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Progress in Polyarsolyl Chemistry

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Dedicated to Professor Heinrich Lang on the occasion of his 60th birthday

Abstract: The synthesis of heteroatom analogues of the cyclopentadienyl anion Cp^- is a fascinating and challenging field of research. The replacement of methine moieties by phosphorus is well investigated for the synthesis of mono-, tri- and pentaphospholyl ligands. On the other hand, arsenic derivatives are rare and 1,2,4-triarsolyl and tetraarsolyl salts are unknown. Herein, we report on the synthesis of $Cs[E_3C_2(trip)_2]$ (**1a**: E = P; **1b**: E = As; trip = 2,4,6-triisopropylphenyl) and $Cs[E_4C(trip)]$ (**2a**: E = P; **2b**: E = As). Compound **1b** represents the first 1,2,4-triarsolyl and **2b** the first tetraarsolyl anion. All salts are obtained in one-pot syntheses using $E(SiMe_3)_3$, 2,4,6-triisopropylbenzoyl chloride and CsF. The products **1a**·2 $C_4H_8O_2$, **2a**·Et_2O and **2b**·3 $C_4H_8O_2$ were characterized by X-ray structural analysis, which revealed planar heterocycles. Nucleus-independent chemical shifts (NICS) confirmed the aromaticity of these anions. Notably, compound **2a**·Et_2O is only the second tetraphospholyl ligand which is structurally characterized.

According to the Nobel Prize lecture of Roald Hoffmann in 1981,[1] the isolobal analogy builds bridges between organometallic, organic and inorganic chemistry. To date, the substitution of CH_x ($x = 1, 2, 3$) units by heteroatoms is of special interest in the fundamental research of all these subfields. In particular, the incorporation of group 15 elements in aromatic molecules is a fascinating area. For example, replacement of methine groups in the cyclopentadienyl anion Cp^- by phosphorus or arsenic leads to the class of phospholyl and arsolyl rings $[E_n(CR)_{5-n}]$ (E = P, As; $n = 1–5$), respectively (Figure 1). The monosubstituted derivatives **I** are well known and were intensively studied for both, P and As.[2] The all-pnictogen analogue **VI** is mostly observed in metallocenes and triple decker complexes by co-thermolysis of the molecular allotropes P_4 and As_4, respectively, with transition metal precursor complexes.[3] The substituent-free ring P_5^- is far more difficult to handle, though it is stable in solution.[3d,4] Recently, Cummins et al. were able to synthesize the sodium salt of the free diphosphatriazolate anion $P_2N_3^-$.[5] On the other hand, numerous investigations for the 1,2,4-triphospholyl ligand **III**[6] and at least a few for the 1,3-diphospholyl derivative **II** have been reported,[6f,7] whereby their syntheses mostly start either from phospha-alkenes or -alkynes. Due to the lower stability of As–C multiple bonds, compounds of type **II** and **III** are not yet known for the heavier homologue arsenic. Similar synthetic approaches only result in the formation of the $[As(CtBu)]_4$ cubane.[8] Only the mixed heterocycle $[AsP_2(CtBu)_2]^-$ is known,[9] with structural characterization being made possible through coordination to a $W(CO)_5$ fragment in $[CpFe\{AsP_2(CtBu)_2\}W(CO)_5]$.[10] Different approaches are needed for the synthesis of the also very rare 1,2,3-isomers **IV**, that is, starting from phosphines[11] or reactions of alkynes either with P_4 butterfly complexes[12] or with the Zintl anions $[E_7]^{3-}$ (E = P, As).[13] The latter route yields the only example known of an 1,2,3-triarsolyl ligand. The lowest number of publications can be found for the derivative **V**, the nitrogen derivatives of which are high-performing energetic materials.[14] However, type **V** is unknown for E = As, and only two structurally characterized complexes are reported for E = P.[6b,15] Ionkin et al. introduced a three-component reaction of CsF, $P(SiMe_3)_3$ and 2,4,6-tri-*tert*-butylbenzoyl chloride yielding a mixture of $Cs[1,2,4\text{-}P_3C_2Mes^*_2]$ and $Cs[P_4CMes^*]$ (Mes* = 2,4,6-tri-*tert*-butylphenyl), both stabilized by bulky supermesityl groups.[6b,16] Since no intermediates have to be isolated using this one-pot reaction, this strategy seems promising for the synthesis of the corresponding arsenic analogue. Furthermore, we were interested in the transfer of this synthetic route to slightly smaller R groups, such as the triisopropylphenyl (trip) derivative.

