added to a stirred solution of **3** (1.22 g, 2.90 mmol) in pyridine (8 mL) at 60 °C. After 3 h the solution had turned red and was kept at 60 °C for additional 18 h without stirring. After standing at room temperature for 24 h cyclohexane (2.5 mL) was added. A ^{31}P NMR spectrum was recorded and showed the signals of **10** (7 %) and **4b** (73 %). After 12 d orange crystals of **13** $\cdot$ 2.5 C_5H_5N began to form, and were filtered off after 11 months and dried in vacuo. Yield 0.69 g (62 %), m.p > 137 °C (decomp); ^{1}H NMR (CD_2Cl_2): $\delta = 7.27-7.39$ (m, 27 H, *m*-H/*p*-H), 7.43–7.48 (m, 18 H, *o*-H), 7.52–7.56 (m, 6 H, *m*-H), 7.59–7.63 (m, 6 H, 3-H, Py), 7.67–7.71 (m, 3 H, *p*-H), 7.74–7.77 (m, 6 H, *o*-H), 7.87–7.90 (m, 3 H, 4-H, Py), 8.12–8.17 (m, 6 H, 2-H, Py); elemental analysis calcd (%) for $C_{76}H_{60}As_5Cl_7P_4 \cdot 2.5\,C_5H_5N$ (1917.73): C 55.42, H 3.78, N 1.83; found C 55.33, H 4.05, N 1.56.

2,2-Dimethyl-1,3-bis(triphenylphosphoranediyl)-2-silaindane (11): *o*-Xylylene bis(triphenylphosphonium) dibromide (147.6 g, 187.2 mmol) and $NaN(SiMe_3)_2$ (136.0 g, 741.5 mmol) in benzene (1000 mL) gave a dark red solution, which was cooled to 0 °C. Dimethyldichlorosilane (24.08 g, 186.6 mmol) was added dropwise over 45 min, and the resulting suspension was stirred at RT for an additional 24 h. The precipitate was filtered off and washed with benzene (2 × 100 mL). The filtrate was concentrated in vacuo to half its original volume and heptane (25 mL) was added. After 24 h dark red crystals of **11** $\cdot$ C_6H_6 were filtered off, washed twice with benzene/heptane (1:1), and dried in vacuo. After further concentration of the filtrate a second crop was obtained. Yield 57.7 g (41 %) of **11** $\cdot$ C_6H_6; m.p. > 94 °C (decomp); ^{31}P{^{1}H} NMR (C_6H_6): $\delta = 8.9$ (s, 94 %; d, 6 %, $^2J_{SiP} = 27.6$ Hz); ^{29}Si INEPT NMR (C_6H_6, C_6D_6): $\delta = 11.4$ (t, $^2J_{SiP} = 27.8$ Hz); ^{1}H NMR (C_6D_6): $\delta = -0.19$ (s, 6 H, CH_3), 6.44–6.62 (m, 4 H, 4-H/5-H), 6.90–7.02 (m, 18 H, *m*-H/*p*-H), 7.15 (s, 6 H, C_6H_6), 7.84–7.88 (m, 12 H, *o*-H); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 8.2$ (s, CH_3), 29.4 (dd, $^1J_{PC} = 100.7$ Hz, $^3J_{PC} = 12.2$ Hz, C=PPh$_3$), 116.2 (s, 5-C), 119.6 (t, $J_{PC} = 4.6$ Hz, 4-C), 128.4 (m, *i*-C), 128.5 (s, *m*-C), 131.1 (s, *p*-C), 134.6 (m, *o*-C), 148.3 (m, 3a-C); elemental analysis calcd (%) for $C_{52}H_{46}P_2Si$ (760.97): C 82.08, H 6.09; found C 82.65, H 6.53.

1,3-Bis(triphenylphosphonio)isoarsindolide tetrachloroarsenate(III) (12): A solution of $AsCl_3$ (0.34 g, 1.9 mmol) in benzene (5 mL) was added dropwise at RT over 10 min to a stirred solution of **11** (1.21 g, 1.8 mmol) in benzene (30 mL). After 24 h of additional stirring, a percipitate was filtered off. It was recrystallized from dichloromethane and dried in vacuo. Yield 0.6 g (37 %) of **12**; m.p. 213–216 °C; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 17.5$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 6.64-6.96$ (m, 4 H, 4-H/5-H), 7.47–7.73 (m, 30 H, aromatic H); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 120.9$ (s, 5-C), 122.1 (t, $J_{PC} = 3.8$ Hz, 4-C), 122.5 (dd, $^1J_{PC} = 89.3$ Hz, 11.5 Hz, C=PPh$_3$), 122.8 (d, $^1J_{PC} = 90.8$ Hz, *i*-C), 129.7 (m, *m*-C), 133.6 (m, *o*-C), 134.1 (s, *p*-C), 146.1 (m, 3a-C); elemental analysis calcd (%) for $C_{44}H_{34}P_2As_2Cl_4$ (916.36): C 57.67, H 3.74; found C 57.04, H 3.83.

