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Cationic Brønsted Acids for the Preparation of Sn^{IV} Salts: Synthesis and Characterisation of $[Ph_3Sn(OEt_2)][H_2N\{B(C_6F_5)_3\}_2]$, $[Sn(NMe_2)_3(HNMe_2)_2][B(C_6F_5)_4]$ and $[Me_3Sn(HNMe_2)_2][B(C_6F_5)_4]$

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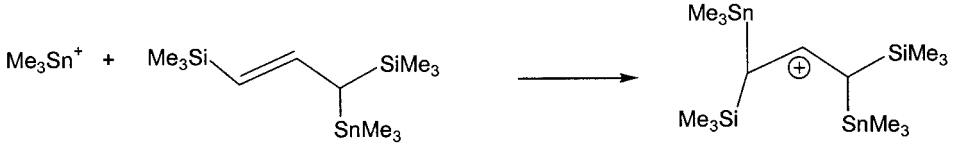
Keywords: Tin / Cations / N ligands / Anions

$Ph_3SnN(SiMe_3)_2$ (**1**) was prepared in good yields by reaction of $[\{NaN(SiMe_3)_2\}_2{\cdot}THF]$ (**2**) with Ph_3SnF. Treatment of **1** with $[H(OEt_2)_2][H_2N\{B(C_6F_5)_3\}_2]$ (**4**) in dichloromethane afforded the stannylium cation $[Ph_3Sn(OEt_2)][H_2N\{B(C_6F_5)_3\}_2]$ (**5**), which was characterised by ^1H, $^{13}C\{^1H\}$, ^{11}B, ^{19}F and ^{119}Sn NMR spectroscopy. The reaction of $Sn(NMe_2)_4$ with $[Ph_2MeNH][B(C_6F_5)_4]$ (**3**) gave the amidotin(IV) compound $[Sn(NMe_2)_3(HNMe_2)_2][B(C_6F_5)_4]$ (**6**) which proved very stable towards ligand substitution and resisted treatment with Et_2O, THF, TMEDA and pyrazine. Two new Brønsted acid salts $[H(NMe_2H)_2][B(C_6F_5)_4]$ (**7**) and $[(C_4H_4N_2)H{\cdot}OEt_2][H_2N\{B(C_6F_5)_3\}_2]$ (**8**) were synthesised. The reaction of **7** with $Sn(NMe_2)_4$ in Et_2O allowed the preparation of **6** in a much improved yield (83 %). The treatment of **7** with $Me_3SnN(SiMe_3)_2$ in Et_2O yielded $[Me_3Sn(HNMe_2)_2][B(C_6F_5)_4]$ (**9**) nearly quantitatively. Compounds **1**, **2**, **6**, **8** and **9** were characterised by single-crystal X-ray diffraction analyses; **6** is the first example of a structurally characterised amidotin(IV) cation.

Introduction

Organotin(IV) compounds have long attracted interest due to their reactivity, their industrial applications and their intriguing biological activity.[1,2] In particular, organotin(IV) cations are thought to play an essential part in the cytotoxicity of organotin compounds[3] or in their catalytic activity for esterification reactions,[4] and the search for stable examples of Sn^{IV} cations was initiated over half a century ago.[5–19] However, to this date only few cationic complexes of tin have been isolated. Even though in the past decade or so fundamental breakthroughs have been achieved where tin cations free of donor atoms have been characterised in the solid state,[20–25] stannylium cations stabilised by donor heteroatoms appear to be more readily accessible.[2] For instance, cationic tin species stabilised by a Y,C,Y-chelating pincer-type ligand (where Y is an heteroatom such as oxygen or nitrogen) have been prepared very successfully in the past 15 years.[26–32] The utilisation of N,C,N-coordinating ligands has even enabled the preparation of air-stable organotin cations.[33,34] Our interest in the chemistry of cationic tin species is based on our recent isolation of a thermally remarkably stable sec-alkyl carbocation that was generated by the attack of a Me_3Sn^+ intermediate on a suitably substituted propene (Scheme 1).[35,36]



Scheme 1. Involvement of Me_3Sn^+ in the formation of a tin-stabilised carbocation.

This prompted us to investigate the chemistry of cationic tin species in more detail. We report here the reactions of a number of tin amides with cation-generating agents. To the best of our knowledge, simple Sn^{IV}-amide precursors have never been employed efficiently for this purpose.

A convenient way of generating cationic metal species is the reaction of protolysis-sensitive metal complexes with

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Brønsted acidic salts of very weakly coordinating anions. For example, the oxonium ions $[H(L)_x]^+$ [L = Et_2O, THF, x = 2; L = $(MeC{=}NC_6H_3\text{-}iPr_2\text{-}2,6)_2$, x = 1] as salts of perfluorinated anions have been synthesised and used with great success in recent years;[37–43] we have shown that they can be applied as a very clean way to abstract alkyl, alkoxy and amido groups from various metals such as Mg, Zr, Zn or Cd.[43–47] For instance, the reactions of ZnR_2 [R = C_6F_5, Me, Et, $N(SiMe_3)_2$], MgR_2 [R = Bu, $N(SiMe_3)_2$], or $Cp_2Zr(O\text{-}iPr)_2$ with $[H(OEt_2)_2]^+[X]^-$ [X = $H_2N\{B(C_6F_5)_3\}_2$ or $B(C_6F_5)_4$] allowed the characterisation of, respectively, $[(Et_2O)_3ZnR][X]$,[44–45] $[(Et_2O)_3MgR][X]$[45] and $[Cp_2Zr(O\text{-}iPr)(HO\text{-}iPr)][X]$.[46] In addition, the anilinium salts $[PhNMe_2H][B(C_6F_5)_4]$ and $[Ph_2NMeH][B(C_6F_5)_4]$ have long been known and used as activating agents in olefin-polymerisation catalysis.[48–49]

As part of our ongoing studies on the preparation and the reactivity of main-group element cations,[43–45,47,50] we describe here the preparation and reactions of the stannylium compounds $[Ph_3Sn(OEt_2)][H_2N\{B(C_6F_5)_3\}_2]$, $[Sn(NMe_2)_3(HNMe_2)_2][B(C_6F_5)_4]$ and $[Me_3Sn(HNMe_2)_2]$-$[B(C_6F_5)_4]$. The structures of $[\{NaN(SiMe_3)_2\}_2{\cdot}THF]$, $Ph_3SnN(SiMe_3)_2$ and $[(C_4H_4N_2)H{\cdot}OEt_2][B(C_6F_5)_4]$ are also presented.

Results and Discussion

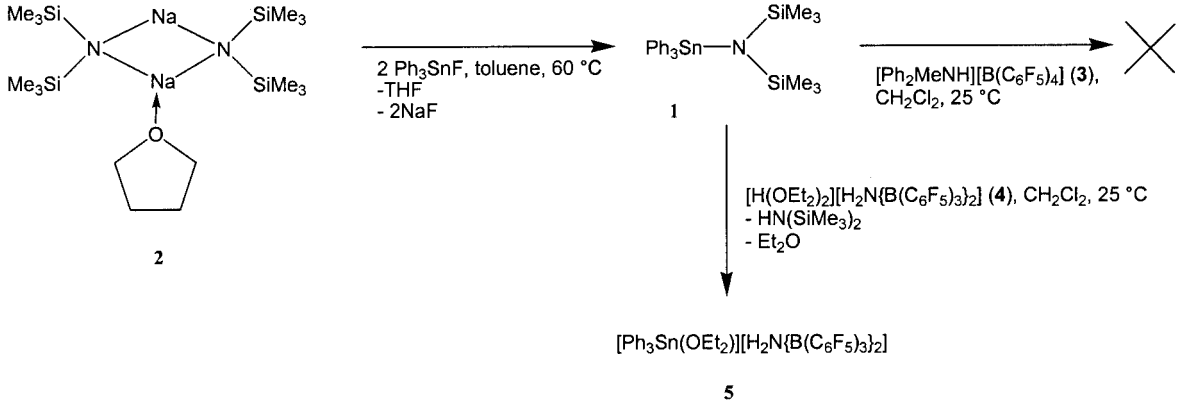
Synthesis and Structure of $Ph_3SnN(SiMe_3)_2$

First attempts to generate a sterically relatively unencumbered stannyl cation involved the reaction of $Ph_3SnN(SiMe_3)_2$ (**1**) with one equiv. of $[Ph_2MeNH][B(C_6F_5)_4]$ (**3**). Compound **1** is conveniently accessible from Ph_3SnF and 0.5 equiv. of $[\{NaN(SiMe_3)_2\}_2{\cdot}THF]$ (**2**) in hot toluene (Scheme 2). The ^{119}Sn NMR spectrum of **1** exhibited a single peak at δ –106.4 ppm, i.e. there was a noticeable highfield shift of ca. 145–185 ppm when compared to other known $R_3Sn{-}NR'_2$ trialkyltin amides.[1] **1** is very soluble both in polar (CH_2Cl_2, Et_2O, THF) and non-polar (toluene, light petroleum) organic solvents.

