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COMMUNICATION

Me_3P complexes of p-block Lewis acids $SnCl_4$, $SnCl_3^+$ and $SnCl_2^{2+}$ †‡

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Reactions of Me_3P with $SnCl_4$ in the presence of $nAlCl_3$ (n = 0, 1, 2) yields a series of P-Sn complexes illustrating new bonding environments for tin.

Coordination chemistry of the p-block elements is considered distinct from the coordination chemistry of the transition metals in that the acceptor orbitals are p-orbitals rather than d-orbitals. Consequently, p-block acceptors typically engage a single donor to adopt a four coordinate, tetrahedral geometry, *e.g.* H_3NBH_3. Although heavier p-block elements are capable of accessing higher coordination numbers, the coordination chemistry of the p-block elements is superficially developed compared to that of transition metals.

Coordination chemistry of tin(IV) has been demonstrated for neutral complexes with phosphines,[1–3] phosphine oxides,[1] sulphides,[3] ethers,[2,4,5] amines,[1,6] and mixed amine-ether[7] ligands. The enhanced Lewis acidity of cationic tin centres offers a more diverse coordination chemistry involving chelating or pincer ligands.[4,8–13] We now report the preparation, isolation and comprehensive characterization of prototypical Me_3P complexes of the fundamental cations $SnCl_3^+$ and $SnCl_2^{2+}$, and compare analogous data for the neutral Me_3P complex of $SnCl_4$, which was previously characterized spectroscopically.[14] The complexes represent new bonding environments for tin, demonstrate a preference for a 1 : 2 coordination stoichiometry (*i.e.* $R_3P \rightarrow Sn \leftarrow PR_3$) with a *trans* configuration of phosphine ligands, and introduce new Lewis acidic p-block centres with potential catalytic utility.

Reaction mixtures of Me_3P with $SnCl_4$ give $SnCl_4(PMe_3)_2$ in high yield, independent of the stoichiometry of the mixture. The *trans* configuration of the complex (Fig. 1) in the solid state is analogous to those reported for $SnCl_4(PEt_3)_2$,[1] $SnF_4(PCy_3)_2$,[2] and $SnI_4(PEt_3)_2$.[3] However, the Sn–P bond in $SnCl_4(PMe_3)_2$ [2.5654(7) Å] is significantly shorter than in these derivatives [2.615(5), 2.6538(11), 2.69(1) Å, respectively], consistent with the relative donor strengths of the phosphines. Equimolar mixtures of $AlCl_3$, Me_3P and $SnCl_4$ give the ionic compound $[SnCl_3(PMe_3)_2][AlCl_4]$ in high yield (91%), and in the presence of excess $AlCl_3$, $[SnCl_2(PMe_3)_2][AlCl_4]_2$ is formed in high yield (96%).

The solid state structures of the new cations are compared with that of the neutral complex $SnCl_4(PMe_3)_2$ in Fig. 1. The monocation $[SnCl_3(PMe_3)_2]^+$ adopts a trigonal bipyramidal geometry at tin with a *trans* configuration of the phosphine ligands. Consistently, the dication $[SnCl_2(PMe_3)_2]^{2+}$ accommodates the phosphine ligands in a *trans* configuration about a distorted square planar $SnCl_4$, which involves two short Sn–Cl bonds in a *cis* configuration. Two additional Sn···Cl inter-ion contacts, also in a *cis* configuration, engage two separate tetrachloroaluminate anions.

Table 1 compares characterization data for $SnCl_4(PMe_3)_2$, $[SnCl_3(PMe_3)_2][AlCl_4]$ and $[SnCl_2(PMe_3)_2][AlCl_4]_2$, including solution and solid state NMR data, selected solid state structural parameters, selected vibrational frequencies, and the corresponding results from *ab initio* and DFT calculations. The experimental bond distances within the Me_3P–Sn–PMe_3 fragment show only slight adjustment with increasing molecular charge. However, the P–Sn–P angle decreases substantially with increasing charge despite the expected D_{3h} molecular symmetry of the monocation and the presence of weak inter-ion contacts to the dication. The similar Sn–P bond distances in the neutral, monocationic and dicationic complexes are

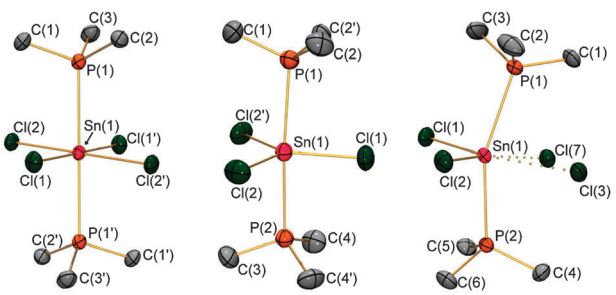

Fig. 1 POV-Ray views of $SnCl_4(PMe_3)_2$ (left), the cation in $[SnCl_3(PMe_3)_2][AlCl_4]$ (middle) and the cation in $[SnCl_2(PMe_3)_2][AlCl_4]_2$ (right) including the interion contacts between tin and chlorine atoms of two anions. Thermal ellipsoids are at the 50% probability level, hydrogen atoms and counter ions are omitted for clarity.

