Hydrogen activation using a novel tribenzyltin Lewis acid

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Over the last decade there has been an explosion in the reactivity and applications of frustrated Lewis pair (FLP) chemistry. Despite this, the Lewis acids (LAs) in these transformations are often boranes, with heavier p-block elements receiving surprisingly little attention. The novel LA Bn3SnOTf 1 has been synthesized from simple, inexpensive starting materials and has been spectroscopically and structurally characterized. Subtle modulation of the electronics at the tin centre has led to an increase in its Lewis acidity in comparison with previously reported R3SnOTf LAs, and has facilitated low temperature hydrogen activation and imine hydrogenation. Deactivation pathways of the R3Sn+ LA core have also been investigated.

This article is part of the themed issue ‘Frustrated Lewis pair chemistry’.

1. Introduction

Since the concept of ‘frustrated Lewis pairs’ (FLPs) was formalized a decade ago [1], there has been a rapid increase in interest and activity in this area of chemistry [2–4]. The combination of a Lewis acid and base (LA and LB, respectively), which are prevented from forming a strong classical adduct by steric and/or electronic factors [3], can possess unquenched reactivity that has been shown to allow activation of a range of small molecules. Following initial observations of the heterolytic cleavage of H2 [5–7] (which had traditionally only been achieved using...
transition metals), subsequent application to metal-free catalytic hydrogenation has brought great interest, with the scope progressing from imines, aziridines and protected nitriles substrates [8,9], to activated alkenes [10], and, most recently, aldehydes and ketones [11,12].

To date the vast majority of the focus in this diverse, rapidly expanding field of chemistry has been directed towards the use of boron-centred LAs [13]; by comparison equivalent FLP chemistry with heavy p-block elements has received far less attention [14–17]. Nevertheless, our current interest has been drawn to the use of stannylium ion R₃Sn⁺ (R = alkyl) based LAs, which possess several properties very similar to the most commonly used LA in FLP chemistry, B(C₆F₅)₃ [13]. In particular these LAs are isoelectronic, isolobal, and have been calculated to have comparable hydride ion affinities (ΔGₓ = 65.83 and 64.95 kcal mol⁻¹ for nBu₃Sn-H and [(C₆F₅)₃B-H]⁻ respectively) [18], indicating that these species could show analogous reactivity in H₂ activation and hydrogenation chemistry. Accordingly, we recently described the use of iPr₃SnOTf (a surrogate for iPr₃Sn⁺; OTf⁻ = CF₃SO₃) in FLP-mediated H₂ activation chemistry when partnered with amine/pyridine LBs. Furthermore, iPr₃SnOTf could successfully be employed in the catalytic hydrogenation of a variety of functional groups (C=C, C≡N and C=O bonds), and demonstrated an unparalleled tolerance to moisture for FLP catalysis [14]. Nevertheless, we noted that one factor limiting the rate of some catalytic hydrogenations using iPr₃SnOTf as a LA was the ease of H₂ activation. In this respect, it is notable that earlier work by Manners and co-workers showed similar FLP systems based on nBu₃SnOTf were unreactive towards H₂, although they were capable of dehydrogenating amine-boranes. We proposed that this resulted from an overly strong interaction between the less bulky R₃Sn⁺ and TfO– moieties, which would result in significant quenching of the Lewis acidity at Sn [15]; this hypothesis drove us to pursue the synthesis of the more sterically encumbered yet electronically similar iPr analogue. These results clearly indicate that the reactivity of R₃Sn⁺-based FLPs can be highly sensitive to the identity of R, and clearly there exists scope for further modification and optimization of such Sn(IV) LAs, which are appealing given their relative ease of synthesis, and the abundance and low cost of Sn [14].

Previously, computational calculations have reported that the successful activation of H₂ is strongly correlated to the cumulative proton and hydride affinities of LB and LA, respectively [19], for which pKₐ values of [LB-H]+ and Lewis acidity measurements (e.g. Gutmann–Beckett method) can be used as guiding experimental proxies. With this in mind, we speculated that increasing the Lewis acidity of R₃Sn⁺ via the use of a more electron-withdrawing R group would facilitate faster FLP-mediated H₂ activation and hence improved catalytic hydrogenation kinetics. Herein we report the targeted high yielding synthesis and characterization of the new LA Bn₃SnOTf (Bn = PhCH₂; 1) which, by virtue of the greater inductive electron-withdrawing effect of the sp²-hybridized phenyl C atom versus an sp³-alkyl substituent, displays an enhanced Lewis acidity over iPr₃SnOTf. Furthermore, we show that 1 displays facile H₂ activation at lower temperatures than its iPr analogue under comparable conditions, and examine its activity for the catalytic hydrogenation of an imine substrate.