Crystals of **1** suitable for X-ray diffraction crystallography were isolated as large colourless blocks by recrystallisation from a concentrated toluene solution stored at –26 °C. The tin atom in **1** has a tetrahedral coordination geometry, while the nitrogen atom is trigonal planar coordinated. A view of a molecule of **1** is depicted in Figure 1. Viewed down the N(4)–Sn bond, the N(4)–Si(5) bond eclipses the Sn–C(11) bond. The Si(5)–N(4)–Sn–C(11) torsion angle is 0.8(4)°. The Sn–C(11), Sn–C(21) and Sn–C(31) bond lengths in **1** of 2.149(6), 2.154(6) and 2.114(6) Å, respectively, are typical of Sn^{IV}–aryl bonds.[31–32,51] The Sn–N(4) bond is 2.060(5) Å, i.e. greater than the two Sn–N bond lengths reported for $(Me_2N)_2Sn(O\text{-}2,6\text{-}tBu_2\text{-}C_6H_3)_2$ [1.980(4) and 1.997(4) Å][52] and the Sn–NMe_2 bond length [2.013(3) Å] found in $\{(2,2,6,6\text{-}Me_4C_5H_6N){-}P{=}C(SiMe_3)\}$-$Sn\{NMe_2\}\{N(SiMe_3)_2\}_2$,[53] but comparable to the two Sn–$N(SiMe_3)_2$ bond lengths [2.070(2) and 2.080(2) Å] also identified in the latter compound. In the crystal packing, there is no stacking of parallel phenyl rings; instead, the principal packing features are those of hydrogen atoms (both of phenyl and methyl groups) pointing into the centre of phenyl rings, and of methyl–methyl interactions.

During the course of this work large crops of the crystalline sodium amide **2** were obtained fortuitously from a concentrated light petroleum solution stored at –26 °C. The molecular structure of **2** was determined and, interestingly, confirmed the presence of only 0.5 molecules of THF per sodium atom.

The molecule of **2** contains a Na_2N_2 ring with a C_2 axis passing through the two sodium atoms (Figure 2). Na(1) is bound only to the two bridging nitrogen atoms, whereas Na(2) is coordinated to the same N atoms as well as to one THF ligand. Examination of the region on the "open" side of Na(1) shows its closest neighbours to be two C(21) methyl groups of neighbouring molecules, with Na(1)···C(21′′) and Na(1)···C(21′′′) distances of 3.104(6) Å; the closest H atoms are the H(21c) atoms of these methyl groups, at 2.61 Å. The shortest distances between the methyl groups (about the twofold symmetry axis) are: C(21′′)···C(21′′′) 3.756(9), H(21b′′)···H(21b′′′) 2.62, and H(21b′′)···H(21c′′′) 2.79 Å. Because the contact distance between two hydrogen atoms is ca. 2.4 Å, there is negligible space for any other atom or group in this region; the methyl groups cover this 'open' side of Na(1). There are other short



Scheme 2. Synthesis of $Ph_3SnN(SiMe_3)_2$ (**1**) and its subsequent reactions with Brønsted acids $[Ph_2MeNH][B(C_6F_5)_4]$ (**3**) and $[H(OEt_2)_2][H_2N\{B(C_6F_5)_3\}_2]$ (**4**).

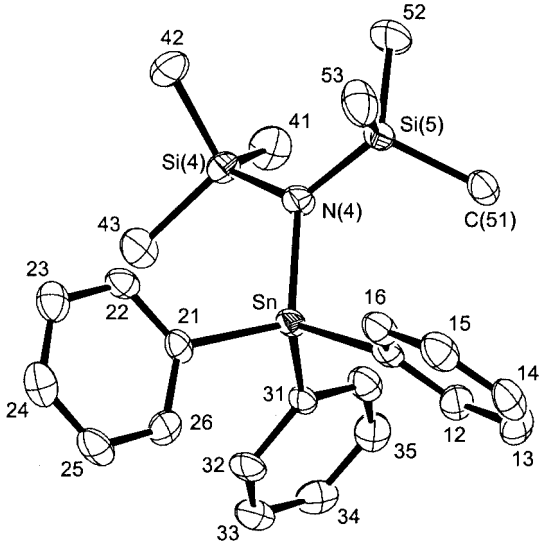


Figure 1. View of a molecule of **1**, indicating the atom numbering scheme; atoms labelled '*n*' represent the carbon atoms C(*n*). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Sn–C(11) 2.149(6), Sn–C(21) 2.154(6), Sn–C(31) 2.114(6), Sn–N(4) 2.060(5), N(4)–Si(4) 1.738(5), N(4)–Si(5) 1.743(5); C(11)–Sn–C(21) 102.5(2), C(31)–Sn–C(11) 109.5(2), C(31)–Sn–C(21) 114.0(2), N(4)–Sn–C(11) 112.9(2), N(4)–Sn–C(21) 112.8(2), N(4)–Sn–C(31) 105.3(2).

Na···H contacts of similar distance in this structure, viz. Na(1)···H(12a) 2.62, Na(1)···H(12c) 2.64 and Na(2)···H(22a) 2.66 Å. There are also Me···Me contacts between each of these C(21) groups and methyl groups of the Na(1) complex, e.g. H(12a)···H(21b′) 2.76 Å, H(21a)···H(21a′) 2.80 Å and H(11c)···H(21a′) 2.73 Å. These contacts effectively shield Na(1) from approach by any other ligand. The arrangement around Na(2) is trigonal planar, while each of the two nitrogen atoms are in a slightly distorted tetrahedral environment. The two N–Na(1)–N and N–Na(2)–N angles are almost identical [99.7(2)° and 99.0(2)°, respectively]. The presence of a THF molecule coordinated to Na(2) has very little influence on the N–Na(2) distance, because the N–Na(1) bond length of 2.388(5) Å is only marginally shorter than the 2.400(5) Å found for N–Na(2). It is remarkable that despite the presence of a unique molecule of THF in the dimeric **2**, all bond lengths and angles correspond closely to those already reported for the bis-THF adduct [{$NaN(SiMe_3)_2$}$_2$·2THF].[54] For instance, the N–Na(1), N–Na(2) and Na(2)–O(3) bond lengths of 2.388(5), 2.400(5) and 2.285(6) Å, respectively in **2** compare very well with the Na(1)–N(1) and Na(1)–O(1) lengths of 2.399 and 2.267 Å given for [{$NaN(SiMe_3)_2$}$_2$·2THF], and the N–Na(2)–N in **2** [99.0(2)°] is very close to the 101.7° found for N(1)–Na(1)–N(1) in the bis-THF adduct.

