Hydrogen activation using a novel tribenzyltin Lewis acid

Robert T. Cooper, Joshua S. Sapsford, Roland C. Turnell-Ritson, Dong-Hun Hyon, Andrew J. P. White and Andrew E. Ashley

Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

Electronic supplementary material is available online at https://dx.doi.org/10.6084/m9.figshare.c.3807280.

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 Bn$_3$SnOTf (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 R$_3$SnOTf LAs, and has facilitated low temperature hydrogen activation and imine hydrogenation. Deactivation pathways of the R$_3$Sn$^+$ 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 H$_2$ [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 $\text{R}_3\text{Sn}^+$ ($\text{R} = \text{alkyl}$) based LAs, which possess several properties very similar to the most commonly used LA in FLP chemistry, $\text{B(C}_6\text{F}_5)_3$ [13]. In particular these LAs are isoelectronic, isolobal, and have been calculated to have comparable hydride ion affinities ($\Delta G_{\text{H}^-} = 65.83$ and $64.95$ kcal mol$^{-1}$ for $\text{nBu}_3\text{Sn-H}$ and $(\text{C}_6\text{F}_5)_3\text{B-H}^-$ respectively) [18], indicating that these species could show analogous reactivity in H$_2$ activation and hydrogenation chemistry. Accordingly, we recently described the use of $\text{iPr}_3\text{SnOTf}$ (a surrogate for $\text{iPr}_3\text{Sn}^+; \text{OTf} = \text{CF}_3\text{SO}_3$) in FLP-mediated H$_2$ activation chemistry when partnered with amine/pyridine LBs. Furthermore, $\text{iPr}_3\text{SnOTf}$ could successfully be employed in the catalytic hydrogenation of a variety of functional groups (C=C, C=Na nand 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 $\text{iPr}_3\text{SnOTf}$ as a LA was the ease of H$_2$ activation. In this respect, it is notable that earlier work by Manners and co-workers showed similar FLP systems based on $\text{nBu}_3\text{SnOTf}$ were unreactive towards H$_2$, although they were capable of dehydrogenating amine-boranes. We proposed that this resulted from an overly strong interaction between the less bulky $\text{R}_3\text{Sn}^+$ and $\text{OTf}^-$ 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 $\text{iPr}$ analogue. These results clearly indicate that the reactivity of $\text{R}_3\text{Sn}^+$-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 H$_2$ is strongly correlated to the cumulative proton and hydride affinities of LB and LA, respectively [19], for which $pK_a$ values of $[\text{LB-H}]^+$ 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 $\text{R}_3\text{Sn}^+$ via the use of a more electron-withdrawing R group would facilitate faster FLP-mediated H$_2$ activation and hence improved catalytic hydrogenation kinetics. Herein we report the targeted high yielding synthesis and characterization of the new LA $\text{Bn}_3\text{SnOTf}$ ($\text{Bn} = \text{PhCH}_2$; 1) which, by virtue of the greater inductive electron-withdrawing effect of the sp$^2$-hybridized phenyl C atom versus an sp$^3$-alkyl substituent, displays an enhanced Lewis acidity over $\text{iPr}_3\text{SnOTf}$. Furthermore, we show that 1 displays facile H$_2$ activation at lower temperatures than its $\text{iPr}$ 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; Et$_2$O was distilled from Na/fluorenone and stored over K; CHCl$_3$ was dried and stored over 3 Å molecular sieves; C$_6$D$_6$ and CDC$_3$/CD$_2$Cl$_2$ were freeze–pump–thaw degassed and dried over a K mirror and 3 Å molecular sieves, respectively. H$_2$ 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=NH...
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 (EI 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.

\[ \delta: 2.22 \text{[s, } 8 \text{H, CH}2\text{], 6.74 \text{[s, } 8 \text{H, Ph}], 7.01 \text{[s, } 4 \text{H, Ph}], 7.16 \text{[s, } 8 \text{H, Ph}].} \]