2. Experimental details

(a) General considerations

Unless otherwise stated, all reactions were conducted under an inert atmosphere of dinitrogen using standard Schlenk techniques on a dual-vacuum-inlet gas manifold or MBraun DP Labmaster glovebox. All glassware was heated to 180°C overnight prior to use. All solvents were dried and degassed before use: pentane was dried using an Innovative Technology Pure Solv™ SPS-400 and stored over K; Et₂O was distilled from Na/fluorenone and stored over K; CHCl₃ was dried and stored over 3 Å molecular sieves; C₆D₆ and CDCl₃/CD₂Cl₂ were freeze–pump–thaw degassed and dried over a K mirror and 3 Å molecular sieves, respectively. H₂ was purchased from BOC (research grade) and dried by passage through a Matheson Tri-Gas Weldassure™ Purifier drying column. 2,4,6-Collidine (hereafter referred to as collidine) and Ph(H)C=NHPh
were purchased from major suppliers, degassed and dried over 4 Å molecular sieves before use. Bn₃SnCl was purchased from Alfa Aesar and dried under vacuum. Benzyl chloride (BnCl), SnCl₄, Mg, LiAlH₄, I₂ and trifluoromethanesulfonic acid (TfOH) were purchased from major suppliers and used as received.

(b) Analytical measurements

NMR spectra were recorded on Bruker AV-400 MHz and DRX-400 spectrometers. ¹H and ¹³C spectra were referenced internally to the residual solvent signals and reported in parts per million (ppm). ¹⁹F, ³¹P and ¹¹⁹Sn spectra were referenced externally to CFCl₃, 85% H₃PO₄(aq) and Me₄Sn respectively. High resolution mass spectrometry was recorded using a Micromass Autospec Premier (El mode) by Dr Lisa Haigh at Imperial College London. Single crystal X-ray diffraction data were collected and refined by Dr Andrew White (full details can be found in the electronic supplementary material). Elemental microanalysis was conducted by Stephen Boyer at London Metropolitan University.

(c) Synthesis

(i) Tetrabenzylstannane (Bn₄Sn)

A modified procedure of Smith & Kipping [20] and Huber and colleagues [21] was employed: SnCl₄ (6.70 g, 25.71 mmol) was added slowly to Et₂O (100 ml) at 0°C to give a milky-white suspension. Mg powder (2.50 g, 102.84 mmol) was added, followed by a single crystal of I₂ (0.05 g, 0.20 mmol). Benzyl chloride (13.02 g, 102.84 mmol) in Et₂O (80 ml) was added dropwise over a period of 90 min at 0°C. Following addition, the reaction was heated to reflux for 3 h followed by further stirring at room temperature for 24 h. The reaction was carefully quenched with water and the aqueous phase extracted with CHCl₃. The remaining work-up was performed under air: the combined organic phases were dried over Na₂SO₄ and filtered, and the volatiles removed under reduced pressure resulting in an oil. Bn₄Sn was crystallized from a slow cooled pentane solution at −45°C, affording 8.50 g (17.59 mmol) of a white crystalline solid in 68.4% yield.

1H NMR (400 MHz, CDCl₃) δ: 2.22 [8H, s, 2J(119,117Sn-1H) = 58.3 Hz, CH₂], 6.74 [8H, m, Ph], 7.01 [4H, m, Ph], 7.16 [8H, m, Ph]. ¹¹⁹Sn {¹H} NMR (149 Hz, CDCl₃) δ: −37.1 (s); these values are consistent with those previously reported [22].

(ii) Tribenzyltin triflate (Bn₃SnOTf), (1)

Trifluoromethanesulfonic acid (TfOH, 0.63 g, 4.21 mmol) was added dropwise to a solution of Bn₄Sn (2.14 g, 4.43 mmol) in CHCl₃ (50 ml), causing the mixture to immediately become turbid. The reaction was stirred at room temperature for 18 h before the solvent was removed in vacuo and the solid subjected to a dynamic vacuum for 6 h. The solid was subsequently washed with pentane (4 × 15 ml) to furnish pure Bn₃SnOTf as a white solid (2.01 g, 3.71 mmol) in 88% yield.

1H NMR (400 MHz, CDCl₃) δ: 2.92 [6H, s, 2J(117,119Sn-1H) = 66.02 Hz, CH₂], 6.79 [6H, m, Ph], 7.12 [3H, m, Ph], 7.20 [6H, m, Ph]. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 26.8 [s, 1J(117Sn-1H) = 258.4 Hz, 1J(1¹¹⁹Sn-¹H) = 271.2 Hz, CH₂], 118.9 [q, 1J(F-¹³C) = 317.2 Hz, CF₃], 125.9 [s, 5J(1¹¹⁷,1¹¹⁹Sn-¹³C) = 21.6 Hz, Ph], 128.1 [s, 3J(1¹¹⁷,1¹¹⁹Sn-¹³C) = 33.4 Hz, Ph], 129.4 [s, 4J(1¹¹⁷,1¹¹⁹Sn-¹³C) = 18.2 Hz, Ph], 135.9 [s, Ph]. ¹⁹F NMR (376 MHz, CDCl₃) δ: −77.0. ¹¹⁹Sn{¹H} NMR (149 Hz, CDCl₃) δ: 87.4 [br s, Δν½ = 48.4 Hz]. Elemental analysis found (calculated) for C₂₂H₂₁O₃F₃SSn: C 48.69 (48.83), H 4.01 (3.91). HRMS (EI): m/z found (calculated) for C₂₂H₂₁O₃F₃SSn: 542.0202 (542.0186).

