

Research



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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 Bn_3SnOTf (**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_3SnOTf LAs, and has facilitated low temperature hydrogen activation and imine hydrogenation. Deactivation pathways of the R_3Sn^+ 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 stannylum ion R_3Sn^+ (R = alkyl) based LAs, which possess several properties very similar to the most commonly used LA in FLP chemistry, $B(C_6F_5)_3$ [13]. In particular these LAs are isoelectronic, isolobal, and have been calculated to have comparable hydride ion affinities (ΔG_{H^-} = 65.83 and 64.95 kcal mol $^{-1}$ for $^nBu_3Sn-H$ and $[(C_6F_5)_3B-H]^-$ respectively) [18], indicating that these species could show analogous reactivity in H_2 activation and hydrogenation chemistry. Accordingly, we recently described the use of $^iPr_3SnOTf$ (a surrogate for $^iPr_3Sn^+$; $OTf = CF_3SO_3$) in FLP-mediated H_2 activation chemistry when partnered with amine/pyridine LBs. Furthermore, $^iPr_3SnOTf$ 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 $^iPr_3SnOTf$ 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 $^nBu_3SnOTf$ 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 R_3Sn^+ 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 R_3Sn^+ -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 $[LB-H]^+$ 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 R_3Sn^+ 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 Bn_3SnOTf ($Bn = PhCH_2$; **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 $^iPr_3SnOTf$. Furthermore, we show that **1** displays facile H_2 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 SolvTM SPS-400 and stored over K; Et_2O was distilled from Na/fluorenone and stored over K; $CHCl_3$ was dried and stored over 3 Å molecular sieves; C_6D_6 and $CDCl_3/CD_2Cl_2$ 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 WeldassureTM Purifier drying column. 2,4,6-Collidine (hereafter referred to as collidine) and $Ph(H)C=NPh$

were purchased from major suppliers, degassed and dried over 4 Å molecular sieves before use. Bn_3SnCl was purchased from Alfa Aesar and dried under vacuum. Benzyl chloride (BnCl), SnCl_4 , Mg , LiAlH_4 , I_2 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 ^{13}C spectra were referenced internally to the residual solvent signals and reported in parts per million (ppm). ^{19}F , ^{31}P and ^{119}Sn spectra were referenced externally to CFCl_3 , 85% $\text{H}_3\text{PO}_4(\text{aq})$ and Me_4Sn 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 (Bn_4Sn)

A modified procedure of Smith & Kipping [20] and Huber and colleagues [21] was employed: SnCl_4 (6.70 g, 25.71 mmol) was added slowly to Et_2O (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 I_2 (0.05 g, 0.20 mmol). Benzyl chloride (13.02 g, 102.84 mmol) in Et_2O (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 CHCl_3 . The remaining work-up was performed under air: the combined organic phases were dried over Na_2SO_4 and filtered, and the volatiles removed under reduced pressure resulting in an oil. Bn_4Sn 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, CDCl_3) δ : 2.22 [8H, s, $^2J(^{119,117}\text{Sn}-^1\text{H}) = 58.3 \text{ Hz}$, CH_2], 6.74 [8H, m, Ph], 7.01 [4H, m, Ph], 7.16 [8H, m, Ph]. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149 Hz, CDCl_3) δ : -37.1 (s); these values are consistent with those previously reported [22].

(ii) Tribenzyltin triflate (Bn_3SnOTf), (1)

Trifluoromethanesulfonic acid (TfOH , 0.63 g, 4.21 mmol) was added dropwise to a solution of Bn_4Sn (2.14 g, 4.43 mmol) in CHCl_3 (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 ($4 \times 15 \text{ ml}$) to furnish pure Bn_3SnOTf as a white solid (2.01 g, 3.71 mmol) in 88% yield.

^1H NMR (400 MHz, CDCl_3) δ : 2.92 [6H, s, $^2J(^{117,119}\text{Sn}-^1\text{H}) = 66.02 \text{ Hz}$, CH_2], 6.79 [6H, m, Ph], 7.12 [3H, m, Ph], 7.20 [6H, m, Ph]. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 26.8 [s, $^1J(^{117}\text{Sn}-^1\text{H}) = 258.4 \text{ Hz}$, $^1J(^{119}\text{Sn}-^1\text{H}) = 271.2 \text{ Hz}$, CH_2], 118.9 [q, $^1J(^{19}\text{F}-^{13}\text{C}) = 317.2 \text{ Hz}$, CF_3], 125.9 [s, $^5J(^{117,119}\text{Sn}-^{13}\text{C}) = 21.6 \text{ Hz}$, Ph], 128.1 [s, $^3J(^{117,119}\text{Sn}-^{13}\text{C}) = 33.4 \text{ Hz}$, Ph], 129.4 [s, $^4J(^{117,119}\text{Sn}-^{13}\text{C}) = 18.2 \text{ Hz}$, Ph], 135.9 [s, Ph]. ^{19}F NMR (376 MHz, CDCl_3) δ : -77.0 . $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149 Hz, CDCl_3) δ : 87.4 [br s, $\Delta\nu^{1/2} = 48.4 \text{ Hz}$]. Elemental analysis found (calculated) for $\text{C}_{22}\text{H}_{21}\text{O}_3\text{F}_3\text{SSn}$: C 48.69 (48.83), H 4.01 (3.91). HRMS (EI): m/z found (calculated) for $\text{C}_{22}\text{H}_{21}\text{O}_3\text{F}_3\text{SSn}$: 542.0202 (542.0186).

