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Hexacoordinated tin complexes catalyse imine hydrogenation with H₂†

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Frustrated Lewis pair (FLP) hydrogenation catalysts predominantly use alkyl- and aryl-substituted Lewis acids (LA) that offer a limited number of combinations of substituents, limiting our ability to tune their properties and, ultimately, their reactivity. Nevertheless, main-group complexes have numerous ligands available for such purposes, which could enable us to broaden the range of FLP catalysis. Supporting this hypothesis, we demonstrate here that hexacoordinated tin complexes with Schiff base ligands catalyse imine hydrogenation via activation of H_{2(g)}. As shown by hydrogen–deuterium scrambling, [Sn(^tBu₂Salen)(OTf)₂] activated H_{2(g)} at 25 °C and 10 bar of H₂. After tuning the ligands, we found that [Sn(Salen)Cl₂] was the most efficient imine hydrogenation catalyst despite having the lowest activity in H_{2(g)} activation. Moreover, various imines were hydrogenated in yields up to 98% thereby opening up opportunities for developing novel FLP hydrogenation catalysts based on hexacoordinated LA of main-group elements.

Frustrated Lewis pairs (FLPs)¹ combining bulky Lewis acids (LAs) with Lewis bases (LBs) catalyse imine hydrogenation via H₂ activation (Fig. 1A).^{2–4} Tuning their electronic and steric properties improves the FLP hydrogenation activity, expands the substrate scope^{5,6} and, in some cases, imparts water tolerance.^{7–10} Notwithstanding these outcomes, tuning predominantly involves triaryl-substituted Lewis acids^{8,11,12} of boron, aluminium, gallium and indium¹³ with a narrow margin of manoeuvre, preventing us from further enhancing their reactivity. As a case in point, some authors argue that we cannot electronically tune the BAR₃ LAs any further.⁷

FLP reactivity has nevertheless been further modified by using group 15 and 14 LAs.^{14–21} In particular, R₃SnX (R = alkyl or aryl, X = halogen, [–]OTf, [–]NTf₂, and [–]CIO₄) Lewis acids (Fig. 1B) in their cationic form are isolobal to group 13-based LAs,¹⁵ so they can act as their direct substitutes. In fact, tin-based FLPs effectively hydrogenate many functional groups and small molecules,^{14–16,22–25} but lack the diversity of metal complexes.

In addition to simple tetravalent alkyl- and aryl-substituted LAs, tin(IV) also forms hexacoordinated complexes with various ligands, including bipyridine,²⁶ benzoylpyridine²⁷ and Schiff bases.²⁸ In particular, Schiff base ligands can stabilize various tin oxidation states, and their complexes are known LA catalysts.^{28,29} Moreover, they have been used in asymmetric

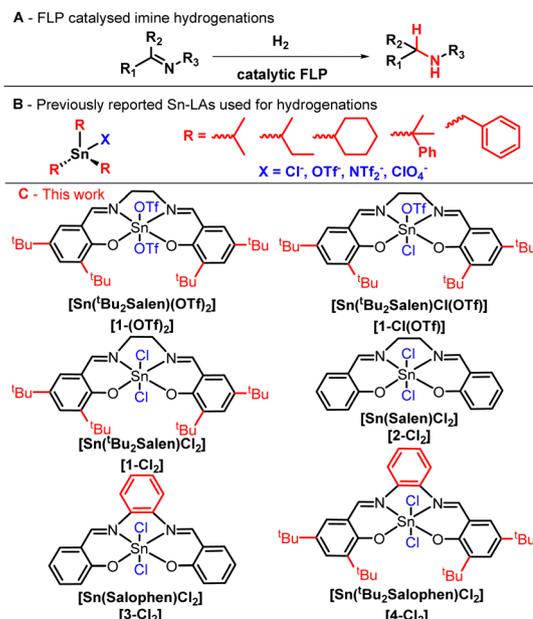


Fig. 1 (A) Reaction scheme of FLP-catalysed imine hydrogenation, (B) previously reported Sn-based LAs used in FLP-catalysed hydrogenations, and (C) L₄SnX₂ catalysts developed for H₂ activation and imine hydrogenations in this study.

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catalysis,^{30,31} which is currently a prominent target of FLP chemistry.^{32,33} Despite the fact that a few main group complexes act as hydrogenation catalysts,^{34–36} we hypothesized that hexacoordinated tin complexes with Schiff base ligands may be applied as LAs in FLPs to catalyse imine hydrogenation.

In this study, we report that hexacoordinated complexes of tin with Schiff base ligands in the form L_4SnX_2 , containing N and O donor atoms (Fig. 1C), activate H_2 gas and act as hydrogenation catalysts for imine reduction. The presence of labile or hemi-labile axial ligands X^- , such as triflate (OTf^-) and chloride, promotes the formation of a vacant site on the LA metal centre, which is necessary for efficient catalysis.

