

Versatile Catalytic Hydrogenation Using A Simple Tin(IV) Lewis Acid

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Abstract: Despite the rapid development of frustrated Lewis pair (FLP) chemistry over the last ten years, its application in catalytic hydrogenations remains dependent on a narrow family of structurally similar early main-group Lewis acids (LAs), inevitably placing limitations on reactivity, sensitivity and substrate scope. Herein we describe the FLP-mediated H_2 activation and catalytic hydrogenation activity of the alternative LA iPr_3SnOTf , which acts as a surrogate for the trialkylstannylum ion iPr_3Sn^+ , and is rapidly and easily prepared from simple, inexpensive starting materials. This highly thermally robust LA is found to be competent in the hydrogenation of a number of different unsaturated functional groups (which is unique to date for main-group FLP LAs not based on boron), and also displays a remarkable tolerance to moisture.

Since the formalization of the concept within the last decade, great attention has been focused on the development and study of frustrated Lewis pairs (FLPs): Lewis acid (LA) and base (LB) combinations that fail to form the classically expected strong adduct, typically because it is sterically precluded.^[1] The resulting combined reactivity has been found to lead to a range of novel bond activation reactions that do not require the involvement of a transition metal (TM).^[2] Of particular interest has been the activation and cleavage of H_2 , which has allowed the development of the first general methodology for TM-free catalytic hydrogenation.^[3]

Computational investigations have suggested that the primary requirements for successful activation of H_2 by an FLP are a sufficient cumulative LA/LB strength, and a suitable steric profile.^[4] One appealing aspect of FLP chemistry is therefore the generality of the concept; indeed, FLP-type reactions have been identified for a broad spectrum of LAs and LBs.^[2,5] Nevertheless inspection of the literature reveals that, despite the apparent breadth of the field, investigations into TM-free FLP-catalyzed hydrogenation have focused overwhelmingly on a very narrow range of LAs; thus far this has exclusively been achieved using B-based acceptors^[6] [predominantly (fluoroaryl)borane derivatives, of which $B(C_6F_5)_3$ is prevalent],^[7] with the exception of a single report using P-based LAs (for a limited range of

activated olefins).^[8] This constrained focus is far from ideal, as examining and developing a wider variety of LAs can be expected to produce novel FLP-catalyzed protocols that display different substrate scope and/or more favorable functional group tolerance.^[9] For example, the application of highly Lewis acidic boranes to the FLP-catalyzed hydrogenation of organic carbonyls has been notably challenging: whilst stoichiometric reductions were reported as early as 2007,^[9] it took until 2014 until catalytic protocols were developed.^[10] This difficulty can be attributed to the strength of the interaction between the alcohol (ROH) products and the LAs, which renders the LA-ROH adducts strongly acidic [cf. $H_2O \cdot B(C_6F_5)_3$; $pK_a = 8.4$ (MeCN), < 1 (H_2O , est.)],^[11] consequently, these adducts are fundamentally incompatible with the moderately strong N/P-centered LBs typically incorporated into active FLP catalysts. Ultimately, turnover can only be achieved when such LBs are strictly excluded, due to the necessarily highly Brønsted acidic media [for example, protonated ethers, $pK_a(H_2O) \ll 0$].^[10,12]

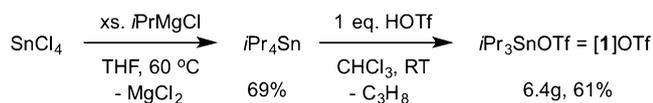
Based on the above, we were motivated to investigate FLPs based on heavier p-block LAs, which have thus far attracted scant attention for use in FLP applications.^[13] Specifically, our interest was drawn to stannylum ion " R_3Sn^+ " (R = alkyl) LAs;^[14] these are isolobal with Ar_3B species commonly employed in FLP chemistry, and have been calculated to possess similar hydride ion affinities ($\Delta G_{H^-} = 65.83$ and 64.95 kcal mol⁻¹ for nBu_3Sn-H and $[H-B(C_6F_5)_3]^-$ respectively),^[15] suggesting that they ought to demonstrate comparable reactivity in FLP H_2 activation and hydrogenation reactions. Furthermore, C=O reductions by R_3SnH in protic media are well known to occur via ionic hydride transfer.^[16] Crucially, however, these LAs interact only much more weakly with hydroxylic species [for example, $(nBu_3Sn \cdot x H_2O)^+$; $pK_a(H_2O) = 6.25$].^[17]

