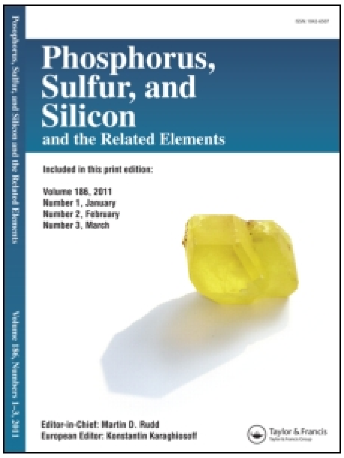

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How To Tame Planar and Main Group Metal-Substituted Onium Ions of Phosphorus and Arsenic

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HOW TO TAME PLANAR AND MAIN GROUP METAL-SUBSTITUTED ONIUM IONS OF PHOSPHORUS AND ARSENIC

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The P^+-transfer abilities of 1,1,1,3,3,3-hexakis(dimethylamino)-triphosphenium tetraphenylborate were investigated. Reaction with Schwartz reagent lead to the first planar tetracoordinated phosphonium salt $P[ZrCp_2H]_4^+BPh_4^+$. The theoretical background of this unusual planar geometry at the phosphorus atom is discussed. The first arsenic analogue $[As(P(NMe_2)_3)2]^+BPh_4^-$ of the respective triphosphenium salt was prepared, which surprisingly can act as a P^+- and As^+-transfer reagent at the same time. Furthermore, the synthesis of perstannylated ($[(Me_3Sn)_4E]OSO_2CF_3$, $E=N$, P) and persilylated ($[(Me_3Si)_4E]^+\ B(C_6F_5)_4^-$, $E=P$, As) onium ions of nitrogen, phosphorus, and arsenic are reported, which are potential starting materials for an independent access to $E[ZrCp_2X]_4$ salts.

Keywords: Arsenic; onium ions; phosphorus; silicon; tin; zirconium

The ability of terminal zirconium phosphinidene complexes to act as a source of the phosphinidene moiety has been reported.[1] We attempted to extend the range of phosphorus transfer reagents to ionic nonbasic zirconium complexes. In order to gain access to cationic zirconium phosphanides we investigated the metalation of a triphosphenium salt with Schwartz reagent. The latter reaction surprisingly furnished the first tetrametalated phosphonium cation with an "anti-van't Hoff–Le Bel" configuration.[2] In this paper we show the factors that are sustaining this unusual geometry and report the synthesis of the analogous arsenic compound.

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RESULTS AND DISCUSSION

Reaction of 1,1,1,3,3,3-hexakis(dimethylamino)-triphosphenium tetraphenylborate **1a** with Schwartz reagent [Cp_2ZrHCl] **2** in tetrahydrofuran (THF) generates the phosphonium salt $P[ZrCp_2H]_4^+ BPh_4^-$ **3a** (Figure 1), which can be obtained in the form of green crystals in 11% yield.

The ^{31}P-NMR spectrum of solutions of **3a** in (d^6)DMF shows a quintet signal at $\delta = 254.2$ due to ^2J(P—H) couplings of the four chemically equivalent ZrH protons. The ^2J(P—H) coupling ($J = 29.5$ Hz) can also be observed in the ^{1}H-NMR spectrum, which shows a characteristic doublet at $\delta = -3.8$, besides the expected sets of phenyl and C_5H_5 proton resonances. The high-field resonance of the ZrH protons clearly indicates the presence of Zr—H—Zr bridging. The bridging hydrogen atoms were also confirmed by x-ray diffraction analysis of **3a**. The Zr—P [2.616(1) and 2.610(2) Å] and Zr—H (1.91, 1.93, and 2.07 Å) distances are unremarkable. The Zr—P—Zr angles [89.84(4) and 90.16(4)°] show almost ideal values for the planar tetracoordinated geometry of the P atom in **3a**.

This **3a** is the first phosphonium cation, which has exclusively electropositive organometallic zirconocene substituents and an "anti-van't Hoff–Le Bel" configuration. Density Functional Theory (DFT) calculations of **3a** comparing the D_{4h}-S_4- geometry reveal a strong destabilization for the Zr—P—Zr angles smaller than 135°, the stage where the hydrogen bridges are rather fragile. The planar D_{4h} structure of $P[ZrCp_2H]_4^+$ is favored by 220 kJ mol^{-1} with respect to the classical tetrahedral one. The second stabilizing factor besides the hydrogen bridges is the nature of the highest occupied molecular orbital (HOMO), which alows the p_z lone-pair electrons of the phosphorus center to be delocalized by π back-bonding to the symmetry-adopted empty d orbitals of the metal centers.