Determination of the crystal and molecular structures of 2b, 5b, 8b, 10, and 13: A Siemens P4 X-ray diffractometer equipped with an LT2 low-temperature device and a CCD area detector was used for all measurements with $Mo_{K\alpha}$ radiation and a graphite monochromator. The selected single crystals were covered with a film of perfluoroether oil, mounted on a glass fibre, and cooled to 193 K on the goniometer head. The preliminary determination of the dimensions of the unit cell used all data collected on 60 frames recorded in groups of 15 for different φ and χ angles. The final cell dimensions were calculated from the data on all frames, each of them recorded with 10 s exposure time. The data were then reduced by using the program SAINT.[37] Empirical absorption correction (either semiempirical or by program SADABS[37]) was employed by using all data with $I > 20\sigma(I)$. The structures were solved by the heavy-atom method as implemented in the program SHELXTL.[38] Non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated and included in the final refinement with a riding model and a fixed isotropic U adjusted to 1.2 U_{eq} of the respective carbon atom. Typical data referring to crystallography, data collection, and structure solution are collected in Table 7. Crystallographic data (excluding structure factors) for the structures

Table 7. Crystallographic data and details of data collection and structure refinement of compounds **2b** and **5b**, **8b**, **10**, and **11**.

	2b	**5b**	**8b** $(C_6H_6)_{5/2}$[a]	**10** $(C_6H_6)_{2/3}$[b]	**11** $(C_5H_5N)_5$
formula	$C_{20}H_{18}AsCl_2P$	$C_{19}H_{15}As_2Cl_4P$	$C_{53}H_{46}As_2Cl_3P_2$	$C_{61}H_{49}As_4Cl_6P_3$	$C_{101}H_{85}As_5Cl_7N_5P_4$
M_w	435.13	565.92	1001.03	1387.29	2115.37
crystal size [mm]	0.45 × 0.47 × 0.5	0.40 × 0.50 × 0.60	0.45 × 0.25 × 0.12	0.5 × 0.5 × 0.1	0.45 × 0.35 × 0.20
crystal system	orthorhombic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2_12_12_1$	$P\bar{1}$	Cc	$P2_1/c$	$P\bar{1}$
a [Å]	9.162(4)	9.233(3)	36.9216(3)	14.2254(1)	13.1057(2)
b [Å]	13.956(8)	10.889(4)	11.9700(1)	14.9927(3)	18.2564(2)
c [Å]	15.121(9)	11.695(4)	22.9826(2)	28.5916(6)	21.5034(2)
α [°]	90	77.84(1)	90	90	77.352(1)
β [°]	90	69.53(1)	103.736(1)	91.329(1)	78.366(1)
γ [°]	90	79.13(1)	90	90	73.949(1)
V [Å^3]	1933(2)	1068.3(6)	9866.7(1)	6096.3(2)	4769.5(1)
Z	4	2	8	4	2
ρ_{calcd} [Mg m^{-3}]	1.495	1.759	1.554	1.512	1.473
μ [mm^{-1}]	2.116	3.705	2.320	2.553	2.046
$F(000)$	880	556	4088	2776	2140
index ranges	$-10 \leq h \leq 10$ $-18 \leq k \leq 18$ $-19 \leq l \leq 19$	$-11 \leq h \leq 11$ $-13 \leq k \leq 13$ $-14 \leq l \leq 15$	$-34 \leq h \leq 33$ $-14 \leq k \leq 14$ $-28 \leq l \leq 26$	$-17 \leq h \leq 17$ $-18 \leq k \leq 20$ $-35 \leq l \leq 35$	$-16 \leq h \leq 16$ $-19 \leq k \leq 24$ $-27 \leq l \leq 27$
2Θ [°]	58.70	58.06	55.62	58.76	58.68
T [K]	193(2)	183(2)	193(2)	193(2)	193(2)
reflns collected	11368	6326	23770	33935	28153
reflns unique	4009	3403	13767	12206	15205
reflns observed	3848	3189	11279	10297	8238
R (int.)	0.0317	0.0129	0.0637	0.0553	0.0818
parameters	289	235	1056	686	1127
weighting scheme[c] x/y	0.0212/0.6392	0.0420/0.5488	0.0760/69.264	0.0367/27.271	0.06820/1.0790
GOOF	1.087	1.110	1.168	1.190	0.971
R (4σ)	0.0216	0.0271	0.0707	0.0600	0.0641
$wR2$	0.0514	0.0695	0.1696	0.1325	0.1246
largest residual peak [e Å^{-3}]	0.226	0.641	1.249	0.718	0.888