Manners et al. have previously investigated the use of nBu_3SnOTf (an nBu_3Sn^+ equivalent; Tf = CF_3SO_2) as a LA partner in FLP chemistry,^[13a] but reported that it was not capable of activating H_2 when combined with the strong amine base TMP (2,2,6,6-tetramethylpiperidine) at 50 °C, whereas the $B(C_6F_5)_3/TMP$ FLP readily cleaves H_2 , even at room temperature;^[18] this result was attributed to the poorer electrophilicity of the Sn compound, and it is evident that the Sn-OTf interaction is strong enough to substantially reduce the Lewis acidity of the nBu_3Sn^+ fragment.

We envisioned that it should be possible to increase the Lewis acidity, to the threshold necessary for favorable H_2 heterolysis, by simply increasing the size of the alkyl groups on Sn, thereby increasing the degree of "internal frustration"^[19] between the R_3Sn^+ and TfO^- moieties. To this end, we targeted the bulkier trialkylstannyl compound iPr_3SnOTf ([I]OTf), which was readily prepared via reaction of excess

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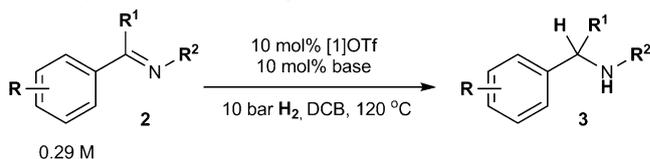
Scheme 1. Synthesis of [1]OTf.

*i*PrMgCl and SnCl₄ to generate *i*Pr₄Sn, followed by facile protodealkylation with HOTf (Scheme 1). This straightforward and inexpensive two-step procedure furnishes pure [1]OTf in good yield (42%, 2 steps), and can easily be performed on a multi-gram scale. [1]OTf is a white solid that shows moderate solubility in polar halogenated solvents and its ¹¹⁹Sn{¹H} spectrum shows a single broad resonance at δ = 156 ppm (Δ_{v/2} = 130 Hz, CDCl₃). The high chemical shift is consistent with significant stannylum ion character, although it is considerably upfield of the value reported for [*n*Bu₃Sn]-[CB₁₁Me₁₂] (δ = 454 ppm), which displays the least coordinated trialkylstannylum core to date.^[20] Gutmann–Beckett Lewis acidity measurements support this conclusion,^[21] indicating increased electrophilicity in comparison with *n*Bu₃SnOTf, although still lower than B(C₆F₅)₃^[22] {AN = 64.2 *n*Bu₃SnOTf; 68.0 [1]OTf; 78.1 B(C₆F₅)₃}. [1]OTf has also been characterized by ¹H, ¹³C and ¹⁹F NMR spectroscopy, MS and elemental analysis (see the Supporting Information (SI)).

Addition of DABCO (1,4-diazabicyclo[2.2.2]octane) to [1]OTf (1:1) leads to an upfield shift in the ¹¹⁹Sn{¹H} resonance (which remains similarly broad) to 39 ppm, consistent with a donor–acceptor interaction. However, the corresponding ¹H NMR spectrum shows only a single resonance for the DABCO protons, suggesting rapid exchange between an adduct and FLP. Admission of H₂ (4 bar) leads to the appearance of resonances in the room temperature ¹H [5.12 ppm, SnH, ¹J(¹¹⁹Sn/¹¹⁷Sn-¹H) = 1471/1405 Hz; 10.93 ppm, NH] and ¹¹⁹Sn{¹H} (−46 ppm) NMR spectra, that are consistent with formation of *i*Pr₃SnH ([1]H) and DABCO·HOTf, and hence H₂ heterolysis by the N/Sn Lewis pair. Further, conclusive proof for H₂ activation is provided by replacing H₂ with D₂, which causes the new ¹¹⁹Sn{¹H} resonance to split into a triplet [1:1:1, ¹J(¹¹⁹Sn-²H) = 226 Hz], and the new resonances in the ¹H NMR spectrum to be replaced by equivalent signals in the ²H spectrum. This represents the first example of FLP H₂ activation using a LA based on Sn, or any p-block element beyond the 3rd row of the periodic table.