Given the large positive polarization of tin(IV) and their labile triflate ligand(s), $[Sn(tBu_2Salen)(OTf)_2]$ (**1-OTf**)₂ and $[Sn(tBu_2Salen)Cl(OTf)]$ (**1-Cl(OTf)**) showed high Lewis acidity, assessed using the Guttmann–Beckett (GB) method (AN = 83.6 and AN = 71.8, respectively), where **1-OTf**₂ presumably dissociates both triflate ligands and **1-Cl(OTf)** dissociates the triflate but retains the chloride to form the Lewis acidic ions $[Sn(tBu_2Salen)]_2^+$ and $[Sn(tBu_2Salen)Cl]^+$, respectively. Their Lewis acidity is similar to that of $B(C_6F_5)_3$ (AN = 78.1). $B(C_6F_5)_3$ is frequently used in FLP hydrogenations and is known to activate H_2 with bases as weak as THF or dioxane.^{9,10,37,38} Calculation of hydride affinities (HIA) (Table 1, entries 1 and 2), following a protocol described by Greb *et al.*, also indicates that HIA is much higher than $B(C_6F_5)_3$ (HIA = 481 $kJ\ mol^{-1}$).³⁹ Accordingly, **1-OTf**₂ and **1-Cl(OTf)** may activate H_2 together with Lewis bases (LBs) comparable to FLPs based on $B(C_6F_5)_3$ if a favourably oriented encounter complex forms.

As expected, **1-OTf**₂ and **1-Cl(OTf)** activated H_2 gas in the presence of THF, as shown by hydrogen–deuterium scrambling to H_2 and D_2 at 10 bar and at 25 and 60 °C, respectively (Fig. 2). Conversely, the dichloride complex $[Sn(tBu_2Salen)Cl_2]$ (**1-Cl**₂) does not possess a free binding site, at least at 25 °C, and in effect has the measured AN = 0 and the hydride affinity of 660 $kJ\ mol^{-1}$ (Table 1, entry 3) remains masked by the Cl^- ligands that must dissociate to reveal the cationic LA site. In line with Cl^- coordination and the lack of binding site at low temperatures, **1-Cl**₂ failed to activate H_2 , even with additional base, 2,4,6-collidine, or DABCO, at temperatures between 25 and 60 °C. These results indicate that H_2 activation requires a free binding site *via* a labile ligand.

Under the reaction conditions used for H_2 activation, however, neither of the complexes **1-OTf**₂ and **1-Cl(OTf)**₂ displayed

Table 1 Guttmann–Beckett Lewis acidity measurement and hydride affinities of the tested complexes and their ions

Entry	Lewis acid	AN ^a	Ionic form ^b	HIA ($kJ\ mol^{-1}$) ^c
1	1-OTf ₂	83.6	$[Sn(tBu_2Salen)]_2^+$	1170
2	1-Cl(OTf)	71.8	$[Sn(tBu_2Salen)Cl]^+$	660
3	1-Cl ₂	0	$[Sn(tBu_2Salen)Cl]^+$	660
4	2-Cl ₂	0	$[Sn(Salen)Cl]^+$	688
5	3-Cl ₂	0	$[Sn(Salophen)Cl]^+$	701
6	4-Cl ₂	0	$[Sn(tBu_2Salophen)Cl]^+$	682

^a Acceptor number. ^b Probable ionic fragments used for the calculation of hydride affinities assume dissociation of at least one ligand and all weakly coordinating anionic ligands. ^c Hydride ion affinities (HIA) were calculated at the DSD-PBEB86-D3BJ/def2-QZVP level.

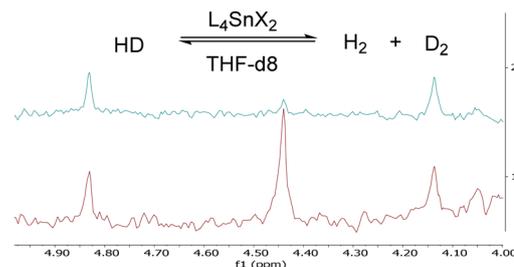


Fig. 2 ²D NMR spectra of HD scrambling by **1-OTf**₂ in THF-*d*₈ at 25 °C and 10 bar of HD. The blue trace is $T = 0$ h, and the red trace is $T = 19$ h. The peak at 4.45 ppm corresponds to D_2 gas, suggesting HD scrambling. Comparable spectra are obtained with **1-Cl(OTf)** (ESI†).

any hydrogenation activity, suggesting that hydride transfer could be hindering the desired catalytic reactivity in line with the high HIA of 1170 and 660 $kJ\ mol^{-1}$ respectively and associated poor hydride donor ability. Catalytic hydrogenation of the FLP model substrate, *N-tert*-butyl-1-phenylmethanimine, was observed only at 180 °C and 50 bar of H_2 in sulfolane with **1-OTf**₂, **1-Cl(OTf)** and even **1-Cl**₂, in 10, 49 and 29% yield, respectively (Table 2, entries 1–3). These findings suggest that chloride becomes a sufficient leaving group for H_2 activation at high temperatures, albeit less so than triflate.