(iii) Tribenzyltin hydride (Bn_3SnH), (2)

A modified procedure of Miura and colleagues [23] was employed for the independent synthesis of Bn_3SnH (2): Bn_3SnCl (1.00 g, 2.34 mmol) was added to LiAlH_4 (0.08 g, 2.13 mmol) in Et_2O

(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, C_6D_6) δ : 2.17 [6H, d, $J = 1.5$ Hz, $^2J(^{117,119}\text{Sn}-^1\text{H}) = 61.5$ Hz, CH_2], 5.71 [1H, sept, $J = 1.5$ Hz, $^1J(^{117}\text{Sn}-^1\text{H}) = 1693.8$ Hz, $^1J(^{119}\text{Sn}-^1\text{H}) = 1773.1$ Hz], 6.79 [6H, m, Ph], 6.94 [3H, m, Ph], 7.09 [6H, m, Ph]. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6) δ : 17.9 [s, $^1J(^{117}\text{Sn}-^1\text{H}) = 277.0$ Hz, $^1J(^{119}\text{Sn}-^1\text{H}) = 289.5$ Hz, CH_2], 124.2 [s, $^5J(^{117,119}\text{Sn}-^{13}\text{C}) = 16.1$ Hz, Ph], 127.9 [s, Ph], 128.9 [s, $^4J(^{117,119}\text{Sn}-^{13}\text{C}) = 13.6$ Hz, Ph], 142.1 [s, $^2J(^{117,119}\text{Sn}-^{13}\text{C}) = 39.6$ Hz, Ph]. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149 Hz, C_6D_6) δ : −85.4 (s); these values are consistent with those previously reported [23].

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

Et_3PO (3.6 mg, 0.02 mmol) and Bn_3SnOTf (32.4 mg, 0.06 mmol) were dissolved in CD_2Cl_2 (0.4 ml) and added to a NMR tube with a capillary insert containing 1 M Et_3PO in CD_2Cl_2 . Based on the $^{31}\text{P}\{^1\text{H}\}$ chemical shift of the resulting Et_3PO adduct relative to the insert, the acceptor number (AN) was calculated using the formula of Mayer *et al.* [25] and Beckett *et al.* [26] $\text{AN} = [(\delta(\text{sample}) - 41.0) \times 100 / (86.14 - 41.0)]$. $^{31}\text{P}\{^1\text{H}\}$ NMR, $\delta_{\text{adduct}} = 74.41$ ppm gave an acceptor number of 74.0.

(e) H_2 activation procedure using Bn_3SnOTf , (**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_6D_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 ^1H , ^{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 $^{117/119}\text{Sn}-^1\text{H}$ 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_3SnOTf , (**1**)

A sample of **1** (16.2 mg, 0.03 mmol) was dissolved in C_6D_6 (0.4 ml) and transferred into a NMR tube fitted with a Young's valve. The reaction was followed by ^1H and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectroscopy but no reaction was observed, even after heating to 70°C for 72 h.

(ii) Thermal stability of Bn_3SnOTf (**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_6D_6 (0.4 ml), which led to the formation of an adduct by $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectroscopy. However, no further change was observed by ^1H and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectroscopy, even after heating to 70°C for 72 h.

(iii) Thermal stability of Bn_3SnOTf (**1**) and Bn_3SnH (**2**)

Inside a glovebox **1** (16.2 mg, 0.03 mmol) and **2** (11.8 mg, 0.03 mmol) were combined in C_6D_6 (0.4 ml) and transferred into a NMR tube fitted with a Young's valve. The mixture was monitored by ^1H and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectroscopy at regular intervals for 60 h at RT. Complete decomposition of **1** and **2** was observed with concomitant formation of Bn_4Sn ($^{119}\text{Sn}\{^1\text{H}\}$ 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 Bn_3SnOTf (**1**), Bn_3SnH (**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_6D_6 (0.4 ml) and transferred into a NMR tube fitted with a Young's valve. The mixture was monitored by ^1H 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_4Sn 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 Bn_3SnOTf (**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 C_6D_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 ^1H , ^{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 ^1H resonances belonging to the amine product [$\text{PhCH}_2\text{-NPh}$, (**4**)], residual starting material [Ph(H)C=NPh , (**3**)]. This procedure was repeated at 70°C and room temperature.