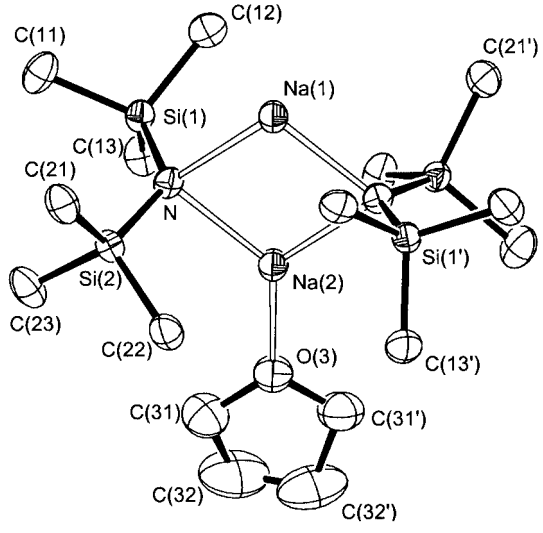


Figure 2. View of a molecule of [{$NaN(SiMe_3)_2$}$_2$·THF] (**2**), indicating the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Na(1)–N 2.388(5), Na(2)–N 2.400(5), Na(2)–O(3) 2.285(6), N–Si(1) 1.696(5), N–Si(2) 1.688(6); N–Na(1)–N′ 99.7(2), N–Na(2)–N′ 99.0(2), N–Na(2)–O(3) 130.5(1).

Synthesis of [$Ph_3Sn(OEt_2)$][$H_2N\{B(C_6F_5)_3\}_2$] (5)

Treatment of **1** with an equimolar amount of [$H(OEt_2)_2$]-[$H_2N\{B(C_6F_5)_3\}_2$][38] (**4**) in dichloromethane yielded a viscous oil, from which a fine white powder was obtained upon repeated washing with light petroleum. NMR spectroscopic data of this solid were consistent with the formulation [$Ph_3Sn(OEt_2)$][$H_2N\{B(C_6F_5)_3\}_2$] (**5**), and the composition was confirmed by elemental analysis. Compound **5** is very soluble in chlorinated solvents and diethyl ether, but is only sparingly soluble in toluene and insoluble in light petroleum. The ^{119}Sn NMR resonance for **5** was found at δ –76.0 ppm, i.e. at much higher field than reported for the free ions (mesityl)$_3Sn^+$ (δ +806 ppm)[21] and (2,4,6-triisopropylphenyl)$_3Sn^+$ (δ +714 ppm).[23] All attempts to determine the molecular structure of **5** proved unsuccessful, possibly due to its high air- and moisture-sensitivity. It was not possible to remove the coordinated Et_2O molecule, even upon heating under vacuum.

Attempts to generate a stannyl cation free of coordinating ether by reacting **1** with [Ph_2MeNH][$B(C_6F_5)_4$] (**3**) in dichloromethane at room temperature gave dark blue mixtures from which no tractable material could be isolated.

Synthesis, Characterisation and Reactivity of [$Sn(NMe_2)_3$-$(HNMe_2)_2$][$B(C_6F_5)_4$] (6), [$H(HNMe_2)_2$][$B(C_6F_5)_4$] (7) and [$(C_4H_4N_2)H\cdot OEt_2$][$H_2N\{B(C_6F_5)_3\}_2$] (8)

To the best of our knowledge simple amidotin(IV)–amide complexes have never been used for the preparation of organotin cations, and it prompted us to investigate the potential of these simple precursors for such purposes.

The sterically very hindered amide $MeSn[N(SiMe_3)_2]_3$ was treated with the cation-generating agents **3**, **4**, [Ph_3C][$H_2N\{B(C_6F_5)_3\}_2$] or $B(C_6F_5)_3$ in dichloromethane. However, none of these reactions proceeded to give the expected organotin cations, but instead the starting material $MeSn[N(SiMe_3)_2]_3$ was recovered in all cases.[55]

By contrast, the less encumbered $Sn(NMe_2)_4$ can be employed effectively for reactions with Brønsted acids. On addition of one equiv. of $Sn(NMe_2)_4$ to a colourless solution of **3** in dichloromethane, a pale yellow, slightly cloudy solution was obtained (Scheme 3, Method A). The crude product was isolated as a viscous yellow oil. Attempts to purify the compound adequately with light petroleum failed. Nevertheless, crystals were grown from a concentrated dichloromethane solution, and crystallographic studies carried out on these colourless plates indicated the structure $[Sn(NMe_2)_3(HNMe_2)_2][B(C_6F_5)_4]$ (**6**), with two molecules of dimethylamine coordinated to the metal centre. Elemental analysis and NMR characterisation were in agreement with the proposed structure. The ^1H NMR spectrum displayed a single sharp singlet for all methyl groups at δ 2.76 ppm, while the N–H protons gave rise to a broad singlet centred at δ 3.25 ppm. Whereas in the ^{119}Sn NMR spectrum the starting material $Sn(NMe_2)_4$ exhibited a resonance at δ –122.4 ppm, the peak for **6** was high-field shifted by about 190 ppm, to δ –311.4 ppm. The borate anion showed an ^{11}B NMR signal at δ –13.6 ppm, while the ^{19}F NMR resonances at δ –133.4, –160.6 and –166.1 ppm are typical of a noncoordinated borate. Compound **6** is highly soluble in diethyl ether, THF and dichloromethane, moderately soluble in toluene and insoluble in light petroleum. It is very air- and moisture-sensitive, but is thermally stable for periods of weeks at room temperature, and does not show any sign of deterioration upon prolonged exposure to light.

The structure of the $[Sn(NMe_2)_3(HNMe_2)_2]^+$ cation ($\mathbf{6^+}$) is shown in Figure 3. The complex is trigonal-bipyramidal, with the two dimethylamine ligands *trans* to one another [angle N(11)–Sn–N(12) 176.0(2)°; angle sum for N_{eq}–Sn–N_{eq} 360.0°]. The Sn–N distances to the axial $HNMe_2$ ligands [Sn–N(11) 2.382(7), Sn–N(12) 2.321(7) Å] are substantially longer than those to the equatorial amido groups [Sn–N(13) 2.013(7) Å, Sn–N(14) 2.005(6) and Sn–N(15) 1.990(7) Å]. The average Sn–N_{eq} length in $\mathbf{6^+}$ (2.003 Å) is somewhat shorter than the average Sn–N_{eq} length of 2.038 Å found in the geometrically comparable neutral complex $Me_2NSn(MeNCH_2CH_2N)_3N$,[56] which presumably reflects the influence of the positive charge on the metal centre in $\mathbf{6^+}$. To the best of our knowledge, **6** is the first example of a structurally characterised five-coordinate amido Sn^{IV}-cation paired with a noncoordinating counteranion.

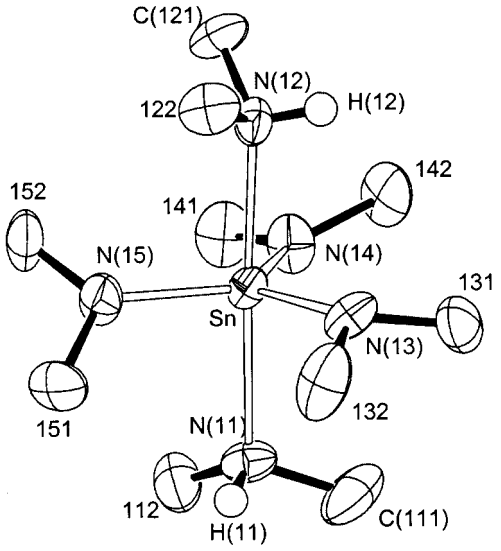
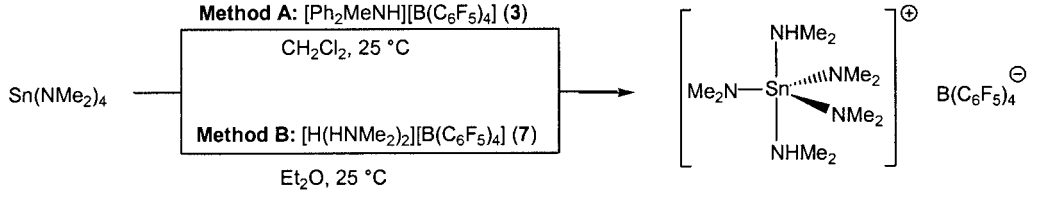


Figure 3. View of the $[Sn(NMe_2)_3(HNMe_2)_2]^+$ cation ($\mathbf{6^+}$), indicating the atom numbering scheme. Atoms labelled 'n' represent the carbon atoms C(n). Hydrogen atoms (except for the amino H atoms) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Sn–N(11) 2.382(7), Sn–N(12) 2.321(7), Sn–N(13) 2.013(7), Sn–N(14) 2.005(6), Sn–N(15) 1.990(7); N(12)–Sn–N(11) 176.0(2), N(13)–Sn–N(11) 91.4(3), N(14)–Sn–N(11) 90.4(3), N(15)–Sn–N(11) 89.9(3), N(13)–Sn–N(12) 84.6(3), N(14)–Sn–N(12) 92.1(3), N(15)–Sn–N(12) 91.5(3), N(14)–Sn–N(13) 120.8(3), N(15)–Sn–N(13) 118.7(3), N(15)–Sn–N(14) 120.5(3).