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Table 1 NMR data, selected structural parameters and vibrational assignments (experimental and calculated) for $SnCl_4(PMe_3)_2$, $[SnCl_3(PMe_3)_2][AlCl_4]$ and $[SnCl_2(PMe_3)_2][AlCl_4]_2$. HF values enclosed in square parentheses. PBE0 values enclosed in curly parentheses

	$SnCl_4(PMe_3)_2$	$[SnCl_3(PMe_3)_2][AlCl_4]$	$[SnCl_2(PMe_3)_2][AlCl_4]_2$
$^{31}P\{^1H\}$ NMR: δ, ppm ($^1J_{PSn}$,119/117 Hz)	1.6(2635/2517)	10.8(2725/2604)	16.9(2591/2476)
^{31}P CP/MAS: δ, ppm ($^1J_{PSn}$, Hz)	6.8(2772)	15.9(2706)	46.3(2125); 45.8(2125)
^{119}Sn NMR: δ, ppm ($^1J_{PSn}$, Hz)	−554(2635)	−456(2725)	−333(2591)
Sn–P (Å)[a]	2.5654(7) [2.641] {2.612}	2.5439(12) *P(1)* [2.622] {2.596} 2.5347(12) *P(2)*	2.5390(6) *P(1)* [2.568] {2.570} 2.5414(6) *P(2)*
Sn–Cl (Å)[a]	2.4762(6) *Cl(1)* 2.4565(7) *Cl(2)* [2.432, 2.416, 2.404][b] {2.446, 2.426, 2.411}[b]	2.3490(12) *Cl(1)* [2.328] {2.349} 2.3955(10) *Cl(2)*	2.3367(5) *Cl(1)* [2.254] {2.273} 2.3575(5) *Cl(2)*
Sn···Cl (Å)	—	—	2.9233(6) *Cl(3)* 2.9907(6) *Cl(7)*
P–Sn–P (°)	180.0 [174.6] {173.1}	172.67(4) [180.0] {180.0}	157.554(19) [123.3] {128.4}
Cl–Sn–Cl (°)	90.53(2), 89.47(2) [90.5, 89.5]{90.6, 89.4}	113.49(2), 133.00(5) [120.0] {120.0}	102.25(2), [115.1] {115.0}
∑ Cl–Sn–Cl (°)	360.00(2) [360.0] {360.0}	359.98(2) [360.0] {360.0}	360.19(4) [360.0] {360.0}
ν_{sym}(P–Sn) (cm^{-1})	334 [348] {319}	321 [349] {323}	329 [354] {328}
ν_{sym}(Sn–Cl) (cm^{-1})	289 [301] {285}	309 [327] {309}	360 [414] {390}
ν_{sym}(P–C) (cm^{-1})	664 [708] {685}	668 [699] {680}	667 [678] {668}

[a] For comparison: $SnCl_4(PEt_3)_2$, Sn–Cl = 2.455(5) Å and 2.445(5) Å, Sn–P = 2.615(5) Å.[1] $SnCl_3Bu(PPh_3)$, Sn–Cl = 2.339(3) Å and 2.404(2) Å, Sn–P = 2.862(2) Å.[23] [b] DFT and *ab initio* calculations give the C_{2v} conformer as the minimum, which is related to the experimentally observed C_{2h} conformer by an eclipsed (calcd) *versus* staggered (expt.) arrangement of methyl groups in the Me_3P donors. The reduced symmetry in the C_{2v} conformer gives rise to three unequal Sn–Cl bond lengths.

surprising in light of the reported Sn–P distances, which vary widely as a function of charge and geometry [2.5–3.5 Å].[1–3,15–20]

In contrast, the Sn–Cl distances in the monocationic salt $[SnCl_3(PMe_3)_2][AlCl_4]$, are significantly shorter than those in $SnCl_4(PMe_3)_2$, indicating that the charge is accommodated by the $SnCl_3$ moiety. The Sn–Cl distances in the dicationic salt $[SnCl_2(PMe_3)_2][AlCl_4]_2$ are further contracted but by a smaller amount due to the *trans* influence imposed by Sn···Cl inter-ion contacts, which are well within the sum of the Sn···Cl van der Waals radii (3.92 Å). All observed Sn–Cl bonds are significantly longer than those in solid (tetrahedral) $SnCl_4$ (average 2.279 Å)[21] and shorter than those in solid $SnCl_2$ (average 2.72 Å).[22]

