function of time by ^{1}H NMR spectroscopy. Since the observed rate decreased with decreasing amine concentration it was clear that k_{obs} decreases with decreasing amine concentration.

[7] The mathematical derivation of Equation (2) can be found in the Supporting Information.

[8] a) The kinetic experiments carried out in this work do not give any information about the ligands L^1 and L^2 remaining at the titanium center. b) A recently published study suggests that a cyclopentadienide ligand (L^1 = Cp) and an amide ligand (L^2 = 4-MeC$_6$H$_4$NH) are bound to the titanium center. J. S. Johnson, R. G. Bergman, *J. Am. Chem. Soc.* **2001**, *123*, 2923–2924.

[9] The calculated parameters for the coefficients in Equation (3) are: $p_1 = 8.4574 \times 10^{-7} \pm 0.00087\,\mathrm{s^{-1}}$; $p_2 = (3.775 \pm 1.06) \times 10^{-7}\,\mathrm{L\,mol^{-1}\,s^{-2}}$, $p_3 = -2.1873 \times 10^{-5} \pm 0.000849\,\mathrm{s^{-1}}$.

[10] The calculated parameters for the coefficients in Equation (4) are: $p_4 = (3.1595 \pm 0.802) \times 10^{-5}\,\mathrm{L^2\,mol^{-2}\,s^{-1}}$; $p_5 = (3.8245 \pm 0.871) \times 10^{-9}\,\mathrm{L^2\,mol^{-2}\,s^{-2}}$.

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[13] Investigations dealing with the catalytic activity of [CpTi(NHPh)$_3$], [Cp$_2$Ti=N*t*BuPy] and [Cp(Ph$_3$P=N)TiMe$_2$] which are also active hydroamination catalysts will be published in due course.

[14] This observation suggests that in accord with Bergman's observations[8b] a mono-Cp complex is the catalytically active species. For [Cp$_2$TiMe$_2$]-catalyzed reactions this species must be formed by a loss of CH$_4$ and an exchange of one Cp ligand during the induction period.

$E(SiMe_3)_4^+$ Ions ($E = P, As$): Persilylated Phosphonium and Arsonium Ions[**]

Matthias Driess,[*] Rainer Barmeyer, Christian Monsé, and Klaus Merz

Dedicated to Professor Bob West

It is known that increasing or even reversing (umpolung) the bond polarity in isoelectronic compounds greatly increases the synthetic utility of a functional group. With this in mind we have been interested in the existence of organometallic-substituted cations of the Group 15 elements, EM_4^+ (E = N, P, As, Sb, Bi; M = semimetal, metal), depending upon the nature and number of the bound metal atoms the structure and reactivity of these compounds could be very different from that of the classical parent compounds as well as from the analogous halogen and organo-substituted EX_4^+ ions (X = H, halogen, alkyl, aryl). Thus, phosphonium ions bound exclusively to organometallic groups can be regarded most simply as masked *anionic* P centers, enclosed within a protective positively charged shell, whereas the PX_4^+ ions, in which X = halogen, represent the opposite (umpolung) extreme and have masked, strongly *cationic* P centers surrounded by a halide shell. To date few completely organometallic-substituted onium ions of the Group 15 elements are known, these compounds however, have remarkable structures and reactivities. The tetragold- and the tetrazirconocenyl-substituted onium ions $E(AuPR_3)_4^+$ (E = N, P, As)[1] and $E[Zr(\eta^5\text{-}C_5H_5)_2H]_4^+$ (E = P, As)[2] are the only transition metal derivatives of the EH_4^+ ions (E = N, P, As) to be described so far and show striking electronic and geometric differences. Recently we reported the first main group metal substituted ammonium and phosphonium ions of the type $E(SnMe_3)_4^+$ (E = N, P), which can also be regarded as base-stabilized stannylium ions and are only stable in nonpolar solvents and in the presence of noncoordinating counterions.[3] They are formed with surprising ease by the stannylation of $E(SnMe_3)_3$ with Me_3SnOTf (OTf = OSO_2CF_3, triflate) in toluene. In contrast, the simple $E(SiMe_3)_4^+$ ions are not so accessible.[4] In addition, attempts to make the $P(SiMe_3)_4^+$ ions from [$Me_3Si\text{-}Co(CO)_4$], as the silylation agent, and $P(SiMe_3)_3$ were not successful, although Me_3P, Me_2PSiMe_3, and $MeP(SiMe_3)_2$ could be converted by this method into the corresponding mono-, di-, and trisilylphosphonium ions.[5] The desired tetrasilylonium ions should therefore be accessible from the more electrophilic silylium salts $R_3Si^+X^-$ containing noncoordinating anions. The easily prepared arene solvates $[Me_3Si(L)^+B(C_6F_5)_4^-]$ (L = C_6H_6, $C_6H_5CH_3$) **1a**, **b**[6] do indeed react smoothly with $P(SiMe_3)_3$ in toluene to give the desired $P(SiMe_3)_4$ salt **2**, which was isolated in the form of colorless cubic crystals in 87% yield. In contrast, $N(SiMe_3)_3$ is inert to **1a**, **b**, whereas the quarternization of the weakly basic $As(SiMe_3)_3$ takes place without problem, giving the colorless crystalline $As(SiMe_3)_4$ salt **3** in 78% yield. Compound **3**, however, cannot be prepared from the toluene solvate **1b** for kinetic reasons because in the presence of toluene the arsonium salt **3** is as stable as the phosphonium salt **2**.

