Experimental Section

1: Microcrystalline **1**[1] was slowly precipitated from CH_2Cl_2, purified, and dried in dynamic vacuum at −40 °C (10^{-3} bar). Under an argon atmosphere, the residue was spread smoothly on a polymer foil at −100 °C using a spatula precooled to −196 °C. To prevent a loss of substance, the sample carrier was coated with perfluorinated silicon grease (Voltaleff). Samples prepared in this manner were additionally dried in vacuo at −40 °C and then transferred to the sample chamber of the X-ray powder diffractometer (Huber G645) at −100 °C, which was cooled to −223 °C for collecting diffraction data.

Caution! Pure $Xe(C_6F_5)_2$ is thermally unstable and may vigorously explode on contact. Protection glasses and Kevlar gloves were worn throughout all manipulations.

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$As[P(NMe_2)_3]_2^+$ as Simultaneous As^I and P^I Source: Synthesis and Density Function Calculations of Planar Tetracoordinate Arsonium and Phosphonium Ions[**]

Matthias Driess,[*] Holger Ackermann, Joachim Aust, Klaus Merz, and Christoph von Wüllen

Dedicated to Professor Rolf Gleiter
on the occasion of his 65th birthday

Recently we reported on the unusual organometallic phosphonium ion $P[Zr(H)Cp_2]_4^+$ ($Cp = \eta\text{-}C_5H_5$) in the BPh_4

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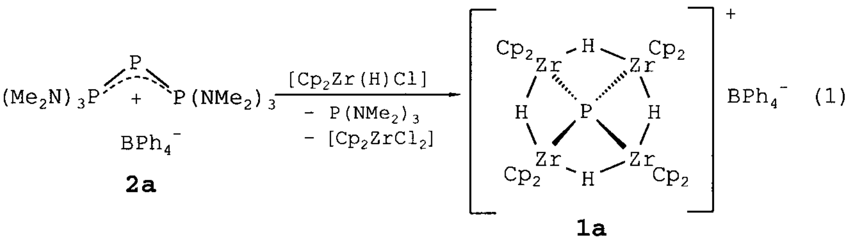
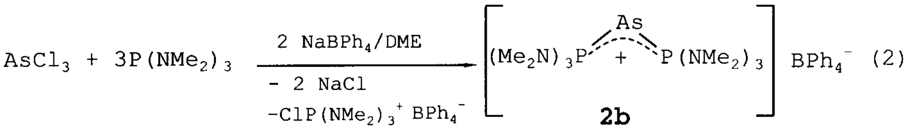
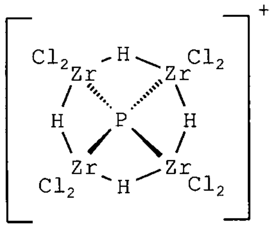
salt **1a**, which surprisingly exhibited a planar tetracoordinate P atom and four Zr-bridging H atoms.[1] The cation is unprecedented amongst the previously known organometallic PR_4^+ derivatives and forms the first phosphorus analogue of planar tetracoordinate methane derivatives.[2] Previously only tetragonal-pyramidal tetraauryl[3] and tetrahedral tetrastannyl-[4] and tetrasilylphosphonium ions[5] could be prepared. Compound **1a** is formed by the reaction of the triphosphenium salt $P[P(NMe_2)_3]_2^+BPh_4^-$ (**2a**) with the Schwartz reagent $[Cp_2Zr(H)Cl]$ in the presence of an auxiliary base; the diphosphane donor stabilized phosphenium ion functions as the P^I source and reacts by cleavage of the $P(NMe_2)_3$ ligands and redox reactions to form the PR_4^+ ion ($R = Zr(H)Cp_2$) [Eq (1)].

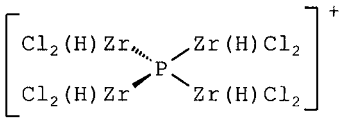




According to ab initio calculations for the model cation $P[Zr(H)Cl_2]_4^+$ the anti-van't Hoff–Le Bel configuration **A**, unusual for a PR_4^+ moiety with eight valence electrons, is 290 kJ mol^{-1} more favorable than the tetrahedral configuration **B**. The preference for the planar configuration is attributed predominantly to the Zr–P π backbonds and delocalization of the lone pair electrons on the P atom in the HOMO as well as stabilization by the μ_2-bridging H atoms at the Zr atoms by chelation.