The preparation described above gave **6** in low yield (24% based on Sn). Consequently, a more economical route was developed, which consisted of protonating $Sn(NMe_2)_4$ while at the same time offering a second molecule of dimethylamine (Scheme 3, Method B). For this purpose, the new Brønsted acid $[H(HNMe_2)_2][B(C_6F_5)_4]$ (**7**) was prepared. The low basicity of $NMePh_2$ compared to that of $HNMe_2$ was exploited for the nearly-quantitative synthesis of **7** (Scheme 4, top). Thus, the straightforward reaction of **3** with a large excess of $HNMe_2$ in diethyl ether at room temperature yielded a white solid after removal of the volatiles. Upon thorough washing with light petroleum, a fine white powder was obtained, and the composition of **7** was confirmed by elemental analysis and NMR spectroscopy. In the ^1H NMR spectrum (in CD_2Cl_2), all four methyl groups appear as a sharp singlet at δ 2.61 ppm, while the three N–H protons are equivalent and give rise to a sharp singlet at



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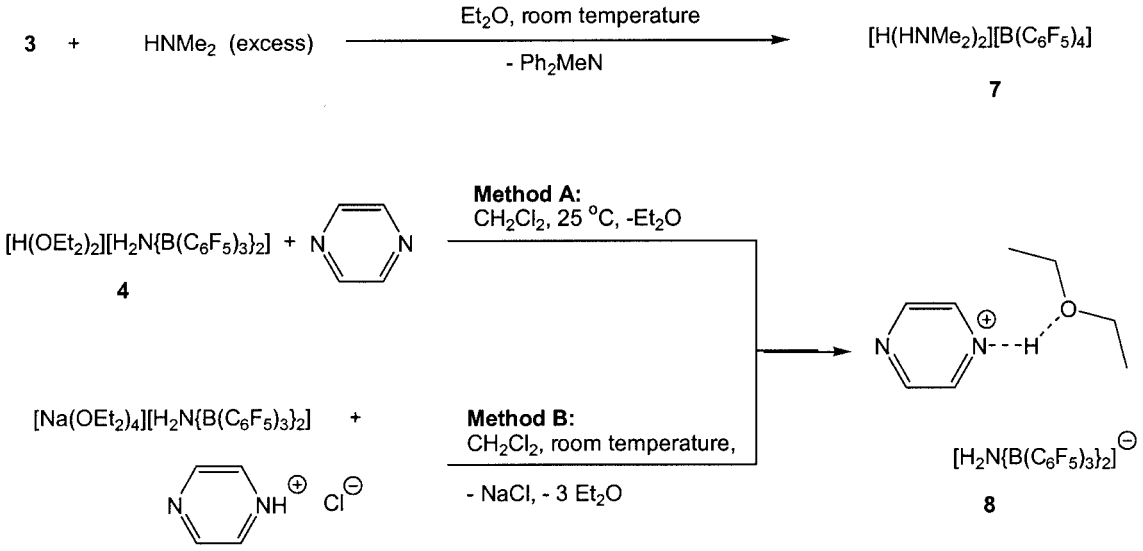
Scheme 3. Preparation of $[Sn(NMe_2)_3(HNMe_2)_2][B(C_6F_5)_4]$ (**6**).



Scheme 4. Preparation of new Brønsted acids stabilised by weakly coordinating perfluorinated anions.

δ 7.04 ppm. It is worth noting that this reaction must not be conducted in dichloromethane, as in this case crystalline $Me_2NH{\cdot}HCl$ is slowly formed in quantitative yield. For this reason, highly concentrated solutions of **7** and short acquisition times were used to record its NMR spectra. Compound **7** dissolves in Et_2O and THF but is hardly soluble in toluene and insoluble in light petroleum. As anticipated, the reaction of $Sn(NMe_2)_4$ with an equimolar amount of **7** in diethyl ether proceeded cleanly to yield ether-free **6** in a substantially improved yield (83%; Scheme 3, Method B).

The stability of **6** was demonstrated by its remarkable inertness towards ligand substitution. There is no reaction with diethyl ether, THF or even a chelating ligand such as tetramethylethylenediamine (TMEDA). Moreover, **6** was also isolated as the only product of the reaction between **3** and $Sn(NMe_2)_4$ carried out in Et_2O or THF instead of CH_2Cl_2 (yield 10–20% with respect to Sn).

Because adding an excess of pyrazine to **6** proved ineffective in displacing one of the dimethylamine ligands, we envisaged adding $[(C_4H_4N_2)H{\cdot}OEt_2][H_2N\{B(C_6F_5)_3\}_2]$ (**8**) to $Sn(NMe_2)_4$, with the rationale that such reaction would lead to the formation of a Sn^{IV} cation coordinated by at least one bifunctional pyrazine ligand. Thus, the new Brønsted acid **8** was conveniently prepared by addition of pyrazine to a solution of **4** in dichloromethane (Scheme 4, bottom, Method A). After removal of the volatile fraction and several washings with light petroleum, analytically pure **8** was recovered in high yield (88%). Product **8** was also readily obtained in 77% yield by reaction of solid pyrazinium chloride with $[Na(OEt_2)_4][H_2N\{B(C_6F_5)_3\}_2]$ in dichloromethane (Scheme 4, bottom, Method B). Compound **8** can easily be dissolved in Et_2O and chlorinated solvents, but shows poor solubility in aromatic solvents and light petroleum. Unexpectedly, no clean product could be recovered from the reaction of $Sn(NMe_2)_4$ and **8** performed in CH_2Cl_2; instead a complicated mixture of products was obtained.

The anion $[H_2N\{B(C_6F_5)_3\}_2]^-$ was chosen in preference to $B(C_6F_5)_4^-$ because of its better crystallisation properties, and indeed crystals of **8** suitable for X-ray crystallography were grown as colourless shards from a concentrated

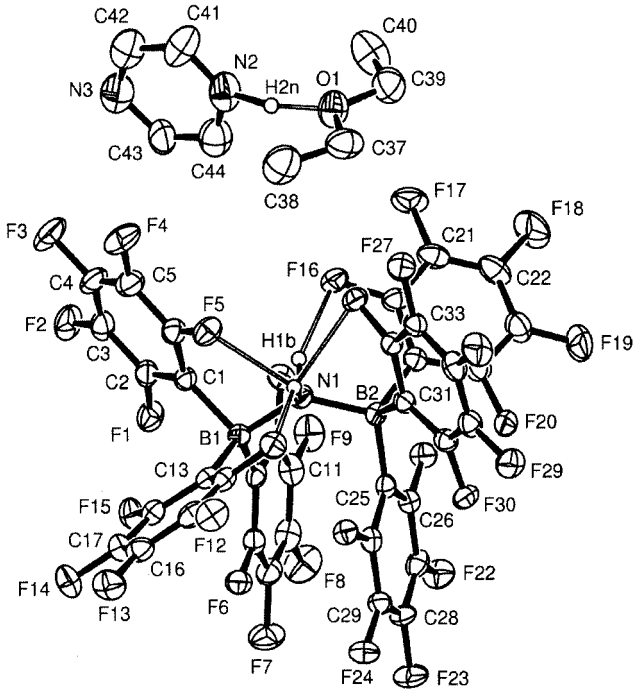
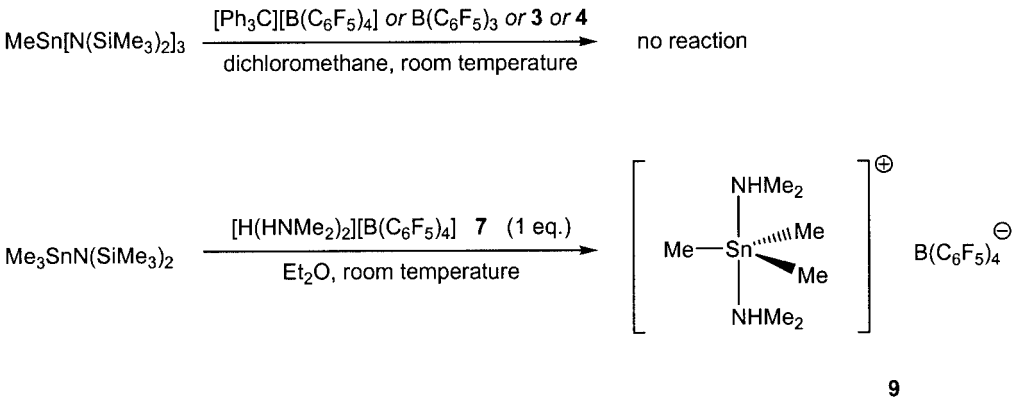