$$[Me_3Si(L)]^+X^- \xrightarrow[-\,L]{E(SiMe_3)_3} [(Me_3Si)_4E]^+X^-$$

1a: L = C_6H_6
1b: L = $C_6H_5CH_3$
X = $B(C_6F_5)_4$

2: E = P
3: E = As

Compounds **2** and **3** are soluble in CH_2Cl_2 and do not dissociate in this solvent. The ^{1}H NMR spectrum of a highly dilute solution of **2** displays a doublet at $\delta = 0.64$ ($^3J(H,P) = 6.3$ Hz) arising from the $SiMe_3$ protons, this signal is temperature independent between −30 and +30 °C. The arsonium ion in **3** behaves similarly, and gives a singlet at $\delta = 0.58$. The ^{31}P NMR spectrum of **2** shows a sharp singlet at $\delta = -200.1$, thus indicating that the ^{31}P nucleus is approximately 50 ppm more deshielded than in $P(SiMe_3)_3$. The deshielding is almost identical to the $\Delta\delta$ values of the corresponding $Me_{3-n}P(SiMe_3)_n/[Me_{3-n}P(SiMe_3)_{n+1}]^+$ pair, however, the latter species does dissociate slightly in solution.[5] In addition a ^{75}As NMR

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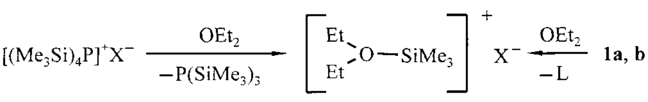
spectrum ($I = 3/2$, 100%) from **3** in CD_2Cl_2 could also be obtained: the singlet at $\delta = -325.4$ (standard: $KAsF_6$) indicates a deshielding of the As atom by more than 500 ppm, which is unusually large for an arsonium ion. In contrast, the $\delta(^{75}As)$ values of AsR_4^+ ions with R = alkyl and phenyl are in the relatively narrow range from +206 to +258.[7] As expected **2** shows a doublet at $\delta = 12.70$ in the ^{29}Si NMR spectrum, but with an unusually small coupling constant of $^1J(^{29}Si,^{31}P) = 1.4$ Hz ($P(SiMe_3)_3$: $^1J(Si,P) = 27.5$ Hz). That there is no dissociation of $SiMe_3^+$ in CH_2Cl_2 was further demonstrated by the addition of $P(SiMe_3)_3$ and $As(SiMe_3)_3$ to solutions of **2** and **3**, respectively. The multinuclear NMR spectra of the resulting mixtures show the unchanged signals of $E(SiMe_3)_3$ and $E(SiMe_3)_4^+$ (E = P, As). In contrast, with the $P(SnMe_3)_4$ salts, a ready $SnMe_3^+$ exchange occurs in spite of the presence of triflate and $B(C_6H_5)_4$ ions as slightly and noncoordinating counterions, respectively;[3] presumably this can be attributed to the weak Sn–P bond and Me_3Sn^+ ions having a lower Lewis acidity than Me_3Si^+ ions. In agreement with this premise **2** and **3** react on addition of Et_2O readily to give the silyloxonium salt **4** and free $E(SiMe_3)_3$ (E = P, As). Whereas up to now the $Et_2(Me_3Si)O^+$ ion could only be identified in solution by means of ^{29}Si NMR spectroscopy at −30°C,[8] we could successfully isolate its room-temperature stable salt **4**, which is obtained in crystalline form through the equimolar reaction of **2** or **3** with Et_2O. However, compound **4** can be prepared more easily, and in crystalline form (87%), from the direct solvation of **1a** with a mixture of Et_2O and C_6H_6.