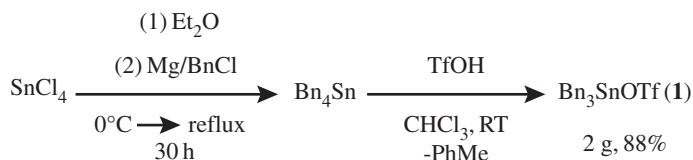
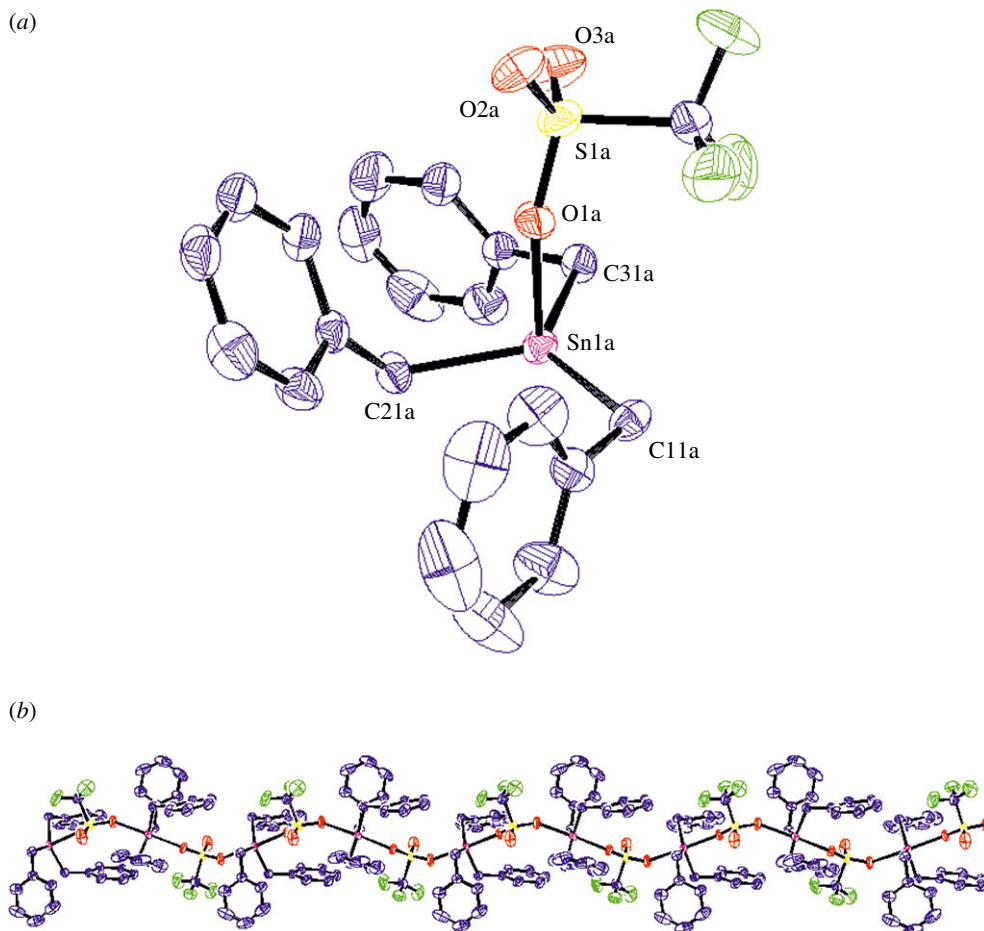
3. Results and discussion

(a) Synthesis and characterization of Bn_3SnOTf (**1**)

The target compound Bn_3SnOTf (**1**) was synthesized by the facile proteodealkylation of Bn_4Sn (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 , ^{13}C , ^{19}F and ^{119}Sn NMR spectroscopy, elemental analysis, HRMS (EI) and X-ray crystallography. Single crystals were grown from a cooled (-20°C) saturated Et_2O 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_3Sn 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 $\tau = 1$, versus $\tau = 0$ for square-based-pyramidal).

1 is isostructural with Ph_3SnOTf [27], one of only two triorganotin triflates that have previously been structurally characterized, the other being the molecular species $[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{SnOTf}$ [29]. These structural variations are likely attributed to the differing steric bulk of the R groups around Sn, with the very large $[(\text{Me}_3\text{Si})_2\text{CH}]$ 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_3SnOTf are almost identical within experimental error [27]. However, the latter are considerably longer than those observed in $[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{SnOTf}$ (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**.**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 Bn_3SnOTf 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 ^1H 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_4Sn ($\delta = 2.22$ 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

Table 1. Selected bond lengths and angles for isomorphous **1** and Ph₃SnOTf [27]. ESDs are given in parentheses.