(iii) Tribenzyltin hydride (Bn₃SnH), (2)

A modified procedure of Miura and colleagues [23] was employed for the independent synthesis of Bn₃SnH (2): Bn₃SnCl (1.00 g, 2.34 mmol) was added to LiAlH₄ (0.08 g, 2.13 mmol) in Et₂O
(20 ml) at 0°C and stirred for 30 min. The suspension was filtered via cannula before the volatiles were removed in vacuo. The solid was extracted into pentane (3 × 10 ml) and filtered. The volatiles were removed under reduced pressure to furnish 0.294 g (0.75 mmol) of 2, as a viscous oil in 37% yield, which solidified upon cooling to −20°C in a glovebox freezer for storage.

$^1$H NMR (400 MHz, C$_6$D$_6$) δ: 2.17 [6H, d, $J = 1.5$ Hz, $^2J(117,119Sn-1H) = 61.5$ Hz, CH$_2$], 5.71 [1H, sept, $J = 1.5$ Hz, $^1J(117Sn-1H) = 1693.8$ Hz, $^1J(119Sn-1H) = 1773.1$ Hz], 6.79 [6H, m, Ph], 6.94 [3H, m, Ph], 7.09 [6H, m, Ph]. $^{13}$C$^\text{H}$ NMR (101 MHz, C$_6$D$_6$) δ: 17.9 [s, $^1J(117Sn-1H) = 277.0$ Hz, $^1J(119Sn-1H) = 289.5$ Hz, CH$_2$], 124.2 [s, $^3J(117,119Sn-13C) = 16.1$ Hz, Ph], 127.9 [s, Ph], 128.9 [s, $^4J(117,119Sn-13C) = 13.6$ Hz, Ph], 142.1 [s, $^2J(117,119Sn-13C) = 39.6$ Hz, Ph]. $^{119}$Sn$^\text{H}$ NMR (149 Hz, C$_6$D$_6$) δ: −85.4 (s); these values are consistent with those previously reported [23].

(d) Gutmann–Beckett Lewis acidity measurements [24]

Et$_3$PO (3.6 mg, 0.02 mmol) and Bn$_3$SnOTf (32.4 mg, 0.06 mmol) were dissolved in CD$_2$Cl$_2$ (0.4 ml) and added to a NMR tube with a capillary insert containing 1 M Et$_3$PO in CD$_2$Cl$_2$. Based on the $^{31}$P$^\text{H}$ chemical shift of the resulting Et$_3$PO adduct relative to the insert, the acceptor number (AN) was calculated using the formula of Mayer et al. [25] and Beckett et al. [26]

$$AN = [(\delta(\text{sample}) − 41.0) \times 100/(86.14 − 41.0)]$$

$^{31}$P$^\text{H}$ NMR, $\delta_{\text{adduct}} = 74.41$ ppm gave an acceptor number of 74.0.

(e) H$_2$ activation procedure using Bn$_3$SnOTf, (1) and collidine

Inside a glovebox 1 (16.2 mg, 0.03 mmol) and collidine (3.6 mg, 0.03 mmol) were combined in C$_6$D$_6$ (0.4 ml) and transferred into a NMR tube fitted with a Young’s valve. The solution was freeze–pump–thaw degassed and H$_2$ (1 bar) was admitted while the solution was at −196°C (which equates to a pressure of approximately 4 bar at room temperature) and the reaction was analysed by $^1$H, $^{19}$F and $^{119}$Sn spectroscopy. The reaction was then heated in an oil bath to 50°C for 2 h, after which it was reanalysed by NMR techniques. This revealed the formation of 2 by the diagnostic Sn-H septet resonance at $\delta = 5.71$ ppm accompanied by $^{117}$/$^{119}$Sn$^\text{H}$ satellites and the $^{119}$Sn resonance at $\delta = −85.4$ ppm.

(f) Investigations into PhCH$_2$/H scrambling and deactivation routes

(i) Thermal stability of Bn$_3$SnOTf, (1)

A sample of 1 (16.2 mg, 0.03 mmol) was dissolved in C$_6$D$_6$ (0.4 ml) and transferred into a NMR tube fitted with a Young’s valve. The reaction was followed by $^1$H and $^{119}$Sn$^\text{H}$ NMR spectroscopy but no reaction was observed, even after heating to 70°C for 72 h.