[a] There are four additional peaks which form a trapezoid. They were considered to be carbon atoms and were refined only isotropically. [b] One of the phenyl rings is rotationally disordered and was refined without attached hydrogen atoms. One of the benzene molecules was refined as an ideal hexagon with SOF = 0.5 and isotropic thermal parameters. A second molecule has a crystallographic C_2 axis with SOF = 0.5; one of its carbon atoms coincides with a carbon atom of the first benzene molecule. [c] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137226 (**2b**), 137225 (**5b**), 137222 (**8b**), 137223 (**10**), and 137224 (**13**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

---

[1] A. Schmidpeter, G. Jochem, *Tetrahedron Lett.* **1992**, *33*, 471–474.

[2] A. Schmidpeter, H. Nöth, G. Jochem, H.-P. Schrödel, K. Karaghiosoff, *Chem. Ber.* **1995**, *128*, 379–393.

[3] A. Schmidpeter, G. Jochem, C. Klinger, C. Robl, H. Nöth, *J. Organomet. Chem.* **1997**, *529*, 87–102.

[4] H.-P. Schrödel, G. Jochem, A. Schmidpeter, H. Nöth, *Angew. Chem.* **1995**, *107*, 2006–2010; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1853–1856.

[5] H.-P. Schrödel, A. Schmidpeter, H. Nöth, M. Schmidt, *Z. Naturforsch. B* **1996**, *51*, 1022–1032.

[6] G. Jochem, A. Schmidpeter, *Z. Naturforsch.* B **1996**, *51*, 773–777.

[7] G. Jochem, F. Breitsameter, A. Schier, A. Schmidpeter, *Heteroatom Chem.* **1996**, *7*, 239–247.

[8] H.-P. Schrödel, A. Schmidpeter, *Chem. Ber./Recueil* **1997**, *130*, 1519–1527.

[9] H.-P. Schrödel, A. Schmidpeter, *Z. Naturforsch. B* **1997**, *52*, 162–168.

[10] H.-P. Schrödel, A. Schmidpeter, H. Nöth, *Z. Naturforsch. B* **1998**, *53*, 1285–1293; H.-P. Schrödel, Ph.D. Thesis, Universität München, **1997**.

[11] H. Schmidbaur, W. Tronich, *Chem. Ber.* **1968**, *101*, 3545–3555.

[12] W. Malisch, M. Kuhn, W. Albert, H. Rößner, *Chem. Ber.* **1980**, *113*, 3318–3333.

[13] H. Schmidbaur, P. Nußstein, G. Müller, *Z. Naturforsch. B* **1984**, *39*, 1456–1462.

[14] H. Schmidbaur, P. Nußstein, *Chem. Ber.* **1987**, *120*, 1281–1285.

[15] H. Grützmacher, H. Pritzkow, *Chem. Ber.* **1989**, *122*, 1417–1421.

[16] F. Breitsameter, H.-P. Schrödel, A. Schmidpeter, H. Nöth, S. Rojas-Lima, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1293–1300.

[17] H. Schmidbaur, U. Deschler, B. Milewski-Mahrla, *Chem. Ber.* **1983**, *116*, 1393–1402.

[18] T. M. Klapötke, A. Schulz, *Quantenmechanische Methoden in der Hauptgruppenchemie*, Spektrum, Heidelberg, **1996**; *Quantum Chemical Methods in Main-Group Chemistry*, Wiley, Chichester, **1998**.

[19] C–As single bond length: 196 pm, *Interatomic Distances Supplement, Special Publ. No. 18*, The Chemical Society, London **1965**.

[20] Compounds with a (partial) C–As double bond which offer themselves for a comparison: arsaalkenyl complex, 182.1 pm, L. Weber, G. Meine, R. Boese, *Angew. Chem.* **1986**, *98*, 463–465; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 469–471; unsubstituted arsinine, 185 pm, A. J. Ashe, III, *Top. Curr. Chem.* **1982**, *105*, 125–152; 2,3,6-triphenylarsinine, 185.9 and 188.4 pm, F. Sanz, J. J. Daly, *Angew. Chem.* **1972**, *84*, 679–681; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 630–632.