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

significant stannylum ion character in **1**, which is usually typified by a strongly downfield ¹¹⁹Sn NMR chemical shift. However, the single broad resonance seen for **1** in the ¹¹⁹Sn{¹H} NMR spectrum ($\delta = 87.4$ ppm; $\Delta\nu_{1/2} = 48.4$ Hz) is considerably upfield relative to the value reported for [nBu₃Sn][CB₁₁Me₁₂] ($\delta = 454$ ppm), which exhibits the least coordinated trialkylstannylum core reported to date [30], and the related trialkyltin triflates R₃SnOTf (R = nBu [31], ⁱPr [14]; $\delta = 168$ and 156 ppm, respectively). These data, in combination with the ¹J(¹³C–¹¹⁹Sn) values for the R₃SnOTf compounds (R = nBu 383; ⁱPr 316; Bn 258 Hz) where higher values are proposed to be an indicator of increasing stannylum character [31], might imply that **1** should be the weakest LA of the R₃SnOTf series. However, the ¹¹⁹Sn 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 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 ³¹P NMR chemical shift of Et₃P=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 the nucleophilic O atom in Et₃P⁺–O[–] is competent at displacing bridging OTf interactions, thus providing a valid assessment of the Lewis acidity of the Bn₃SnOTf monomer. The AN value of **1** was experimentally determined to be 74.0, and indicates that Bn₃SnOTf is significantly more Lewis acidic than the related R₃SnOTf (R = nBu, ⁱPr; AN = 64.2 and 68.0, respectively) [14], albeit less so than the commonly used FLP LA B(C₆F₅)₃ (AN = 78.1). This indicates, as intended by design, that **1** is the strongest LA in the R₃SnOTf series and a strong candidate for improved heterolytic H₂ activation and subsequent reactivity.

(b) Hydrogen activation studies of Bn₃SnOTf (**1**)

Combination of **1** and collidine in a 1:1 ratio in C₆D₆ led to an upfield shift in the ¹¹⁹Sn{¹H} resonance from $\delta = 74.9$ to 33.6 ppm (br), concomitant with a slight shift of the ¹H 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 B(C₆F₅)₃ which generates the free FLP upon heating which subsequently cleaves H₂ [33]; furthermore strongly bound adducts such as the silylium/phosphine species [ⁱPr₃Si–P^tBu₃]⁺ (for which no stable FLP counterpart can exist) can also engage in H₂ heterolysis [34] (note that in our previous studies the ⁱPr₃SnOTf/DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane) Lewis pair was found to activate H₂ despite evidence for similar adduct formation [14]). With this in mind, admission of H₂ (4 bar, 50°C, 2 h) led to