(ii) Thermal stability of Bn$_3$SnOTf (1) and collidine

A NMR tube was loaded with 1 (16.2 mg, 0.03 mmol), collidine (3.6 mg, 0.03 mmol) and C$_6$D$_6$ (0.4 ml), which led to the formation of an adduct by $^{119}$Sn$^\text{H}$ NMR spectroscopy. However, no further change was observed by $^1$H and $^{119}$Sn$^\text{H}$ NMR spectroscopy, even after heating to 70°C for 72 h.

(iii) Thermal stability of Bn$_3$SnOTf (1) and Bn$_3$SnH (2)

Inside a glovebox 1 (16.2 mg, 0.03 mmol) and 2 (11.8 mg, 0.03 mmol) were combined in C$_6$D$_6$ (0.4 ml) and transferred into a NMR tube fitted with a Young’s valve. The mixture was monitored by $^1$H and $^{119}$Sn$^\text{H}$ NMR spectroscopy at regular intervals for 60 h at RT. Complete decomposition of 1 and 2 was observed with concomitant formation of Bn$_4$Sn ($^{119}$Sn$^\text{H}$ NMR $\delta = −37.5$ ppm), along with the formation of an intractable precipitate, after this time. An analogous reaction conducted with heating to 50°C for 5 h gave identical results.
(iv) Thermal stability of $\text{Bn}_3\text{SnOTf (1)}, \text{Bn}_3\text{SnH (2)}$ and collidine

1 (8.1 mg, 0.015 mmol), 2 (5.9 mg, 0.015 mmol) and collidine (3.6 mg, 0.03 mmol) were combined in C$_6$D$_6$ (0.4 ml) and transferred into a NMR tube fitted with a Young’s valve. The mixture was monitored by $^1\text{H}$ and $^{119}\text{Sn}$($^1\text{H}$) NMR spectroscopy at regular intervals over the course of 60 h at RT, during which partial decomposition of 1 and 2 to Bn$_4$Sn was observed ($^{119}\text{Sn}$($^1\text{H}$) NMR $\delta = -37.5$ ppm). An analogous reaction conducted with heating to 50°C for 5 h showed complete decomposition.

(g) Imine hydrogenation procedure using $\text{Bn}_3\text{SnOTf (1)}$ and collidine

Inside a glovebox 1 (10.8 mg, 0.02 mmol), collidine (2.4 mg, 0.02 mmol) and Ph(H)C=NHPh (3) (36.2 mg, 0.20 mmol) were dissolved in C$_6$D$_6$ (0.4 ml) and transferred into a Wilmad high pressure NMR tube fitted with a PV-ANV PTFE valve. H$_2$ was admitted to a pressure of 10 bar (at room temperature) and analysed by $^1\text{H}$, $^{19}$F and $^{119}$Sn NMR spectroscopy. The reaction was heated in an oil bath to 50°C without active mixing and monitored at regular intervals. The conversion (%) was determined by relative integration of $^1\text{H}$ resonances belonging to the amine product [PhC$_2$NHPh, (4)], residual starting material [Ph(H)C=NPh, (3)]. This procedure was repeated at 70°C and room temperature.

3. Results and discussion

(a) Synthesis and characterization of $\text{Bn}_3\text{SnOTf (1)}$

The target compound $\text{Bn}_3\text{SnOTf (1)}$ was synthesized by the facile proteodealkylation of Bn$_4$Sn (synthesized by a modified procedure of Smith & Kipping [20] and Huber et al. [21]) with TfOH (figure 1). Subsequent work-up yielded 1 as a white solid in excellent yield (88%). 1 has been characterized by $^1\text{H}$, $^{13}\text{C}$, $^{19}\text{F}$ and $^{119}\text{Sn}$ NMR spectroscopy, elemental analysis, HRMS (EI) and X-ray crystallography. Single crystals were grown from a cooled (~20°C) saturated Et$_2$O solution under an inert atmosphere, for which X-ray diffraction data were collected and refined, and the structure is shown in figure 2.

1 crystallizes in the chiral space group P2$_1$ and contains four independent molecules (molecules 1a–d; see table 1 for more details) in the asymmetric unit, which are geometrically closely related. Each independent molecule forms its own unique extended polymer structure along the b axis, in which the TfO moieties bridge two separate Bn$_3$Sn centres. The ligands are coordinated in a distorted trigonal bipyramidal arrangement around Sn, with the three benzyl groups occupying the equatorial positions and oxygens from the bridging triflate moieties occupying the axial positions. The degree of distortion from an idealized trigonal bipyramidal structure can be quantified using the parameter $\tau$ [28]; the range 0.94–0.96 obtained for the four independent molecules in 1 indicates a near perfect trigonal bipyramidal geometry (idealized $\tau = 1$, versus $\tau = 0$ for square-based-pyramidal).

