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## Synthesis, characterization and mass-spectrometric analysis of $[\text{LSn(IV)F}_{4-x}]^{x+}$ salts [L = tris ((1-ethyl-benzoimidazol-2-yl)methyl)amine, $x = 1-4$ ]<sup>†</sup>

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A series of complexes with the formulae  $[(\text{BIMe}_3)\text{SnF}_{4-x}][\text{OTf}]_x$  with  $x = 1-4$  has been synthesized by successive fluoride abstraction from  $\text{SnF}_4$  with TMSOTf in the presence of the tetradentate nitrogen donor BIMe<sub>3</sub> (tris ((1-ethyl-benzoimidazol-2-yl)methyl)amine). Single crystal X-ray diffraction and heteronuclear NMR spectroscopic analysis provided insight into these new main group cations. Electrospray ionization mass spectrometric analysis on solutions containing the different salts allowed for successful detection of the cations  $[(\text{BIMe}_3)\text{SnF}]^{3+}$ ,  $[(\text{BIMe}_3)\text{SnF}_2]^{2+}$  and  $[(\text{BIMe}_3)\text{SnF}_3]^+$ .

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## Introduction

Weakly coordinating anions (WCAs) have been studied intensively and have enabled the isolation of salts containing cationic main group centers that have otherwise only been observed in the gas phase.<sup>1</sup> Such cationic centers are also stabilised with neutral donors or solvent molecules and show only weak interactions with their counter anions making them significantly more acidic and reactive.<sup>2</sup> In this context, Lewis acids are capable of activating small molecules including dihydrogen, carbon monoxide and carbon dioxide, which makes them potential catalysts, especially with regards to the concept of frustrated Lewis pairs (FLPs).<sup>3</sup> While tricationic triel(III)<sup>3+</sup> salts are known, the analogous ligand stabilized tetrel(IV)<sup>4+</sup> and pnictogen(V)<sup>5+</sup> derivatives have not been isolated. We have recently reported the investigation of multidentate ligand scaffolds which encapsulate the main group cation without occupying all the available coordination sites, allowing for metal centered reactivity. The tetradentate ligand BIMe<sub>3</sub> (tris ((1-ethyl-benzoimidazol-2-yl)methyl)amine) has been identified as a versatile and strong ligand, which allowed for successful isolation of dicationic germanium(IV) and tricationic phos-

phorus(V) complexes,  $[(\text{BIMe}_3)\text{GeF}_2]^{2+}$  and  $[(\text{BIMe}_3)\text{PF}_2]^{3+}$  by the oxidation of the parent Ge(II)<sup>2+</sup> and P(III)<sup>3+</sup> cations with XeF<sub>2</sub>.<sup>5</sup> We now report the sequential fluoride abstraction from  $\text{SnF}_4$  in the presence of BIMe<sub>3</sub> to isolate salts of tin complexes with the generic formula  $[(\text{BIMe}_3)\text{SnF}_{4-x}][\text{OTf}]_x$  and  $x = 1-4$ .

## Results

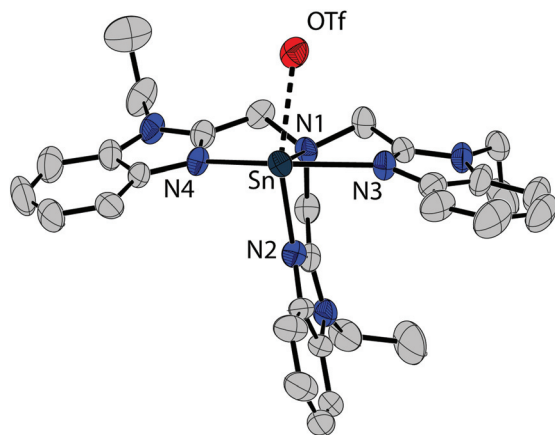
By extrapolation of our experience with the ligand stabilized germanium cation in  $[(\text{BIMe}_3)\text{Ge}][\text{OTf}]_2$ , addition of excess TMSOTf to an equimolar mixture of BIMe<sub>3</sub> and  $\text{SnCl}_2$  in acetonitrile gives  $[(\text{BIMe}_3)\text{Sn}][\text{OTf}]_2$ .<sup>5a</sup> X-ray diffraction analysis of single crystals grown from the reaction mixture confirm the structure of  $[(\text{BIMe}_3)\text{Sn}][\text{OTf}]_2$  (Fig. 1), which includes one contact to a triflate anion ( $\text{Sn}\cdots\text{OTf}$  2.663(4) Å) in contrast to the structure observed for the analogous  $[(\text{BIMe}_3)\text{Ge}][\text{OTf}]_2$ .

Addition of XeF<sub>2</sub> to a solution of  $[(\text{BIMe}_3)\text{Sn}][\text{OTf}]_2$  resulted in vigorous evolution of xenon gas, consistent with a redox process. The <sup>19</sup>F NMR spectrum of the reaction mixture indicates consumption of XeF<sub>2</sub>, but numerous fluorine containing compounds are observed. Reaction of  $\text{SnF}_4$  with one equivalent of BIMe<sub>3</sub> and one equivalent of TMSOTf in acetonitrile (Scheme 1) gives a colorless solution. Addition of diethyl ether effects rapid precipitation of a colorless solid that has been identified as  $[(\text{BIMe}_3)\text{SnF}_3][\text{OTf}]$  on the basis of a quartet resonance in the <sup>119</sup>Sn NMR spectrum ( $\delta = -763.6$  ppm with  $J_{\text{SnF}} = 1895$  Hz) and a singlet resonance in the <sup>19</sup>F NMR spectrum with resolved tin satellites ( $\delta = -112.2$  (s),  $J_{\text{SnF}} = 1893$  Hz and  $J_{\text{SnF}} = 1808$  Hz).

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**Fig. 1** Structure of the cation in  $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_2$ . Thermal ellipsoids are shown at a 50% probability level. Hydrogen atoms, solvent molecules and non-coordinating anions are omitted for clarity. For weakly interacting triflate anions only the coordinating oxygen atoms are shown. Interatomic distances and angles are summarized in Table 1.