A



B

In view of the existence of **1a** the question arises whether in analogy the homologous As salt $As[Zr(H)Cp_2]_4^+BPh_4^-$ (**1b**) exhibits a planar configurated AsR_4^+ ion, since ab initio calculations for the hypothetical ammonium ion $N[Zr(H)Cl_2]_4^+$ have shown that a highly distorted tetrahedral configuration would be preferred, not the planar or tetrahedral configurations.[1] In analogy to the synthesis of **1a**, the synthesis of **1b** should be possible by reaction of the diphosphane donor stabilized arsenium salt $As[P(NMe_2)_3]_2^+BPh_4^-$ (**2b**) with $[Cp_2Zr(H)Cl]$; however, the precursor **2b** was hitherto unknown. In the following we therefore first describe the synthesis of **2b**, which surprisingly reacted with $[Cp_2Zr(H)Cl]$ not only to the planar arsonium ion in **1b**, but simultaneously also to the planar phosphonium ion in **1a**. In addition we report on the density functional theory (DFT) calculations for the homologous "real cations" $E[Zr(H)Cp_2]_4^+$ (E = N, P, As, Sb) which confirm that the "magic" hydridozirconocenyl substituent is the ligand of choice to realize an anti-van't Hoff–Le Bel configuration in ER_4 fragments with eight valence electrons.

As in the synthesis of **2a** described by Schmidpeter et al.,[6] the synthesis of **2b** is also simple. First the As^{III} ion in $AsCl_3$ is reduced by $P(NMe_2)_3$ in the presence of $NaBPh_4$ to the As^I ion, which is donor-stabilized by the addition of two $P(NMe_2)_3$ ligands [Eq. (2)]. Compound **2b** can be isolated in the form of colorless, highly air-sensitive crystals in 53% yield.

Compound **2b** is stable only for a short time in polar, aprotic solvents such as THF, DME, or CH_2Cl_2 at room temperature; after a few hours unknown orange-colored decomposition products are formed. The $^{31}P\{^1H\}$ NMR spectrum of freshly prepared solutions at −30 °C also shows a singlet at $\delta = 89.0$, which indicates a degenerate, resonance-stabilized P-As-P π system, a heteroallyl cation. In agreement with this a single-crystal X-ray structure analysis[7] of the THF solvate of **2b** shows only almost equal As–P distances of 2.266(2) and 2.236(2) Å (Figure 1). Very similar and almost identical As–P distances (2.24–2.27 Å) were also observed in the only previously known cyclic analogues **3**[8] and **4**,[9] which equally exhibit P donor-stabilized As^I centers. The P1-As1-P2 angle in **2b** (103.26(6)°) is as expected larger than the corresponding endocyclic angles in **3** (93.0(1)°) and **4** (69.90(2)° and 69.45(2)°).

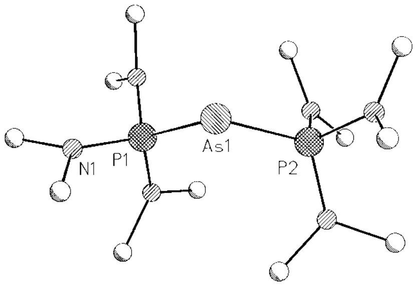
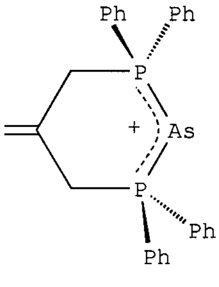


Figure 1. Molecular structure of **2b** in the crystal; selected distances [Å] and angles [°]: As1-P1 2.266(2), As1-P2 2.236(2), P1-N1 1.641(5); P1-As1-P2 103.26(6), As1-P1-N1 102.4(2).