The gas phase optimized structures of $SnCl_4(PMe_3)_2$, $[SnCl_3(PMe_3)_2]^+$ and $[SnCl_2(PMe_3)_2]^{2+}$ appropriately model the trends in experimental values for bond lengths observed in the solid state, as illustrated in Fig. 2. The calculated Sn–Cl bond distances in the dication are anomalously short since the *trans* influence of the inter-ion contacts observed in the solid state is absent. In contrast to the experimental data, the $[SnCl_3(PMe_3)_2]^+$ cation is modelled as a D_{3h} structure in the gas phase indicating that the solid state distortion of the P–Sn–P axis [P–Sn–P (°) = 172.67(4) *vs.* 180.0] is due to crystal packing (see supplementary information).

The gas phase optimized structure of $[SnCl_2(PMe_3)_2]^{2+}$ reveals Cl–Sn–Cl and P–Sn–P angles that are substantially smaller than those in the solid state and the gas phase geometry at tin is best described as a tetrahedron distorted by steric interactions between the phosphine ligands. The solid state geometry deviates from the tetrahedron due to the Sn···Cl inter-ion contacts. The influence of these solid state contacts is also evident in the comparison between solution and solid state ^{31}P CP/MAS NMR data, which reveals substantially different chemical shifts between the two phases for the dication than for the neutral and monocation complexes.

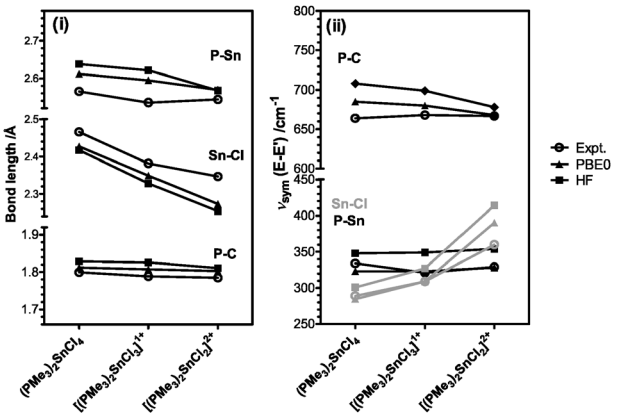

Fig. 2 Comparison of experimental and calculated (i) average E–E′ bond lengths, and (ii) symmetric E–E′ stretching frequencies.

Consistent with the conclusions from experimental and calculated structural data that the molecular charge is accommodated primarily by the Sn–Cl framework, the chemical shifts of the phosphorus centres exhibit only minor deshielding with increasing charge, while the ^{119}Sn shift is deshielded by approximately 100 ppm for each unit of added charge.

DFT and *ab initio* calculations have allowed for unambiguous assignment of the key E–E′ stretching frequencies. The calculated trends are in agreement with experimental observations [Fig. 2, (ii)] for symmetric stretching frequencies [υ_{sym}(P–Sn), υ_{sym}(Sn–Cl), and υ_{sym}(P–C)] in the solid state structural parameters, in that the Sn–Cl stretching frequencies exhibit larger adjustments with increasing molecular charge than do the Sn–P and P–C frequencies.

The characterization data for the feature compounds classify them as *trans* bis-phosphine complexes of $SnCl_4$, $[SnCl_3]^+$ and $[SnCl_2]^{2+}$, respectively. The compounds complement the coordination chemistry of neutral and cationic tin(IV) that has been

developed using chelating and crown ligands.[1–10] In addition, the compounds illustrate new structure and bonding for tin, with $[SnCl_3]^+$ behaving as a tetrael analogue of an isoelectronic triel Lewis acid [*cf.* $InCl_3(PMe_3)_2$][24] and $[SnCl_2]^{2+}$ behaving as an analogue of an isoelectronic group 12 metal halide [*cf.* $CdCl_2(PPh_3)_2$].[25] The gas phase D_{3h} structure modelled for $[SnCl_3(PMe_3)_2]^+$ is consistent with the observed solid state structure of $InH_3(PCy_3)_2$,[26] and the distorted tetrahedral solid state geometry at tin in $[SnCl_2(PMe_3)_2]^{2+}$ is consistent with the structure of $Cd(OAr)_2(PMe_3)_2$.[27] However, the In–P bonds [2.9869(5) Å] and Cd–P bonds [2.737(5) Å] are substantially longer than the Sn–P bonds, despite the similar covalent radii of Sn, In, and Cd (1.41, 1.44, and 1.48 Å, respectively, demonstrating the greater Lewis acidity of the tin centre.

Lewis acidic tin centres have been shown to exhibit valuable catalytic activity.[28,29] In the context of the extensive utility of phosphine ligands in transition metal catalysis, the development of phosphine complexes of tin represents an important and enabling step towards unlocking the catalytic potential of such main group elements.

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