The high yield crystallization of  $[(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$  provided a synthon for more highly charged tin cations (Scheme 1). Addition of one equivalent of TMSOTf to  $[(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$  with stirring for 5 minutes at room temperature yielded a colorless solution. A triplet resonance in the  $^{119}\text{Sn}$  NMR spectrum ( $\delta = -556.2$  ppm with  $J_{\text{SnF}} = 2223$  Hz) and one major broad singlet in the  $^{19}\text{F}$  NMR spectrum with broad tin-satellites ( $\delta = -157.9$  ppm with  $J_{\text{SnF}} = 2220$  Hz) are assigned to  $[(\text{BIMeEt}_3)\text{SnF}_2][\text{OTf}]_2$ , invoking fast exchange of the fluoride substituents in solution. In contrast, the isoelectronic complexes  $[(\text{BIMeEt}_3)\text{PF}_2]^{3+}$  and  $[(\text{BIMeEt}_3)\text{GeF}_2]^{2+}$  exhibit two distinct fluorine substituents.<sup>5</sup> The solid state structure obtained from single crystal X-ray diffraction analysis (Fig. 2) shows a dimeric  $\text{Sn}_2\text{F}_2$ -core involving seven-coordinate tin centers, which provides a rationale for the exchange observed in solution. Mixtures of two equivalents of TMSOTf with  $[(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$  exhibit a doublet resonance in the  $^{119}\text{Sn}$  NMR spectrum (at  $\delta = -543.0$  ppm) with tin-fluorine coupling constants ( $J_{\text{SnF}} = 2450$  Hz) expected for  $[(\text{BIMeEt}_3)\text{SnF}][\text{OTf}]_3$ . A sharp singlet resonance in the  $^{19}\text{F}$  NMR spectrum was observed at significantly lower frequency ( $\delta = -164.8$  ppm) with tin-satellites ( $J_{\text{SnF}} = 2450$  Hz and  $J_{\text{SnF}} = 2332$  Hz) implicating a more resilient metal fluoride complex.

The last fluoride in  $[(\text{BIMeEt}_3)\text{SnF}][\text{OTf}]_3$  can be substituted with a triflate anion using an excess of TMSOTf. The tetratriflate salt,  $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_4$  has been identified in solution by its singlet resonance in the  $^{119}\text{Sn}$  NMR spectrum ( $\delta = -571.1$  ppm), the absence of signals corresponding to a Sn-F in the  $^{19}\text{F}$ -NMR spectrum and X-ray diffraction analysis of the

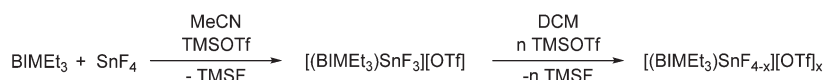
isolated crystalline solid (Fig. 2). Slow decomposition of  $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_4$  in acetonitrile or DCM solutions is evident by the emergence of  $^1\text{H}$ -NMR signals corresponding to  $[(\text{BIMeEt}_3)\text{H}]^+$ .

The Gutmann Beckett method<sup>6</sup> was applied to assess the Lewis acidity of the new cations. Equimolar mixtures of  $[(\text{BIMeEt}_3)\text{SnF}][\text{OTf}]_3$  and triethylphosphine oxide in dichloromethane exhibit a sharp doublet resonance at  $^{31}\text{P}$   $\delta = 90.4$  ppm with  $J_{\text{PF}} = 3.8$  Hz. This is a substantial chemical shift of  $\Delta\delta = 49.4$  ppm compared to the free phosphine oxide and is interpreted as an acceptor number of 109. The singlet resonance in the  $^{19}\text{F}$  NMR spectrum ( $\delta = -158.5$  ppm with  $J_{\text{SnF}} = 2399$  and 2292 Hz) and the doublet resonance in the  $^{119}\text{Sn}$  NMR spectrum ( $\delta = -540.0$  ppm with  $J_{\text{SnF}} = 2399$  Hz) are similar to  $[(\text{BIMeEt}_3)\text{SnF}][\text{OTf}]_3$ . Addition of two equivalents of OPET<sub>3</sub> to  $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_4$  resulted in a broad resonance in the  $^{31}\text{P}$  NMR spectrum ( $\delta = 91.4$  ppm) with a very similar chemical shift to  $[(\text{BIMeEt}_3)(\text{OPET}_3)\text{SnF}][\text{OTf}]_3$ . The broad heteronuclear resonances and the fact that none of the proton resonances are resolved at room temperature indicate a fast exchange between the two phosphine oxide donors, while the sharp singlet resonance in the  $^{19}\text{F}$  NMR spectrum suggest dissociated (non-interacting) triflate anions. These observations indicate that the Lewis acidities of the new cations are comparable to that of boron Lewis acids,<sup>7</sup> with the trend  $\text{B}(\text{C}_6\text{F}_5)_3$  (82) <  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (89) <  $\text{BCl}_3$  (106) <  $\text{BBR}_3$  (109) =  $[(\text{BIMeEt}_3)\text{SnF}][\text{OTf}]_3$  =  $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_4$  <  $\text{BI}_3$  (115).

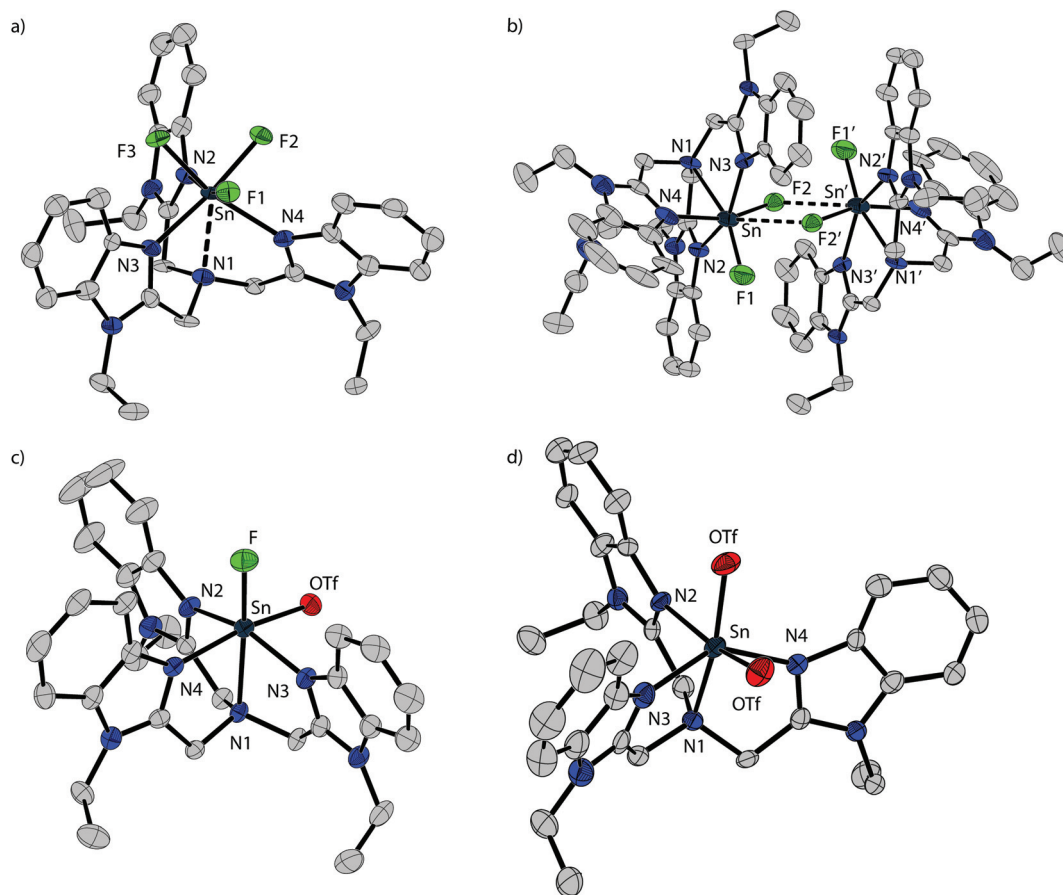
Table 1 lists the  $^{119}\text{Sn}\{^1\text{H}\}$  NMR chemical shift for each of the new tin salts together with data for related compounds. The chemical shift for  $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_2$  is found at high frequency compared to salts of tin(II)<sup>2+</sup> which form acetonitrile complexes in solution<sup>9,10</sup> or [18]crown-6,<sup>8</sup> and is comparable to that for  $[(\text{bipy})_2\text{Sn}][\text{OTf}]_2$ .<sup>11</sup> Replacement of fluoride substituents in  $\text{SnF}_4$  with triflate anions yielded the salts that resonate at higher frequency,  $^{119}\text{Sn}$   $\delta = [(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$  ( $-763.6$  ppm) <  $[(\text{BIMeEt}_3)\text{SnF}_2][\text{OTf}]_2$  ( $-556.2$  ppm) <  $[(\text{BIMeEt}_3)\text{SnF}][\text{OTf}]_3$  ( $-543.4$  ppm). The chemical shift of  $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_4$  ( $^{119}\text{Sn}$   $\delta = -571.1$  ppm) is at a lower frequency than those of the mono and difluoride species, perhaps correlated to the coordination geometry of the tris-benzoimidazole ligand.  $[(\text{PMe}_3)_2\text{SnCl}_2][\text{AlCl}_4]_2$  represents a rare example of a complex of  $\text{Sn}(\text{IV})^{2+}$  salt and resonates at higher frequency ( $^{119}\text{Sn}$   $\delta = -333$  ppm).