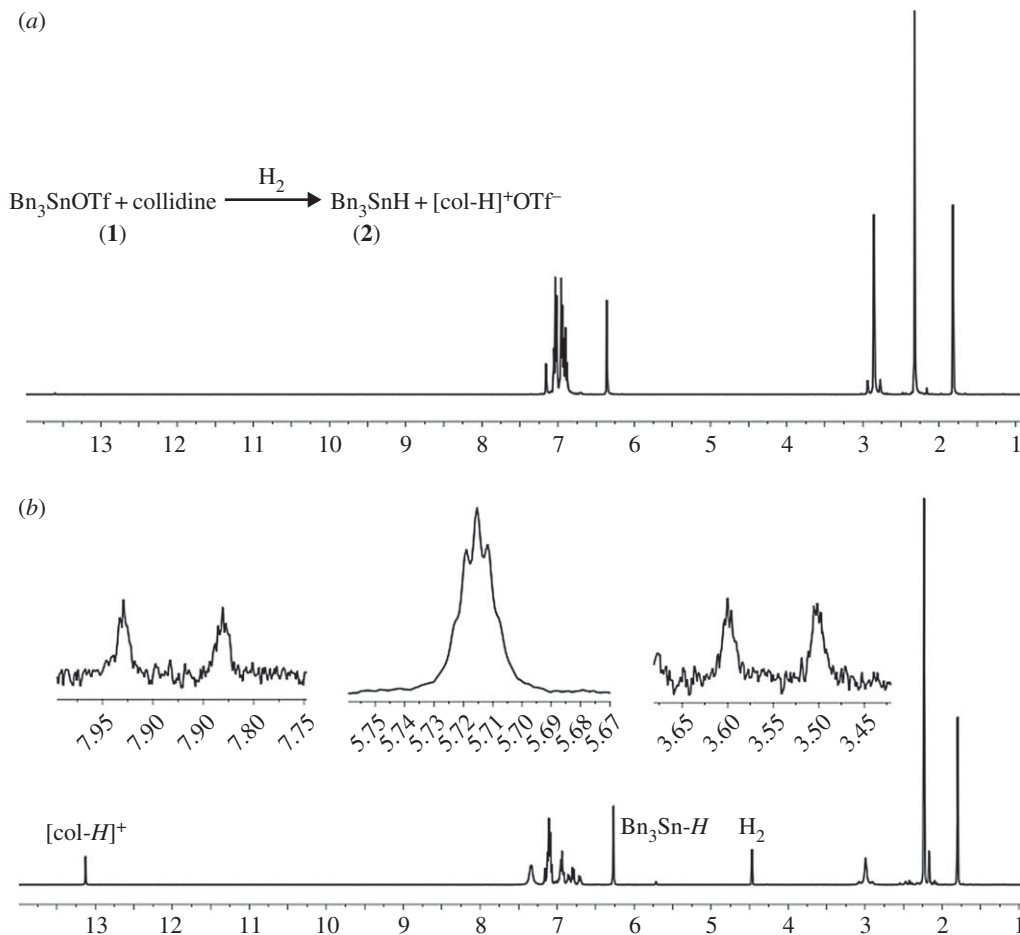


Figure 3. ¹H NMR spectra of **1** and collidine in C₆D₆ before (a) and after (b) admission of H₂ (4 bar). Insets show Sn-H resonance and ¹J(^{117/119}Sn-¹H) satellites.

the appearance of resonances in the ¹H NMR [5.72 ppm, SnH, ¹J(^{117/119}Sn-¹H) = 1693/1773 Hz; 13.13 ppm, NH] and ¹¹⁹Sn{¹H} NMR (−84.8 ppm) spectra, which are consistent with formation of Bn₃SnH (**2**) and [col-H]⁺[TfO][−], formed through H₂ 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 H₂ activation using a Sn(IV) based LA.

It is interesting to note that the equivalent H₂ activation by ⁱPr₃SnOTf and collidine required higher pressure (10 bar) and longer times (20 h) [14]. Similarly, no H₂ activation was reported with ⁿBu₃SnOTf 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 R₃SnOTf series (R = ⁿBu, ⁱPr, Bn).

Inspection of ¹H NMR integrals revealed incomplete conversion of **1** to **2** (17% as ascertained by ¹H NMR using a 2,5-dimethylfuran insert), which contrasts with the outcome of similar reactions using B(C₆F₅)₃ whose H₂ 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 CH₂Ph resonances in **1**. However, similar observations were reported for ⁱPr₃SnOTf, which is nonetheless catalytically active for a variety of C=X (X = C, N, O) bond

hydrogenations [14]. It was noted that alongside appreciable H_2 activation at 50°C , several other new resonances were observed in the ^1H and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra (such peaks had not been observed during earlier investigations using $^1\text{Pr}_3\text{SnOTf}$). 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 Bn_3SnX ($\text{X} = \text{H}, \text{TfO}$) deactivation pathways

On closer inspection of the hydrogen cleavage experiments the diagnostic chemical shifts of Bn_4Sn were noted in the ^1H and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra ($\delta = 2.17$ and -37.5 ppm respectively; C_6D_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 ^1H and $^{119}\text{Sn}\{^1\text{H}\}$ NMR) even at temperatures above those used for 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 hexabenzylidistannane ($\text{Bn}_3\text{SnSnBn}_3$) with concomitant evolution of 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 ($1:1$, C_6D_6) 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 Bn_4Sn 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 Bn_2SnH_2 [37]. Interestingly, the diagnostic downfield resonance is almost identical to the related diorganotin hydride species, $\text{Bu}_2\text{Sn}(\text{H})\text{OTf}$ ($\delta = 8.99$ ppm; C_6D_6) [38], strongly indicating the possibility that a benzyl-substituted analogue might be transiently formed. The resonances for Bn_4Sn steadily grew in intensity at room temperature, while those for **1** and **2** decreased, until after 60 h the dominant species present was Bn_4Sn ; when this reaction mixture was heated to 50°C from the start rapid conversion of **1** and **2** to Bn_4Sn 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 Bn_4Sn 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 $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra were **1** and **2**; only after heating at 50°C for a further 5 h did Bn_4Sn become the predominant species. Interestingly, the resonance at $\delta = 5.28$ ppm attributed to Bn_2SnH_2 was again present, and a characteristic resonance attributed to $[\text{col-H}^+]$ 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 (Bn_2), a proposed mechanism which rationalizes the incomplete **1**/collidine-mediated 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 ^1H NMR spectrum. Rearrangement of this intermediate through PhCH_2/H exchange between Sn centres could then lead to formation of the observed Bn_4Sn and $\text{Bn}_2\text{Sn}(\text{H})\text{OTf}$ (corresponding to the $\delta = 9.01$ ppm resonance in the ^1H NMR spectrum). $\text{Bn}_2\text{Sn}(\text{H})\text{OTf}$ is expected to be highly reactive by analogy with its ^nBu analogue (hence its low steady-state intensity). Subsequently $\text{Bn}_2\text{Sn}(\text{H})\text{OTf}$ reacts with the more powerful hydride donor **2**, which reforms **1** and accordingly produces the observed Bn_2SnH_2 (^1H NMR: $\delta = 5.28$ ppm). R_2SnH_2 , 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