Having demonstrated H₂ activation, our focus shifted to achieving catalytic hydrogenation using [1]OTf. Gratifyingly, heating the archetypal FLP substrates PhCH=N*t*Bu (**2a**) and PhC(Me)=N*t*Bu (**2b**) with 10 mol% [1]OTf to 120 °C under H₂ (10 bar) led to conversion to the respective amines (**3a** and **3b**; Table 1, entries 1 and 2). Conversely, the *N*-phenyl analogue PhCH=NPh (**2c**) is reduced far less effectively (Table 1, entry 3), which is attributed to the reduced basicity of both the imine and amine product, which makes H₂ activation less favorable. Consistent with this interpretation, addition of 2,4,6-collidine [Col; p*K*_a(MeCN) = 14.98]^[23] as an auxiliary base leads to a dramatic improvement in performance (Table 1, entry 4), and also allows for reduction of the related ketimine PhC(Me)=NPh (**2d**; Table 1, entry 5), and

Table 1: [1]OTf-catalyzed hydrogenation of imines.



Entry ^[a]	Substrate	R	R ¹	R ²	Base	t [h]	Conversion [%] ^[b]
1	2a	H	H	<i>t</i> Bu	–	12	97
2	2b	H	Me	<i>t</i> Bu	–	16	85
3	2c	H	H	Ph	–	16	4
4	2c	H	H	Ph	Col	24	> 99
5	2d	H	Me	Ph	Col	32	96
6	2e	H	H	Ts	Col	80	65
7	2f	4-Br	H	<i>t</i> Bu	Col	16	96

[a] 10 bar refers to initial pressure at RT. [b] Conversions determined by ¹H NMR spectroscopic analysis (see the SI).

even PhCH=NTs (**2e**; Ts = O₂SC₆H₄Me, 4-toluenesulfonyl), although the latter reaction is appreciably slower, presumably as the substrate is less basic still (Table 1, entry 6). Notably, the bromoaryl imine **2f** also undergoes efficient C=N hydrogenation (Table 1, entry 7); no evidence of hydrodebromination is observed during this reaction (no NMR resonances attributable to **2a/3a**, [1]Br or [1]₂),^[24] supporting the idea that radical Sn species do not appear to be involved in this reaction. Accordingly, we propose that hydrogenation occurs via a polar mechanism analogous to that for related borane-catalyzed systems:^[1d,e,25] H₂ activation by an FLP consisting of [1]OTf/imine is followed by hydride transfer and release of amine at elevated temperature (Figure S15). This is further supported by the observation that pre-formed **2a**·HOTf is rapidly reduced by [1]H even at RT,^[26] whereas the equivalent reactions with unprotonated **2a**, either alone or in the presence of [1]OTf, do not lead to significant reduction at 120 °C (see SI). Interestingly, there is evidence for autocatalysis during the course of the reaction (16% conversion observed after 3 h, 60% after 6 h); comparable observations have been made by Paradies et al. for imine hydrogenations catalyzed by B(2,6-F₂C₆H₃)₃, and are attributed to the increased basicity of the product amines, relative to the imine substrate, rendering H₂ activation more favorable as more product is formed.^[25]

Following success in the hydrogenation of imines, we were interested to see whether [1]OTf might also be capable of mediating the hydrogenation of closely related carbonyl compounds. Satisfyingly, when acetone (**4a**) is exposed to reaction conditions similar to those used to hydrogenate **2c** catalytic conversion to 2-propanol (**5a**) is observed (Table 2, entry 1). Whilst the reaction at 120 °C is somewhat slow, at 180 °C near-quantitative conversion can be observed within 32 h (Table 2, entry 2). Significantly, no evidence of catalyst decomposition is observed in this homogeneous reaction, either by ¹H or ¹¹⁹Sn{¹H} NMR spectroscopy,^[27] in comparison with analogous FLP protocols mediated by B(C₆F₅)₃.^[1f,28] To the best of our knowledge this is the first example of a catalytically active FLP system capable of tolerating such conditions without degradation, and illustrates the impressive

Table 2: [1]OTf-catalyzed hydrogenation of ketones and aldehydes.

