Perstannylated Ammonium and Phosphonium Ions: Organometallic Onium Ions That Are also Base-Stabilized Stannylium Ions**

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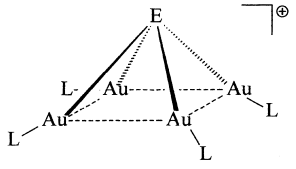
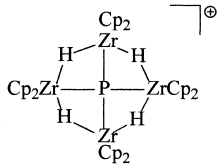
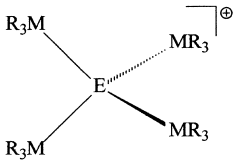
Among the four-coordinate onium ions of Group 15 elements (N, P, As, Sb, and Bi) the derivatives with organometallic subsituents are a special case.[1] In fact, only a few discrete tetra-metal ammonium, phosphonium, and arsonium ions of the form $[EL_4]^+$ (L = metal or metalloid; E = N, P, As) have been described. For transition metal derivatives the initial work of Schmidbaur et al. on the tetrahedral tetraaurated ammonium ion $[\{(Ph_3P)Au\}_4N]^+$ and the phosphorus and the arsenic analogues $[\{(Ph_3P)Au\}_4E]^+$ (E = P, As) **A** that have a nonclassical quadratic-pyramidal structure, in which the P and As atoms are found at the apex of the pyramid, have attracted considerable attention.[2] Recently we reported the first planar tetracoordinate phosphonium ion $[\{(C_5H_5)_2(H)Zr\}_4P]^+$ **B** (Cp = C_5H_5), which has an "anti-van't-Hoff-Le-Bel" configuration caused mainly by the strong π-acceptor character of the Zr center.[3]



A: E = P, As; L = PPh_3



B



C: E = N, P; M = Si, Ge, Sn
R = H, Alkyl, Aryl

In contrast permetalated ammonium and phosphonium ions with main group element substituents are so far unknown. Noteworthy is that even the apparently simple tetrasilyl, tetragermyl, or tetrastannyl derivatives of the form $[(R_3M)_4E]^+$ (R = H, alkyl, aryl; M = Si, Ge, Sn; E = N, P) **C** have eluded unequivocal characterization.[4, 5] Herein we demonstrate that the high liability of these onium ions is based on a tug-of-war between $(R_3M)_3E$, the anion, and solvent molecules as Lewis bases on one side and the Me_3M^+ ion on the other, in which the presence of sufficient weakly coordinating anions and solvent molecules favors the formation of the onium ion. With the synthesis of the partially silated ammonium ion $[(Me_3Si)_2NH_2]^+$, the unusual solid-state polymer $BaYbSi_4N_7$, which contains linked Si_4N tetrahedra, and other related partially stannylated complexes Schnick et al. and Dehnicke et al. have made exceptional advances;[6–8] in this context the recently synthesized cubic Si_3N_4 species is also worth mentioning.[7b] Herein we report the surprisingly simple synthesis of the first tetrakis(trimethylstannyl)ammonium and -phosphonium cations **1** and **2**, respectively, that dissociate slightly in solution and thus represent masked Me_3Sn^+ ions. The triflate salts of **1** and **2** are isolated as colorless crystals from the reaction of $(Me_3Sn)_3E$ (E = N, P) with the strong Lewis acid Me_3SnOTf (OTf = OSO_2CF_3) in toluene in 50 and 82 % yield, respectively.

$$E(SnMe_3)_4^+ BPh_4^- \xleftarrow[-\ NaF]{Me_3SnF/\ NaBPh_4} E(SnMe_3)_3 \xrightarrow{Me_3SnOTf} E(SnMe_3)_4^+ OTf^-$$

2': E = P

1: E = N
2: E = P

The ammonium salt **1** crystallized in the trigonal space group *R*3; only three of the Me_3Sn groups per cation interact weakly with an oxygen atom from one of three OTf anions (Figure 1).[9] The Sn···O interaction (3.07 Å)[10] results in a

