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 \( \text{H}_2 \) activation and catalytic hydrogenation activity of the alternative LA \( \text{iPrSnOTf} \), which acts as a surrogate for the trialkylstannylium ion \( \text{iPrSn}^+ \), and is readily 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 \( \text{H}_2 \), 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 \( \text{H}_2 \) 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 \( \text{B(C}_6\text{F}_5\text{)}_3 \) 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 carbylons 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. \( \text{H}_2\text{O-B(C}_6\text{F}_5\text{)}_3 \); \( \text{pK}_a = 8.4 \text{ (MeCN), < 1 (H}_2\text{O, ext.)} \)[11] consequently, these adducts are fundamentally incompatible with the moderately strong N/P-centered LAs typically incorporated into active FLP catalysts. Ultimately, turnover can only be achieved when such LAs are strictly excluded, due to the necessarily highly Bronsted acidic media [for example, protonated ethers, \( \text{pK}_a(\text{H}_2\text{O}) < 0 \)[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 stannylium ion “\( \text{R}_3\text{Sn}^- \)” (R = alkyl) LAs:[14] these are isosolable with Ar,B species commonly employed in FLP chemistry, and have been calculated to possess similar hydride ion affinities (\( \Delta G_{\text{H}^+} = 65.83 \text{ and } 64.95 \text{ kcalmol}^{-1} \) for \( \text{nBu}_3\text{Sn-H} \) and \( \text{H-B(C}_6\text{F}_5\text{)}_3^- \) respectively)[13] suggesting that they ought to demonstrate comparable reactivity in FLP \( \text{H}_2 \) activation and hydrogenation reactions. Furthermore, C=O reductions by \( \text{R}_3\text{SnH} \) 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, \( \text{nBu}_3\text{Sn} \times \text{H}_2\text{O} \); \( \text{pK}_a(\text{H}_2\text{O}) = 6.25 \)[17]

Manners et al. have previously investigated the use of \( \text{nBu}_3\text{SnOTf} \) (an \( \text{nBu}_3\text{Sn} \) equivalent; \( \text{TF} = \text{CF}_3\text{SO}_3 \)) as a LA partner in FLP chemistry,[2a] but reported that it was not capable of activating \( \text{H}_2 \) when combined with the strong amine base TMP (2,2,6,6-tetramethylpipеридине) at 50°C, whereas the \( \text{B(C}_6\text{F}_5\text{)}_3/\text{TMP FLP readily cleaves H}_2 \), even at room temperature.[16] 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 \( \text{nBu}_3\text{Sn} \) fragment.

We envisioned that it should be possible to increase the Lewis acidity, to the threshold necessary for favorable \( \text{H}_2 \) heterolysis, by simply increasing the size of the alkyl groups.
on Sn, thereby increasing the degree of “internal frustration”\cite{20} between the R$_2$Sn$^+$ and TiO$^-$ moieties. To this end, we targeted the bialkyl triarylstannyl compound $\text{PrR}_2\text{SnOTf}$ ([1]OTf), which was readily prepared via reaction of excess $\text{PrR}_2\text{MgCl}$ and SnCl$_4$ to generate $\text{PrR}_2\text{Sn}$, 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 $^{119}$Sn$^{[1]H}$ spectrum shows a single broad resonance at $\delta = 156$ ppm ($\Delta \nu_{\text{H}} = 130$ Hz, CDCl$_3$). The high chemical shift is consistent with significant stannyl ion character, although it is considerably upfield of the value reported for [nBu$_2$Sn]-[CB$_3$Me$_2$] ( $\delta = 454$ ppm), which displays the least coordinated triarylstannylum core to date.\cite{21} Gutmann–Beckett Lewis acidity measurements support this conclusion,\cite{22} indicating increased electrophilicity in comparison with nBu$_2$SnOTf, although still lower than B(C$_6$F$_5$)$_2$.\cite{23} [AN = 64.2 nBu$_2$SnOTf; 68.0 [1]OTf; 78.1 B(C$_6$F$_5$)$_2$]. [1]OTf has also been characterized by $^1$H, $^13$C and $^{19}$F 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 $^{119}$Sn$^{[1]H}$ resonance (which remains similarly broad) to 39 ppm, consistent with a donor-acceptor interaction. However, the corresponding $^1$H NMR spectrum shows only a single resonance for the DABCO protons, suggesting rapid exchange between an adduct and FLP. Admission of H$_2$ (4 bar) leads to the appearance of resonances in the room temperature $^1$H [5.12 ppm, SnH, $J(119$Sn$^{[1]}$Sn$^{[1]}) = 1471/1405$ Hz; 10.93 ppm, NH] and $^{119}$Sn$^{[1]}$H (−46 ppm) NMR spectra, that consist of formation of $\text{Pr}_2\text{SnH}$ ([1]H) and DABCO–HOTf, and hence H$_2$ heterolysis by the N/Sn Lewis pair. Further, conclusive proof for H$_2$ activation is provided by replacing H$_2$ with D$_2$, which causes the new $^{119}$Sn$^{[1]}$H resonance to split into a triplet [1:1:1, $J(119$Sn$^{[1]}$Sn$^{[1]}$H) = 226 Hz], and the new resonances in the $^1$H NMR spectrum to be replaced by equivalent signals in the $^2$H spectrum. This represents the first example of FLP H$_2$ activation using a LA based on Sn, or any p-block element beyond the 3rd row of the periodic table.