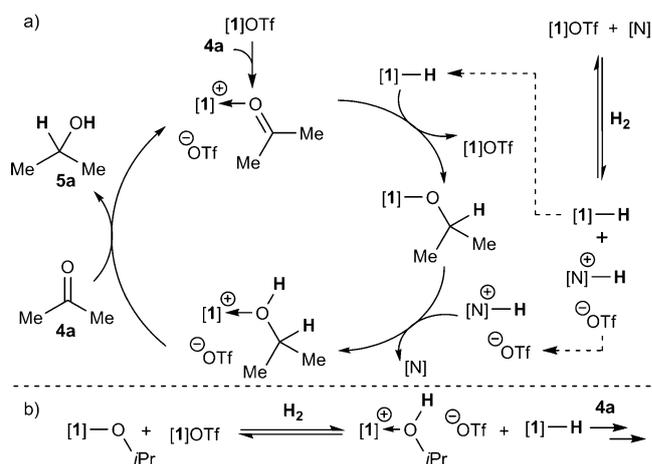
Entry ^[a]	Substrate	R	R ¹	Base	t [h]	Conversion [%] ^[b]
1 ^[c]	4a	Me	Me	Col	96	78
2 ^[d]	4a	Me	Me	Col	32	97
3 ^[d]	4b	Ph	Me	Col	48	91 ^[f]
4 ^[d]	4c	tBu	H	Col	48	79
5 ^[d]	4d	2,6-Cl ₂ C ₆ H ₃	H	Col	32	91
6	4a	Me	Me	Col	16	57
7	4a	Me	Me	Lut	16	48
8	4a	Me	Me	DABCO	16	14
9	4a	Me	Me	[1]OiPr ^[e]	16	32
10 ^[g]	4a	Me	Me	Col	32	95

[a] 10 bar refers to initial pressure at RT. [b] Conversions determined by ¹H NMR spectroscopic analysis (see the SI). [c] Reaction run at 120 °C, repressurized after 48 h. [d] Repressurized at 16 h intervals. [e] Generated in situ from [1]H and **4a** (see the SI). [f] Based on consumption of **4b**; reaction produces **5b** in addition to **6** and **7** as side-products in a ca. 74:18:8 molar ratio (see the SI). [g] Using undried reagents, solvent and catalyst (see the SI).

thermal stability of [1]OTf, which enables the use of more forcing conditions in order to achieve an improved rate of turnover. As well as **4a**, other aliphatic and aromatic ketones and aldehydes (**4b–d**) can be reduced under these conditions (Table 2, entries 3–5). In the case of acetophenone (**4b**), ¹H NMR spectroscopic analysis indicates formation of the expected alcohol **5b**, in addition to smaller quantities of styrene (**6**) and α -methylbenzyl ether (**7**). Similar side-reactions were observed in our previous attempts to reduce **4b** using B(C₆F₅)₃ in 1,4-dioxane,^[10b,12c] but in those cases this led to severe reductions in conversion and rate of turnover.

The ease and speed with which it was possible to apply this system to carbonyl hydrogenation stands in contrast to the extended period of development required before more conventional B-based FLPs were successfully used in this transformation.^[10a,b] It is also noteworthy that the [1]OTf-catalyzed reaction can proceed using a rather conventional, moderately-strong, N-centered LB, which again contrasts with B-based systems and is consistent with less acidic adducts forming between the product alcohols (e.g. **5a**) and [1]OTf. The choice of LB is important to the outcome of the hydrogenation of **4a** (Table 2, entries 6–8), with inferior results obtained using either a weaker or stronger base [2,6-lutidine (Lut), DABCO; pK_a(MeCN) = 14.13, 18.29].^[29]