The solid state structures for derivatives of  $[(\text{BIMeEt}_3)\text{SnF}_{4-x}][\text{OTf}]_x$  with  $x = 1-4$  were determined from single crystal X-ray diffraction analysis on crystals grown from saturated acetonitrile solutions layered with diethyl ether (Table 2).

The fluoride substituent in  $[(\text{BIMeEt}_3)\text{SnF}]^{3+}$  is *trans* to the apex amine donor, as in  $[(\text{BIMeEt}_3)\text{GeF}(\text{OTf})][\text{OTf}]_2$ , which is consistent with the amine (N1) being the weakest donor.<sup>5a</sup> The



**Scheme 1** Sequential fluoride abstraction from  $\text{SnF}_4$  to form  $[(\text{BIMeEt}_3)\text{SnF}_{4-x}][\text{OTf}]_x$ ,  $x = 1-4$ ,  $n = 1-3$ .



**Fig. 2** Solid state structure of the cations in [(BIMeEt<sub>3</sub>)SnF<sub>3</sub>][OTf] (a) [(BIMeEt<sub>3</sub>)SnF(μ<sub>2</sub>-F)]<sub>2</sub>[OTf]<sub>4</sub> (b), [(BIMeEt<sub>3</sub>)SnF][OTf]<sub>3</sub> (c) and [(BIMeEt<sub>3</sub>)Sn][OTf]<sub>4</sub> (d). Thermal ellipsoids are shown at a 50% probability level. Hydrogen atoms, solvent molecules and non-coordinating anions are omitted for clarity. For weakly interacting triflate anions only the coordinating oxygen atoms are shown. Interatomic distances and angles are summarized in Table 1.

**Table 1** <sup>119</sup>Sn δ chemical shifts for selected tin cations in solution if not otherwise stated

	<sup>119</sup> Sn{ <sup>1</sup> H} δ	Ref.
[[18]crown-6)Sn][OTf] <sub>2</sub>	-1578 <sup>a</sup>	8
(MeCN) <sub>6</sub> Sn][Al(OR <sup>F</sup> ) <sub>4</sub> ] <sub>2</sub>	-1490	9
(C <sub>7</sub> H <sub>8</sub> ) <sub>3</sub> Sn][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sub>2</sub>	-1468 <sup>b</sup>	10
(bipy) <sub>2</sub> Sn][OTf] <sub>2</sub>	-728.6	11
(BIMeEt <sub>3</sub> )Sn][OTf] <sub>2</sub>	-628.7	
(bipy) <sub>2</sub> SnCl][OTf]	-577.0	11
(BIMeEt <sub>3</sub> )SnF <sub>3</sub> ][OTf]	-763.6	
(bipy)SnF <sub>4</sub> ]	-708.2	12
(BIMeEt <sub>3</sub> )(OPeT <sub>3</sub> ) <sub>2</sub> Sn][OTf] <sub>4</sub>	-582.7	
(BIMeEt <sub>3</sub> )Sn][OTf] <sub>4</sub>	-571.1	
(BIMeEt <sub>3</sub> )SnF <sub>2</sub> ][OTf] <sub>2</sub>	-556.2	
(BIMeEt <sub>3</sub> )SnF][OTf] <sub>3</sub>	-543.4	
(BIMeEt <sub>3</sub> )(OPeT <sub>3</sub> )SnF][OTf] <sub>3</sub>	-540.0	
(PMe <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ][AlCl <sub>4</sub> ] <sub>2</sub>	-333	13
(DMAP) <sub>2</sub> Me <sub>2</sub> Sn][OTf] <sub>2</sub>	-175.0	14

<sup>a</sup> Chemical shift of sample in the solid state. <sup>b</sup> Replacement of the toluene donors and formation of [(CH<sub>3</sub>CN)<sub>6</sub>Sn]<sup>2+</sup> in solution.

subsequent fluoride abstraction results in a formal increase of cationic charge at the tin center. This electron deficiency results in a significantly greater Lewis acidity emphasized by