Compound **2b** reacts with a molar excess of $[Cp_2Zr(H)Cl]$ in THF to form a red suspension. Deep green crystals could be obtained from these solutions, which surprisingly turned out to be a mixture of the phosphonium and arsonium salts **1a** and



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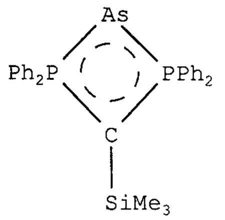
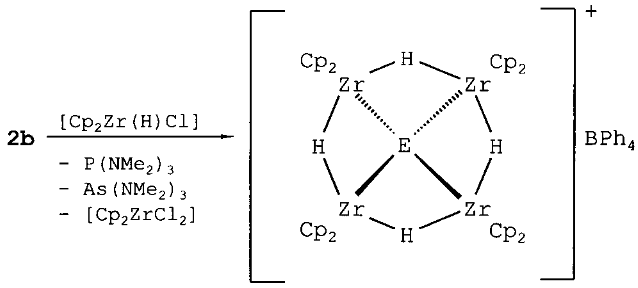


4

1b, respectively [Eq. (3)]. That both onium ions really exist in the mixtures followed from the electrospray ionization (ESI) mass spectra, in which the signals for the molecular ions occur at *m/z* 920.4 (**1a**; calcd 920.6) and 964.1 (**1b**; calcd 964.5) as base peaks.



(3)

1a: E = P
1b: E = As

The composition of the mixtures was established unequivocally by the simple and readily distinguishable ^1H and ^{31}P NMR spectra. The signals of the highly deshielded ^1H nuclei of the bridging hydrogen atoms, which form different splitting patterns in the high-field region, are particularly characteristic. The doublet at $\delta = -3.85$ ($^2J(H,P) = 29.5$ Hz) could be unambiguously assigned to **1a**, the singlet at $\delta = -3.99$ to **1b**. The ^{31}P NMR spectrum of [D$_8$]THF solutions shows a quintet for **1a** at $\delta = 252.0$ ($^2J(P,H) = 29.5$ Hz).[1] By fractional crystallization from CH_2Cl_2/pentane the **1a**/**1b** ratio could be enriched from an initial 1:1 to a maximum of about 2:3 in favor of **1b**. Why formation of both onium ions occurs simultaneously, however, is still unknown. However, it is clear that "free" **2b** in solution does not rearrange to "free" **2a**. The As/P interchange necessary for the formation of **1a** must therefore presumably take place within the coordination sphere of the Zr atoms.

By single-crystal X-ray structure analysis[7] of the **1a**/**1b** mixed crystal (monoclinic space group *C*2/*c* as in pure **1a**)[1] in the ratio of 2:3, it was possible to show that in agreement with the ^1H NMR spectroscopic results the two onium ions are indeed isostructural and exhibit a planar tetracoordinate phosphorus and arsenic atom, respectively (Figure 2). Naturally, mean Zr–E distances (E = P, As) are obtained which as expected are larger than the distances in pure **1a**.

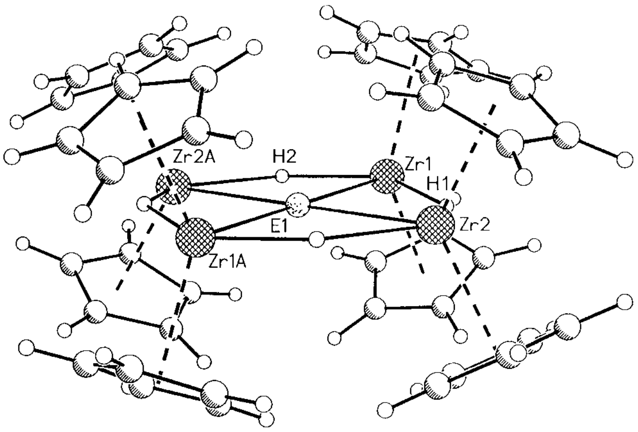


Figure 2. Molecular structure of the isostructural cations in **1a** (E = P) and **1b** (E = As) in the mixed crystal (ratio ca. 2:3); selected distances [Å] and angles [°]: E1-Zr1 2.6563(7), E1-Zr2 2.6470(8), Zr1-H1 1.97(6), Zr1-H2 1.99(7), Zr2-H2 2.03(7), Zr2-H1 2.10(7); Zr1-E1-Zr2 89.82(2), Zr1A-E1-Zr2 90.18(2), E1-Zr1-H1 68(2), E1-Zr1-H2 66(2), H1-Zr1-H2 135(2), Zr1-H1-Zr2 134(2); sum of angles at E1 360.0.