Given the low Brønsted basicity of **4a** we propose a slightly different mechanism for its reduction than for **2a**,^[30] with the substrate activated by [1]⁺ rather than via H-bonding to [Col-H]⁺ (Scheme 2a).^[16b] Evidence for this comes from the significantly upfield-shifted ¹¹⁹Sn{¹H} NMR resonance ($\delta = 92$ ppm) observed upon addition of **4a** (10 equiv.) to [1]OTf, indicative of Sn–O binding.^[31] A proposed subsequent H⁺ transfer from [1]H to adduct {[1]-**4a**}OTf, to form [1]OiPr and regenerate [1]OTf, is supported by the observation that [1]H is capable of reducing **4a** in the presence of [1]OTf even at RT, whereas no appreciable



Scheme 2. a) Proposed mechanism for catalytic hydrogenation of **4a** using [1]OTf ([N] = 2,4,6-collidine) and b) alternative H₂ activation using in situ generated [1]OiPr.

conversion is observed in its absence either at RT or 120 °C. Conversely, if [1]OTf is replaced by Col·HOTf, only slow release of H₂ is observed at RT.^[32] In order for the final H⁺ transfer step to occur efficiently it should be recognized that Col and [1]OiPr must be comparable in base strength and, therefore, it may be envisaged that once [1]OiPr is formed in the reaction mixture, it could also activate H₂ in conjunction with [1]OTf (Scheme 2b). In fact, catalytic hydrogenation *can* be observed by substituting Col with [1]OiPr (generated in situ from [1]H and **4a**; Table 2, entry 9), thus demonstrating its competence in this role. Even so, the reduced rate of turnover in this reaction indicates that the auxiliary base does play a beneficial role beyond simply facilitating formation of some initial [1]OiPr, presumably by rendering H₂ activation more favorable.^[33]

Clear tolerance of alcohol products suggested that these reactions might also demonstrate appreciable moisture tolerance.^[10,12] Remarkably, when the hydrogenation of model substrate **4a** (chosen over an imine to avoid hydrolysis) was prepared on the open bench, with non-anhydrous reagents and solvent, and using [1]OTf that had been exposed to air for 1 week, the reaction was observed to proceed without any noticeable reduction in rate (Table 2, entry 10; details in SI). This is unprecedented in FLP catalysis, where even the most tolerant of previously reported reactions have been dramatically slowed by adventitious H₂O,^[12] and suggests a major advantage of using Sn-based LAs.

Finally, we investigated the use of [1]OTf in the catalytic hydrogenation of compounds containing other unsaturated functionalities; the heteroaromatic ring of acridine, and the C=C bonds in *n*-butyl acrylate and 1-piperidino-1-cyclohexene could all be effectively reduced (yields 83–99%), further demonstrating the versatility of this Sn^{IV} compound (Figure S33).

In summary, we have demonstrated the use of readily accessible and inexpensive *i*Pr₃SnOTf as a main-group LA catalyst for the hydrogenation of C=C, C=N and C=O bonds; this constitutes only the second example of an FLP hydrogenation protocol utilizing a p-block LA not incorporating

boron, and the first such example shown to be applicable to the reduction of a range of different functional groups. Despite the ubiquity of Sn in industrial catalysis this also represents, to the best of our knowledge, the first example of homogeneous catalytic hydrogenation using a Sn-based system of any kind.^[34] Of particular interest is the ready applicability of this protocol to C=O bond hydrogenation, in a reaction that displays an unparalleled level of H₂O tolerance. This neatly demonstrates the value of pursuing alternative FLP LAs, and can be jointly attributed to the formation of weakly acidic LA-ROH adducts; a thermally robust [iPr₃Sn]⁺ core, allowing access to high reaction temperatures; and the stability of the Sn–C bonds towards protolytic cleavage for example, by H₂O. Clearly there is significant scope for variation of the triorganotin(IV) framework in “R₃Sn⁺” species; investigations into how this affects their reactivity, functional group tolerance, and substrate scope are currently underway.