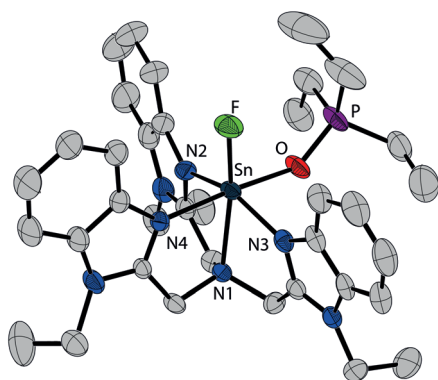
shorter average N–Sn bond; [(BIMeEt<sub>3</sub>)SnF<sub>3</sub>]<sup>+</sup> 2.192(6)<sub>av</sub> > [(BIMeEt<sub>3</sub>)SnF<sub>2</sub>]<sup>2+</sup> 2.140(6)<sub>av</sub> > [(BIMeEt<sub>3</sub>)SnF]<sup>3+</sup> 2.098(4)<sub>av</sub> ≈ [(BIMeEt<sub>3</sub>)Sn]<sup>4+</sup> 2.095(6)<sub>av</sub>. Correspondingly, the apex N–Sn bond distance is shorter too; 2.639(6) [(BIMeEt<sub>3</sub>)SnF<sub>3</sub>]<sup>+</sup> > 2.362(6) [(BIMeEt<sub>3</sub>)SnF<sub>2</sub>]<sup>2+</sup> > 2.271(4) [(BIMeEt<sub>3</sub>)SnF]<sup>3+</sup> ≈ 2.293(6)<sub>av</sub> [(BIMeEt<sub>3</sub>)Sn]<sup>4+</sup>. The tin center in [(BIMeEt<sub>3</sub>)SnF<sub>2</sub>]<sup>2+</sup> engages a fluoride substituent of a neighbouring cation to impose a *hepta*-coordinate environment for tin, similar to the main group center in [(BIMeEt<sub>3</sub>)SnF<sub>3</sub>]<sup>+</sup>. Notably, [(BIMeEt<sub>3</sub>)SnF]<sup>3+</sup> has the shortest Sn–F interactions (1.905(3) Å) compared to the ones in [(BIMeEt<sub>3</sub>)SnF<sub>2</sub>]<sup>2+</sup> (1.938(4) and 1.966(4) Å) and those in [(BIMeEt<sub>3</sub>)SnF<sub>3</sub>]<sup>+</sup> (1.963(4) and 1.979(4) Å), which is due to the increased cationic charge and the complex geometry which allows for closer interactions. The tetratriflate salt [(BIMeEt<sub>3</sub>)Sn][OTf]<sub>4</sub> adopts a tripodal geometry at tin imposed by strong interactions with two triflate anions (Sn...OTf 2.026(5), 2.106(5) Å and 2.031(6), 2.102(6) Å for the other isomer present in the asymmetric unit). One sharp signal is observed in the <sup>19</sup>F NMR spectrum that is assigned to the triflate anions, implicating a fast anion exchange that is not resolved on NMR timescale. The presence of only one set of signals for the protons of the benzoimidazole substituents in the <sup>1</sup>H-NMR spectrum suggests a similar structure in solution.

**Table 2** Bond distances in Å, angles in degrees (°), chemical shifts in ppm and coupling constants in Hz for the featured cations (L = BIMEt<sub>3</sub>, L' = OPEt<sub>3</sub>)

	[LSn] <sup>2+</sup>	[LSnF <sub>3</sub> ] <sup>+</sup>	[LSnF <sub>2</sub> ] <sup>2+</sup>	[LSnF] <sup>3+</sup>	[LSn] <sup>4+</sup>	[LL'SnF] <sup>3+</sup>
Sn N	2.399(5) 2.419(5) 2.288(5)	2.167(6) 2.191(6) 2.217(6)	2.123(7) 2.148(6) 2.149(5)	2.109(4) 2.098(4) 2.086(4)	2.086(5), 2.085(7) <sup>a</sup> 2.098(6), 2.099(6) <sup>a</sup> 2.100(6), 2.099(6) <sup>a</sup>	2.99(3) 2.109(3) 2.119(3)
Sn N1	2.541(5)	2.639(6)	2.362(6)	2.271(4)	2.268(7), 2.318(7) <sup>a</sup>	2.293(3)
Sn OTf	2.633(4)	—	—	2.097(3)	2.106(5), 2.031(6) <sup>a</sup> 2.026(5), 2.102(6) <sup>a</sup>	—
Sn F	—	1.963(4) 1.979(4) 1.979(4)	1.938(5) 1.966(5) 2.754(5)	1.905(3)	—	1.915(2)
Sn...OPEt <sub>3</sub>	—	—	—	—	—	2.026(3)
O-PEt <sub>3</sub>	—	—	—	—	—	1.539(3)
Σ°P (OPEt <sub>3</sub> )	—	—	—	—	—	327.1
<sup>119</sup> Sn{ <sup>1</sup> H} δ	-628.7	-763.6	-556.2	-543.4	-571.1 -582.7 <sup>b</sup>	-543.4 -540.0
<sup>19</sup> F{ <sup>1</sup> H} δ	—	-112.2	-157.9	-164.8	—	-164.8 -158.5
J <sub>SnF</sub> [Hz]	—	1893, 1808	2220	2450	—	2450, 2328 2399, 2292
<sup>31</sup> P{ <sup>1</sup> H} δ	—	—	—	—	91.4 <sup>b</sup>	90.4

<sup>a</sup> Bond distances for the second molecule in the asymmetric unit. <sup>b</sup> Chemical shift for solutions containing two equivalents of OPEt.

[(BIMEt<sub>3</sub>)(OPEt<sub>3</sub>)SnF][OTf]<sub>3</sub> was crystallized from a saturated DCM solution of [(BIMEt<sub>3</sub>)SnF][OTf]<sub>3</sub> in the presence of excess triethylphosphine oxide layered with diethyl ether at -35 °C. The short Sn...OPEt<sub>3</sub> bond (2.026(3) Å) in [(BIMEt<sub>3</sub>)(OPEt<sub>3</sub>)SnF][OTf]<sub>3</sub> (Fig. 3) lies just within the sum of the covalent radii for tin and oxygen (2.03 Å)<sup>15</sup> and is consistent with a significant elongation of the O-P bond (1.539(3) Å) compared to the free phosphine oxide (1.489(2) Å in O-P(<sup>n</sup>Bu)<sub>3</sub>)<sup>16</sup>. This suggests a significant charge delocalization over the Sn-O-P unit. Compared with phosphine oxide adducts of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (P-O 1.4973(17) Å)<sup>17</sup> and B(C<sub>6</sub>H<sub>4</sub>F)<sub>3</sub> (P-O 1.5251(8) Å)<sup>18</sup> this effect is much more pronounced. This contact is in the same order of magnitude as the shortest interaction with a tri-



**Fig. 3** Solid state structure of the cation in [(BIMEt<sub>3</sub>)(OPEt<sub>3</sub>)SnF][OTf]<sub>3</sub>. Thermal ellipsoids are shown at a 50% probability level. Hydrogen atoms, solvent molecules and non-coordinating anions are omitted for clarity. For weakly interacting triflate anions only the coordinating oxygen atoms are shown. Interatomic distances and angles are summarized in Table 1.