Figure 4. View of the salt $[(C_4H_4N_2)H{\cdot}OEt_2][H_2N\{B(C_6F_5)_3\}_2]$ (**8**), indicating the atom numbering scheme. Hydrogen atoms (except for the amido and acidic atoms) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: N(2)–H(2n) 1.27(5), O(1)–H(2n) 1.38(5), N(2)–C(41) 1.335(6), N(2)–C(44) 1.337(6), N(3)–C(42) 1.321(6), N(3)–C(43) 1.331(6), N(1)–B(1) 1.627(4), N(1)–B(2) 1.638(4), N(1)–H(1a) 0.90, N(1)–H(1b) 0.90, H(1a)–F(5) 2.24, H(1a)–F(11) 2.13, H(1a)–F(26) 2.32, H(1b)–F(16) 1.98; N(2)–H(2n)–O(1) 156(5), C(41)–N(2)–C(44) 120.6(4), C(42)–N(3)–C(43) 114.9(4), B(1)–N(1)–B(2) 133.2(2).

dichloromethane solution cooled to –26 °C (Figure 4). The acidic proton in the cation was refined freely. It lies between the oxygen and nitrogen atoms and is located somewhat closer to the latter [N(2)–H(2n) 1.27(5) Å, O(1)–H(2n) 1.38(5) Å]; the N(2)–H(2n)–O(1) angle is 156(5)°. The C–N bonds of the protonated nitrogen [1.335(6) and 1.337(6) Å] are marginally longer than those to the nonprotonated nitrogen atom [1.321(6) and 1.331(6) Å]. The structure of the anion resembles strongly that in $[Na(OEt_2)_2][H_2N\{B(C_6F_5)_3\}_2]$ reported previously.[38]

Synthesis and Characterisation of $[Me_3Sn(HNMe_2)_2][B(C_6F_5)_4]$ (9)

As discussed above, no stannyl cation could be generated from $MeSn[N(SiMe_3)_2]_3$ upon treatment with various cation-generating agents. On the other hand, the sterically less hindered mono-amide $Me_3SnN(SiMe_3)_2$ reacted successfully with one equiv. of **7** in Et_2O to yield $[Me_3Sn(HNMe_2)_2][B(C_6F_5)_4]$ (**9**) in a near-quantitative yield (Scheme 5). Compound **9** was fully characterised by NMR



Scheme 5. Preparation of $[Me_3Sn(HNMe_2)_2][B(C_6F_5)_4]$ (**9**).

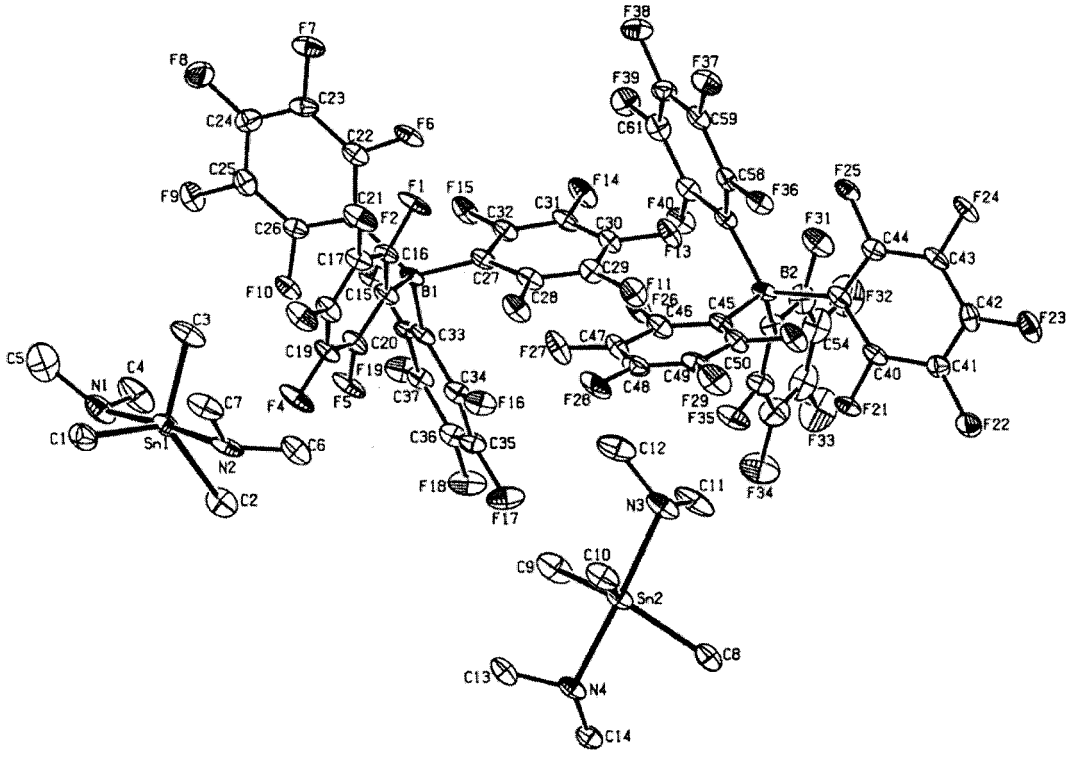


Figure 5. View of the two independent ion pairs in the salt $[Me_3Sn(HNMe_2)_2][B(C_6F_5)_4]$ (**9**), indicating the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: For the first cation, Sn(1)–N(1) 2.405(6), Sn(1)–N(2) 2.323(6), Sn(1)–C(1) 2.036(6), Sn(1)–C(2) 2.404(6), Sn(1)–C(3) 2.085(6); N(1)–Sn(1)–N(2) 176.3(2), N(1)–Sn(1)–C(1) 78.4(2), N(1)–Sn(1)–C(2) 93.0(2), N(1)–Sn(1)–C(3) 94.0(2), N(2)–Sn(1)–C(1) 100.2(2), N(2)–Sn(1)–C(2) 84.9(2), N(2)–Sn(1)–C(3) 89.7(2), C(1)–Sn(1)–C(2) 124.5(2), C(2)–Sn(1)–C(3) 127.9(2), C(1)–Sn(1)–C(3) 107.5(3). For the second cation, Sn(2)–N(3) 2.263(5), Sn(2)–N(4) 2.272(4), Sn(2)–C(8) 2.417(7), Sn(2)–C(9) 2.049(6), Sn(2)–C(10) 2.154(6); N(3)–Sn(2)–N(4) 177.0(2), N(3)–Sn(2)–C(8) 98.8(2), N(3)–Sn(2)–C(9) 80.2(2), N(3)–Sn(2)–C(10) 91.7(2), N(4)–Sn(2)–C(8) 84.0(2), N(4)–Sn(2)–C(9) 97.7(2), N(4)–Sn(2)–C(10) 87.3(2), C(8)–Sn(2)–C(9) 116.8(3), C(9)–Sn(2)–C(10) 116.1(3), C(8)–Sn(2)–C(10) 127.1(3).

spectroscopy in CD_2Cl_2, and its composition was confirmed by elemental analysis. It is readily soluble in ethers and chlorinated solvents, but only poorly soluble in aromatic hydrocarbons and totally insoluble in light petroleum. It is air- and moisture-sensitive, but is thermally stable and does not deteriorate when exposed to light.

