Phosphorus–Tin Compounds

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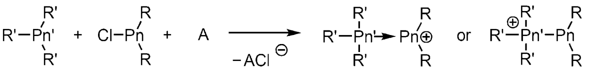
Stannylphosphonium Cations**

Elizabeth MacDonald, Lauren Doyle, Neil Burford, Ulrike Werner-Zwanziger, and Andreas Decken*

Compounds containing bonds between heavy p-block elements (E) are promising as materials that exhibit new properties,[1] however synthetic approaches to E−E′ bonds are limited. We have exploited coordination chemistry between pnictogen (Pn = P, As, Sb, or Bi) elements as a versatile and high yield method to form new or rare Pn−Pn′ bonds,[2–8] as in the general reaction Equation (1) involving the combination of a pnictine, a chloropnictine and a halide abstracting agent (e.g. A = $Me_3SiOSO_2CF_3$, $AlCl_3$). The reaction is envisaged to proceed by the heterolytic cleavage of the Pn−Cl bond and coincident or subsequent Pn′–Pn coordination of the pnictine R'_3Pn' (Lewis donor) to the pnictenium R_2Pn^+ center (Lewis acceptor) **1a**. The framework can also be viewed as a pnictinopnictonium cation **1b**. We have now extrapolated this reaction to form P−Sn coordinate bonds (illustrated by **2a**) in a series of stannylphosphonium cations (illustrated by **2b**). The versatility of this synthetic approach bodes well for the extensive and diverse development of E–E′ frameworks that provide opportunities for the discovery of new inorganic materials.



1a **1b** (1)

Equimolar reaction mixtures of Me_3P with Me_3SnCl and $AlCl_3$ [Eq. (2)] exhibit a single signal in the ^{31}P NMR spectrum that is assigned to $[Me_3PSnMe_3][AlCl_4]$, **2**, which has been isolated and characterized. The solid state structure of **2** is shown in Figure 1 (In all structural drawings hydrogen atoms are omitted for clarity), and selected structural features for **2** and other compounds are compared in Table 1. The cation in **2** represents a prototypical example of a stannylphosphonium, and the P−Sn bond [2.5861(9) Å] is predictably at the short end of the range [2.521–3.528(1) Å][9–15] of P–Sn bond distances in examples of neutral complexes containing phosphine ligands on tin acceptors and slightly longer than [2.547(1) Å] in the only example of a stannylphosphonium salt, $[P(SnMe_3)_4][SO_3CF_3]$.[16] Cation **2** adopts an eclipsed conformation with a predictable tetrahedral geometry at phosphorus and a distorted tetrahedral geometry at tin in which the $SnMe_3$ pyramid is "flattened" [Σ3(C-Sn-C) = 344.5°] due to a weak cation–anion interaction between tin and chlorine *trans* to the phosphorus center.

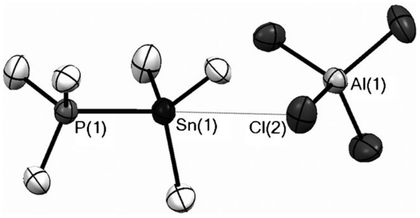
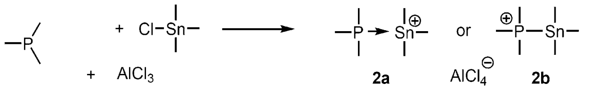


Figure 1. View of $[Me_3PSnMe_3][AlCl_4]$ (**2**) in the solid state (thermal ellipsoids at 50% probability).

Analogous reactions to Equation (2) involving tetramethyldiphosphinoethane (dmpe) with a chlorostannane and a halide abstracting agent give a variety of stannylphosphonium salts depending on the stannane derivative, the stoichiometry, and the methods of combination of the reagents. Reaction Equation (3) involving excess Me_3SnCl and $Me_3SiOSO_2CF_3$ with dmpe gives the bistriflate salt of a distannyldiphosphonium cation **3**. As shown in Figure 2a, the diphosphine ligand links two tin centers, each of which adopts a substantially distorted tetrahedral geometry due to interactions of the tin centers with an oxygen atom of each anion. In contrast to the formation of **3**, the equimolar combination of dmpe, Me_3SnCl and $AlCl_3$ in Equation (4) gives a stannylphosphoniumphosphine aluminate **4** (Figure 2b) together with the aluminate salt of aluminum complex **5** (see Supporting Information), which have been separately isolated. In the solid, **4** adopts a coordination polymeric structure in which tin has a penta-