119Sn NMR (149 Hz, CDCl3) \( \delta: -37.1 \text{ (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 \( \times \) 15 ml) to furnish pure Bn3SnOTf as a white solid (2.01 g, 3.71 mmol) in 88% yield.

\[ \delta: 2.92 \text{[s, } 6 \text{H, CH}2\text{], 6.79 \text{[s, } 6 \text{H, Ph}], 7.12 \text{[s, } 3 \text{H, Ph}], 7.20 \text{[s, } 6 \text{H, Ph}.} \]

13C NMR (101 MHz, CDCl3) \( \delta: 26.8 \text{[s, } 1 \text{C}, 117\text{Sn}] \]), 118.9 \[ \text{[s, } 1 \text{C}, 119\text{Sn}] \]), 125.9 \[ \text{[s, } 1 \text{C}, 119\text{Sn}].\]

19F NMR (376 MHz, CDCl3) \( \delta: -77.0 \text{.} \]

Elemental analysis found (calculated) for C22H21O3F3SSn: C 48.69 (48.83), H 4.01 (3.91). HRMS (EI): \( m/z: 542.0202 \) (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.

1H NMR (400 MHz, C6D6) δ: 2.17 [6H, d, J = 1.5 Hz, 2J(117,119Sn-1H) = 61.5 Hz, CH2], 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]. 13C{1H} NMR (101 MHz, C6D6) δ: 17.9 [s, 1J(117Sn-1H) = 277.0 Hz, 1J(119Sn-1H) = 289.5 Hz, CH2], 124.2 [s, 5J(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]. 119Sn{1H} NMR (149 Hz, C6D6) δ: −85.4 (s); these values are consistent with those previously reported [23].

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

Et3PO (3.6 mg, 0.02 mmol) and Bn3SnOTf (32.4 mg, 0.06 mmol) were dissolved in CD2Cl2 (0.4 ml) and added to a NMR tube with a capillary insert containing 1 M Et3PO in CD2Cl2. Based on the 31P{1H} chemical shift of the resulting Et3PO adduct relative to the insert, the acceptor number (AN) was calculated using the formula of Mayer et al. [25] and Beckett et al. [26]

\[ \text{AN} = \frac{[\delta (\text{sample}) - 41.0] \times 100}{86.14 - 41.0} \]

31P{1H} NMR, δadduct = 74.41 ppm gave an acceptor number of 74.0.

(e) H2 activation procedure using Bn3SnOTf, (1) and collidine

Inside a glovebox 1 (16.2 mg, 0.03 mmol) and collidine (3.6 mg, 0.03 mmol) were combined in C6D6 (0.4 ml) and transferred into a NMR tube fitted with a Young’s valve. The solution was freeze–pump–thaw degassed and H2 (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 1H, 19F and 119Sn 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 δ = 5.71 ppm accompanied by 117/119Sn-1H satellites and the 119Sn resonance at δ = −85.4 ppm.

(f) Investigations into PhCH2/H scrambling and deactivation routes

(i) Thermal stability of Bn3SnOTf, (1)

A sample of 1 (16.2 mg, 0.03 mmol) was dissolved in C6D6 (0.4 ml) and transferred into a NMR tube fitted with a Young’s valve. The reaction was followed by 1H and 119Sn{1H} NMR spectroscopy but no reaction was observed, even after heating to 70°C for 72 h.

(ii) Thermal stability of Bn3SnOTf (1) and collidine

A NMR tube was loaded with 1 (16.2 mg, 0.03 mmol), collidine (3.6 mg, 0.03 mmol) and C6D6 (0.4 ml), which led to the formation of an adduct by 119Sn{1H} NMR spectroscopy. However, no further change was observed by 1H and 119Sn{1H} NMR spectroscopy, even after heating to 70°C for 72 h.