flate anion in [(BIMEt<sub>3</sub>)Sn][OTf]<sub>4</sub> (Sn...OTf 2.026(5) or 2.031(6) Å). These Sn-O bonds are significantly shorter than the bis-stannylyne stabilized Sn=O (Sn1-O1 2.079(2) Å), which has been described as a heavier homologue of carbon monoxide and suggests the presence of a very Lewis acidic tin center.<sup>19</sup>

All derivatives of [(BIMEt<sub>3</sub>)SnF<sub>x</sub>][OTf]<sub>4-x</sub> (x = 1-4) have been analyzed by ESI-MS in positive mode under inert conditions.<sup>20</sup> The spectrum of [(BIMEt<sub>3</sub>)SnF<sub>3</sub>][OTf] shows only the expected signal for [(BIMEt<sub>3</sub>)SnF<sub>3</sub>]<sup>+</sup> at m/z = 668 (see ESI Fig. S1†). Spectra of the polycationic species show signals corresponding to complexes with water<sup>21</sup> and one or more triflate anions. The spectrum of [(BIMEt<sub>3</sub>)SnF<sub>2</sub>][OTf]<sub>2</sub> contains a major signal for [(BIMEt<sub>3</sub>)SnF<sub>2</sub>]<sup>2+</sup> (m/z = 325) as well as [(BIMEt<sub>3</sub>)SnF<sub>2</sub>(H<sub>2</sub>O)]<sup>2+</sup>, [(BIMEt<sub>3</sub>)SnF<sub>2</sub>(OTf)]<sup>+</sup>, and [(BIMEt<sub>3</sub>)SnF<sub>3</sub>]<sup>+</sup> (Fig. 4 top). For [(BIMEt<sub>3</sub>)SnF][OTf]<sub>3</sub> the major signals correspond to [(BIMEt<sub>3</sub>)SnF(OTf)]<sup>2+</sup> and [(BIMEt<sub>3</sub>)SnF(OTf)<sub>2</sub>]<sup>+</sup>. Additionally, a signal corresponding to [(BIMEt<sub>3</sub>)SnF<sub>2</sub>]<sup>2+</sup> (Fig. 4 bottom), indicates that fluoride transfer has occurred in the source. Minor signals corresponding to [(BIMEt<sub>3</sub>)SnF]<sup>3+</sup>, [(BIMEt<sub>3</sub>)SnF(H<sub>2</sub>O)]<sup>3+</sup> and [(BIMEt<sub>3</sub>)SnF(CH<sub>3</sub>CN)]<sup>3+</sup> are also observed (Fig. 4 bottom highlighted section). Attempts to detect a signal for the tetracation in [(BIMEt<sub>3</sub>)Sn][OTf]<sub>4</sub> were not successful, but the mass spectrum showed signals for [(BIMEt<sub>3</sub>)Sn(OTf)]<sup>3+</sup> (m/z = 253), indicating that highly charged tin cations engage in significant interactions with triflate anions in solution and in the gas phase. Addition of a small excess of OPEt<sub>3</sub> enabled observation of [(BIMEt<sub>3</sub>)(OPEt<sub>3</sub>)Sn]<sup>2+</sup> (m/z = 372) and [(BIMEt<sub>3</sub>)(OPEt<sub>3</sub>)<sub>2</sub>Sn]<sup>2+</sup> (m/z = 439) (see ESI Fig. S3 and S4†), indicating that the phosphine oxide stabilizes the tetracation during the desolvation process towards fragmentation, but not towards reduction. The mass spectrometric analysis confirms the high Lewis acidity of the complexes thanks to observation of the coordinated water surviving the ESI desolvation process. The appearance of the aggregate ions involving the dication and

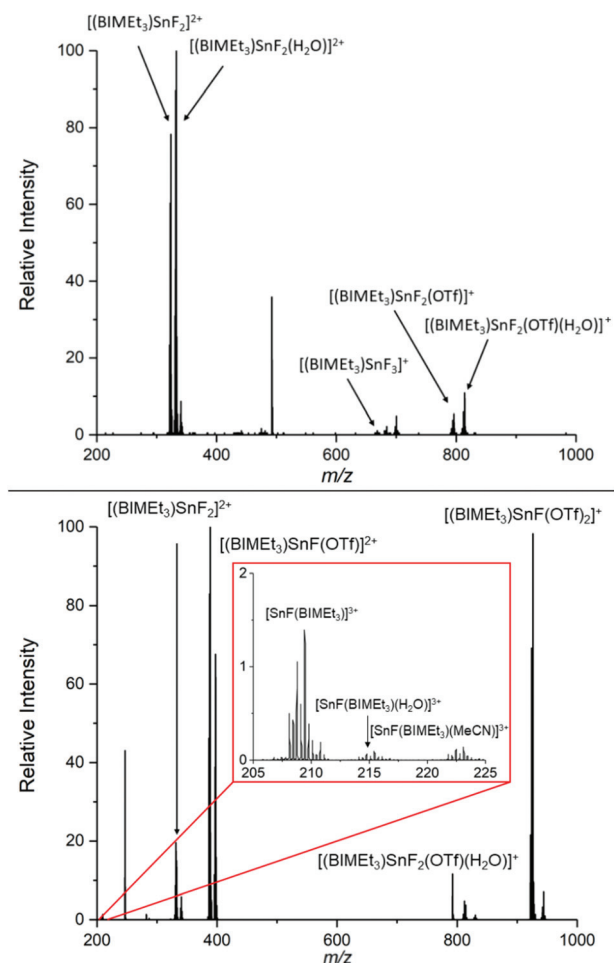


Fig. 4 Positive ion ESI-MS spectrum of  $[(\text{BIMe}_3)\text{SnF}_2][\text{OTf}]_2$  (top) and  $[(\text{BIMe}_3)\text{SnF}][\text{OTf}]_3$  (bottom) in MeCN.

the triflate counterion is a function of the electrostatic attraction between the two, and is a well-known phenomenon in the ESI-MS analysis of dicationic salts with monoanionic ligands.<sup>22</sup>

## Conclusion

A reliable procedure has been developed for the synthesis of coordinatively unsaturated and Lewis acidic tin compounds with the generic formula  $[(\text{BIMe}_3)\text{SnF}_{4-x}][\text{OTf}]_x$  for  $x = 1-4$ . Structural analysis and heteronuclear NMR spectroscopic data indicates that the compounds are ionic. Positive mode ESI mass spectrometric analysis of acetonitrile solutions confirm the existence of the complex cations in the gas phase, including the trication  $[(\text{BIMe}_3)\text{SnF}]^{3+}$  and its water and acetonitrile adducts. As there is no commercially available tin tetracation, this straight forward synthetic approach may allow for an in depth study of such species as Lewis acid catalysts or components for FLPs.