2a **2b** (2)

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[*] Dr. N. Burford
Department of Chemistry, University of Victoria
P.O. Box 3065, Stn CSC, Victoria, BC (Canada)
E-mail: nburford@uvic.ca

E. MacDonald, L. Doyle, Dr. N. Burford, Dr. U. Werner-Zwanziger
Department of Chemistry, Dalhousie University
1459 Oxford Street, Halifax, NS (Canada)

Dr. A. Decken
Department of Chemistry, University of New Brunswick
P.O. Box 4400, Fredericton, NB (Canada)

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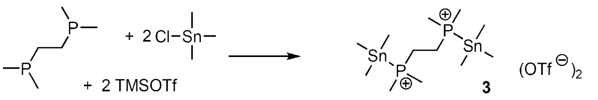
Table 1: Selected interatomic distances, bond angles and NMR spectroscopic parameters for **2**, **3**, **4**, **6**, and **7**.

	2	**3**	**4**	**6**	**7**
Sn(1)-P(1) [Å]	2.5861(9)	2.6146(12)	2.826(17)	2.5696(8)	2.5654(9)
Sn(1)-P(2) [Å]	–	–	2.8221(17)	2.7601(8)	2.521(9)
Sn(2)-P(2) [Å]	–	2.6257(12)	–	–	–
Sn(1)-Cl(1) [Å]	–	–	–	2.5756(8)	–
Shortest [Å]	Sn···Cl	Sn···O	H···Cl: 2.827	H···Cl: 2.853	Sn···Cl
Cation–Anion	3.596	2.784, 2.994	Sn···Cl: 4.188	Sn···Cl: 3.997	3.474, 3.498
Σ3(C-Sn-C) [°]	344.5	348.5 (Sn1) 353.6 (Sn2)	359.7	–	–
P-Sn-P [°]	–	–	177.21(6)	77.15(3)	82.59(3)
^{31}P{^{1}H} δ [ppm]	−37.1	−38.5	−37.1	−30.4	−27.9
^{31}P CP-MAS δ_{iso} [ppm]	−38.8	−29.6, −30.9 (AB)	−38.4, −42.8 (AB)	−17.8, −38.5 (AB)	−9.0, −9.8 (AB)
$^2J_{PP}$ [Hz]	–	0 (^{3}JPP)	158	223	80
$^1J_{SnP}$ [Hz]	329	542, 559	950, 821	282, 1091	474, 449

coordinate, trigonal bipyramidal geometry with two axial phosphonium centers, and no significant interaction with the anion.

Equimolar mixtures of dmpe with nBu$_2$SnCl$_2$ and AlCl$_3$ give an aluminate salt of a C$_2$P$_2$Sn heterocyclic cation **6** via



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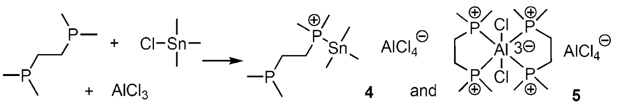


(4)

Equation (5), and the structure is shown in Figure 2c. One of the tetracoordinate phosphorus centers adopts an axial position and the other an equatorial position around a pentacoordinate tin center. The chlorine atom on tin occupies a *trans* axial position to one of the phosphorus centers, which renders the Sn–P$_{ax}$ and the Sn–P$_{eq}$ bond distances distinctly different (Table 1). In the presence of excess AlCl$_3$, dmpe affects the abstraction of two chloride ions from nBu$_2$SnCl$_2$, as in Equation (6), to give the corresponding cyclostannyldiphosphonium bisaluminate salt **7** shown in Figure 2d.

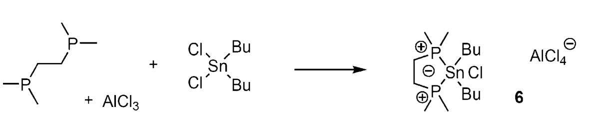
The cations in compounds **6** and **7** can be considered as chelate complexes of nBu$_2$SnCl$^+$ and nBu$_2$Sn^{+2}, respectively. The P-Sn-P bite angles in these compounds are less than 90° and compare with the chelate complexes of diphosphines with SnCl$_4$ and SnF$_4$.[10]