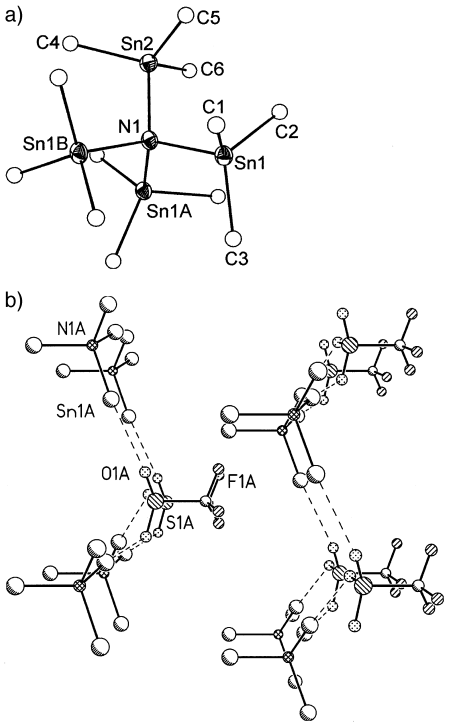


Figure 1. a) Molecular structure of the $[N(SnMe_3)_4]^+$ ion in **1**. Selected bond lengths [Å] and angles [°]: Sn1-N1 2.178(5), Sn2-N1 2.177(5), Sn1-C1 2.120(11), Sn1-C2 2.137(11), Sn1-C3 2.159 (12); C1-Sn1-C2 113.1(5), Sn1-N1-Sn2 108.6(4), Sn1A-N1-Sn1 110.3(4), Σ(C-Sn1-C) 340.1. b) Crystal packing diagram of **1**. For clarity the Me groups of the Sn atoms are not shown.

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strongly distorted trigonal-bipyramidal coordination at the Sn center (sum of the C-Sn-C bond angles 340.1°), whereas the Sn atom normally has a perfect tetrahedral coordination geometry.

The N atom has an almost perfect tetrahedral coordination sphere (108.6 and 110.3(4)°, respectively); however, the average Sn–N bond length (2.178(5) Å) is about 7% longer than the Sn–N bond in $(Me_3Sn)_3N$ (2.038 Å).[11] Similar Sn–N bond lengths are found in the ions $[(Me_3Sn)_2NH_2]^+$ (av. 2.171(9) Å) and $[(Me_3Sn)_3NH]^+$ (2.168(3) Å),[8] which clearly indicates that steric effects play only a subordinate role. This idea is supported by density functional calculations (DFT) on EL_3 and $[EL_4]^+$ (E = N, P; L = silyl, stannyl) which show that in going from NL_3 to $[NL_4]^+$ the M–N bonds (M = Si, Sn) become significantly longer than the corresponding M–P bonds in the phosphorus analogues (Table 1).[12]

Table 1. DFT-calculated N–L and P–L bond lengths [Å] (experimental values in parentheses).[12]

L	$r(NL_3)$	$r([NL_4]^+)$	$r(PL_3)$	$r([PL_4]^+)$
SiH_3	1.769	1.891	2.280	2.318
$SiMe_3$	1.794	1.948	2.293 (2.244)[c]	2.357
SnH_3	2.065	2.200	2.559	2.600
$SnMe_3$	2.083 (2.036)[a]	2.232 (2.178)[b]	2.567	2.623 (2.547)[d]

[a] See reference [11]. [b] See Figure 1. [c] See reference [15]. [d] See Figure 2.

The increase in the M–N bond lengths in the ammonium system (M = Si 7–8%, M = Sn 6–7%) can be explained most simply in ionic models through electrostatic repulsion between the four strongly electropositive R_3M groups. This repulsion arises through the electronegativity differences in the Si/N and Sn/N pairs. In agreement with this explanation the natural bond orbital (NBO) analysis of $[E(MMe_3)_4]^+$ (E = N, P; M = Si and Sn) shows that the Si and Sn atoms in the ammonium ions have an approximately 20% greater partial charge than in the phosphonium ions.[11] As a result of its significantly less polar Sn–P bonds the $[P(SnMe_3)_4]^+$ ion in **2** has an Sn–P bond length (2.547(1) Å) similar to that in stannylphoshanes (ca. 2.52 Å)[13]. Compound **2** crystallizes in the tetragonal space group *P4/nmm*, which implies that there is one Sn···O interaction per Me_3Sn group of the cation (Figure 2).[9] Thus as in **1** the Sn atoms have a strongly distorted trigonal-bipyramidal coordination (Sn···O 3.12 Å, sum of the C-Sn-C bond angles 342°). The perfectly tetrahedral Sn_4P framework is not disordered, unlike the methyl groups attached to the Sn atoms and also the O and F atoms of the OTf anions.

Like **1**, compound **2** is only soluble enough for room-temperature multinuclear NMR experiments in polar solvents such as THF. The ^1H and ^{31}P NMR spectra of **1** and **2** each show only one broad signal, without Sn satellites, at $\delta = 0.43$ and -325, respectively. Correspondingly the ^{119}Sn NMR spectra does not show the expected doublets but a broad signal at $\delta = 37.6$ ($\nu_{1/2} = 430$ Hz); the position of this signal indicates a five-coordinate base-stabilized stannylium ion.[14]