## Experimental

### General considerations

All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in an MBraun Labmaster inert atmosphere dry-box containing an atmosphere of purified nitrogen. THF-*d*<sub>8</sub>, CD<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>D<sub>6</sub> were purchased from Sigma Aldrich. CD<sub>2</sub>Cl<sub>2</sub> was dried over CaH<sub>2</sub> and distilled, THF-*d*<sub>8</sub> and C<sub>6</sub>D<sub>6</sub> were distilled over potassium. All glassware was stored in a 170 °C oven for several hours and was degassed prior to use. Solvents were distilled over the appropriate drying agent. Anhydrous grade MeCN was obtained from Sigma-Aldrich and used without distillation but stored over 3 Å molecular sieves. Solvents were additionally tested using a ketyl test to guarantee oxygen and moisture free conditions. TMSOTf (99%) was distilled before use. BIMe<sub>3</sub><sup>23</sup> was synthesized following literature procedures. NMR tubes were charged and sealed inside the glovebox. <sup>1</sup>H NMR spectra were recorded on Bruker spectrometers operating at 300 MHz, <sup>13</sup>C NMR at 76 MHz, <sup>31</sup>P NMR at 121.6 MHz, <sup>19</sup>F NMR at 282.5 MHz, <sup>119</sup>Sn NMR at 134 MHz. All <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported relative to SiMe<sub>4</sub> using the <sup>1</sup>H (residual) and <sup>13</sup>C chemical shifts of the solvent as a secondary standard. Elemental analysis was performed at the University of Windsor Mass Spectrometry Service Laboratory using a PerkinElmer 2400 combustion CHN analyser. Crystals for investigation were covered in Paratone®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N<sub>2</sub> of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXII (Bruker AXS) software suite on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with MoK<sub>α</sub> ( $\lambda = 0.71073 \text{ \AA}$ ). For each sample, data were collected at low temperature. APEXII software was used for data reductions and SADABS (Bruker AXS) was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX<sup>24</sup> software suite as implemented in the WinGX<sup>25</sup> or OLEX2<sup>26</sup> program suites. Validation of the structures was conducted using PLATON.<sup>27</sup>

For mass spectrometric analysis, a solution was prepared from 1 mg sample dissolved in 3 ml acetonitrile (~30 μM) in a glovebox. This solution was then injected into a Micromass QTOF *micro* spectrometer that had been pre-rinsed with dried acetonitrile for at least 1 hour. PTFE tubing (1/16 in. o.d., 0.005 in. i.d.) were used. A capillary voltage was set at 3000 V with source and desolvation gas temperatures at 80 °C and 185 °C, respectively, with a desolvation gas flow at 400 L h<sup>-1</sup>.

### Synthesis of $[(\text{BIMe}_3)\text{Sn}][\text{OTf}]_2$

SnCl<sub>2</sub> (0.5 mmol, 95 mg) and BIMe<sub>3</sub> (0.5 mmol, 250 mg) were combined in 4 mL of MeCN, TMSOTf (1.5 mmol, 300 μL) was added. The suspension was stirred for two hours to yield a clear light yellow solution. The mixture was then passed through a glass filter to remove unreacted insoluble starting materials and the clear solution was layered with 4 mL of

diethyl ether and placed in the freezer at  $-35\text{ }^{\circ}\text{C}$  for 72 hours. Colourless crystals (312 mg) were isolated from the solution by decanting off the supernatant. The mother liquor was then concentrated and proceeded as before to yield another 56 mg. Yield: 368 mg (81% for  $\text{C}_{32}\text{H}_{33}\text{F}_6\text{N}_7\text{O}_6\text{S}_2\text{Sn}$ ),  $\text{MW} = 909.1\text{ g mol}^{-1}$ .  $\text{MP} = 262\text{ }^{\circ}\text{C}$  (dec.). EA [calc.]: C, 42.31; H, 3.66; N, 10.79; EA [found]: C, 42.54; H, 3.55; N, 10.689;  $^1\text{H NMR}$  (300 MHz,  $\text{CD}_3\text{CN}$ )  $\delta = 8.07\text{--}7.95$  (m, 3H,  $\text{CH}_{\text{arom}}$ ),  $7.69\text{--}7.58$  (m, 3H,  $\text{CH}_{\text{arom}}$ ),  $7.48\text{--}7.35$  (m, 6H,  $\text{CH}_{\text{arom}}$ ),  $4.87$  (s, 6H,  $\text{CH}_2$ ),  $4.28$  (q,  $^3J_{\text{HH}} = 7.33\text{ Hz}$ , 6H,  $\text{CH}_2$ ),  $1.38$  (t,  $^3J_{\text{HH}} = 7.33\text{ Hz}$ , 9H,  $\text{CH}_3$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR (283 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -79.4$ .  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = 152.5$  (s),  $137.5$  (s),  $135.0$  (s),  $124.6$  (s),  $124.3$  (s),  $117.1$  (s),  $111.5$  (s),  $54.4$  (s),  $39.6$  (s),  $13.8$  (s).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (134 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = -628.7$  (s).

#### Attempted oxidation of $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_2$

$[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]$  (0.1 mmol, 97 mg) was dissolved in 4 mL of DCM,  $\text{XeF}_2$  (0.1 mmol, 17 mg) was added at room temperature resulting in a vigorous evolution of xenon gas. Numerous signals were observed in the  $^{19}\text{F}$  NMR spectrum of the reaction mixture.

#### Synthesis of $[(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$

$\text{BIMeEt}_3$  (1.5 mmol, 750 mg) and  $\text{TMSOTf}$  (1.5 mmol, 288  $\mu\text{L}$ ) were mixed in 4 mL of MeCN to give a light yellow solution.  $\text{SnF}_4$  (294 mg, 1.5 mmol) was added. The suspension was stirred for 16 hours at room temperature and a new colourless precipitate was formed. The solid was filtered and washed with diethyl ether, the volatiles were removed under reduced pressure to obtain 1.004 g of a colourless solid. The mother liquor was concentrated and layered with diethyl ether and placed in the freezer at  $-35\text{ }^{\circ}\text{C}$  to obtain another 228 mg. Yield: 1.232 g (96% for  $\text{C}_{31}\text{H}_{33}\text{F}_6\text{N}_7\text{O}_3\text{SSn-MeCN}$ ),  $\text{MW} = 857.5\text{ g mol}^{-1}$ ,  $\text{MP} = 242\text{ }^{\circ}\text{C}$  (dec.), EA [calc.]: C, 46.22; H, 4.23; N, 13.07; EA [found]: C, 46.72; H, 4.51; N, 12.99.  $^1\text{H NMR}$  (300 MHz,  $\text{CD}_3\text{CN}$ )  $\delta = 8.60\text{--}8.70$  (m, 3H),  $7.55\text{--}7.75$  (m, 3H),  $7.35\text{--}7.55$  (m, 6H),  $4.62$  (s, 6H),  $4.28$  (q,  $J = 7.33\text{ Hz}$ , 6H),  $1.39$  (t,  $J = 7.33\text{ Hz}$ , 9H).  $^{19}\text{F}\{^1\text{H}\}$  NMR (283 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -79.34$  (OTf)  $-112.2$  (s,  $J_{\text{SnF}} = 1893.4$  and  $1807.9\text{ Hz}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = 150.9$  (s),  $136.9$  (s),  $134.3$  (s),  $124.7$  (s),  $124.2$  (s),  $121.0$  (broad-s),  $110.3$  (s),  $49.2$  (s,  $\text{CH}_2$ ),  $39.2$  (s,  $\text{CH}_2$ ),  $13.5$  (s,  $\text{CH}_3$ ).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (134 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = -763.6$  (q,  $J_{\text{SnF}} = 1895\text{ Hz}$ ).