Having demonstrated H$_2$ activation, our focus shifted to achieving catalytic hydrogenation using [1]OTf. Gratifyingly, heating the archetypal FLP substrates PhCH$\equiv$N–Bu (2a) and Ph(CH(Me)=–N–Bu (2b) with 10 mol % [1]OTf to 120°C under H$_2$ (10 bar) led to conversion to the respective amines (3a and 3b; Table 1, entries 1 and 2). Conversely, the N-phenyl analogue PhCH$\equiv$N–Ph (2c) is reduced far less effectively (Table 1, entry 3), which is attributed to the reduced basicity of both the imine and amine products, which makes H$_2$ activation less favorable. Consistent with this interpretation, addition of 2,4,6-collidine [Col; pK$_f$(MeCN) = 14.98]$^{[24]}$ as an auxiliary base leads to a dramatic improvement in performance (Table 1, entry 4), and also allows for reduction of the related ketimine Ph(CH)=–NPh (2d; Table 1, entry 5), and even PhCH=NTs (2e; Ts = O$_2$SC$_6$H$_4$Me, 4-toluene sulfonyl), although the latter reaction is appreciably slower, presumably as the substrate is less basic still (Table 1, entry 6). Notably, the bromoamine imine 2f also undergoes efficient C=N hydrogenation (Table 1, entry 7); no evidence of hydrodeboronation is observed during this reaction (no NMR resonances attributable to 2a3a, 1|Br or 1|3).\cite{25} 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.\cite{26} H$_2$ 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,\cite{27} 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-F$_2$-C$_6$H$_4$n), and are attributed to the increased basicity of the product amines, relative to the imine substrate, rendering H$_2$ activation more favorable as more product is formed.\cite{28}

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,

![Table 1: [1]OTf-catalyzed hydrogenation of imines.](image)

**Scheme 1.** Synthesis of [1]OTf.
It is also noteworthy that the reaction produces evidence for this comes in the in 1,4-dioxane, Angew. Chem. Int. Ed. = in conjunction transfer from \[4c\] in addition to To \[5a\] Me Me \[7\] Aroposed activation \[6\] Base Substrate RR (chosen over an imine to avoid hydrolysis) was \[4a\]; reaction produces 5b in comparison \[4b\] reactions were observed in our previous attempts to reduce \[4b\] can be reduced under these conditions (Table 2, entries 3–5). In the case of acetophenone \[4b\], \[1\] H NMR spectroscopic analysis indicates formation of the expected alcohol \[5b\] in addition to smaller quantities of styrene \[6\] and \[\alpha\]-methylbenzyl ether \[7\]. Similar side-reactions were observed in our previous attempts to reduce \[4b\] using B(CF\(_3\))\(_3\) in 1,4-dioxane, \[10\] 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.\[11\] 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 [\[2,6-Cl\_2C,H\_2\] H Col 32 91\[11\]] (Table 2, entries 9, 10). Based on consumption of \[4a\] in the presence of [\[1\]OTf even at RT, whereas no appreciable conversion is observed in its absence either at RT or 120°C. Conversely, if [\[1\]OTf is replaced by Col:HO?.Ti, only slow release of H\(_2\) is observed at RT.\[28\] In order for the final H\(_2\) transfer step to occur efficiently it should be recognized that Col and [\[1\]OPr must be comparable in base strength and, therefore, it may be envisaged that once [\[1\]OPr is formed in the reaction mixture, it could also activate H\(_2\) in conjunction with [\[1\]OTf (Scheme 2b). In fact, catalytic hydrogenation can be observed by substituting Col with [\[1\]OPr (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 [\[1\]OPr, presumably by rendering H\(_2\) activation more favorable.\[31\]