1 is isostructural with Ph$_3$SnOTf [27], one of only two triorganotin triflates that have previously been structurally characterized, the other being the molecular species [(Me$_3$Si)$_2$CH]$_3$SnOTf [29]. These structural variations are likely attributed to the differing steric bulk of the R groups around Sn, with the very large [(Me$_3$Si)$_2$CH] substituents favouring a distorted tetrahedral geometry over a polymer which necessitates higher coordination numbers. For Ph and Bn, the substituents are small enough for the LA Sn centres to bond in a hypervalent manner, resulting in the polymeric 5-coordinate geometry. The Sn-C and Sn-O bond lengths within 1 and Ph$_3$SnOTf are almost identical within experimental error [27]. However, the latter are considerably longer than those observed in [(Me$_3$Si)$_2$CH]$_3$SnOTf (2.139(4) Å) [29], presumably because the lower coordination number enables closer approach of the triflate moiety, compared to the more sterically congested 5-coordinate species.
**Figure 1.** Synthesis of 1.

1 is highly soluble in polar halogenated solvents, displays appreciable solubility in benzene, yet is completely insoluble in aliphatic hydrocarbon solvents. The solution-phase room temperature $^1$H NMR spectrum in the non-donor solvent CDCl$_3$ reveals a notably downfield shift of the methylene resonance ($\delta = 2.92$ ppm; CDCl$_3$) compared to Bn$_4$Sn ($\delta = 2.22$ ppm; CDCl$_3$), with the same trend observable for the methylene carbon resonances ($^{13}$C NMR: $\delta = 26.8$ and 18.9 ppm respectively), which reflects the enhanced electron deficiency upon substituting the benzyl for a weakly coordinating triflate ligand. This might be expected to result in
significant stannylium ion character in 1, which is usually typified by a strongly downfield \(^{119}\text{Sn}\) NMR chemical shift. However, the single broad resonance seen for 1 in the \(^{119}\text{Sn}\)(\(^{1}\text{H}\)) NMR spectrum (\(\delta = 87.4\) ppm; \(\Delta \nu_{3/2} = 48.4\) Hz) is considerably upfield relative to the value reported for \([\text{nBu}_{3}\text{Sn}][\text{CB}_{11}\text{Me}_{12}]\) (\(\delta = 454\) ppm), which exhibits the least coordinated trialkylstannylium core reported to date [30], and the related trialkyltin triflates \(\text{R}_{3}\text{SnOTf}\) (\(\text{R} = \text{nBu} [31], \text{iPr} [14]; \delta = 168\) and \(156\) ppm, respectively). These data, in combination with the \(^{1}J(\text{\textsuperscript{13}C,\text{\textsuperscript{119}Sn}})\) values for the \(\text{R}_{3}\text{SnOTf}\) compounds \((\text{R} = \text{nBu} 383; \text{iPr} 316; \text{Bn} 258\) Hz) where higher values are proposed to be an indicator of increasing stannylium character [31], might imply that 1 should be the weakest LA of the \(\text{R}_{3}\text{SnOTf}\) series. However, the \(^{119}\text{Sn}\) NMR chemical shift is not a direct correlation to Lewis acidity and can be highly dependent on solvent, degree of aggregation in solution, and the substituents of the stannylium core [32]; in this instance it may be conceived that the propensity to aggregate within the solution-phase (in the absence of external strong donor species) is enhanced due to a more electron-deficient Sn core. A more rigorous, quantitative method was developed by Gutmann and Beckett which uses the change in \(^{31}\text{P}\) NMR chemical shift of \(\text{Et}_{3}\text{P}=\text{O}\) upon coordination to a LA to provide an AN value, the magnitude of which positively correlates with Lewis acidity; this is a more reliable indicator of Lewis acidity since it is expected that coordination to a LA to provide an AN value, the magnitude of which positively correlates with Lewis acidity and can be highly dependent on solvent, degree of aggregation in solution, and the substituents of the stannylium core [32]; in this instance it may be conceived that the propensity to aggregate within the solution-phase (in the absence of external strong donor species) is enhanced due to a more electron-deficient Sn core. A more rigorous, quantitative method was developed by Gutmann and Beckett which uses the change in \(^{31}\text{P}\) NMR chemical shift of \(\text{Et}_{3}\text{P}=\text{O}\) upon coordination to a LA to provide an AN value, the magnitude of which positively correlates with Lewis acidity; this is a more reliable indicator of Lewis acidity since it is expected that coordination to a LA to provide an AN value, the magnitude of which positively correlates with Lewis acidity.