Herein we report on the synthesis of $Cs[E_3C_2(trip)_2]$ (**1a**: E = P; **1b**: E = As; trip = 2,4,6-triisopropylphenyl) and $Cs[E_4C(trip)]$ (**2a**: E = P; **2b**: E = As). Thereby compound **1b** displays the first 1,2,4-triarsolyl ligand and **2b** the first tetraarsolyl ligand, both fill significant gaps in the series of arsenic-containing analogues of the cyclopentadienyl anion. Furthermore, the salts

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504961; including the experimental section, selected NMR spectra, X-ray diffraction data and details of the NICS computations.

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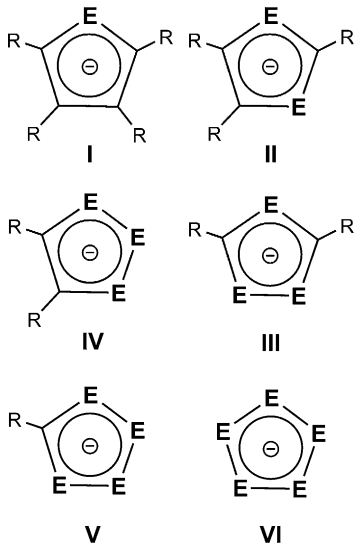
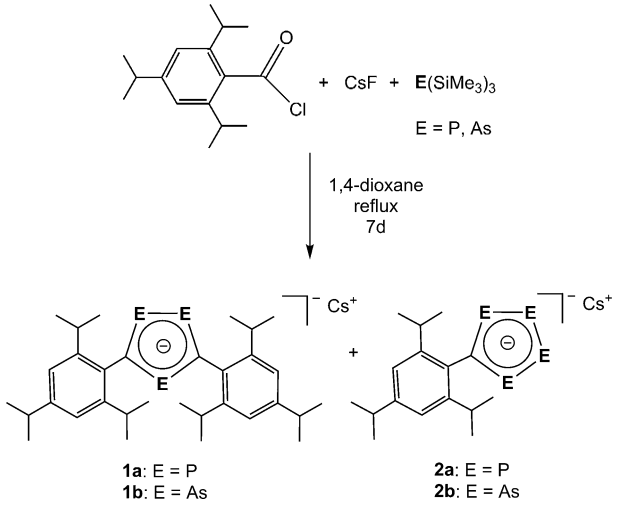


Figure 1. Selected types of phospholyl (E = P) and arsolyl (E = As) rings.

1a·2 $C_4H_8O_2$, **2a**·Et_2O and **2b**·3 $C_4H_8O_2$ could also be characterized by X-ray structural analysis.

Following the synthetic route for the preparation of $Cs[P_3C_2Mes^*_2]$ and $Cs[P_4CMes^*]$, 2,4,6-triisopropylbenzoyl chloride bearing the smaller trip substituent was treated with $P(SiMe_3)_3$ and CsF in 1,4-dioxane (Scheme 1). Already while combining the reagents, the colorless solutions became yellow-orange and, when refluxing, a darkening to deep red with turbidity was observed.



Scheme 1. Synthesis of **1a** and **1b** and **2a** and **2b**.

The reaction progress can easily be monitored by NMR spectroscopy. After one day, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed three main signals corresponding to $P(SiMe_3)_3$, **1a** and **2a** in the ratio 2:2:1. In the corresponding spectrum after three days of reflux the ratio was determined to be 1.1:1.8:1. After seven days of reflux the intensity of the signal of $P(SiMe_3)_3$ still decreased, however signals appeared that could be assigned to byproducts according to reference [6b]. The ratio **1a**/**2a** = 1.8:1 remained constant at this stage. After filtration of the hot solution, separation of **1a** and **2a** was achieved by fractional crystallization, since the solubility of **2a** containing only one trip ligand in dioxane was lower compared to **1a** (for details see the Supporting Information). By this method, pure **1a** (third crop of crystals) and pure **2a** (first crop of crystals) can be isolated in yields of 15 and 4%, respectively. Taking also the second crop of crystals into account, which consists of a mixture of both, the overall yield amounts to 16% for **1a** and 12% for **2a**, which is usual for this kind of reaction in high boiling solvents. However, the separation procedure is very sensitive to the concentration, temperature and diffusion time, and hence often recrystallization is required.[16]