Replacing the bulky ^tBu groups with -H on **1-Cl**₂ to form $[Sn(Salen)Cl_2]$ (**2-Cl**₂) improved the product yield from 29 to 53% (Table 2, entries 3 and 4), implicating steric hindrance in the low hydrogenation activity of the complexes. This hypothesis was tested with $[Sn(Salophen)Cl_2]$ (**3-Cl**₂) and $[Sn(tBu_2Salophen)Cl_2]$ (**4-Cl**₂), which yielded the desired product in 42 and 28% yield, respectively (Table 2, entries 5 and 6), thus confirming that ^tBu groups on complexes **1-Cl**₂, and **4-Cl**₂ hinder substrate access to the metal centre. Moreover, the ^tBu-substituted complexes **1-Cl**₂

Table 2 Optimization table for *N-tert*-butyl-1-phenylmethanimine reduction by L_4SnX_2 complexes with Schiff base ligands

Entry	Catalyst	Solvent	Temperature (°C)	Yield (%)
1	1-OTf ₂	Sulfolane	180	10
2	1-Cl(OTf)	Sulfolane	180	49
3	1-Cl ₂	Sulfolane	180	29
4	2-Cl ₂	Sulfolane	180	53
5	3-Cl ₂	Sulfolane	180	42
6	4-Cl ₂	Sulfolane	180	28
7	1-OTf ₂	Toluene	180	30
8	1-Cl(OTf)	Toluene	180	86
9	1-Cl ₂	Toluene	180	84
10	2-Cl ₂	Toluene	180	98
11	1-Cl ₂	Toluene	150	NR
12	2-Cl ₂	Toluene	150	27
13	2-Cl ₂	Collidine	180	85

Reaction conditions: *N-tert*-butyl-1-phenylmethanimine (1 mmol), reaction solvent (4 mL), catalyst (0.05 mmol), H_2 (50 bar), 17 h. All reactions were performed in triplicate, quantifying the reaction product by ¹H NMR with CH_2Br_2 as the internal standard and confirming the structure by ESI-MS.



and **4-Cl₂** had similar yields of the target product, at 29 and 28%, respectively (Table 2, entries 3 and 6) and the HIA of the best catalyst **2-Cl₂** without the ^tBu groups and the worst **4-Cl₂** with ^tBu groups are almost identical (Table 1, entries 4 and 6), further demonstrating that steric hindrance of ^tBu groups is the limiting factor of the activity of chloride complexes. Attempts to calculate an optimized FLP structure were only successful for **2-Cl₂** (Fig. 4B) as the ^tBu groups on **1-Cl₂** and **4-Cl₂** prevented FLP formation.

Substituting sulfolane for toluene improved the catalytic performance of **1-OTf₂**, **1-Cl(OTf)** and **1-Cl₂** reaching 30, 86 and 84% yields of the desired amine, respectively (Table 2, entries 7–9), thus approximately doubling and trebling those obtained in sulfolane (Table 2, entries 1, 2 and 3). Among other solvent effects, this can be attributed to the enhanced solubility of H₂ gas in toluene⁴⁰ that can promote tin hydride formation *via* the Le Chatelier principle. As a result, **1-Cl(OTf)** and **1-Cl₂** showed similar activities. The failure to further improve the yield of **1-(OTf)₂** was attributed to the instability of this catalyst under these reaction conditions. **2-Cl₂** also demonstrated improved activity in toluene and the desired product was obtained in 98% yield (Table 2, entry 10). The use of 2,4,6-collidine as the solvent, which can also act as an FLP base and enhance H₂ activation, decreased the yield from 98 to 85% (Table 2, entries 10 and 13). Lowering the temperature to 150 °C, in toluene, also decreased the yield and confirmed **2-Cl₂** as the best catalyst (Table 2, entries 11 and 12). Based on these results, we established the optimal reaction conditions, which were 180 °C, toluene, 50 bar of H₂ and 17 hours over the catalyst **2-Cl₂** (5 mol%).