Furthermore calculations for isovalence electronic $E[ZrCp_2H]_4$ species predict a planar geometry for $E = Al^-$, Si, As^+, whereas for isoelectronic elements of the second period ($E = B^-$, C, N^+) a distorted

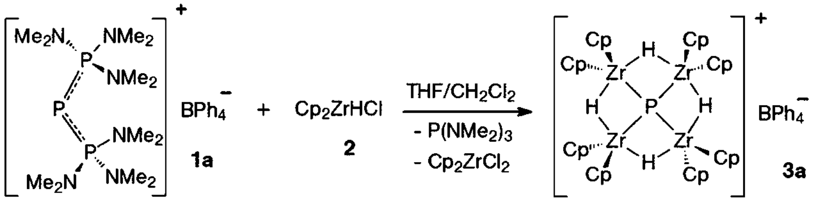


FIGURE 1

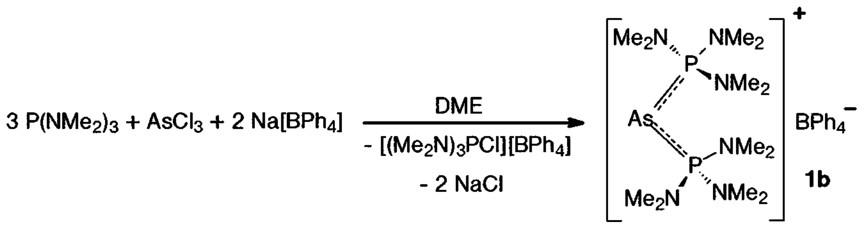


FIGURE 2

tetrahedral structure is expected. In consideration of the promising quantum chemical calculations we tried to generate the analogous arsenium salt.

The preparation of the hitherto unknown arsenium salt **1b** is analogous to the procedure for the triphosphenium salt.[3] This led to **1b** achieved in the form of crystals in 53% yield (Figure 2).

The ^{31}P-NMR spectrum in (d^8)THF shows a singlet for the terminal phosphorus atoms at $\delta = 89$. An x-ray diffraction analyis of **1b** revealed AsP distances of 2.265(2) and 2.235(2) Å, and the angle at the arsenic atom [P—As—P 103.26(6)°] is slightly smaller than the respective P—P—P angle [104.9(1)°] in the triphosphenium ion analogue.

Reaction of **1b** with Schwartz reagent **2** leads to the desired planar arsonium salt $As[ZrCp_2H]_4^+BPh_4^-$ **3b** but also, quite unexpectedly, to the phosphonium salt **3a**:

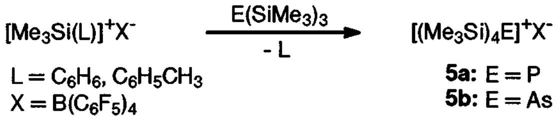
$$\mathbf{1b} + \mathbf{2} \xrightarrow[\substack{-\,P(NMe_2)_3\ \ -\,As(NMe_2)_3 \\ -\,Cp_2ZrCl_2}]{THF/CH_2Cl_2} \mathbf{3a} + \mathbf{3b}$$

The ^{1}H-NMR spectrum in CD_2Cl_2 shows the characteristic doublet for the ZrHZr bridging protons in the phosphonium cation in **3a** at $\delta = -4$, while the cation in **3b** gives a singlet at $\delta = -3.8$ for the respective ZrHZr protons. The ratio of **3a**:**3b** is 1:1.1, which is in accordance with x-ray diffraction analysis.

An alternative synthetic route to generate planar onium ions could be enabled by novel permetalated onium species, which were previously prepared:[4,5]

$$(Me_3Sn)_3E \xrightarrow[Toluene]{+\ Me_3SnOTf} (Me_3Sn)_4E[OTf]$$

4a: E = N
4b: E = P



The work to employ the cations **4a–b** and **5a–b** as starting materials for σ-metathesis reactions with [Cp_2ZrXY] reagents is in progress.

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