Both compounds **1a** and **2a** have good solubility in donor solvents such as dioxane, DME, CH_3CN and THF. In contrast, they are only poorly soluble in nonpolar solvents such as toluene and hexane. The $^{31}P\{^1H\}$ spectrum of **1a** in $[D_8]$THF shows a triplet at $\delta = 273.9$ ppm for the isolated P atom in the ring and a doublet at $\delta = 270.5$ ppm for the adjacent P atoms with an integral ratio of 1:2 ($^2J_{PP} = 38$ Hz). In comparison with $Cs[P_3C_2Mes^*_2]$ the former signal is therefore slightly upfield-shifted ($\delta = 287.6$ ppm), whereas the latter signal shows a small shift to lower field ($\delta = 267.9$ ppm). In the ^1H NMR spectrum of **1a** two sets of signals of the trip ligand are observed (see the Supporting Information). In the $^{31}P\{^1H\}$ NMR spectrum of **2a** in $[D_8]$THF, mulitplets characteristic for an AA′MM′ spin system at $\delta = 372.8$ and 366.0 ppm with respective coupling constants of $^1J_{AA'} = 488.2$ Hz, $^2J_{AM'} = -1.6$ Hz, $^3J_{MM'} = 52.0$ Hz and $^1J_{AM} = 492.0$ Hz (simulated values; for experimental and simulated spectra see the Supporting Information) are obtained. The same trend is observed for the bulkier $Cs[P_4CMes^*]$ salt ($\delta =$ 386.5 and 341.6 ppm). Both anions, $[P_3C_2(trip)_2]^-$ and $[P_4C(trip)]^-$, were also detected in the negative ion ESI-MS spectrum.

This one-pot synthesis was subsequently extended to reactions with $As(SiMe_3)_3$ as the starting material. The addition of CsF to a solution of $As(SiMe_3)_3$ in 1,4-dioxane immediately leads to a very dark, almost black slurry suspension. After adding a solution of triisopropylbenzoyl chloride in the same solvent and refluxing for 1.5 h the color of the reaction mixture changed to deep red, as observed in the synthesis of **1a** and **2a**. In the ^1H NMR spectrum of the reaction mixture several overlapping sets of signals corresponding to the trip ligand (one big and some smaller ones) as well as of the protons of $As(SiMe_3)_3$ are recorded, hence a reliable statement of the ratio of the formed products cannot be made. After six days of reflux the same work-up strategy like for the phosphorus derivatives **1a** and **2a** was performed, and several crops of crystals were obtained (for details see the Supporting Information). Unfortunately, a fractional crystallization of **1b** and **2b** was only partially successful. Pure **1b** cannot be obtained and **2b** contained very minor impurities of **1b** (see the Supporting Information). The majority of the first crop of crystals consisted of yellow rods, the X-ray structural characterization of which revealed the first tetraarsolyl anion **2b** (vide infra). In addition, a small amount of a beige microcrystalline powder was ob-

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tained. Subsequently, the mother liquor was decanted and the solid (crystals and powder) was dissolved in CD_3CN. The main signals in the recorded ^1H NMR spectrum were assigned to the trip ligand of **2b** considering almost identical chemical shifts in comparison to **2a**. In addition, two small sets of signals (intensity 10%) for the trip ligand with an integral ratio of 1:1 appear, though partially overlapping. These indicate the presence of the triarsolyl ligand **1b**. A further clear hint is the negative ion ESI-MS spectrum of every crop of crystals, which always shows peaks at *m/z* 514.9 and 655.2, that can be assigned to $[As_4C(trip)]^-$ and $[As_3C_2(trip)_2]^-$, respectively. Taking this molar ratio (determined by ^1H NMR spectroscopy: 10% of **1b**, 90% of **2b**) into account, the yield of the isolated crystals amounts to 33%, which is even slightly better than for the phosphorus derivatives.

Hence it can be stated that the one-pot route described above can also be transferred for the synthesis of a tri- and tetraarsolyl ligand, though with **2b** as main product besides a small amount of **1b**.