### (b) Hydrogen activation studies of \(\text{Bn}_{3}\text{SnOTf}(1)\)

Combination of 1 and collidine in a 1:1 ratio in \(\text{C}_{6}\text{D}_{6}\) led to an upfield shift in the \(^{119}\text{Sn}\)(\(^{1}\text{H}\)) resonance from \(\delta = 74.9\) to \(33.6\) ppm (br), concomitant with a slight shift of the \(^{1}\text{H}\) NMR resonances of 1, consistent with a donor–acceptor interaction. Nevertheless, it is well known that certain ordinary Lewis pair adducts can exhibit FLP reactivity, as exemplified by the classical adduct between lutidine and \(\text{B(C}_{6}\text{F}_{5})_{3}\) which generates the free FLP upon heating which subsequently cleaves H\(_{2}\) [33]; furthermore strongly bound adducts such as the silylium/phosphine species \([\text{Pr}_{3}\text{Si-P}^{+}\text{Bu}_{3}]^{+}\) (for which no stable FLP counterpart can exist) can also engage in H\(_{2}\) heterolysis [34] (note that in our previous studies the \([\text{Pr}_{3}\text{SnOTf/DABCO}]\) (DABCO=1,4-diazabicyclo[2.2.2]octane) Lewis pair was found to activate H\(_{2}\) despite evidence for similar adduct formation [14]). With this in mind, admission of H\(_{2}\) (4 bar, 50°C, 2 h) led to

### Table 1. Selected bond lengths and angles for isomeric 1 and \(\text{Ph}_{3}\text{SnOTf}[27].\) ESDs are given in parentheses.

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the appearance of resonances in the $^1$H NMR (5.72 ppm, SnH, $^1J(^{117}/^{119}$Sn-$^1$H) = 1693/1773 Hz; 13.13 ppm, NH) and $^{119}$Sn($^1$H) NMR (−84.8 ppm) spectra, which are consistent with formation of Bn$_3$SnH (2) and [col-H]$^+$[TfO]$^-$, formed through H$_2$ activation by the 1/collidine Lewis pair (figure 3). These resonances were verified by comparison with literature values [23], and the independent synthesis of 2. Significantly, this is only the second reported example of H$_2$ activation using a Sn(IV) based LA.

It is interesting to note that the equivalent H$_2$ activation by iPr$_3$SnOTf and collidine required higher pressure (10 bar) and longer times (20 h) [14]. Similarly, no H$_2$ activation was reported with nBu$_3$SnOTf in combination with the stronger amine base 2,2,6,6-tetramethylpiperidine (TMP) [15], even with prolonged heating (18 h, 50°C), which is consistent with the suggestion from our Gutmann–Beckett measurements that 1 is the strongest LA in the R$_3$SnOTf series (R = nBu, iPr, Bn).

Inspection of $^1$H NMR integrals revealed incomplete conversion of 1 to 2 (17% as ascertained by $^1$H NMR using a 2,5-dimethylfuran insert), which contrasts with the outcome of similar reactions using B(C$_6$F$_5$)$_3$ whose H$_2$ activation reactions have been reported to proceed to completion when using similarly strong LBs [19,33], along with a downfield shift and concomitant broadening of the CH$_2$Ph resonances in 1. However, similar observations were reported for iPr$_3$SnOTf, which is nonetheless catalytically active for a variety of C=X (X = C, N, O) bond
hydrogenations [14]. It was noted that another appreciable \( \text{H}_2 \) activation at 50°C, several other new resonances were observed in the \( \text{H}^1 \) and \( \text{Sn}^{119} \) NMR spectra (such peaks had not been observed during earlier investigations using \( \text{Pr}_3\text{SnOTf} \)). These were postulated to result from deactivation/decomposition pathways operating within the system, which could provide one explanation for the incomplete conversion of 1 to 2. As such, the origin of these resonances was investigated further.

(c) Investigations into potential \( \text{Bn}_2\text{SnX} \) (\( X = \text{H}, \text{TfO} \)) deactivation pathways

On closer inspection of the hydrogen cleavage experiments the diagnostic chemical shifts of \( \text{Bn}_4\text{Sn} \) were noted in the \( \text{H}^1 \) and \( \text{Sn}^{119} \) NMR spectra (\( \delta = 2.17 \) and \( -37.5 \) ppm respectively; \( \text{C}_6\text{D}_6 \)). This, in combination with the incomplete conversion of 1 to 2, led us to conclude that additional side-reactions must also be operating. The thermal stability of 1 was established with and without the presence of collidine; samples remained stable (no change observed by \( \text{H}^1 \) and \( \text{Sn}^{119} \) NMR) even at temperatures above those used for \( \text{H}_2 \) activation (70 versus 50°C). Our initial suspicion related to decomposition of the hydride 2; although 2 has been demonstrated to be an effective reagent in many organic transformations [23], it is known to be unstable at elevated temperatures [35], converting smoothly to hexabenzyldistannane (\( \text{Bn}_3\text{SnSnBn}_3 \)) with concomitant evolution of \( \text{H}_2 \) [36]. However, at no time was this distannane observed by NMR spectroscopy, indicating that 2 does not decompose via this pathway.