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- [1] For key publications, see: a) G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126; b) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881; c) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050–8053; *Angew. Chem.* **2007**, *119*, 8196–8199; d) P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, 1701–1703; e) D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, 2130–2131; f) A. E. Ashley, A. L. Thompson, D. O'Hare, *Angew. Chem. Int. Ed.* **2009**, *48*, 9839–9843; *Angew. Chem.* **2009**, *121*, 10023–10027; g) K. Chernichenko, Á. Madarász, I. Pápai, M. Nieger, M. Leskelä, T. Repo, *Nat. Chem.* **2013**, *5*, 718–723; h) M.-A. Légaré, M.-A. Courtemanche, É. Rochette, F.-G. Fontaine, *Science* **2015**, *349*, 513–516.
- [2] For reviews of FLP chemistry, see: a) “Frustrated Lewis Pairs”: G. Erker, D. W. Stephan, *Topics in Current Chemistry, Vols. I and II*, Springer, Berlin, **2013**; b) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306–316; c) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541; d) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018–10032.
- [3] For reviews of FLP-catalyzed hydrogenation, see: a) D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch, M. Ullrich, *Inorg. Chem.* **2011**, *50*, 12338–12348; b) J. Paradies, *Angew. Chem. Int. Ed.* **2014**, *53*, 3552–3557; *Angew. Chem.* **2014**, *126*, 3624–3629; c) L. J. Hounjet, D. W. Stephan, *Org. Process Res. Dev.* **2014**, *18*, 385–391.
- [4] T. A. Rokob, A. Hamza, I. Pápai, *J. Am. Chem. Soc.* **2009**, *131*, 10701–10710.
- [5] S. A. Weicker, D. W. Stephan, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1003–1016.
- [6] A few examples of catalytic hydrogenation using TM-based FLPs have also been reported. See: a) M. P. Boone, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 8508–8511; b) A. T. Normand, C. G. Daniliuc, B. Wibbeling, G. Kehr, P. Le Gendre, G. Erker, *J. Am. Chem. Soc.* **2015**, *137*, 10796–10808; c) X. Xu, C. G. Daniliuc, G. Erker, *J. Am. Chem. Soc.* **2015**, *137*, 4550–4557; d) N. S. Lambic, R. D. Sommer, E. A. Ison, *J. Am. Chem. Soc.* **2016**, *138*, 4832–4842; e) S. R. Flynn, O. J. Metters, I. Manners, D. F. Wass, *Organometallics* **2016**, *35*, 847–850.
- [7] For catalytic hydrogenation using much weaker boranes paired with strong bases, see: S. Mummadi, D. K. Unruh, J. Zhao, S. Li, C. Krempner, *J. Am. Chem. Soc.* **2016**, *138*, 3286–3289.