$$[(Me_3Si)_4P]^+X^- \xrightarrow[-P(SiMe_3)_3]{OEt_2} \left[\begin{matrix}Et\\ \end{matrix}\!\!>\!O{-}SiMe_3\ \begin{matrix}\\ Et\end{matrix}\right]^+ X^- \xleftarrow[-L]{OEt_2} \mathbf{1a, b}$$

2 **4**

The crystal structure analyses of **2** and **3** show almost perfect tetrahedral coordination of the P and As centers to the Me_3Si groups (Figure 1).[9] The average Si–P bond length in **2** (2.300(2) Å) is only about 2% longer than in $P(SiMe_3)_3$.[10] The corresponding average Si–As bond in **3** is 2.386(3) Å and is thus hardly longer than those in other silylarsanes.[11] This result is in agreement with density functional calculations, that also predict a relatively small increase in the natural bond orbital (NBO) partial charges for the Si–E bonds in persilylated onium complexes of phosphorous and arsenic.[3, 12]

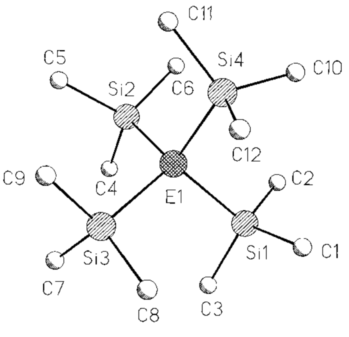


Figure 1. Molecular structure of the $[E(SiMe_3)_4]^+$ ions in the $[B(C_6F_5)_4]$ salts **2** (E = P) and **3** (E = As). Selected distances [Å] and angles [°] for $[P(SiMe_3)_4]^+$: P1-Si1 2.310(2), P1-Si2 2.290(2), P1-Si3 2.307(2), P1-Si4 2.294(2), Si1-C1 1.855(5), Si1-C2 1.851(5), Si1-C3 1.845(5); Si2-P1-Si4 109.65(8), Si2-P1-Si3 109.41(7), Si4-P1-Si3 111.06(7), Si2-P1-Si1 110.74(7), Si4-P1-Si1 108.65(7), Si3-P1-Si1 107.30(7). Selected distances [Å] and angles [°] for $[As(SiMe_3)_4]^+$: As1-Si1 2.379(3), As1-Si4 2.380(3), As1-Si3 2.388(3), As1-Si2 2.397(3); Si1-As1-Si4 108.8(1), Si1-As1-Si3 109.6(1), Si4-As1-Si3 109.4(1), Si1-As1-Si2 109.9(1), Si4-As1-Si2 110.0(1), Si3-As1-Si2 109.1(1).

The crystal structure of **4**[9] shows that the C_1 symmetric silyloxonium ion has a trigonal planar geometry (Figure 2) and the geometric parameters are in good agreement with the calculated values.[13] The Si–O bond (1.777(3) Å) is about 9% longer than that in $(Me_3Si)_2O$ (1.63 Å) and in silylalkyl ethers,[14] but almost identical to the Si–O bond in the $tBu_3SiOH_2^+$ ion.[15] The C–O bonds (1.495(4) and 1.485(5) Å) are indistinguishable from those in trialkyloxonium ions,[16] and the C-O-C angle at 114.2(3)° is, as expected, smaller than the C-O-Si angles (121.1(2) and 123.3(2)°).