The mutual compatibility of 1 and 2 were subsequently probed (1 : 1, \( \text{C}_6\text{D}_6 \)) which led to an instant interaction as evidenced by the broadening of both sets of resonances (most notably methylene) in the \( \text{H}^1 \) NMR spectrum (electronic supplementary material, figure S6a). After 30 min at RT there were distinctive resonances indicating the formation of \( \text{Bn}_4\text{Sn} \) and after a further hour, broad resonances at \( \delta = 9.01 \) and 5.28 ppm appeared (albeit in low intensity), the latter being identical to that previously reported for \( \text{Bn}_2\text{SnH}_2 \) [37]. Interestingly, the diagnostic downfield resonance is almost identical to the related diorganotin hydride species, \( \text{Bu}_2\text{Sn(H)OTf} \) (\( \delta = 8.99 \) ppm; \( \text{C}_6\text{D}_6 \)) [38], strongly indicating the possibility that a benzyl-substituted analogue might be transiently formed. The resonances for \( \text{Bn}_4\text{Sn} \) steadily grew in intensity at room temperature, while those for 1 and 2 decreased, until after 60 h the dominant species present was \( \text{Bn}_4\text{Sn} \); when this reaction mixture was heated to 50°C from the start rapid conversion of 1 and 2 to \( \text{Bn}_4\text{Sn} \) and 1H was seen; in both instances a solid material precipitated which proved to be intractable in all non-reacting solvents tested. The same conditions were then applied to a sample of 1 and 2 with collidine also present. After 30 min at RT no change was noted except the expected formation of the 1-collidine adduct, as witnessed in §3(b); while \( \text{Bn}_4\text{Sn} \) was similarly observed to appear and grow in intensity concomitant with the decrease of 1 and 2, this was at an appreciably retarded rate in comparison with the results in the absence of collidine. After 60 h at RT the predominant species in the \( \text{H}^1 \) and \( \text{Sn}^{119} \) NMR spectra were 1 and 2; only after heating at 50°C for a further 5 h did \( \text{Bn}_4\text{Sn} \) become the predominant species. Interestingly, the resonance at \( \delta = 5.28 \) ppm attributed to \( \text{Bn}_2\text{SnH}_2 \) was again present, and a characteristic resonance attributed to \( \text{[coll-H}^+ \text{]} \) had appeared in significant intensity (\( \delta = 13.38 \) ppm), upon heating.

Based on the observations above and the lack of any formation of \( \text{Bn}_3\text{SnSnBn}_3 \) or dibenzyl (\( \text{Bn}_2 \)), a proposed mechanism which rationalizes the incomplete 1/collidine-mediated \( \text{H}_2 \) heterolysis reaction, and observed decomposition products, is outlined in figure 4a.

It is postulated that the combination of 1 and 2 leads to formation of a binuclear complex (figure 4b), as evidenced by a broadening of resonances in the \( \text{H}^1 \) NMR spectrum. Rearrangement of this intermediate through PhCH\(_2\)/H exchange between Sn centres could then lead to formation of the observed \( \text{Bn}_4\text{Sn} \) and \( \text{Bn}_2\text{Sn(H)OTf} \) (corresponding to the \( \delta = 9.01 \) ppm resonance in the \( \text{H}^1 \) NMR spectrum). \( \text{Bn}_2\text{Sn(H)OTf} \) is expected to be highly reactive by analogy with its \(^{n}\text{Bu} \) analogue (hence its low steady-state intensity). Subsequently \( \text{Bn}_2\text{Sn(H)OTf} \) reacts with the more powerful hydride donor 2, which reforms 1 and accordingly produces the observed \( \text{Bn}_2\text{SnH}_2 \) (\( \text{H}^1 \) NMR: \( \delta = 5.28 \) ppm). \( \text{R}_2\text{SnH}_2 \), especially those containing R groups of a low steric threshold (e.g. \(^{n}\text{Bu} \), \( \text{Bn} \)) are also highly reactive compounds which are prone to decomposition via a radical
Figure 4. (a, b) Proposed deactivation pathways for Bn₃SnX (X = TfO, H; 1, 2) during H₂ heterolysis reactions.

chain mechanism, forming H₂ and complex mixtures of oligo/polystannanes {R₂Sn}ₙ, which for Ph-rich species can display poor solubility, especially when cross-branching occurs [from dehydrocoupling with (PhCH₂)₃SnH] [39]; the latter explains the observation of a precipitate and overall loss of ¹H NMR signal intensity during the reaction, as the PhCH₂ groups are sequestered from solution.

The stabilizing effect when collidine is present may thus be explained by its ability to form a 1-collidine adduct which competes with, and effectively retards, the formation of the complex between 1 and 2, thereby inhibiting the rate of decomposition; this result corroborates the idea that facile formation of the binuclear complex is key to the deactivation mechanism. It should also be emphasized that the presence of [col-H]⁺ in this reaction can be rationalized from the 1/collidine-mediated cleavage of H₂, the latter formed from decomposition of Bn₂SnH₂, which leads to 2 (which re-enters the cycle) and the build-up of [col-H]⁺, as observed. It is hence plausible that this constant syphoning of 2 from the system via ligand scrambling and subsequent decomposition may explain the incomplete conversion of 1 to 2 during the normal H₂ activation reaction by 1/collidine under a H₂ atmosphere (§3(b)). Finally, H₂ activation by the incipiently formed Bn₄Sn, in conjunction with collidine, can be discounted since an independent experiment of this combination under H₂ failed to show any reaction; this observation is in line with the poor Lewis acidity of tetralkyltin compounds.