- [8] a) T. vom Stein, M. Pérez, R. Dobrovetsky, D. Winkelhaus, C. B. Caputo, D. W. Stephan, *Angew. Chem. Int. Ed.* **2015**, *54*, 10178–10182; *Angew. Chem.* **2015**, *127*, 10316–10320; imine hydrogenation is also known using an Al-based LA or a pyridylidene as catalyst, but in both cases was reported not to proceed via an FLP mechanism: b) J. A. Hatnean, J. W. Thomson, P. A. Chase, D. W. Stephan, *Chem. Commun.* **2014**, *50*, 301–303; c) J. Auth, J. Padevet, P. Mauleón, A. Pfaltz, *Angew. Chem. Int. Ed.* **2015**, *54*, 9542–9545; *Angew. Chem.* **2015**, *127*, 9678–9681.
- [9] P. Spies, G. Erker, G. Kehr, K. Bergander, R. Frohlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, 5072–5074.
- [10] a) T. Mahdi, D. W. Stephan, *J. Am. Chem. Soc.* **2014**, *136*, 15809–15812; b) D. J. Scott, M. J. Fuchter, A. E. Ashley, *J. Am. Chem. Soc.* **2014**, *136*, 15813–15816.
- [11] C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner, G. Parkin, *J. Am. Chem. Soc.* **2000**, *122*, 10581–10590.
- [12] a) T. Mahdi, D. W. Stephan, *Angew. Chem. Int. Ed.* **2015**, *54*, 8511–8514; *Angew. Chem.* **2015**, *127*, 8631–8634; b) Á. Gyömöre, M. Bakos, T. Földes, I. Pápai, A. Donján, T. Soós, *ACS Catal.* **2015**, *5*, 5366–5372; c) D. J. Scott, T. R. Simmons, E. J. Lawrence, G. G. Wildgoose, M. J. Fuchter, A. E. Ashley, *ACS Catal.* **2015**, *5*, 5540–5544; d) V. Fasano, J. E. Radcliffe, M. J. Ingleson, *ACS Catal.* **2016**, *6*, 1793–1798.
- [13] a) G. R. Whittell, E. I. Balmont, A. P. M. Robertson, S. K. Patra, M. F. Haddow, I. Manners, *Eur. J. Inorg. Chem.* **2010**, 3967–3975; b) S. Freitag, J. Henning, H. Schubert, L. Wesemann, *Angew. Chem. Int. Ed.* **2013**, *52*, 5640–5643; *Angew. Chem.* **2013**, *125*, 5750–5754; c) S. Freitag, K. M. Krebs, J. Henning, J. Hirdler, H. Schubert, L. Wesemann, *Organometallics* **2013**, *32*, 6785–6791; d) F. A. Tsao, L. Cao, S. Grimme, D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 13264–13267; e) Y. Yu, J. Li, W. Liu, Q. Ye, H. Zhu, *Dalton Trans.* **2016**, *45*, 6259–6268; f) K. M. Krebs, J.-J. Maudrich, L. Wesemann, *Dalton Trans.* **2016**, *45*, 8081–8088.
- [14] The use of “R₃Sn⁺” LAs need not present excessive safety concerns. While certain organotin(IV) species are highly toxic (notably for R = Me), this is highly dependent on the organic skeleton. See, for example: T. Gadja, A. Jancsó, *Met. Ions Life Sci.* **2010**, *7*, 111–151, and references therein.
- [15] Z. M. Heiden, A. P. Lathem, *Organometallics* **2015**, *34*, 1818–1827.
- [16] For example, see: a) K. Kamiura, M. Wada, *Tetrahedron Lett.* **1999**, *40*, 9059–9062; b) T. X. Yang, P. Four, F. Guibé, G. Balavoine, *New J. Chem.* **1984**, *8*, 611–614, and references therein.
- [17] C. G. Arnold, A. Weidenhaupt, M. M. David, S. R. Müller, S. B. Haderlein, R. P. Schwarzenbach, *Environ. Sci. Technol.* **1997**, *31*, 2596–2602.
- [18] V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo, B. Rieger, *Angew. Chem. Int. Ed.* **2008**, *47*, 6001–6003; *Angew. Chem.* **2008**, *120*, 6090–6092.