#### Synthesis of $[(\text{BIMeEt}_3)\text{SnF}_2][\text{OTf}]_2$

$[(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$  (0.25 mmol, 204 mg) and  $\text{TMOSTf}$  (0.25 mmol, 48  $\mu\text{L}$ ) were mixed in 4 mL of DCM stirring for 15 minutes at room temperature yielded a colourless solution, the mixture was filtered through a glass filter pipette and the reaction mixture was layered with 4 mL of diethyl ether and was placed in the freezer at  $-35\text{ }^{\circ}\text{C}$  for 16 h. The colourless precipitate was filtered off and washed with ether and was dried under reduced pressure to isolate 170 mg. The mother liquor was concentrated layered again with diethyl ether and placed in the freezer to isolate another 34 mg of solid. Total yield: 204 mg (77% for  $\text{C}_{32}\text{H}_{33}\text{F}_8\text{N}_7\text{O}_6\text{S}_2\text{Sn}(\text{DCM})_{1.5}$ ),

$\text{MW} = 1073.9\text{ g mol}^{-1}$ ,  $\text{MP} = 270\text{ }^{\circ}\text{C}$  (dec.), EA [calc.]: C, 37.47; H, 3.38; N, 9.90; EA [found]: C, 37.32; H, 3.25; N, 9.34.  $^1\text{H NMR}$  (300 MHz,  $\text{CD}_3\text{CN}$ )  $\delta = 8.00\text{--}8.20$  (m, 3H),  $7.65\text{--}7.80$  (m, 3H),  $7.45\text{--}7.65$  (m, 6H),  $5.34$  (s, 6H),  $4.31$  (q,  $J = 7.36\text{ Hz}$ , 6H),  $1.43$  (t,  $J = 7.36\text{ Hz}$ , 9H).  $^{19}\text{F}\{^1\text{H}\}$  NMR (283 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -79.34$  (OTf)  $-157.7$  (s broad,  $J_{\text{SnF}} = 2220\text{ Hz}$ ),  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = 149.9$  (s),  $135.7$  (s),  $135.0$  (s),  $127.7$  (s),  $127.5$  (s),  $116.8$  (broad-s),  $113.7$  (s),  $58.1$  (s,  $\text{CH}_2$ ),  $41.7$  (s,  $\text{CH}_2$ ),  $14.4$  (s,  $\text{CH}_3$ ).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (134 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = -556.2$  (t,  $J_{\text{SnF}} = 2223\text{ Hz}$ ). Single crystals suitable for X-ray diffraction analysis were grown from a saturated acetonitrile solution layered with diethyl ether, stored at  $-35\text{ }^{\circ}\text{C}$  for one week.

#### Synthesis of $[(\text{BIMeEt}_3)\text{SnF}][\text{OTf}]_3$

$[(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$  (0.25 mmol, 204 mg) and  $\text{TMOSTf}$  (0.5 mmol, 96  $\mu\text{L}$ ) were mixed in 4 mL of DCM stirring for 15 minutes at room temperature yielded a colourless solution, the mixture was filtered through a glass filter pipette and the reaction mixture was concentrated to roughly 2 mL and was layered with 4 mL of diethyl ether and was placed in the freezer at  $-35\text{ }^{\circ}\text{C}$  for 16 h. The colourless precipitate was filtered off and washed with ether and was dried under reduced pressure to isolate 230 mg. Total yield: 230 mg (83% for  $\text{C}_{33}\text{H}_{33}\text{F}_{10}\text{N}_7\text{O}_9\text{S}_3\text{Sn}$ ),  $\text{MW} = 1077.0\text{ g mol}^{-1}$ ,  $\text{MP} = 258\text{ }^{\circ}\text{C}$  (dec.), EA [calc.]: C, 36.82; H, 3.09; N, 9.11; EA [found]: C, 36.22; H, 2.89; N, 8.83;  $^1\text{H NMR}$  (300 MHz,  $\text{CD}_3\text{CN}$ )  $\delta = 8.05\text{--}8.25$  (m, 3H),  $7.70\text{--}7.90$  (m, 3H),  $7.50\text{--}7.70$  (m, 6H),  $5.53$  (s, 6H,  $J_{\text{SnH}} = 26.9\text{ Hz}$ ),  $4.38$  (q,  $J = 7.36\text{ Hz}$ , 6H),  $1.45$  (t,  $J = 7.36\text{ Hz}$ , 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = 149.7$  (s),  $135.7$  (s),  $134.6$  (s),  $128.1$  (s),  $128.0$  (s),  $116.8$  (d,  $J = 4.4\text{ Hz}$ ),  $114.0$  (s),  $58.8$  (s,  $\text{CH}_2$ ),  $42.0$  (s,  $\text{CH}_2$ ),  $14.3$  (s,  $\text{CH}_3$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR (283 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -79.34$  (OTf)  $-164.8$  (s,  $J_{\text{SnF}} = 2450.0\text{ Hz}$  and  $J_{\text{SnF}} = 2328.0\text{ Hz}$ )  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (134 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = -543.4$  (d,  $J_{\text{SnF}} = 2450$ ).