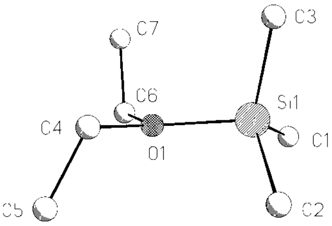
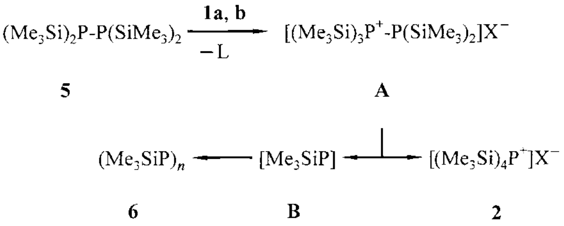


Figure 2. Molecular structure of the $[Et_2(Me_3Si)O]^+$ ion in **4**. Selected distances [Å] and angles [°]: Si1-O1 1.777(3), Si1-C1 1.829(4), Si1-C2 1.836(4), Si1-C3 1.842(5), C4-O1 1.485(5), C6-O1 1.495(4); Si1-O1-C6 123.3(2), Si1-O1-C4 121.1(2), C4-O1-C6 114.2(3).

With unexpected ease the $P(SiMe_3)_4^+$ ion can also be obtained from the reaction of the diphosphane $P_2(SiMe_3)_4$ (**5**) with **1a, b** (Scheme 1). This reaction also produces the insoluble yellow polymer **6**, which has a composition corresponding to $(PSiMe_3)_n$ but, as yet, could not be structurally characterized. Presumably the reaction proceeds via the intermediate **A**, from which the salt **2** and the carbene-like silylphosphandiyl **B** are formed through P–P bond cleavage and a simultaneous silyl migration; **B** then polymerizes to **6**. Whether stable salts of the still unknown tetrasilylonium ions $E(SiMe_3)_4^+$ (E = N, Sb, Bi) can be obtained through analogous reactions with the homologous $E_2(SiMe_3)_4$ compounds of nitrogen, antimony, and bismuth remains to be seen.



Scheme 1.

Experimental Section

2: **1a** was formed in situ by dissolving the required equimolar amount of $[Me_3Si]^+[B(C_6F_5)_4]^-$[6] in warm benzene (50 mL); $P(SiMe_3)_3$ (0.50 g, 2.00 mmol) was added at room temperature to such a solution of **1a**

(2.00 mmol), immediately a colorless solid precipitated, the solid was redissolved by addition of CH_2Cl_2 (2 mL) at around 40 °C. Colorless cubes were obtained by slowly cooling the solution to room temperature, yield: 1.74 g (1.74 mmol, 87 %). Alternatively **2** can be prepared by the reaction of **5** (0.16 g, 0.45 mmol) in toluene (10 mL) with **1a** (0.40 mmol) in toluene (50 mL) at 0 °C. The resulting yellow suspension was treated with CH_2Cl_2 (ca. 2 mL) heated to about 40 °C and the insoluble residues removed by filtration. At room temperature cubic crystals of **2** formed from the colorless filtrate, yield: 0.31 g (0.31 mmol, 67 %); ^{1}H NMR (CD_2Cl_2, 250 MHz): $\delta = 0.64$ (d, 36 H, ^3J(H,P) = 6.3 Hz, $SiMe_3$); ^{31}P NMR: $\delta = -200.1$ (s); ^{29}Si NMR: $\delta = 12.70$ (d, $^1J(^{29}Si,^{31}P) = 1.4$ Hz); correct elemental analysis.

3: Analogous to the preparation of **2** a solution of **1a** (0.43 mmol) was treated with $As(SiMe_3)_3$ (0.13 g, 0.43 mmol) at room temperature. Immediately a colorless, amorphous precipitate was formed, which can be redissolved by the addition of CH_2Cl_2 (5 mL) at about 40 °C. Slowly cooling the solution to room temperature gave colorless needles of the product, yield: 0.35 g (0.33 mmol, 78 %); ^{1}H NMR (CD_2Cl_2, 250 MHz): $\delta = 0.58$ (s, $SiMe_3$); ^{29}Si NMR: $\delta = 12.79$ (s); ^{75}As NMR (CD_2Cl_2, $KAsF_6$ standard): $\delta = -325.4$ (s); correct C,H analysis.

4: Analogous to the preparation of **2** a 1/9 mixture of diethyl ether/benzene (0.35 g) was added to a solution of **1a** (0.38 mmol). The resulting solid was recrystallized from CH_2Cl_2 (ca. 2 mL), yield 0.27 g (0.32 mmol, 83 %); ^{29}Si NMR (CD_2Cl_2): $\delta = 66.3$ (s); correct C,H analysis.

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