- [19] A similar strategy has been documented for silylium species:
a) B. Mathieu, L. Ghosez, *Tetrahedron* **2002**, *58*, 8219–8226;
b) T. J. Herrington, B. J. Ward, L. R. Doyle, J. McDermott, A. J. P. White, P. A. Hunt, A. E. Ashley, *Chem. Commun.* **2014**, *50*, 12753–12756.
- [20] I. Zharov, B. T. King, Z. Havlas, A. Pardi, J. Michl, *J. Am. Chem. Soc.* **2000**, *122*, 10253–10254.
- [21] a) U. Mayer, V. Gutmann, W. Gerger, *Monatsh. Chem.* **1975**, *106*, 1235–1257; b) M. A. Beckett, G. C. Strickland, J. R. Holland, K. S. Varma, *Polymer* **1996**, *37*, 4629–4631; c) G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei, D. W. Stephan, *Dalton Trans.* **2007**, 3407–3414.
- [22] A. E. Ashley, T. J. Herrington, G. G. Wildgoose, H. Zaher, A. L. Thompson, N. H. Rees, T. Krämer, D. O'Hare, *J. Am. Chem. Soc.* **2011**, *133*, 14727–14740.
- [23] I. Kaljurand, A. Kütt, L. Sooväli, T. Rodima, V. Mäemets, I. Leito, I. A. Koppel, *J. Org. Chem.* **2005**, *70*, 1019–1028.
- [24] W. Kitching, H. A. Olszovy, G. M. Drew, *Organometallics* **1982**, *1*, 1244–1246.
- [25] a) S. Tussing, L. Greb, S. Tamke, B. Schirmer, C. Muhle-Goll, B. Luy, J. Paradies, *Chem. Eur. J.* **2015**, *21*, 8056–8059; b) S. Tussing, K. Kaupmees, J. Paradies, *Chem. Eur. J.* **2016**, *22*, 7422–7426.
- [26] Interestingly, while this reaction proceeds initially very rapidly at RT (reaching almost 50% conversion within minutes), the rate drops quickly (e.g. only 65% conv. after 17 h), presumably due to deprotonation of remaining **2a**-HOTf by the more basic **3a**.
- [27] RT NMR spectroscopy on the final reaction mixture shows only one set of Sn-*i*Pr resonances and no unassigned peaks in the ¹H spectrum, and a single broad resonance at around 30 ppm in the ¹¹⁹Sn{¹H} spectrum. A comparable ¹¹⁹Sn{¹H} signal can be obtained by mixing [1]OTf, collidine and **5a** (10 equiv) at the same concentration in DCB.
- [28] L. E. Longobardi, C. Tang, D. W. Stephan, *Dalton Trans.* **2014**, *43*, 15723–15726.
- [29] a) I. Kaljurand, A. Kütt, L. Sooväli, T. Rodima, V. Mäemets, I. Leito, I. A. Koppel, *J. Org. Chem.* **2005**, *70*, 1019–1028; b) J. F. Coatzee, G. R. Padmanabhan, *J. Am. Chem. Soc.* **1965**, *87*, 5005–5010.
- [30] H. J. Campbell, J. T. Edward, *Can. J. Chem.* **1960**, *38*, 2109–2116.
- [31] J. M. Blackwell, W. E. Piers, R. McDonald, *J. Am. Chem. Soc.* **2002**, *124*, 1295–1306.
- [32] If this reaction mixture is subsequently heated to 120°C very slow formation of **5a** is observed. In light of other results, this reduction is most likely mediated by the [1]OTf formed upon H₂ release from [1]H/Col-HOTf.
- [33] The reduced rates of turnover with 2,6-lutidine and DABCO relative to collidine can be attributed to less favorable H₂ activation, and H⁺ transfer, respectively (see the SI). Evidence that collidine is a slightly stronger base than [1]OiPr comes from the observation that addition of collidine to a [1]OTf/**5a** mixture leads to an upfield shift in the LA ¹H and ¹¹⁹Sn resonances and downfield shifts for the collidine ¹H resonances, consistent with deprotonation. Similar shifts in the collidine resonances are observed during catalytic reactions (see the SI).
- [34] We are aware of a single example of heterogeneous Sn-catalyzed hydrogenation: S. Nishiyama, T. Kubota, K. Kimura, S. Tsuruya, M. Masai, *J. Mol. Catal. A* **1997**, *120*, L17–22.

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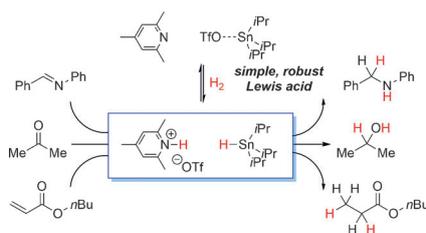
Communications



FLP Hydrogenation

D. J. Scott, N. A. Phillips, J. S. Sapsford,
A. C. Deacy, M. J. Fuchter,
A. E. Ashley* 

Versatile Catalytic Hydrogenation Using A
Simple Tin(IV) Lewis Acid



Less frustration with new FLP: The simple Lewis acid $i\text{Pr}_3\text{SnOTf}$ can be used to activate H_2 in conjunction with common N-centered Lewis bases via a frustrated Lewis pair (FLP) mechanism. These FLP systems are effective for the catalytic hydrogenation of a variety of C=C, C=N, and even C=O bonds and display an unprecedented level of tolerance to moisture.