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 H\(_2\)O.\[29\] 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\(^{\text{II}}\) compound (Figure S33).

**Table 2:** \([\text{1}]\text{OTf-catalyzed hydrogenation of ketones and aldehydes.}^1\)

| Entry\[a\] | Substrate | R    | R\(_1\) | Base | t [h] | Conversion [%]\[b\] |
|----------|-----------|------|--------|------|------|------------------|
| 1\[h\]   | 4a        | Me   | Me     | Col  | 96   | 78               |
| 2\[h\]   | 4a        | Me   | Me     | Col  | 32   | 97               |
| 3\[h\]   | 4b        | Ph   | Me     | Col  | 48   | 91\[f\]         |
| 4\[h\]   | 4c        | iBu  | H Col  | 48   | 79   |
| 5\[h\]   | 4d        | 2,6-Cl\(_2\)C,H\(_2\) | 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     | [\[1\]OPr\[h\]] | 16   | 32               |
| 10\[g\] | 4a        | Me   | Me     | Col  | 32   | 95               |

\[a\] 10 bar refers to initial pressure at RT. \[b\] Conversions determined by \[1\] H NMR spectroscopic analysis (see the SI). \[c\] Reaction run at 120°C, represurized 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).

\[1\]OTf, indicative of Sn—O binding.\[31\] A proposed subsequent H\(_2\) transfer from [\[1\]H to adduct \([\[1\]OTf to form [\[1\]OPr and regenerate [\[1\]OTf, is supported by the observation that [\[1\]H is capable of reducing \[4a\] in its absence either at RT or 120°C. Conversely, if [\[1\]OTf is replaced by Col:HO?.Ti, only slow release of H\(_2\) is observed at RT.\[32\] In order for the final H\(_2\) transfer step to occur efficiently it should be recognized that Col and [\[1\]OPr must be comparable in base strength and, therefore, it may be envisaged that once [\[1\]OPr is formed in the reaction mixture, it could also activate H\(_2\) in conjunction with [\[1\]OTf (Scheme 2b). In fact, catalytic hydrogenation can be observed by substituting Col with [\[1\]OPr (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 [\[1\]OPr, presumably by rendering H\(_2\) activation more favorable.\[31\]

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In summary, we have demonstrated the use of readily accessible and inexpensive \( \text{IPr}_x\text{SnOTf} \) as a main-group LA catalyst for the hydrogenation of \( C=\text{C} \), \( C=\text{N} \) and \( C=\text{O} \) 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 \( \text{H}_2\text{O} \) 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 \([\text{IPr}_x\text{Sn}]^{\text{+}}\) core, allowing access to high reaction temperatures; and the stability of the Sn-C bonds towards protolytic cleavage for example, by \( \text{H}_2\text{O} \). Clearly there is significant scope for variation of the triorganotin(IV) framework in “R-Sn” species; investigations into how this affects their reactivity, functional group tolerance, and substrate scope are currently underway.

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[27] RT NMR spectroscopy on the final reaction mixture shows only one set of Sn-iPr resonances and no unassigned peaks in the $^1$H spectrum, and a single broad resonance at around 30 ppm in the $^{119}$Sn–$^1$H spectrum. A comparable $^{119}$Sn–$^1$H signal can be obtained by mixing [1]OTf, collidine and 5a (10 equiv) at the same concentration in DCB.

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[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 $^1$Ha and $^{119}$Sn resonances and downfield shifts for the collidine $^1$H resonances, consistent with deprotonation. Similar shifts in the collidine resonances are observed during catalytic reactions (see the SI).

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