Compounds **2**, **3**, **4**, **6**, and **7** are all considered to be ionic, although cation–anion interactions are within the sum of the van der Waals radii and distort the tetrahedral environment at tin in **2** and **3**. The P–Sn distance in **2** can be considered as a prototypical representative of a stannylphosphonium P–Sn bond, and the slightly longer bonds observed in **3** are due to a reduced basicity of each phosphine resulting from donation to two stannyl cations. The substantially longer P–Sn distances in **4** and **6** are consistent with a *trans* influence of the phosphine center in **4** and the chlorine center in **6** on the P–Sn bonds in the axial positions at the tin centers. Compound **7** exhibits the shortest P–Sn bonds within this group of compounds, despite the relatively short anion–cation Sn···Cl contacts. In contrast to the structures of **2**, **3**, **4**, and **6**, the tin center in **7** adopts a tetrahedral geometry within the cation. The Sn···Cl contacts in **7** are substantially removed from the *trans* positions with respect to the P–Sn bonds, and all bonds within the dication are enhanced by the double cationic charge.

All compounds have been extensively characterized, and the ^{31}P NMR data is most informative. Spectra obtained for solutions of each compound **2**, **3**, **4**, **6**, and **7** all exhibit a single peak (Table 1). The ^{31}P CP-MAS spectra obtained on a powder sample of each compound, shown in Figure 3 and listed in Table 1, exhibit ^{115}Sn, ^{117}Sn, or ^{119}Sn satellites and for **3**, **4**, **6**, and **7**, reveal the crystallographic distinctions between chemically equivalent phosphorus centers that are imposed in the solid state. For each compound, the chemical shifts in the solid state spectra are similar to those observed in solution. Nevertheless, significant differences are observed in **3**, **6**, and **7** due to the more substantial inter-ion contacts in the solid state that are dissociated in solution. The observed $^2J_{PP}$ coupling occurs between the crystallographically non-equivalent phosphorus centers bound to the tin center in **3**, **4**, **6**, and **7**.

Compound **3** exhibits a two line pattern that is simulated as two distinct phosphorus centers that do not couple to each other but are coupled to their neighboring Sn nuclei. AB patterns observed for **4** and **7** have overlapping Sn satellites, while the greater distinction between the axial and equatorial phosphorus centers in **6** is evident in the chemical shift difference and $^1J_{P\text{-}Sn}$ values (Table 1).

In summary, a series of stannylphosphonium cations has been formed in reactions of Me$_3$P or Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe) with Me$_3$SnCl or nBu$_2$SnCl$_2$ in the presence of a halide abstracting agent. The demonstrated versatility of the reactions, structures, and bonding arrangements bodes well for extensive development of a diverse P–Sn chemistry by exploiting coordination chemistry for P–Sn bond formation.



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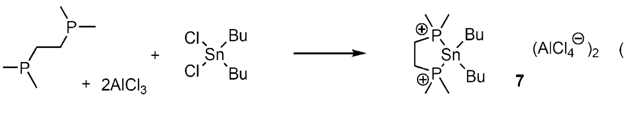

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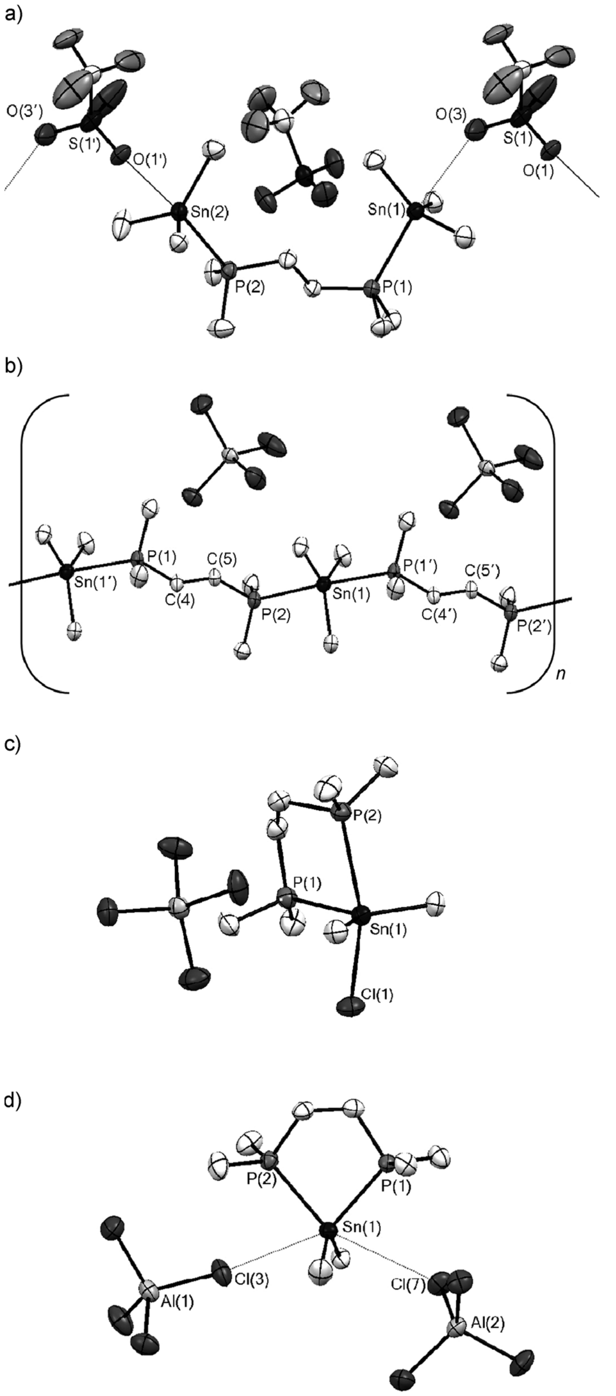