(iii) Thermal stability of Bn3SnOTf (1) and Bn3SnH (2)

Inside a glovebox 1 (16.2 mg, 0.03 mmol) and 2 (11.8 mg, 0.03 mmol) were combined in C6D6 (0.4 ml) and transferred into a NMR tube fitted with a Young’s valve. The mixture was monitored by 1H and 119Sn{1H} NMR spectroscopy at regular intervals for 60 h at RT. Complete decomposition of 1 and 2 was observed with concomitant formation of Bn4Sn (119Sn{1H} NMR δ = −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 Bn₃SnOTf (1), Bn₃SnH (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 C₆D₆ (0.4 ml) and transferred into a NMR tube fitted with a Young’s valve. The mixture was monitored by ¹H and ¹¹⁹Sn HSQC NMR spectroscopy at regular intervals over the course of 60 h at RT, during which partial decomposition of 1 and 2 to Bn₄Sn was observed (¹¹⁹Sn HSQC NMR δ = −37.5 ppm). An analogous reaction conducted with heating to 50°C for 5 h showed complete decomposition.

(g) Imine hydrogenation procedure using Bn₃SnOTf (1) and collidine

Inside a glovebox 1 (10.8 mg, 0.02 mmol), collidine (2.4 mg, 0.02 mmol) and Ph(H)C=NPh (3) (36.2 mg, 0.20 mmol) were dissolved in C₆D₆ (0.4 ml) and transferred into a Wilmad high pressure NMR tube fitted with a PV-ANV PTFE valve. H₂ was admitted to a pressure of 10 bar (at room temperature) and analysed by ¹H, ¹⁹F and ¹¹⁹Sn 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 ¹H resonances belonging to the amine product [PhC≡H₂-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 Bn₃SnOTf (1)

The target compound Bn₃SnOTf (1) was synthesized by the facile proteodealkylation of Bn₄Sn (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 ¹H, ¹³C, ¹⁹F and ¹¹⁹Sn NMR spectroscopy, elemental analysis, HRMS (EI) and X-ray crystallography. Single crystals were grown from a cooled (−20°C) saturated Et₂O 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 P2₁ 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 Bn₃Sn 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 τ [28]; the range 0.94–0.96 obtained for the four independent molecules in 1 indicates a near perfect trigonal bipyramidal geometry (idealized τ = 1, versus τ = 0 for square-based-pyramidal).

1 is isostructural with Ph₃SnOTf [27], one of only two triorganotin triflates that have previously been structurally characterized, the other being the molecular species [(Me₃Si)₂CH]₃SnOTf [29]. These structural variations are likely attributed to the differing steric bulk of the R groups around Sn, with the very large [(Me₃Si)₂CH] 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 Ph₃SnOTf are almost identical within experimental error [27]. However, the latter are considerably longer than those observed in [(Me₃Si)₂CH]₃SnOTf (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.

Figure 2. Molecular structure of 1 (molecule a). Ellipsoids shown at 50% probability, H atoms omitted for clarity (C atoms blue, O atoms red, F atoms green, S atoms yellow, Sn atoms pink). (a) View of one independent Bn₃SnOTf fragment in the asymmetric unit. (b) Extended view of the polymeric structure generated from the independent fragment along the b axis (all four independent molecules form similar polymeric chains).

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 CDCl₃ reveals a notably downfield shift of the methylene resonance ($\delta = 2.92$ ppm; CDCl₃) compared to Bn₄Sn ($\delta = 2.22$ ppm; CDCl₃), 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; $\Delta\nu/2 = 48.4$ 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 $\text{R}_3\text{SnOTf}$ ($\text{R} = ^3\text{Bu}$ [31],$^1\text{Pr}$ [14]; $\delta = 168$ and 156 ppm, respectively). These data, in combination with the $^{13}C$-$^{119}\text{Sn}$ values for the $\text{R}_3\text{SnOTf}$ compounds ($\text{R} = ^3\text{Bu}$ 383; $^1\text{Pr}$ 316; 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 highly depend on solvent, degree of aggregation in solution, and the substituents of the stannyl 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.