The ^{119}Sn NMR spectrum of **9** consists of a single peak located at δ –25.3 ppm, i.e. it has undergone a high-field shift of about 77 ppm when compared to the starting material (δ +52.1 ppm). By contrast, the ^{119}Sn NMR resonance for the free Bu_3Sn^+ appears at the much higher frequency (δ +454 ppm).[22] In the ^1H NMR spectrum, the resonance for the nine Sn–CH_3 protons is found at δ 0.60 ppm, exhibiting a $^2J_{H,Sn}$ coupling of 30.7 Hz; the two N–H protons display a resonance at δ 2.14 ppm, and are considerably more shielded than the two analogous protons in **6** (δ 3.25 ppm). The ^{11}B (δ –13.6 ppm) and ^{19}F (δ –133.6, –164.0 and –168.0 ppm) NMR spectra are characteristic of the noncoordinating nature of the counteranion.

Single crystals of **9** were readily grown from a dichloromethane/light petroleum mixture at –28 °C as colourless slabs, suitable for X-ray diffraction. The crystal structure (Figure 5) indicates the presence of two independent ion pairs per asymmetric unit. The arrangement around the tin atoms of the two cations in **9** resembles that in **6**. Each of the cations has a distorted trigonal-bipyramidal environment, where the two dimethylamine ligands are situated in apical positions [N(1)–Sn(1)–N(2) 176.3(2)°; N(3)–Sn(2)–N(4) 177.0(2)°]. The average angle sums for C_{eq}–Sn(1)–C_{eq} [359.9(2)°] and C_{eq}–Sn(2)–C_{eq} [360.0(3)°] confirm the planarity of the trigonal $SnMe_3$ subunits. In both cations, one of the three equatorial Sn–C bonds is significantly longer than the other two [Sn(1)–C(2) 2.404(6) compared to Sn(1)–C(1) 2.036(6) and Sn(1)–C(3) 2.085(6) Å; Sn(2)–C(8) 2.417(7) compared to Sn(2)–C(9) 2.049(6) and Sn(2)–C(10) 2.154(6) Å], and there are considerable variations in the C_{eq}–Sn–C_{eq} angles [C_{eq}–Sn(1)–C_{eq} 107.5(3)–127.9(2)°; C_{eq}–Sn(2)–C_{eq} 116.1(3)–127.1(3)°]. The axial Sn–N bond lengths in **9** differ slightly between the two independent cations [Sn(1)–N(1) 2.405(6) and Sn(1)–N(2) 2.323(6) Å; Sn(2)–N(3) 2.263(5) and Sn(2)–N(4) 2.272(4) Å], but overall compare well with those found in **6** [2.382(7) and 2.321(7) Å] and in the related ammonia complex $[Me_3Sn(NH_3)_2][N(SO_2Me)_2]$ (Sn–N 2.328 and 2.383 Å; N–Sn–N 179.2°).[57] The equatorial Sn–C bond lengths in **9** are comparable to those reported for the latter compound (Sn–C 2.117–2.124 Å).

Conclusions

We have shown that Brønsted acids paired with weakly coordinating perfluorinated counteranions can be employed as an effective way to generate cationic tin(IV) complexes. With this aim in mind two new nitrogen-based Brønsted acids have been developed. The Sn^{IV} cations formed in such fashion are highly electrophilic. In particular, $[Sn(NMe_2)_3(HNMe_2)_2]^+$ $[B(C_6F_5)_4]^-$ was synthesized as the first example of a structurally characterised cationic amidotin complex. The dimethylamine ligands exhibit a surprising resistance to substitution by other Lewis bases. Future work will involve tailor-made cationic Brønsted acids and their use in combination with other main group precursors for the development of new architectures built around cationic metal centres and weakly coordinating anions.

Experimental Section

General: All manipulations were performed under argon using standard Schlenk techniques. Solvents were pre-dried, and distilled under inert atmosphere over sodium (low-sulfur toluene), sodium–benzophenone (diethyl ether, THF), sodium–potassium alloy (light petroleum, boiling point 40–60 °C) or calcium hydride (dichloromethane). NMR solvents were dried with activated 4-Å molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded with a Bruker Avance DPX-300 spectrometer. Chemical shifts are reported in ppm. ^1H NMR spectra (300.13 MHz) are referenced to the residual protons of the deuterated solvent used. ^{13}C NMR spectra (75.47 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. ^{11}B (96.29 MHz), ^{19}F (282.38 MHz) and ^{119}Sn (111.91 MHz) NMR spectra were referenced externally to $BF_3{\cdot}Et_2O$, $CFCl_3$ and $SnMe_4$, respectively. $HN(SiMe_3)_2$, $NMePh_2$, Ph_3SnF, $SnCl_4$, Me_3SnCl, $MeSnCl_3$, $C_4H_4N_2$, $HNMe_2$ and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine were used as purchased without further purification. $B(C_6F_5)_3$,[58–59] $[Ph_2MeNH][B(C_6F_5)_4]$ (**3**),[49] $[Na(OEt_2)_4][H_2N\{B(C_6F_5)_3\}_2]$,[38] $[H(OEt_2)_2][H_2N\{B(C_6F_5)_3\}_2]$ (**4**),[38] $[Ph_3C][H_2N\{B(C_6F_5)_3\}_2]$,[38] $MeSn[N(SiMe_3)_2]_3$,[60] $Me_3SnN(SiMe_3)_2$[61] and $Sn(NMe_2)_4$[62] were prepared according to the literature methods.

Synthesis of $Ph_3SnN(SiMe_3)_2$ (1): Ph_3SnF (5.0 g, 13.5 mmol) was added rapidly at –78 °C to a suspension of $[\{NaN(SiMe_3)_2\}_2{\cdot}THF]$ (6.0 g, 13.5 mmol) in light petroleum (80 mL). The mixture was warmed slowly to room temperature and was stirred overnight. The volatiles were removed under vacuum, giving a white solid which was suspended in toluene (60 mL). The reaction mixture was stirred at 60 °C for 5 hours. The precipitate of NaF was then removed by filtration, and the supernatant was concentrated to 20 mL. X-ray quality crystals were obtained by recrystallisation at –26 °C. Yield: 4.8 g (70%). ^1H NMR (CD_2Cl_2, 25 °C, 300.13 MHz): δ = 7.66 (m, 6 H, Ar–*H*), 7.44 (m, 9 H, Ar–*H*), 0.10 (s, 18 H, Si*Me*$_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 75.48 MHz): δ = 142.5 (C_i, $^1J_{C,Sn}$ = 298.9 Hz, Sn*Ph*$_3$), 137.0 (C_o, $^2J_{C,Sn}$ = 20.6 Hz, Sn*Ph*$_3$), 129.6 (C_p, $^4J_{C,Sn}$ = 6.2 Hz, Sn*Ph*$_3$), 129.1 (C_m, $^3J_{C,Sn}$ = 28.9 Hz, Sn*Ph*$_3$), 5.6 (Si*Me*$_3$) ppm. ^{119}Sn NMR (CD_2Cl_2, 25 °C, 111.91 MHz): δ = –106.4 ppm. $C_{24}H_{33}NSi_2Sn$ (510.4): calcd. C 56.48, H 6.52, N 2.74; found C 56.71, H 6.52, N 2.87.

Preparation of $[\{NaN(SiMe_3)_2\}_2{\cdot}THF]$(2): The solvent was removed from a solution of $NaN(SiMe_3)_2$ (12.0 g, 65.4 mmol) in THF (125 mL) under vacuum and the resulting solid extracted with light petroleum (2×100 mL). The filtrate was concentrated to 50 mL and stored overnight at –26 °C, affording a large crop of colourless crystals suitable for X-ray diffraction crystallography. Yield 10.0 g, 22.8 mmol, 70%. ^1H NMR (CD_2Cl_2, 25 °C, 300.13 MHz): δ = 3.41 (t, 4 H, J = 6.6 Hz, CH_2–C*H*$_2$–O), 1.22 (m, 4 H, C*H*$_2$–CH_2–O), 0.26 (s, 36 H, Si*Me*$_3$) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C, 75.48 MHz): δ = 68.4 (CH_2–*C*H_2–O), 25.4 (*C*H_2–CH_2–O), 7.0 (Si*Me*$_3$) ppm. $C_{16}H_{44}N_2Na_2OSi_4$ (438.9): calcd. C 43.79, H 10.11, N 6.38; found C 43.01, H 10.10, N 6.40.