The preference for the planar configuration of the P and As onium ions was confirmed by DFT calculations (Figure 3, Table 1).[10] These showed that the planar configurations are

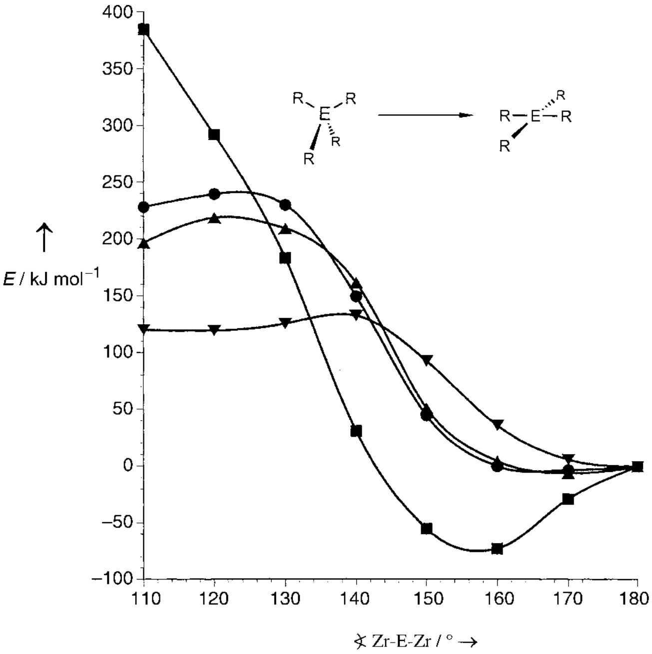


Figure 3. DFT-calculated energy profiles (relative to the energy of the planar form) as a function of the *trans*-Zr-E-Zr angle for the angle distortion of the ER_4^+ ions (E = N, P, As, Sb; R = Zr(H)Cp$_2$) from tetrahedral to planar.[10] ■ = N, ● = P, ▲ = As, ▼ = Sb.

Table 1. DFT-calculated geometric parameters for $E[Zr(H)Cp_2]_4^+$.[10]

E	∢$_{ZrEZr}$ [°]	R_{E-Zr} [Å]	R_{Zr-H} [Å]	∢$_{Zr-H-Zr}$ [°]
N	158.0, 92.0	2.352	1.945	120.9
P	173.4, 90.2[a]	2.647[b]	2.043[c]	133.3
As	173.9, 90.2	2.699	2.065	135.6
Sb	175.4, 90.0	2.830	2.133	139.7

Experimental values: [a] 89.84(4), 90.16(4)°. [b] 2.616(1), 2.610(2) Å. [c] 1.93, 2.07, 2.12 Å.

240 (**1a**) and 195 kJ mol^{-1} (**1b**) more favorable than the tetrahedral configurations. Also for the hypothetical stibonium homologue $Sb[Zr(H)Cp_2]_4^+$ the planar form is favored by about 120 kJ mol^{-1}. In contrast, however, the calculations for the ammonium homologue $N[Zr(H)Cp_2]_4^+$ gave a highly distorted tetrahedral coordination geometry at the N atom with Zr-N-Zr angles of 158.0 and 92.0°, which should be 390 kJ and 75 kJ mol^{-1} more favorable than the tetrahedral (109.47°) and planar forms (180°), respectively. The energy profiles show that the energy hypersurfaces of the P, As, and Sb onium ions in the region of the minimum structure are not only noticeably flat, but also very similar in appearance. The somewhat different curve shape for the $Sb[Zr(H)Cp_2]_4^+$ ion in the region of Zr-Sb-Zr angles $< 140°$ indicates the formation of terminal Zr–H and readily flexible Sb–Zr bonds. In contrast the Zr-N-Zr angles in the ammonium ion are far less flexible, which is attributable to stronger Zr–N bonds arising from isovalent s,p hybridization.[11] The synthesis of the ammonium homologue of **1a** and **1b** appears especially attractive because in that way a novel "intermediate" structural type for ER_4 compounds with eight valence electrons in an anti-van't Hoff–Le Bel configuration would be realized.

Experimental Section

All work was carried out under the strict exclusion of air and water. The solvents used were freshly distilled, dried, and saturated with Ar.