**Table 1.** Selected bond lengths and angles for isomorphic 1 and $\text{Ph}_3\text{SnOTf}$ [27]. ESDs are given in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>1d</th>
<th>$\text{Ph}_3\text{SnOTf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn–R length (Å)</td>
<td>2.141(6)</td>
<td>2.141(7)</td>
<td>2.147(7)</td>
<td>2.141(8)</td>
<td>2.104(6)</td>
</tr>
<tr>
<td></td>
<td>2.147(7)</td>
<td>2.151(6)</td>
<td>2.157(7)</td>
<td>2.143(7)</td>
<td>2.117(6)</td>
</tr>
<tr>
<td></td>
<td>2.154(7)</td>
<td>2.152(7)</td>
<td>2.164(6)</td>
<td>2.146(7)</td>
<td>2.118(5)</td>
</tr>
<tr>
<td>Sn–O length (Å)</td>
<td>2.310(4)</td>
<td>2.288(5)</td>
<td>2.317(5)</td>
<td>2.306(6)</td>
<td>2.310(4)</td>
</tr>
<tr>
<td></td>
<td>2.345(5)</td>
<td>2.351(5)</td>
<td>2.352(5)</td>
<td>2.337(5)</td>
<td>2.375(4)</td>
</tr>
<tr>
<td>O–Sn–O angle (°)</td>
<td>177.7(2)</td>
<td>177.66(18)</td>
<td>176.83(19)</td>
<td>176.1(2)</td>
<td>175.6(1)</td>
</tr>
<tr>
<td>R–Sn–R angle (°)</td>
<td>113.4(3)</td>
<td>115.2(3)</td>
<td>114.4(3)</td>
<td>114.4(3)</td>
<td>116.2(2)</td>
</tr>
<tr>
<td></td>
<td>118.0(3)</td>
<td>117.7(3)</td>
<td>117.0(3)</td>
<td>115.9(3)</td>
<td>117.4(2)</td>
</tr>
<tr>
<td></td>
<td>128.3(3)</td>
<td>126.4(3)</td>
<td>128.3(3)</td>
<td>129.5(3)</td>
<td>126.3(2)</td>
</tr>
</tbody>
</table>

(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 $\text{B(C}_6\text{F}_5)_3\text{ }$ which generates the free FLP upon heating which subsequently cleaves $\text{H}_2$ [33]; furthermore strongly bound adducts such as the silylium/phosphine species $[^1\text{Pr}_3\text{Si}=\text{P}^+\text{Bu}_3]^+$ (for which no stable FLP counterpart can exist) can also engage in $\text{H}_2$ heterolysis [34] (note that in our previous studies the $^1\text{Pr}_3\text{SnOTf}/\text{DABCO}$ (DABCO=1,4-diazabicyclo[2.2.2]octane) Lewis pair was found to activate $\text{H}_2$ despite evidence for similar adduct formation [14]). With this in mind, admission of $\text{H}_2$ (4 bar, 50°C, 2 h) led to
Figure 3. $^1$H NMR spectra of 1 and collidine in $\text{C}_6\text{D}_6$ before (a) and after (b) admission of H$_2$ (4 bar). Insets show Sn-H resonance and $^1J(1^{17}/1^{19}\text{Sn}-^1\text{H})$ satellites.

the appearance of resonances in the $^1$H NMR (5.72 ppm, SnH, $^1J(1^{17}/1^{19}\text{Sn}-^1\text{H}) = 1693/1773$ Hz; 13.13 ppm, NH) and $^{119}\text{Sn}(^1\text{H})$ NMR ($-84.8$ ppm) spectra, which are consistent with formation of Bn$_3$SnH (2) and [col-H]$^+\text{[TfO]}^-$, 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 $^1$Pr$_3$SnOTf and collidine required higher pressure (10 bar) and longer times (20 h) [14]. Similarly, no H$_2$ activation was reported with iPr$_3$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, $^1$Pr, 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 $^1$Pr$_3$SnOTf, which is nonetheless catalytically active for a variety of C=X (X = C, N, O) bond
downfield resonance is almost identical to the related diorganotin hydride species, Bu₂Sn(H)OTf, δ further hour, broad resonances at (Bn₂), a proposed mechanism which rationalizes the incomplete observed during earlier investigations using iPr₃SnOTf. 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 Bn₂SnX (X = H, TfO) deactivation pathways