$[Ph_3Sn(OEt_2)][H_2N\{B(C_6F_5)_3\}_2]$ (5): A colourless solution of **1** (0.5 g, 1.0 mmol) and **4** (1.2 g, 1.0 mmol) in CH_2Cl_2 (8 mL) was stirred at room temperature for 12 hours. The solvent was then removed under vacuum, leaving a sticky foam. Upon repeated washing with light petroleum a white powder was obtained which was suspended in 3 mL of light petroleum, and dichloromethane (ca. 2 mL) was added until the solid was completely dissolved. Cooling to –26 °C for several days gave a white microcrystalline solid, yield 0.5 g (30%). ^{1}H NMR (CD_2Cl_2, 25 °C, 300.13 MHz): δ = 7.92–7.70 (m, 15 H, Ar–*H*), 5.70 (br. s, 2 H, H_2N), 3.61 (q, $^3J_{H,H}$ = 7.0 Hz, 4 H, CH_3–CH_2–O), 0.99 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3–CH_2–O) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 75.48 MHz): δ = 149.8, 146.7, 141.2, 138.7, 137.8, 135.5 (all ArF_5–*C*), 136.9 (C_i, Sn*Ph*$_3$), 136.6 ($^2J_{C,Sn}$ = 22.8 Hz, C_o, Sn*Ph*$_3$), 131.1 (C_p, Sn*Ph*$_3$), 131.0 ($^3J_{C,Sn}$ = 33.8 Hz, C_m, Sn*Ph*$_3$), 67.5 (CH_3–*C*H_2–O), 13.9 (*C*H_3–CH_2–O) ppm. ^{11}B NMR (CD_2Cl_2, 96.29 MHz, 25 °C): δ = –5.3 ppm. ^{19}F NMR (CD_2Cl_2, 282.38 MHz, 25 °C): δ = –133.4 (d, $^3J_{F,F}$ = 19.8 Hz, 12 F, F_o), –160.7 (t, $^3J_{F,F}$ = 19.8 Hz, 6 F, F_p), –166.0 (t, $^3J_{F,F}$ = 19.8 Hz, 12 F, F_m) ppm. ^{119}Sn NMR (CD_2Cl_2, 25 °C, 111.91 MHz): δ = –76.0 ppm. $C_{58}H_{27}B_2F_{30}NOSn$ (1464.1): calcd. C 47.58, H 1.86, N 0.96; found C 47.45, H 2.02, N 1.04.

$[Sn(NMe_2)_3(HNMe_2)_2][B(C_6F_5)_4]$ (6). Method A: To a colourless solution of **3** (1.3 g, 1.5 mmol) in CH_2Cl_2 (15 mL) was added neat $Sn(NMe_2)_4$ (0.5 g, 1.7 mmol). The solution was stirred at room temperature for 5 h, when it gradually turned pale yellow and cloudy. It was then concentrated to ca. 5 mL and crystals suitable for X-ray crystallography were obtained after several days at –26 °C. Yield 0.4 g (24% relative to Sn). ^{1}H NMR (CD_2Cl_2, 25 °C, 300.13 MHz): δ = 3.25 (br., 2 H, N–*H*), 2.76 (s, 30 H, N–CH_3) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 75.48 MHz): δ = 150.0, 146.8, 140.2, 138.2, 136.9, 135.0 (all ArF_5–*C*), 42.0 (br., N–*C*H_3) ppm. ^{11}B NMR (CD_2Cl_2, 96.29 MHz, 25 °C): δ = –13.6 ppm. ^{19}F NMR (CD_2Cl_2, 282.38 MHz, 25 °C): δ = –133.6 (d, $^3J_{F,F}$ = 19.8 Hz, 8 F, F_o), –164.1 (t, $^3J_{F,F}$ = 19.8 Hz, 4 F, F_p), –168.0 (t, $^3J_{F,F}$ = 19.8 Hz, 8 F, F_m) ppm. ^{119}Sn NMR (CD_2Cl_2, 25 °C, 111.91 MHz): δ = –311.4 ppm. $C_{34}H_{32}BF_{20}N_5Sn$ (1020.2): calcd. C 40.03, H 3.16, N 6.87; found C 39.52, H 2.95, N 6.48.

Method B: Neat $Sn(NMe_2)_4$ (0.4 g, 1.4 mmol) was added to a solution of **7** (0.9 g, 1.2 mmol) in Et_2O (30 mL). A white precipitate formed within 2 min. The reaction mixture was stirred overnight, and light petroleum (10 mL) was added, yielding a white precipitate. The supernatant was filtered off. The white solid residue was washed with light petroleum (4 × 30 mL) and dried in vacuo. The product proved to be identical to that prepared by Method A. Yield 1.0 g (83% relative to Sn).

$[H(HNMe_2)_2][B(C_6F_5)_4]$ (7): Dimethylamine (6.6 g, 14.6 mmol) was condensed into a Schlenk tube at –35 °C and transferred rapidly to a solution of **3** (1.2 g, 1.4 mmol) in Et_2O (25 mL). The resulting colourless solution was stirred overnight at room temperature. The volatiles were then removed in vacuo, yielding a white solid which was washed thoroughly with light petroleum (5 × 20 mL) and dried under vacuum. Yield 0.9 g (86%). ^{1}H NMR (CD_2Cl_2, 25 °C, 300.13 MHz): δ = 7.04 (s, 3 H, N–*H*), 2.61 (s, 12 H, N–CH_3) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 75.48 MHz): δ = 150.0, 147.1, 140.1, 138.0, 136.7, 135.0 (all ArF_5–*C*), 36.7 (N–*C*H_3) ppm. ^{11}B NMR (CD_2Cl_2, 96.29 MHz, 25 °C): δ = –11.7 ppm. ^{19}F NMR (CD_2Cl_2, 282.38 MHz, 25 °C): δ = –131.8 (d, $^3J_{F,F}$ = 19.8 Hz, 8 F, F_o), –161.9 (t, $^3J_{F,F}$ = 19.8 Hz, 4 F, F_p), –165.9 (t, $^3J_{F,F}$ = 19.8 Hz, 8 F, F_m) ppm. $C_{28}H_{15}BF_{20}N_2$ (770.2): calcd. C 43.66, H 1.96, N 3.64; found C 43.92, H 1.82, N 3.65.

$[(C_4H_4N_2)H{\cdot}OEt_2][H_2N\{B(C_6F_5)_3\}_2]$ (8). Method A: Pyrazine (0.1 g, 1.2 mmol) was weighed under inert atmosphere and rapidly added to a solution of **4** (1.0 g, 0.8 mmol) in CH_2Cl_2 (25 mL). The colourless mixture was stirred at room temperature overnight, and the solvent was pumped off under vacuum to leave a white solid which was washed with light petroleum (3 × 25 mL) and dried in vacuo. Crystals suitable for X-ray diffraction were obtained by recrystallisation from a concentrated CH_2Cl_2 solution at –26 °C. Yield 0.8 g (88%). ^{1}H NMR (CD_2Cl_2, 25 °C, 300.13 MHz): δ = 16.46 (br., 1 H, N–*H*), 10.36–8.10 (v br, 4 H, C–*H*), 5.70 (br. s, 2 H, H_2N), 3.86 (q, $^3J_{H,H}$ = 7.0 Hz, 4 H, CH_3–CH_2–O), 1.34 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H,CH_3–CH_2–O) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 75.48 MHz): δ = 148.8, 146.6, 141.1, 138.6, 137.8, 135.4 (all ArF_5–*C*), 142.7 ($C_4H_4N_2$), 67.7 (CH_3–*C*H_2–O), 15.0 (*C*H_3–CH_2–O) ppm. ^{11}B NMR (CD_2Cl_2, 96.29 MHz, 25 °C): δ = –5.3 ppm. ^{19}F NMR (CD_2Cl_2, 282.38 MHz, 25 °C): δ = –133.4 (d, $^3J_{F,F}$ = 19.8 Hz, 12 F, F_o), –160.6 (t, $^3J_{F,F}$ = 19.8 Hz, 6 F, F_p), –166.1 (t, $^3J_{F,F}$ = 19.8 Hz, 12 F, F_m) ppm. $C_{44}H_{17}B_2F_{30}N_3O$ (1195.2): calcd. C 44.22, H 1.43, N 3.52; found C 43.91, H 1.58, N 3.43.