(d) Imine hydrogenations

Despite the observation of subsequent decomposition, the successful activation of H₂ encouraged us to proceed to investigate the use of 1 in FLP hydrogenation reactions. It was hoped that, although 2 may exist only transiently in the presence of a suitable unsaturated substrate, the rate of reduction might exceed the rate of any undesirable side-reactions. Thus, as an attempted proof-of-principle, initial attention was focused on the imine Ph(H)C=NPPh, (3), which is an archetypal substrate for FLP-mediated catalytic hydrogenations. When H₂ (10 bar) was added to a solution of imine 3 and 1/collidine (10 mol%) in C₆D₆ and the solution subsequently
heated to 50°C, hydrogenation was indeed observed, with formation of amine PhCH2NHPh (4) (13.9% conversion after 128 h; Table 2, entry 2); it is of note that imine hydrogenation using iPr3SnOTf required significantly higher temperatures (120°C) for any reaction under analogous conditions [14].

Unfortunately, only low conversion is observed, with the rate of conversion decreasing as a function of time (5 h 6%; 21 h 10.1%; 66 h 13.3% and 128 h 13.9%), concomitant with the formation of resonances attributable to Bn4Sn, and hence with decomposition of 1/2 (vide supra).

Nevertheless, this is still one of a very small number of examples of FLP-type hydrogenation using a p-block LA catalyst based on an element other than boron [14,40,41].

Attempts to increase the rate of reaction and percentage of imine conversion by raising the temperature to 70°C led to no more than minor improvements in rate (Table 2), and resulted in the complete decomposition of 1 (via 1/2) to Bn4Sn (as observed by 1H and 119Sn{1H} NMR spectroscopy). Conversely, at ambient temperatures decomposition was observed to a much lesser extent, but at the expense of even poorer conversion (4.3% after 128 h); nonetheless this result does demonstrate that H2 activation occurs even at room temperature for the 1/collidine system. Ultimately, however, it seems clear that the potential for 1 to engage in useful FLP hydrogenation catalysis is unfortunately limited by the reduced chemical stability of the Bn3Sn core (relative to iPr3Sn, for example).

### Table 2. 1-catalysed hydrogenation of Ph(H)C≡NPh. (Online version in colour.)

<table>
<thead>
<tr>
<th>entry</th>
<th>temperature (°C)</th>
<th>time (h)</th>
<th>conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>128</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>128</td>
<td>13.9</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>49</td>
<td>13.2</td>
</tr>
</tbody>
</table>

4. Conclusion

The Sn-based LA, Bn3SnOTf, has been synthesized in excellent yield and fully characterized in both the solution and solid state. X-ray crystallography reveals an extended polymeric structure with triflate anions bridging two Bn3Sn cores and a 5-coordinate, trigonal bipyramidal, geometry around the Sn centre; this is a rare example of a structurally characterized triorganotin triflate. Subtle modulation of the electronics at the Sn centre by incorporating benzyl instead of the more common alkyl ligands on the R3Sn core has allowed for a successful increase in R3SnOTf Lewis acidity, as evidenced by the comparison of AN values calculated from the Gutmann–Beckett spectroscopic method. This increase in Lewis acidity was further corroborated by the lower temperature and pressure at which Bn3SnOTf activates hydrogen in comparison with previously reported alkylated analogues. Competing decomposition/deactivation pathways preclude stable H2 activation for use in catalysis at elevated temperatures, however; these were probed and it was posited that a binuclear complex forming between Bn3SnOTf and the product of H2 activation, Bn3SnH, leads to ligand scrambling and ultimately deactivation to Bn4Sn. Future efforts are focused on the synthesis of new triorganotin LAs which display enhanced Lewis acidity to mediate rapid H2 activation, yet retain a high degree of thermal stability, for use as FLP hydrogenation catalysis.
Data accessibility. Additional data supporting this article have been uploaded as part of the electronic supplementary material. Crystallography data of 1 has been deposited in the CCDC, no. 1534626. They are available online.

Authors’ contributions. R.T.C., J.S.S. (PhD student) and R.C.T.-R. (PhD student) carried out the majority of the experiments and characterization, interpreting the results and writing the manuscript. D.-H.H. (undergrad student) contributed to the experimental data and characterization studies. A.J.P.W. collected and processed X-ray crystallography data. A.E.A. conceived and designed the study with R.T.C. All authors read and approved the manuscript.

Competing interests. We declare we have no competing interests.

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