Compound **1a**·$2C_4H_8O_2$ crystallizes as yellow prisms in the triclinic space group $P\bar{1}$. Its structural analysis reveals a planar (deviation 0.009(2) Å) five-membered P_3C_2-ring with P–C and P–P distances of 1.733(3)–1.743(3) Å and 2.108(1) Å, respectively (Figure 2a). Both values are in the middle range between a single and a double bond,[17] supporting the aromaticity of these systems. Two dioxane molecules show η^1-coordination to the cesium cation with bond lengths of 3.039(2) and 3.100(3) Å, respectively. Cs···H interactions with the *i*Pr ligands of both the corresponding and the adjacent ring (3.265(1)–3.709(1) Å) were also observed. Surprisingly, cesium is also η^6 coordinated by a phenyl ring of the trip ligand with distances of 3.304(1) and 3.298(1) Å. This could not be observed in the Mes* derivative.[6b] Furthermore, short P–Cs distances to the isolated phosphorus atom of the ring (3.795(1) and 3.809(1) Å) as well as to a P atom of the P_2 "dumbbell" of the neighboring anion (3.623(1) and 3.634(1) Å) can be observed. This high coordination number of Cs leads to a 2D polymeric structure of this salt, whereas Cs[P_3C_2Mes*$_2$] is described as a 1D chain.[6b]

In contrast, the same crystallization procedure for **2a** only leads to crystals of insufficient quality for X-ray structural analysis. Gratifyingly, cooling a solution of **2a** in Et_2O turned out to be beneficial. Using this method, compound **2a** crystallized in the monoclinic space group *C*2/*c* as Et_2O solvate. The central structural motif is a five-membered P_4C ring that shows a slightly stronger deviation of 0.024(3) Å from planarity than the P_3C_2 ligand in **1a**·$2C_4H_8O_2$ (Figure 2b). Compared to **1a**·$2C_4H_8O_2$, the P–P distances in **2a**·Et_2O are slightly shorter (2.087(3)–2.102(3) Å), whereas the P–C bond lengths are somewhat elongated (1.742(7)–1.753(7) Å). The coordination sphere of Cs is different, in **2a**·Et_2O it includes a η^1 coordination of the 1,4-dioxane ligand (3.042(5)–3.075(6) Å) and of a P atom (3.651(2)–3.695(2) Å), respectively, as well as short distances to three hydrogen atoms of one *i*Pr substituent (3.051(1)–3.459(1) Å). Furthermore, in contrast to the η^6 coordination of Cs to the phenyl ring in **1a**·$2C_4H_8O_2$, in **2a**·Et_2O a η^5 coordination to the central *cyclo*-P_4C moiety is observed (3.591(1)–3.683(1) Å). Such a η^5 interaction is also found in $[Cp_3Cs_2]^-$,[18] however not in the cesium salts of the phospholyl derivatives obtained by Ionkin et al.[6b] Similarly to **1a**·$2C_4H_8O_2$, the tendency of Cs^+ to form polymeric aggregates can also be observed in **2a**·Et_2O forming 2D layers in the solid state. In addition to Cs[P_4CMes*], compound **2a**·Et_2O is the second example of a structurally characterized tetraphospholyl salt. It is interesting to note that the group of Baudler has reported evidence of $[P_4CH]^-$, yet only based on NMR spectroscopy.[19]

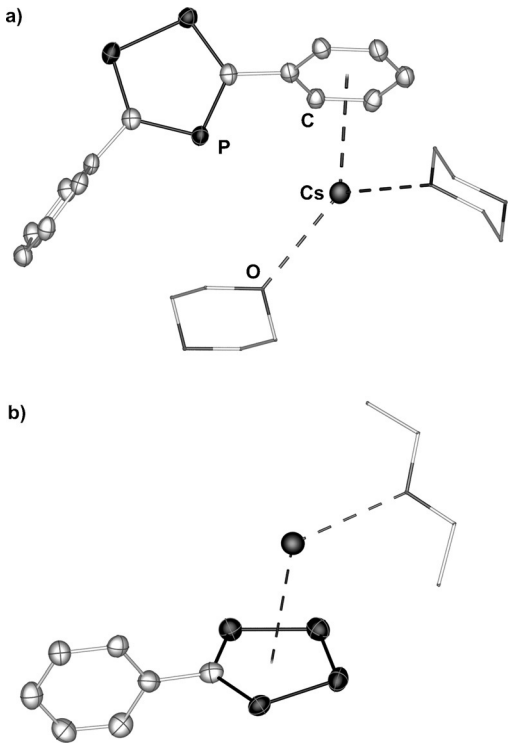

Figure 2. Section of the structure of: a) **1a**·$2C_4H_8O_2$, and b) **2a**·$C_4H_{10}O$. Hydrogen atoms, *i*Pr ligands and minor positions of disorder are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Coordinated solvent molecules are shown in wires-model.