Figure 2. Views (in the solid state) of a) **3**, b) **4**, c) **6**, and d) **7** (thermal ellipsoids at 50% probability).

Experimental Section

2: Me$_3$SnCl (498 mg, 2.5 mmol) and AlCl$_3$ (333 mg, 2.5 mmol) in CH$_2$Cl$_2$ (20 mL), Me$_3$P (257.7 μL, 2.5 mmol) in CH$_2$Cl$_2$ (14 mL). Yield: 460 mg (1.13 mmol, 45 % crystalline material); m.p. 275–277 °C; C,H analysis [%]: obs.: C 16.38, H 4.33; calcd: C 17.63, H 4.44; it was not possible to obtain analytically pure samples. Crystal Data: C$_6$H$_{18}$AlCl$_4$PSn, colorless, parallelepiped, crystal size $0.40 \times 0.30 \times 0.25$ mm^3, orthorhombic, space group *Pnma*, $a = 17.813(2)$, $b = 10.7242(12)$, $c = 8.699(1)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 1661.8(3)$ Å^3, $Z = 4$, $\mu = 2.297$ mm^{-1}, $2\theta_{max} = 54.2°$, collected (independent) reflections = 6116 (1932); 72 refined parameters, $R_1 = 0.0294$, $wR_2 = 0.0677$ for all data, max/min residual electron density = 0.475/−0.421 e Å^{-3}.

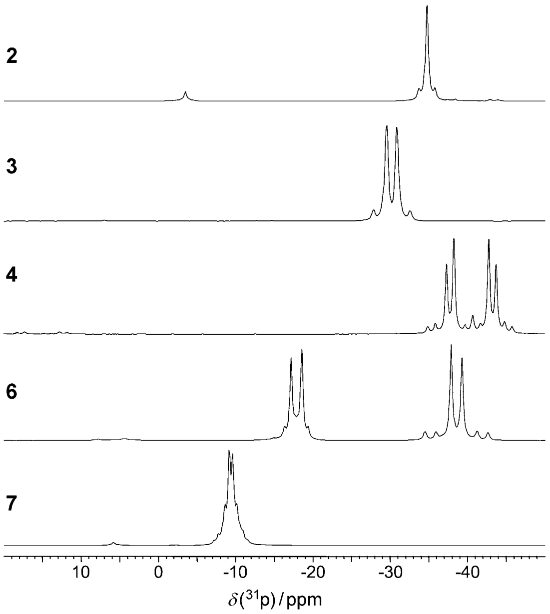

Figure 3. ^{31}P CP/MAS NMR spectra for compounds **2**, **3**, **4**, **6**, and **7**.

3: Me$_3$SnCl (996 mg, 5.0 mmol) and TMSOTf (904.7 μL, 5.0 mmol) in CH$_2$Cl$_2$ (30 mL), dmpe (427.8 μL, 2.5 mmol) in CH$_2$Cl$_2$ (14 mL). Yield: 1.052 g (1.35 mmol, 54 % powder); m.p. 148–150 °C; C,H analysis [%]: obs.: C 21.32, H 4.39; calcd: C 21.67, H 4.42. Crystal Data: C$_{14}$H$_{34}$F$_6$O$_6$P$_2$S$_2$Sn$_2$, colorless, rod, crystal size $0.55 \times 0.10 \times 0.10$ mm^3, monoclinic, space group *P*2$_1$/*c*, $a = 13.348(4)$, $b = 15.848(5)$, $c = 13.795(4)$ Å, $\alpha = 90$, $\beta = 96.132(4)$, $\gamma = 90°$, $V = 2901.5(16)$ Å^3, $Z = 4$, $\mu = 2.039$ mm^{-1}, $2\theta_{max} = 54.2°$, collected (independent) reflections = 18550 (6439); 299 refined parameters, $R_1 = 0.0343$, $wR_2 = 0.0868$ for all data, max/min residual electron density = 0.788/−0.633 e Å^{-3}.