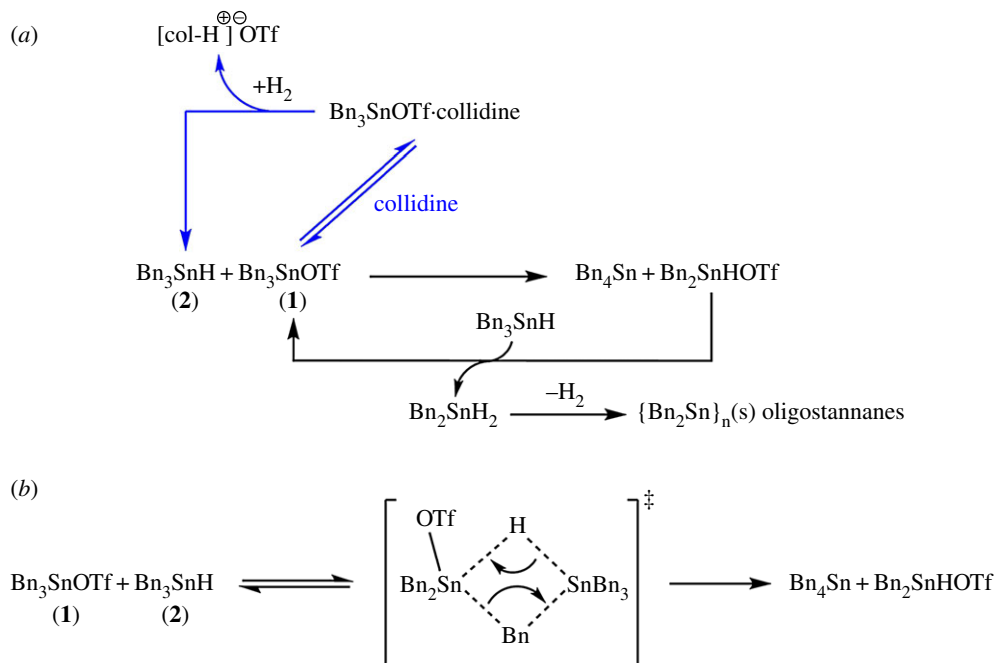


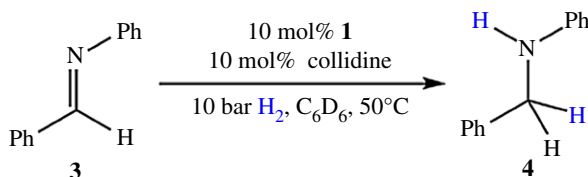
Figure 4. (a,b) Proposed deactivation pathways for Bn_3SnX ($\text{X} = \text{TfO}, \text{H}; \mathbf{1}, \mathbf{2}$) during H_2 heterolysis reactions.

chain mechanism, forming H_2 and complex mixtures of oligo/polystannanes $\{\text{R}_2\text{Sn}\}_n$, which for Ph-rich species can display poor solubility, especially when cross-branching occurs [from dehydrocoupling with $(\text{PhCH}_2)_3\text{SnH}$] [39]; the latter explains the observation of a precipitate and overall loss of ^1H NMR signal intensity during the reaction, as the PhCH_2 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 $[\text{col-H}]^+$ in this reaction can be rationalized from the 1/collidine-mediated cleavage of H_2 , the latter formed from decomposition of Bn_2SnH_2 , which leads to **2** (which re-enters the cycle) and the build-up of $[\text{col-H}]^+$, 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 H_2 activation reaction by **1**/collidine under a H_2 atmosphere (§3(b)). Finally, H_2 activation by the incipiently formed Bn_4Sn , in conjunction with collidine, can be discounted since an independent experiment of this combination under H_2 failed to show any reaction; this observation is in line with the poor Lewis acidity of tetraalkyltin compounds.

(d) Imine hydrogenations

Despite the observation of subsequent decomposition, the successful activation of H_2 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 $\text{Ph}(\text{H})\text{C}=\text{NPh}$, (**3**), which is an archetypal substrate for FLP-mediated catalytic hydrogenations. When H_2 (10 bar) was added to a solution of imine **3** and **1**/collidine (10 mol%) in C_6D_6 and the solution subsequently

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

entry	temperature (°C)	time (h)	conversion (%)
1	25	128	4.3
2	50	128	13.9
3	70	49	13.2

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.