2b: $AsCl_3$ (1.52 g, 8.4 mmol) was added dropwise at -30 °C to a solution of $NaBPh_4$ (6.0 g, 17.4 mmol) and $P(NMe_2)_3$ (4.74 mL, 26.1 mmol) in DME (130 mL). The yellow suspension was warmed to room temperature over 2 h and stirred for a further 2 h. The solid isolated by filtration was taken up in CH_2Cl_2 (100 mL); the suspension was stirred for 15 min and then filtered. After concentration of the clear filtrate to about 10 mL colorless crystals of **2b** were obtained at 6 °C. Yield: 3.20 g (4.45 mmol, 53 %). M.p. 187–189 °C (decomp); ^1H NMR (250 MHz, $[D_8]THF$): $\delta = 2.64$ (m, 36H; $N-CH_3$), 6.81 (m, 4H; arom. H), 6.93 (m, 8H; arom. H), 7.33 (m, 8H; arom. H); $^{31}P\{^1H\}$ NMR (101.3 MHz, $[D_8]THF$): $\delta = 89.0$ (s); correct C,H analysis.

1a/1b: A slurry of $[Cp_2Zr(H)Cl]$ (2.56 g, 9.93 mol) in THF (10 ml) was treated with a solution of **2b** (0.86 g, 1.08 mmol) in THF (20 mL). The red suspension obtained was stirred for four days and then centrifuged. The clear filtrate was evaporated to dryness in vacuum and the residue was dissolved in CH_2Cl_2 (ca. 30 mL). Vapor diffusion of pentane (ca. 30 mL) into this solution gave deep green crystals within seven days at room temperature which were washed with cold CH_2Cl_2 and then dried. Yield: 0.24 g (1:1 mixture of **1a** and **1b**, 24 %). ^1H NMR (250 MHz, $[D_8]THF$): $\delta = -3.99$ (s, AsZr-H of **1b**), -3.85 (d, $^2J(P,H) = 29.5$ Hz, PZr-H of **1a**), 6.00 (s, C_5H_5), 6.80 (m, arom. H), 7.00 (m, arom. H), 7.43 (m, arom. H); ^{31}P NMR (101.3 MHz, $[D_8]THF$): $\delta = 252.0$ (q, $^2J(P,H) = 29.5$ Hz, **1a**); ESI-MS ($CH_2Cl_2/CHCl_3$): *m/z* (%): 920.4 [$\mathbf{1a} - BPh_4^-$] (100), 964.1 [$\mathbf{1b} - BPh_4^-$] (100).

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[7] Crystal structure analysis: A crystal of **1a/1b** and **2b** were each mounted on a glass capillary in perfluorinated oil and measured in a cold gas flow. The intensity data were measured with a Bruker AXS area detector ($Mo_{K\alpha}$ radiation), $\lambda = 0.71073$ Å, ω scan) at -70 °C. **2b** ($C_{40}H_{64}AsBN_6OP_2$): monoclinic, $P2_1/n$, $a = 13.146(3)$, $b = 11.818(2)$, $c = 27.833(6)$ Å, $\beta = 98.87(3)°$, $V = 4269(1)$ Å^3, $Z = 4$, $\mu = 0.909$ mm^{-1}. A total of 13 928 reflections were collected ($2\theta_{max} = 50°$), 6311 independent, 3909 observed ($F_o > 4\sigma(F_o)$), structure solution by direct methods (SHELXS 97), refinement against F^2 with all measured reflections (SHELXL 97) (460 parameters). The positions of the H atoms were calculated und considered isotropically according to a riding model. $R1 = 0.066$, $wR2$ (all data) $= 0.1921$. **1a/b** ($C_{64}H_{64}As_{0.58}BP_{0.42}Zr_4$): monoclinic, $C2/c$, $a = 25.498(3)$, $b = 13.283(2)$, $c = 18.193(2)$ Å, $\beta = 120.404(3)°$, $V = 5314(1)$ Å^3, $Z = 4$, $\mu = 1.174$ mm^{-1}. A total of 8100 reflections were collected ($2\theta_{max} = 58.62°$), 5396 independent, 3052 observed ($F_o > 4\sigma(F_o)$), structure solution by direct methods (SHELXS 97), refinement against F^2 with all measured reflections (SHELXL 97) (276 parameters). Refinement of the pentel atoms with the occupation factors 0.21 for P and 0.29 for As. The positions of the bridging H atoms at the Zr center were calculated and isotropically refined; the remaining H atoms were calculated and considered isotropically according to a riding model. $R1 = 0.0606$, $wR2$ (all data) $= 0.1803$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as "supplementary publication nos." CCDC-170097 (**2b**) and CCDC-170098 (**1a/1b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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