[21] Although the cyclodimerization and trimerization of arsaalkenes is known,[22] we found no evidence that **7b**, **10**, and **13** form via the monomeric compound $Ph_3PCAsCl$ as an intermediate. The products may rather result from a multistep condensation.

[22] L. Weber, *Chem. Ber.* **1996**,*129*, 367–379.

[23] The shifts correspond well with those observed for the analogous protonated diphosphetane **8a** and a similarly large coupling constant $^4J_{PP}$ is known for its bis(diethylamino) derivative.[8]

[24] While the two axial AsCl distances differ by 36 pm in this case, we recently observed in two related ylide adducts of $AsCl_3$ a difference of 15 pm and 60 pm, respectively.[16]

[25] The structure of **8b** shows parallels to those of $(Me_3PNAsCl)_2{}^{2+}(Cl^-)_2$ and $[(Me_3PNAsCl)_2{}^{2+}]_2(Cl^-)_3AsCl_4{}^-$, the cation of which is isoelectronic to **7b**: R. Garbe, S. Wocadlo, H.-C. Kang, W. Massa, K. Harms, K. Dehnicke, *Chem. Ber.* **1996**, *129*, 109–113; R. Garbe, Ph.D. Thesis, Universität Marburg, **1995**.

[26] A closely related structure has been found for a 1,2,6-azadiphosphinane derivative: G. Jochem, M. Schmidt, H. Nöth, A. Schmidpeter, *Z. Naturforsch. B* **1996**, *51*, 1761–1767.

[27] J. Kaub, W. S. Sheldrick, *Z. Naturforsch. B* **1984**, *39*, 1252–1256; A. T. Mohammed, U. Müller, *Acta Crystallogr. C* **1985**, *41*, 329–332; H. Gruber, U. Müller, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1033–1034; W. Czado, S. Rabe, U. Müller, *Z. Naturforsch. B* **1999**, *54*, 288–290.

[28] For the corresponding phospha-phosphocyanines see: A. Schmidpeter, G. Jochem, M. Thiele, *Phosphorus Sulfur Silicon* **1993**, *76*, 13–16.

[29] A. Schmidpeter, M. Thiele, *Angew. Chem.* **1991**, *103* 333–335; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 308–310.

[30] N. Gamon, C. Reichardt, R. Allmann, A. Waskowska, *Chem. Ber.* **1981**, *114*, 3289–3303.

[31] G. Märkl, F. Lieb, *Tetrahedron Lett.* **1967**, *8*, 3489–3493.

[32] Distances as long as dPCl = 285.0 pm[33] and dAsCl = 286.7 pm[16] must still be taken, however, as bonding. They refer to axial bonds in asymmetric ψ-tbp structures.

[33] K. B. Dillon, A. W. G. Platt, A. Schmidpeter, F. Zwaschka, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **1982**, *488*, 7–26.

[34] H. J. Bestmann, A. Bomhard, *Angew. Chem.* **1982**, *94*, 562; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 545–546.

[35] H. J. Bestmann, A. Bomhard, R. Dostalek, R. Pichl, R. Riemer, R. Zimmermann, *Synthesis* **1992**, 787–792.

[36] C. E. Griffin, K. R. Martin, B. E. Douglas, *J. Org. Chem.* **1962**, 27, 1627–1631.

[37] Siemens Analytical Instruments, Versions 3.1 and 4.1, **1996**.

[38] G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1993**.

[39] P. Kisliuk, C. H. Townes, *J. Chem. Phys.* **1950**, *18*, 1109–1111.

[40] R. C. Weast, M. J. Astle, *Handbook of Chemistry and Physics*, 60th ed., CRC, Florida, **1980**.

[41] K. W. Muir, *J. Chem. Soc. Dalton Trans.* **1975**, 259–262.

[42] R. H. Bohra, H. W. Roesky, M. Noltemeyer, G. M. Sheldrick, *Acta Crystallogr. C*, **1984**, *40*, 1150–1152.

[43] N. Burford, C. L. B. Macdonald, T. M. Parks, G. Wu, B. Borecka, W. Kwiatkowski, T. S. Cameron, *Can. J. Chem.* **1996**, *74*, 2209–2216.

[44] M. K. Denk, S. Gupta, A. J. Lough, *Eur. J. Inorg. Chem.* **1999**, 41–49.

[45] C. J. Carmalt, V. Lomeli, B. G. McBurnett, A. H. Cowley, *Chem. Commun.* **1997**, 2095–2096.

Received: December 2, 1999 [F2172]