#### Synthesis of $[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_4$

$[(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$  (0.25 mmol, 204 mg) and  $\text{TMOSTf}$  (2 mmol, 400  $\mu\text{L}$ ) were mixed in 1 mL of DCM stirring for 15 minutes at room temperature yielded a colourless solution, the mixture was filtered through a glass filter pipette and was stirred under dynamic vacuum for 2 hours to drive off  $\text{TMSF}$ . The colourless oily residue was triturated with diethyl ether. The product was dried under reduced pressure to isolate a colourless solid. The product was recrystallized from MeCN layered with diethyl ether to yield a crystalline solid suitable for X-ray diffraction analysis. Total yield: 192 mg (63% for  $\text{C}_{34}\text{H}_{33}\text{F}_{12}\text{N}_7\text{O}_{12}\text{S}_4\text{Sn}$ ),  $\text{MW} = 1206.6\text{ g mol}^{-1}$ ,  $\text{MP} = 94\text{ }^{\circ}\text{C}$  (dec.), EA [calc.]: C, 33.84; H, 2.76; N, 8.13; EA [found]: C, 34.23; H, 2.92; N, 7.88;  $^1\text{H NMR}$  (300 MHz,  $\text{CD}_3\text{CN}$ )  $\delta = 8.0\text{--}8.16$  (m, 3H,  $\text{CH}_{\text{arom}}$ ),  $7.75\text{--}7.90$  (m, 3H,  $\text{CH}_{\text{arom}}$ ),  $7.65$  (ddt,  $J = 1.8, 12.3, 7.4\text{ Hz}$ , 6H),  $5.63$  (s,  $^3J_{\text{SnH}} = 30.9\text{ Hz}$ , 6H,  $\text{CH}_2$ ),  $4.41$  (q,  $J = 7.4\text{ Hz}$ , 6H,  $\text{CH}_2$ ),  $1.45$  (t,  $J = 7.4\text{ Hz}$ , 9H,  $\text{CH}_3$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR (283 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -78.18$  (OTf).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = 148.6$  (s),  $134.4$  (s),  $133.2$  (s),  $127.1$  (s),  $127.0$  (s),  $115.3$  (s),  $113.0$  (s),  $57.1$  (s,  $\text{CH}_2$ ),  $41.0$  (s,  $\text{CH}_2$ ),  $13.0$  (s,  $\text{CH}_3$ ).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (134 MHz  $\text{CD}_3\text{CN}$ ):  $\delta = -571.1$  (s). The tetra-tri-

flate salt slowly decomposes in MeCN to form the protonated ligand  $[\text{BIMeEt}_3\text{H}]^+$ .

### Synthesis of $[(\text{BIMeEt}_3)(\text{OPEt}_3)\text{SnF}][\text{OTf}]_3$

$[(\text{BIMeEt}_3)\text{SnF}_3][\text{OTf}]$  (0.25 mmol, 204 mg) and TMOSTF (0.5 mmol, 100  $\mu\text{L}$ ) were mixed in 4 mL of DCM stirring for 15 minutes at room temperature yielded a colourless solution, the mixture was filtered through a glass filter pipette and  $\text{OPEt}_3$  (0.25 mmol, 34 mg) was added as a solid. The solution was stirred again for 15 min and was then layered with 4 mL of diethyl ether before it was placed in the freezer at  $-35\text{ }^\circ\text{C}$  for 16 h. The colourless precipitate was filtered off and washed with ether and was dried under reduced pressure to isolate 167 mg. The same batch yielded single crystals suitable for X-ray diffraction analysis. The mother liquor was concentrated layered again with ether and placed in the freezer to isolate another 64 mg of solid. Total yield: 231 mg (74% for  $\text{C}_{39}\text{H}_{48}\text{F}_{10}\text{N}_7\text{O}_{10}\text{PS}_3\text{Sn}$ ), MW = 1211.12  $\text{g mol}^{-1}$ , MP = 222  $^\circ\text{C}$  (dec.), EA [calc.]: C, 38.69; H, 4.00; N, 8.10; EA [found]: C, 37.78; H, 3.93; N, 7.88;  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  = 8.0–8.21 (m, 3H,  $\text{CH}_{\text{arom}}$ ), 7.70–7.90 (m, 3H,  $\text{CH}_{\text{arom}}$ ), 7.50–7.70 (m, 6H,  $\text{CH}_{\text{arom}}$ ), 5.58 (s, 6H,  $\text{CH}_2$ ), 4.39 (s, 6H,  $\text{CH}_2$ ), 1.80–2.00 (m, overlaps with MeCN,  $\text{CH}_2$ , 6H), 1.34–1.64 (m, 9H,  $\text{CH}_3$ ), 0.65 (td,  $J$  = 7.7, 19.2 Hz, 9H,  $\text{CH}_3$ )  $^{19}\text{F}\{^1\text{H}\}$  NMR (283 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  =  $-79.3$  (OTf),  $-158.53$  (s,  $J_{\text{SnF}}$  = 2399.0 Hz,  $J_{\text{SnF}}$  = 2292.4 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.6 MHz  $\text{CD}_3\text{CN}$ ):  $\delta$  = 90.4 (d,  $J_{\text{PF}}$  = 3.8,  $J_{\text{SnP}}$  = 142.9 Hz),  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz  $\text{CD}_3\text{CN}$ ):  $\delta$  = 148.3 (s), 134.5 (s), 133.1 (s), 127.0 (s), 126.7 (s), 115.1 (s), 112.9 (s), 57.3 (s,  $\text{CH}_2$ ), 40.8 (s,  $\text{CH}_2$ ), 17.0 (d,  $J_{\text{PC}}$  = 65.9 Hz), 13.0 (s,  $\text{CH}_3$ ) 3.7 (d,  $J_{\text{PC}}$  = 4.9 Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (134 MHz  $\text{CD}_3\text{CN}$ ):  $\delta$  =  $-540.0$  (dd,  $J_{\text{SnF}}$  = 2399.0,  $J_{\text{SnP}}$  = 142.9 Hz).

### In situ formation of $[(\text{BIMeEt}_3)(\text{OPEt}_3)_2\text{Sn}][\text{OTf}]_4$

$[(\text{BIMeEt}_3)\text{Sn}][\text{OTf}]_4$  (0.03 mmol, 38 mg) was dissolved in 0.5 mL of  $\text{CD}_2\text{Cl}_2$  and  $\text{OPEt}_3$  (0.07 mmol, 9 mg) was added as a solid.  $^{19}\text{F}\{^1\text{H}\}$  NMR (283 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  =  $-79.3$  (OTf).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.6 MHz  $\text{CD}_3\text{CN}$ ):  $\delta$  = 91.5 (s, broad)  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz  $\text{CD}_3\text{CN}$ ):  $\delta$  = 150.0 (s), 149.9 (s), 135.5 (s), 135.4 (s), 134.4 (s), 134.0 (s), 127.6 (s), 127.4 (s), 126.8 (s), 125.6 (s), 116.8 (s), 116.6 (s), 113.4 (s), 112.9 (s), 59.2 (s,  $\text{CH}_2$ ), 58.8 (s,  $\text{CH}_2$ ), 42.2 (s,  $\text{CH}_2$ ), 41.7 (s,  $\text{CH}_2$ ), 17.9 (d,  $J_{\text{PC}}$  = 62.7 Hz), 5.22 (d,  $J_{\text{PC}}$  = 5.5 Hz)  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (134 MHz  $\text{CD}_3\text{CN}$ ):  $\delta$  =  $-582.7$  (d,  $J_{\text{SnP}}$  = 145.2 Hz).

CCDC 1822446, 1833324, 1835099, 1835100, 1835101 and 1869786 contain the supplementary crystallographic data for this paper.†

## Conflicts of interest

There are no conflicts to declare.

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