Method B: $[Na(OEt_2)_4][H_2N\{B(C_6F_5)_3\}_2]$ (1.9 g, 1.4 mmol) was added at room temperature to a suspension of solid $C_4H_4N_2{\cdot}HCl$ (0.15 g, 1.3 mmol) in 25 mL of CH_2Cl_2. The pyrazinium chloride reacted immediately, and the resulting solution turned pale yellow while small amounts of NaCl precipitate persisted. The solution was filtered off after 6 h, and the volatiles were removed under vacuum. A white powder was isolated, the composition of which was essentially identical to that of the solid obtained with Method A above. Yield 1.2 g (77%).

$[Me_3Sn(HNMe_2)_2][B(C_6F_5)_4]$ (9): Compound **7** (0.8 g, 1.0 mmol) was rapidly added to a solution of $Me_3SnN(SiMe_3)_2$ (0.6 g, 1.8 mmol) in Et_2O (30 mL). The resulting colourless solution was stirred at room temperature for 1 h. Upon removal of the volatiles in vacuo a white solid was obtained which was washed thoroughly with light petroleum (2 × 50 mL) and dried in vacuo to constant weight. Yield 0.9 g (96%). Recrystallisation from a dichloromethane/light petroleum mixture (4:1) kept at –26 °C afforded single crystals of **9** as colourless slabs. ^{1}H NMR (CD_2Cl_2, 25 °C, 300.13 MHz): δ = 2.42 (s, 12 H, N–CH_3), 2.14 (br., 2 H, N–*H*), 0.60 (s, 9 H, Sn–CH_3) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 75.48 MHz): δ = 150.1, 146.9, 140.2, 138.3, 137.0, 135.0 (all ArF_5–*C*), 37.8 (N–*C*H_3), –5.4 (Sn–*C*H_3) ppm. ^{11}B NMR (CD_2Cl_2, 96.29 MHz, 25 °C): δ = –13.6 ppm. ^{19}F NMR (CD_2Cl_2, 282.38 MHz, 25 °C): δ = –133.6 (d, $^3J_{F,F}$ = 19.8 Hz, 8 F, F_o), –164.0 (t, $^3J_{F,F}$ = 19.8 Hz, 4 F, F_p), –168.0 (t, $^3J_{F,F}$ = 19.8 Hz, 8 F, F_m) ppm. ^{119}Sn NMR (CD_2Cl_2, 25 °C, 111.91 MHz): δ = –25.3 ppm. $C_{31}H_{23}BF_{20}N_2Sn$ (933.0): calcd. C 39.91, H 2.48, N 3.00; found C 40.07, H 2.40, N 3.06.

X-ray Crystallography: Crystal data and refinement results for compounds **1**, **2**, **6**, **8** and **9** are collated in Table 1. In each case, crystals were mounted on glass fibres, either in oil and fixed in the cold nitrogen stream on a Rigaku/MSC AFC7R diffractometer (samples **1**, **2** and **6**) or with epoxy resin on a Nonius KappaCCD diffractometer (samples **8** and **9**). Data were processed with the TeXsan/PROCESS[63] or DENZO program,[64] and absorption corrections applied. The structures were determined by heavy atom methods (compounds **1** and **2**) or direct methods (compounds **6**, **8** and **9**) in SHELXS.[65] Refinement was by full-matrix least-squares methods in SHELXL.[65] In all, non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in idealised positions and their isotropic thermal parameters were set to ride on the U_{eq} values of the parent carbon or nitrogen atoms. Scattering factors for neutral atoms were taken from ref.[66]. The relatively large difference peaks and holes were located close to the tin atoms and arise from inadequate absorption correction. No absorption correction was applied in the case of compound **1**.

Table 1. Crystal and structure refinement data for compounds **1**, **2**, **6**, **8** and **9**.

Compound	**1**	**2**	**6**	**8**	**9**
Elemental formula	$C_{24}H_{33}NSi_2Sn$	$C_{16}H_{44}N_2Na_2OSi_4$	$C_{10}H_{32}N_5Sn$, $C_{24}BF_{20}$	$C_8H_{15}N_2O$, $C_{36}H_2B_2F_{30}N$	$C_{62}H_{46}B_2F_{40}N_4Sn_2$
Formula weight	510.4	438.9	1020.2	1195.2	1866.0
Crystal system	triclinic	monoclinic	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
Unit cell dimensions [Å, °]					
a	11.799(14)	11.195(13)	12.569(10)	13.9820(2)	13.910(4)
b	12.031(12)	21.65(2)	14.304(12)	17.1460(2)	14.102(3)
c	9.405(11)	11.877(13	10.983(8))	18.3470(3)	17.786(4)
α	95.68(9)	90	91.59(7)	90	88.92(2)
β	107.33(9)	109.73(9)	102.48(6)	90	82.07(2)
γ	84.08(9)	90	85.87(7)	90	89.94(2)
Cell volume, V [Å^3]	1264(2)	2710(5)	1923(3)	4398.43(11)	3454.9(15)
No. of formula units/cell, Z	2	4	2	4	2
Density (calculated) [mg/m^3]	1.340	1.076	1.762	1.805	1.794
F(000)	524	960	1012	2360	1832
Absorption coefficient [mm^{-1}]	1.114	0.259	0.796	0.197	0.875
Temperature [K]	140(1)	140(1)	140(1)	293(2)	120(2)
Crystal colour, shape	colourless block	colourless prism	colourless plate	colourless shard	colourless slab
Crystal size [mm]	0.8×0.7×0.5	0.5×0.25×0.2	0.7×0.40×0.15	0.27×0.02×0.02	0.50×0.18×0.08
θ range [°] for data collection	2.3–25.1	1.9–20.0	1.9–25.0	2.9–27.1	1.2–27.5
Index ranges for h, k, l	0/14, –14/14, –11/10	–1/10, –20/20, –11/10	0/13, –16/16, –12/12	–17/16, –19/21, –23/23	–17/17, –18/18, –22/22
Absorption correction	Psi-scans	Psi-scans	Psi-scans	Semi-empirical from equivalents	Semi-empirical from equivalents
Max./min. transmission	1.00/0.584	1.00/0.756	1.00/0.64	0.996/0.949	0.933/0.669
Total no. of reflections measured	4681	2028	5537	63610	70746
No. of unique reflections	4443	1270	5200	9638	14464
R_{int} for equivalents	0.088	0.146	0.104	0.074	0.065
No. of "observed" reflections ($I > 2\sigma_I$)	3851	883	4053	7707	11285
Refinement					
Data/restraints/parameters	4443/0/254	1270/0/121	5200/0/563	9638/0/727	14464/0/1021
Goodness-of-fit on F^2, S	1.048	0.999	0.996	1.065	1.098
Final R indices ("observed" data)	R_1 = 0.061, wR_2 = 0.156	R_1 = 0.058, wR_2 = 0.114	R_1 = 0.063, wR_2 = 0.158	R_1 = 0.047, wR_2 = 0.104	R_1 = 0.055, wR_2 = 0.150
Final R indices (all data)	R_1 = 0.071, wR_2 = 0.164	R_1 = 0.094, wR_2 = 0.126	R_1 = 0.084, wR_2 = 0.170	R_1 = 0.068, wR_2 = 0.113	R_1 = 0.076, wR_2 = 0.160
Largest diff. peak and hole [e·Å^{-3}]	3.23 and –1.92	0.22 and –0.30	1.52 and –2.22	0.60 and –0.29	2.07 and –1.79

CCDC-605857 (for **1**), -605858 (for **2**), -605859 (for **6**), -605860 (for **8**) and -605861 (for **9**) 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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