Yellow needles of **2b**·$3C_4H_8O_2$ are obtained by cooling a hot solution of **2b** in dioxane. Compound **2b**·$3C_4H_8O_2$ crystallizes in the triclinic space group $P\bar{1}$ and its X-ray structural analysis reveals a planar As_4C ring with a similar deviation value of 0.022(3) Å compared to **2a**·Et_2O (0.024(3) Å; Figure 3). Nearly equal As–C bond lengths of 1.857(14) and 1.859(16) Å are found, whereas the As–As distances can be subdivided in two longer ones (2.310(2) and 2.311(2) Å) and one shorter value of 2.287(3) Å for the bond opposite to the carbon atom. These distances are shorter than the average As–As bond length of 2.327(6) Å in the *cyclo*-As_5 ligand of the sandwich complex $[Cp^{Et}Fe(\eta^5\text{-}As_5)]$ ($Cp^{Et}=C_5Me_4Et$).[3c] However, all As–As and As–C distances in **2b**·$3C_4H_8O_2$ are between a single and a double bond.[17] Again, the Cs^+ cation shows a different environment, in **2b**·$3C_4H_8O_2$ it coordinates four dioxane ligands (3.025(9)–52(9) Å) and shows one relatively short As–Cs contact of 3.873(2) Å. In **2b**·$3C_4H_8O_2$, two dioxane molecules bridge two Cs^+ cations and therefore again aggregation is found in two directions in the solid state.

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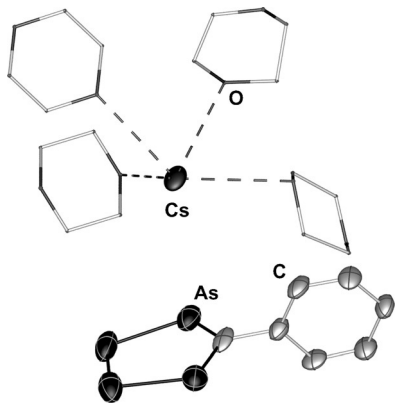

Figure 3. Section of the structure of **2b**·3 $C_4H_8O_2$. Hydrogen atoms and *i*Pr ligands are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Solvent ligands are shown in wires-model.

In order to verify the aromatic character, the nucleus-independent chemical shifts (NICS)[20] were calculated for the [1,2,4-P_3C_2(trip)$_2$]$^-$ and [E_4C(trip)]$^-$ (E = P, As) anions. The NICS values show that the phospholyl and arsolyl derivatives have an aromatic character, which is only slightly lower than that of the cyclopentadienide anion. Their high π-aromaticity is reflected in the high negative NICS(1)$_{zz}$ values (see the Supporting Information). Moreover, the presence of a π-system is obvious by the inspection of the frontier molecular orbitals (see the Supporting Information).

In summary, a one-pot method was successfully applied to the synthesis of the [1,2,4-P_3C_2(trip)$_2$]$^-$ and [P_4C(trip)]$^-$ anions containing the 2,4,6-triisopropylphenyl ligand. The cesium salts of the 1,2,4-triphospholyl substituent (**1a**) as well as the tetraphospholyl ligand (**2a**) were successfully separated from each other by fractional crystallization and were isolated as dioxane solvates. This synthetic approach is also applicable for the synthesis of the respective arsenic derivatives Cs[1,2,4-As_3C_2(trip)$_2$] (**1b**) and Cs[As_4C(trip)] (**2b**). Compounds **1b** and **2b** are the first representatives of a 1,2,4-triarsolyl and tetraarsolyl ligand, respectively. Compounds **1a**, **2a** as well as **2b** could also be structurally characterized revealing planar rings. The cesium cations show interactions with a phenyl ring of **1a**, the *cyclo*-P_4C unit of **2a** and an arsenic atom of **2b**, respectively. In combination with bridging dioxane ligands a two-dimensional polymeric structure is found in all crystals. Furthermore, the NICS values reveal the aromaticity of these compounds, which is only slightly lower than that of the cyclopentadienide anion.

Supporting Information

CCDC 1435933 (**1a**), 1435934 (**2a**) and 1435935 (**2b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Keywords: cyclopentadienyl ligands · heterocycles · inorganic ring systems · polyarsolyl · polyphospholyl

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