4: Me$_3$SnCl (498 mg, 2.5 mmol) and AlCl$_3$ (333 mg, 2.5 mmol) in CH$_2$Cl$_2$ (20 mL), dmpe (257.7 μL, 2.5 mmol) in CH$_2$Cl$_2$ (14 mL). Yield: 600 mg (1.24 mmol, 50 % crystalline material); m.p. 185–187 °C; C,H analysis [%]: obs.: C 21.79, H 5.63; calcd: C 22.39, H 5.22. Crystal Data: C$_9$H$_{25}$AlCl$_4$P$_2$Sn, colorless, block, crystal size $0.12 \times 0.08 \times 0.08$ mm^3, monoclinic, space group Cc, $a = 9.3162(13)$, $b = 16.286(3)$, $c = 14.0784(19)$ Å, $\alpha = 90$, $\beta = 106.382(2)$, $\gamma = 90°$, $V = 2049.3(5)$ Å^3, $Z = 4$, $\mu = 1.950$ mm^{-1}, $2\theta_{max} = 54.2°$, collected (independent) reflections = 7065 (4274); 161 refined parameters, $R_1 = 0.0405$, $wR_2 = 0.0767$ for all data, max/min residual electron density = 0.802/−0.460 e Å^{-3}.

6: *n*Bu$_2$SnCl$_2$ (759 mg, 2.5 mmol) and AlCl$_3$ 333 mg, 2.5 mmol) in CH$_2$Cl$_2$ (25 mL), dmpe (427.8 μL, 2.5 mmol) in CH$_2$Cl$_2$ (14 mL). Yield: 1.058 mg (1.80 mmol, 72 % crystalline material); m.p. 141–143 °C; C,H analysis [%]: obs.: C 28.65, H 5.75); calcd: C 28.63, H 5.83. Crystal Data: C$_{14}$H$_{34}$AlCl$_5$P$_2$Sn, colorless, plate, crystal size $0.55 \times 0.40 \times 0.10$ mm^3, orthorhombic, space group *Pbca*, $a = 20.697(3)$ Å, $b = 12.2475(17)$ Å, $c = 20.815(3)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 5276.5(12)$ Å^3, $Z = 8$, $\mu = 1.627$ mm^{-1}, $2\theta_{max} = 54.2°$, collected (independent) reflections = 33 731 (5818); 214 refined parameters, $R_1 = 0.0264$, $wR_2 = 0.0675$ for all data, max/min residual electron density = 0.711 and −0.478 e Å^{-3}.

7: *n*Bu$_2$SnCl$_2$ (759 mg, 2.5 mmol) and AlCl$_3$ (666 mg, 5.0 mmol) in CH$_2$Cl$_2$ (30 mL), dmpe (427.8 μL, 2.5 mmol) in CH$_2$Cl$_2$ (14 mL). Yield: 1.487 mg (2.06 mmol, 83 % powder); m.p. 168–170 °C; C,H analysis [%]: obs.: C 22.88, H 4.64; calcd: C 23.33, H 4.76. Crystal Data: C$_{14}$H$_{34}$Al$_2$C$_{18}$P$_2$Sn, colorless, irregular, crystal size $0.40 \times 0.30 \times 0.25$ mm^3, monoclinic, space group *P*2$_1$/*n*, $a = 11.629(3)$, $b = 11.765(3)$,

$c = 23.499(6)$ Å, $\alpha = 90$, $\beta = 102.874(4)$, $\gamma = 90°$, $V = 3134.3(15)$ Å^3, $Z = 4$, $\mu = 1.658$ mm^{-1}, $2\theta_{max} = 54.2°$, collected (independent) reflections = 21287 (7013); 254 refined parameters, $R_1 = 0.0286$, $wR_2 = 0.0767$ for all data, max/min residual electron density = 0.822 and −0.533 e Å^{-3}.

CCDC 833306 (**2**), 833307 (**3**), 833304 (**4**), 835246 (**6**), and 833305 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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