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References

- McCahill JSJ, Welch GC, Stephan DW. 2007 Reactivity of 'frustrated Lewis pairs': three-component reactions of phosphines, a borane, and olefins. *Angew. Chem. Int. Ed.* **46**, 4968–4971. (doi:10.1002/anie.200701215)
- Stephan DW. 2016 The broadening reach of frustrated Lewis pair chemistry. *Science* **354**, 1248. (doi:10.1126/science.aaf7229)
- Stephan DW, Erker G. 2015 Frustrated Lewis pair chemistry: development and perspectives. *Angew. Chem. Int. Ed.* **54**, 6400–6441. (doi:10.1002/anie.201409800)
- Stephan DW. 2015 Frustrated Lewis pairs. *J. Am. Chem. Soc.* **137**, 10 018–10 032. (doi:10.1021/jacs.5b06794)
- Welch GC, Juan RRS, Masuda JD, Stephan DW. 2006 Reversible, metal-free hydrogen activation. *Science* **314**, 1124–1126. (doi:10.1126/science.1134230)
- Welch GC, Stephan DW. 2007 Facile heterolytic cleavage of dihydrogen by phosphines and boranes. *J. Am. Chem. Soc.* **129**, 1880–1881. (doi:10.1021/ja067961j)
- Spies P, Erker G, Kehr G, Bergander K, Fröhlich R, Grimme S, Stephan DW. 2007 Rapid intramolecular heterolytic dihydrogen activation by a four-membered heterocyclic phosphane–borane adduct. *Chem. Commun.* **2**, 5072. (doi:10.1039/b710475h)
- Chase PA, Welch GC, Jurca T, Stephan DW. 2007 Metal-free catalytic hydrogenation. *Angew. Chem. Int. Ed.* **46**, 8050–8053. (doi:10.1002/anie.200702908)
- Chase PA, Jurca T, Stephan DW. 2008 Lewis acid-catalyzed hydrogenation: B(C₆F₅)₃-mediated reduction of imines and nitriles with H₂. *Chem. Commun.* **2**, 1701–1703. (doi:10.1039/b718598g)
- Hounjet LJ, Bannwarth C, Garon CN, Caputo CB, Grimme S, Stephan DW. 2013 Combinations of ethers and B(C₆F₅)₃ function as hydrogenation catalysts. *Angew. Chem. Int. Ed.* **52**, 7492–7495. (doi:10.1002/anie.201303166)
- Scott DJ, Fuchter MJ, Ashley AE. 2014 Nonmetal catalyzed hydrogenation of carbonyl compounds. *J. Am. Chem. Soc.* **136**, 15 813–15 816. (doi:10.1021/ja5088979)
- Mahdi T, Stephan DW. 2014 Enabling catalytic ketone hydrogenation by frustrated Lewis pairs. *J. Am. Chem. Soc.* **136**, 15 809–15 812. (doi:10.1021/ja508829x)
- Stephan DW. 2015 Frustrated Lewis pairs: from concept to catalysis. *Acc. Chem. Res.* **48**, 306–316. (doi:10.1021/ar500375j)
- Scott DJ, Phillips NA, Sapsford JS, Deacy AC, Fuchter MJ, Ashley AE. 2016 Versatile catalytic hydrogenation using a simple tin(IV) Lewis acid. *Angew. Chem. Int. Ed.* **55**, 14 738–14 742. (doi:10.1002/anie.201606639)
- Whittell GR, Balmond EI, Robertson APM, Patra SK, Haddow MF, Manners I. 2010 Reactions of amine- and phosphane-borane adducts with frustrated Lewis pair combinations of group 14 triflates and sterically hindered nitrogen bases. *Eur. J. Inorg. Chem.* **2010**, 3967–3975. (doi:10.1002/ejic.201000515)
- Yu Y, Li J, Liu W, Ye Q, Zhu H. 2016 Amino group combined P/Ge and P/Sn Lewis pairs: synthesis and dipolar addition reactions to alkyne and aldehyde molecules. *Dalton Trans.* **45**, 6259–6268. (doi:10.1039/C5DT03873A)