On closer inspection of the hydrogen cleavage experiments the diagnostic chemical shifts of Bn₄Sn were noted in the ¹H and ¹¹⁹Sn[¹H] NMR spectra (δ = 2.17 and −37.5 ppm respectively; C₆D₆). 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 ¹H and ¹¹⁹Sn[¹H] NMR) even at temperatures above those used for H₂ 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 [35], it is known to be unstable at elevated temperatures [35], converting smoothly to hexabenzyldistannane (Bn₃SnSnBn₃) with concomitant evolution of H₂ [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, C₆D₆) which led to an instant interaction as evidenced by the broadening of both sets of resonances (most notably methylene) in the ¹H NMR spectrum (electronic supplementary material, figure S6a). After 30 min at RT there were distinctive resonances indicating the formation of Bn₄Sn and after a further hour, broad resonances at δ = 9.01 and 5.28 ppm appeared (albeit in low intensity), the latter being identical to that previously reported for Bn₂SnH₂ [37]. Interestingly, the diagnostic downfield resonance is almost identical to the related diorganotin hydride species, Bu₂Sn(H)OTf (δ = 8.99 ppm; C₆D₆) [38], strongly indicating the possibility that a benzyl-substituted analogue might be transiently formed. The resonances for Bn₄Sn steadily grew in intensity at room temperature, while those for 1 and 2 decreased, until after 60 h the dominant species present was Bn₄Sn; when this reaction mixture was heated to 50°C from the start rapid conversion of 1 and 2 to Bn₄Sn is 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 Bn₄Sn 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 ¹H and ¹¹⁹Sn[¹H] NMR spectra were 1 and 2; only after heating at 50°C for a further 5 h did Bn₄Sn become the predominant species. Interestingly, the resonance at δ = 5.28 ppm attributed to Bn₂SnH₂ was again present, and a characteristic resonance attributed to [coll-H⁺] had appeared in significant intensity (δ = 13.38 ppm), upon heating.

Based on the observations above and the lack of any formation of Bn₃SnSnBn₃ or dibenzyl (Bn₂), a proposed mechanism which rationalizes the incomplete 1/collidine-mediated H₂ 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 ¹H NMR spectrum. Rearrangement of this intermediate through PhCH₂/H exchange between Sn centres could then lead to formation of the observed Bn₄Sn and Bn₂Sn(H)OTf (corresponding to the δ = 9.01 ppm resonance in the ¹H NMR spectrum). Bn₂Sn(H)OTf is expected to be highly reactive by analogy with its nBu analogue (hence its low steady-state intensity). Subsequently Bn₂Sn(H)OTf reacts with the more powerful hydride donor 2, which reforms 1 and accordingly produces the observed Bn₂SnH₂ (¹H NMR: δ = 5.28 ppm). B₂SnH₂, especially those containing R groups of a low steric threshold (e.g. nBu, Bn) are also highly reactive compounds which are prone to decomposition via a radical
chain mechanism, forming H₂ and complex mixtures of oligo/polystannanes \( \{R_2Sn\}_n \), 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 \(^1\)H 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 tetralkyldtin 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=NPh, (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
Table 2. 1-catalysed hydrogenation of Ph(H)C=NHPh. (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>

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).

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.

Funding. We greatly acknowledge funding for this work from the Royal Society for a University Research Fellowship (A.E.A.; UF110061), the EPSRC for R.T.C. (EP/N026004/1), and Imperial College for a President’s PhD Scholarship (R.C.T.-R.).

Acknowledgements. We would like to thank Pete Haycock, Imperial College London, for NMR spectroscopic measurements.

References


26. Beckett MA, Strickland GC, Holland JR, Varma KS. 1996 A convenient n.m.r. method for the measurement of Lewis acidity at boron centres: correlation of reaction rates of Lewis acid initiated epoxide polymerizations with Lewis acidity. Polymer (Guildf) 37, 4629–4631. (doi:10.1016/0032-3861(96)00323-0)