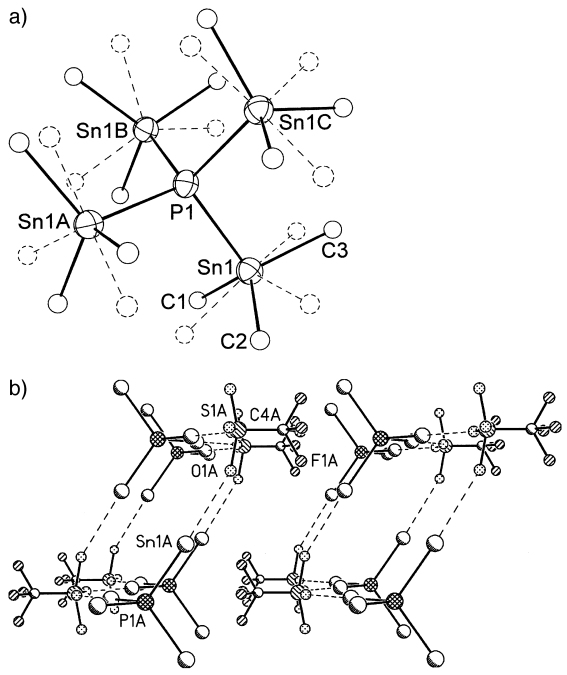

Figure 2. a) Molecular structure of the $[P(SnMe_3)_4]^+$ ion in **2**. The Me groups are to 50% disordered. Selected bond lengths [Å] and angles [°]: Sn1-P1 2.547(1), Sn1-C1 2.11(2), Sn1-C2 2.13(2), Sn1-C3 2.13(2); Sn1-P1-Sn2 108.80(2), Sn1B-P1-Sn1 110.81(5), Σ(C-Sn1-C) 342(2). b) Crystal packing diagram of **2**. For clarity the Me groups of the Sn atoms are not shown. In contrast to the cation the CF_3 and SO_3 groups of the OTf anion are rotation disordered about a fourfold axis.

When "free" $(Me_3Sn)_3P$ (^{31}P NMR (25 °C): $\delta = -328.0$) is added to the THF solution there is no change in the multinuclear NMR spectra. This observation can only be explained by dissociation and a rapid exchange of Me_3Sn^+ on the NMR time scale. The BPh_4 salt **2′**, is more soluble in THF (to −25 °C) and can be prepared from the reaction of $(Me_3Sn)_3P$ with Me_3SnF in the presence of $NaBPh_4$ in THF. The salt **2′**, shows the same NMR behavior as **2**, which implies that the influence of the anion on the dynamics is low. However, below −10 °C an additional sharp singlet appears at $\delta = -314.0$ and has a complicated Sn satellite multiplet. This singlet is not assigned to the intact $[(Me_3Sn)_4P]^+$ ion but to a "frozen" cation–THF complex of a Me_3Sn^+ ion that is simultaneously base stabilized from $(Me_3Sn)_3P$ and THF. Noteworthy is that the nucleophilicity of $E(SiMe_3)_3$ (E = N, P) in hexane is not sufficient compared to that of Me_3SiOTf to form the corresponding onium salts. In contrast the reaction of $E(SnMe_3)_3$ (E = N, P) with Me_3SiOTf leads by metathesis reactions (depending upon molar ratios) to mixed amines and phosphanes, respectively, or to **1** and **2**. By using electrophilic silylation reagents that are stronger than Me_3SiOTf[16] in nonpolar solvents it should be possible to isolate discrete tetrasilyl-substituted ammonium and phosphonium ions.

Experimental Section

1: A solution of Me_3SnOTf (0.71 g, 2.27 mmol) in toluene (20 mL) was added to a solution of $(Me_3Sn)_3N$ (1.16 g, 2.29 mmol) at room temperature. The precipitate was recrystallized from THF and afforded cubic crystals that were insoluble in nonpolar solvents, and were sensitive to air and hydrolysis (0.93 g, 1.14 mmol, 50%). Elemental analysis calcd for

$C_{13}H_{36}F_3O_3NSSn_4$ (817.8) (%): C 19.1, H 4.4, N 1.7; found: C 19.2, H 4.2, N 1.4. The mass spectrum showed only signals from fragments of the Me_3Sn group; ^{1}H NMR ([D$_8$]THF, 28 °C): $\delta = 0.36$ (s, $w_{1/2} = 75$ Hz); ^{13}C{^{1}H} NMR ([D$_8$]THF, 28 °C): $\delta = -1.3$ (s, $w_{1/2} = 40$ Hz); ^{119}Sn{^{1}H} NMR ([D$_8$]THF, 25 °C): $\delta = 88.5$ (s, $w_{1/2} = 430$ Hz); ^{19}F NMR ([D$_8$]THF, 28 °C): $\delta = -79.6$ (s).