17. Tofan D, Gabbaï FP. 2016 Fluorinated antimony(v) derivatives: strong Lewis acidic properties and application to the complexation of formaldehyde in aqueous solutions. *Chem. Sci.* **7**, 6768–6778. (doi:10.1039/C6SC02558G)
18. Heiden ZM, Lathem AP. 2015 Establishing the hydride donor abilities of main group hydrides. *Organometallics* **34**, 1818–1827. (doi:10.1021/om5011512)
19. Rokob TA, Hamza A, Pápai I. 2009 Rationalizing the reactivity of frustrated Lewis pairs: thermodynamics of H₂ activation and the role of acid–base properties. *J. Am. Chem. Soc.* **131**, 10 701–10 710. (doi:10.1021/ja903878z)
20. Smith TA, Kipping FS. 1912 CCLXV.—A study of some organic derivatives of tin as regards their relation to the corresponding silicon compounds. *J. Chem. Soc., Trans.* **101**, 2553–2563. (doi:10.1039/CT9120102553)
21. Schürmann M, Silvestri A, Ruisi G, Girasolo MA, Paulsen AB, Huber F, Barbieri R. 1999 The structure and dynamics of Cl-substituted tetraphenyl- and tetrabenzyl-tin(IV). *J. Organomet. Chem.* **584**, 293–300. (doi:10.1016/S0022-328X(99)00166-7)
22. Petrosyan VS. 1977 NMR spectra and structures of organotin compounds. *Prog. Nucl. Magn. Reson. Spectrosc.* **11**, 115–148. (doi:10.1016/0079-6565(77)80005-8)
23. Yamakawa T, Kinoshita H, Miura K. 2013 Synthetic utility of tribenzyltin hydride and its derivatives as easily accessible, removable, and decomposable organotin reagents. *J. Organomet. Chem.* **724**, 129–134. (doi:10.1016/j.jorganchem.2012.11.007)
24. Welch GC, Cabrera L, Chase PA, Hollink E, Masuda JD, Wei P, Stephan DW. 2007 Tuning Lewis acidity using the reactivity of ‘frustrated Lewis pairs’: facile formation of phosphine-boranes and cationic phosphonium-boranes. *Dalton Trans.* **9226**, 3407–3414. (doi:10.1039/b704417h)
25. Mayer U, Gutmann V, Gerger W. 1975 The acceptor number—a quantitative empirical parameter for the electrophilic properties of solvents. *Monatsh. Chem.* **106**, 1235–1257. (doi:10.1007/BF00913599)
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)
27. Beckmann J, Lork E, Mallow O. 2012 Crystal structure of polymeric triphenyltin triflate. *Main Gr. Met. Chem.* **35**, 183–185. (doi:10.1515/mgmc-2012-0056)
28. Addison AW, Rao TN, Reedijk J, van Rijn J, Verschoor GC. 1984 Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) perchlorate. *J. Chem. Soc. Dalton Trans.* **251**, 1349–1356. (doi:10.1039/DT9840001349)
29. Westerhausen M, Schwarz W. 1997 Synthesis and molecular structures of tris [bis(trimethylsilyl) methyl] stannane and the corresponding stannyl triflate. *Main Gr. Met. Chem.* **20**, 351–360. (doi:10.1515/mgmc.1997.20.6.351)
30. Zharov I, King BT, Havlas Z, Pardi A, Michl J. 2000 Crystal structure of n-Bu₃Sn⁺ CB11Me₁₂[−]. *J. Am. Chem. Soc.* **122**, 10 253–10 254. (doi:10.1021/ja001374v)
31. Farah D, Swami K, Kuivila HG. 1992 Synthesis and spectral characterization of medium ring distannacycloalkanes and their Lewis acid derivatives. *J. Organomet. Chem.* **429**, 311–334. (doi:10.1016/0022-328X(92)83182-H)
32. Davies AG. 2004 *Organotin chemistry*, 2nd edn. Weinheim, Germany: Wiley.
33. Geier SJ, Stephan DW. 2009 Lutidine/B(C₆F₅)₃: at the boundary of classical and frustrated Lewis pair reactivity. *J. Am. Chem. Soc.* **131**, 3476–3477. (doi:10.1021/ja900572x)
34. Herrington TJ, Ward BJ, Doyle LR, McDermott J, White AJP, Hunt PA, Ashley AE. 2014 Bypassing a highly unstable frustrated Lewis pair: dihydrogen cleavage by a thermally robust silylium-phosphine adduct. *Chem. Commun.* **50**, 12 753–12 756. (doi:10.1039/c4cc05905k)
35. Khan A, Gossage RA, Foucher DA. 2010 A convenient route to distannanes, oligostannanes, and polystannanes. *Can. J. Chem.* **88**, 1046–1052. (doi:10.1139/V10-130)
36. Puff H, Breuer B, Gehrke-Brinkmann G, Kind P, Reuter H, Schuh W, Wald W, Weidenbrück G. 1989 Bindungsabstände zwischen organylsubstituierten Zinnatomen. *J. Organomet. Chem.* **363**, 265–280. (doi:10.1016/0022-328X(89)87114-1)

37. Birchall T, Pereira AR. 1975 Nuclear magnetic resonance and Mössbauer spectra of some organotin anions. *J. Chem. Soc. Dalton Trans.* 1087–1092. (doi:10.1039/DT9750001087)
38. Miura K, Wang D, Matsumoto Y, Hosomi A. 2005 Highly regio- and stereoselective hydrostannylation of alkynols with a new Lewis acidic hydrostannane. *Org. Lett.* **7**, 503–505. (doi:10.1021/ol0474397)
39. Davies AG, Gielen M, Pannell KH, Tiekink ERT. 2008 *Tin chemistry: fundamentals, frontiers, and applications*. Chichester, UK: John Wiley & Sons, Ltd.
40. Hatnean JA, Thomson JW, Chase PA, DW. Stephan. 2014 Imine hydrogenation by alkylaluminum catalysts. *Chem. Commun.* **50**, 301–303. (doi:10.1039/C3CC47889K)
41. Vom Stein T, Pérez M, Dobrovetsky R, Winkelhaus D, Caputo CB, Stephan DW. 2015 Electrophilic fluorophosphonium cations in frustrated Lewis pair hydrogen activation and catalytic hydrogenation of olefins. *Angew. Chem. Int. Ed.* **54**, 10 178–10 182. (doi:10.1002/anie.201504109)