2: $(Me_3Sn)_3P$ (1.29 g, 2.47 mmol) was slowly added dropwise to a solution of Me_3SnOTf (0.77 g, 2.46 mmol) in toluene (ca. 20 mL) at room temperature. A colorless precipitate formed immediately and was crystallized from THF (ca. 10 mL) by cooling. This afforded cubic colorless crystals of **2** which were sparingly soluble in THF, insoluble in nonpolar solvents, and completely stable in air and towards hydrolysis (1.69 g, 2.02 mmol, 82 %). Elemental analysis calcd for $C_{13}H_{36}F_3O_3PSSn_4$ (834.8) (%): C 18.7, H 4.3; found: C 18.7, H 4.2. The mass spectrometric investigations (EI) gave signals corresponding to the cleavage of $(Me_3Sn)_3P$ and $(Me_3Sn)_2PH$; ^{1}H NMR: $\delta = 0.43$ (s, $w_{1/2} = 7$ Hz); ^{31}P NMR: $\delta = -325.5$ (s, $w_{1/2} = 50$ Hz); ^{13}C{^{1}H} NMR: $\delta = -3.3$ (s), CF_3 signal not observed; ^{119}Sn{^{1}H} NMR: $\delta = 37.6$ (s, $w_{1/2} = 430$ Hz); ^{19}F NMR: $\delta = -79.5$ (s).

2′: A solution of $NaBPh_4$ (2.01 g, 5.88 mmol) in THF (ca. 10 mL) was added to a suspension of Me_3SnF (1.16 g, 6.35 mmol) and $(Me_3Sn)_3P$ (3.37 g, 6.45 mmol) in THF (ca. 20 mL) at room temperature . The mixture was stirred for 24 h at 45 °C. The solution was separated by centrifugation from the NaF formed and the solvent removed under vacuum. The resulting powder was crystallized from a small amount of THF to give compound **2** which is very soluble in THF and only slightly air and moisture sensitive (3.29 g, 3.27 mmol, 56 %). Elemental analysis calcd for $C_{36}H_{56}BPSn_4$ (1004.6) (%): C 43.0, H 5.6; found: C 42.8, H 5.3; ^{1}H NMR ([D$_8$]THF): $\delta = 7.35$ (m, 8H, *o*-CH), 6.94 (pseudo-t, ^3J(H,H) = 7.2 Hz, 8H, *m*-CH), 6.80 (m, 4H, *p*-CH), 0.40 (s, $w_{1/2} = 4$ Hz, 36H); ^{31}P NMR ([D$_8$]THF): $\delta = -323.6$ (s, $w_{1/2} = 90$ Hz); ^{13}C{^{1}H} NMR ([D$_8$]THF): $\delta = 164.3$ (q, C(1), ^1J(C,B) = 49.4 Hz), 136.6 (q, C(3), ^3J(C,B) = 1.2 Hz), 125.1 (q, C(2), ^2J(C,B) = 3.0 Hz), 121.3 (s, C(4)), −4.2 (s, $w_{1/2} = 11$ Hz); ^{119}Sn{^{1}H} NMR ([D$_8$]THF): $\delta = 38.4$ (s, $w_{1/2} = 180$ Hz).

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[9] **1**: Trigonal, space group *R*3, $a = b = 10.0939(1)$, $c = 21.655(4)$ Å, $Z = 3$, $V = 1910.7(5)$ Å^3. 1064 independent reflections ($I > 2\sigma(I)$), $R1 = 0.0332$ (observed reflections), w$R2 = 0.0895$ (all data). **2**: Tetragonal, space group *P*4/*nmm*, $a = b = 12.4613(19)$, $c = 8.885(2)$ Å, $Z = 2$, $V = 1379.7(4)$ Å^3, 658 independent reflections ($I > 2\sigma$(I)), $R1 = 0.0631$ (observed reflections), w$R2 = 0.1693$ (all data). Intensity data was collected with a Bruker-AXS-SMART diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71707$ Å, ω-Scan, $T = 203$ K). The structure was solved by direct methods (SHELXLS 97), the refinement against F^2 was with all the measured reflections (SHELXLS 97). The non-hydrogen atoms were refined anisotropically and the H atoms isotropically. The methyl groups in the $[P(SnMe_3)_4]^+$ ion of **2** are disordered, with an occupancy of 0.5, while the triflate anion is rotation disordered about a fourfold axis. 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-145133 (**1**) and CCDC-145132 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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New and Facile Entry to Nitrilium Phosphane Ylide Complex Chemistry by Using 7-Phosphanorbornadiene Complexes**

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

It is known that nitrilium phosphane ylide complexes **II** can be efficiently generated by thermally[1] or photochemically[2] induced ring opening of 2*H*-azaphosphirene complexes **I** (Scheme 1) and subsequently trapped by electronically activated π systems such as alkynes,[3] nitriles,[4] or phosphaalkynes,[5] thus providing access to a variety of new unsaturated N,P-heterocyclic ring systems. To develop the synthetic potential of this methodology, it was necessary to find a novel access to nitrilium phosphane ylide complexes **II**, thus providing N,P-heterocycles with more ubiquitous substituents

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