Under optimal reaction conditions, **2-Cl₂** was used as the catalyst to assess the substrate scope of the reaction (Fig. 3). The model substrate *N-tert-butyl-1-phenylmethanimine* was converted into the corresponding amine (**1**) in 98% yield. Introduction of functional group(s) onto the benzene ring such as 4-chloride-, 4-trifluoromethyl- or 4,5-dimethoxy- decreased the reaction yields to 61 (**2**), 42 (**3**) and 50% (**5**) respectively or

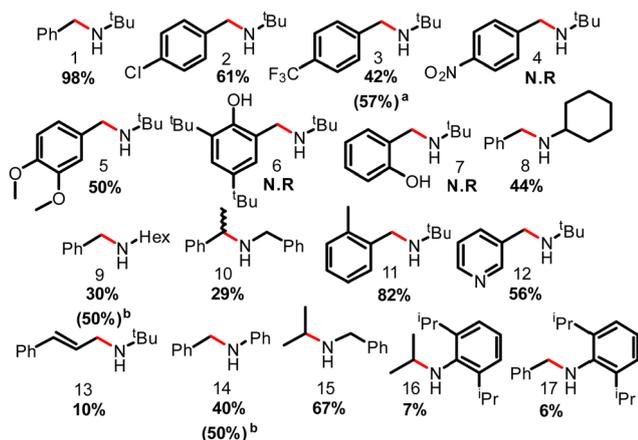


Fig. 3 Substrate scope of the imine hydrogenation reaction with H₂ over **2-Cl₂**. Reaction conditions: imine (1 mmol), toluene (4 mL) and LA (5 mol%), H₂ (50 bars), 180 °C, 17 h. All yields were determined by ¹H NMR with CH₂Br₂ as the internal standard, and all structures were confirmed by ESI-MS. (a) 70 bar (b) Extended reaction time to 48 h.

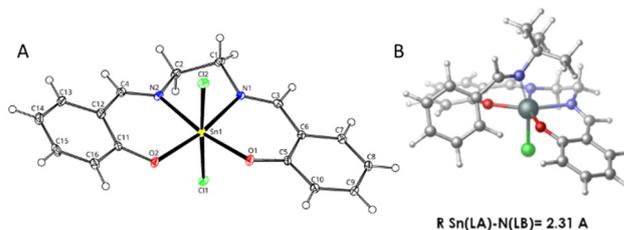


Fig. 4 (A) X-ray structure of **2-Cl₂** and (B) calculated FLP structure at the DSD-PBEB86-D3BJ/def2-QZVP level.

halted the reaction in the case of 4-nitro- (**4**), and 2-hydroxy- (**6** and **7**). As shown by mass spectrometry, nitro- and hydroxy-substitution completely inhibited imine reduction possibly due to the slow but preferential –NO₂ group reduction to –NH₂ and to the relative Brønsted acidity of phenol(s), respectively. Phenols can protonate the hydride formed in the reaction and hence reverse H₂ activation. Simultaneous reduction of an alkene was also observed and *N-(tert-butyl)-N-cinnamylamine* (**13**) was obtained in only 10% yield, while the rest was further hydrogenated to remove the alkene moiety.

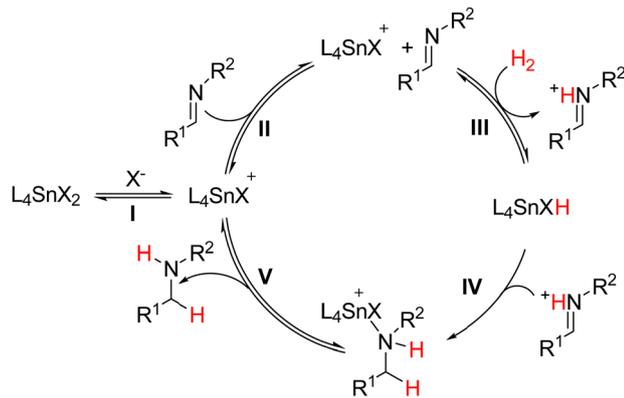
Substitution of the ^tBu group for –Hex, Cy, –Ph, –Bn or other unfunctionalized aliphatic or aromatic hydrocarbon substituents resulted in the corresponding amine formation in 6 to 82% yield (**8** to **17**). Noteworthy is the tolerance of *ortho*-methyl substitution, which yielded the corresponding amine **11** in 82% yield, whereas *ortho*-diisopropyl inhibited the reactivity and the corresponding amine **17** was obtained in 6% yield.

Nevertheless, further reaction trends are difficult to establish and analysis of side reactions, reaction mass balance and catalyst stability indicate that the desired reaction yield is a balance between the rate of substrate hydrogenation, its decomposition and catalyst deactivation, which decomposes to an inactive mixture of metallic tin, tin oxides and ligand fragments under the reaction conditions.

In toluene, the reaction substrate also acts as the Lewis base to activate H₂ because the tin(IV) complexes lack this ability on their own. Furthermore, a ligand must also dissociate from the coordinatively saturated complexes (Fig. 4A) to generate a Lewis acidic site, and generate an active FLP catalyst (Fig. 4B) as shown in our H₂ activation studies (Fig. 2). Based on these observations and on previous literature,^{4,41–44} we propose a catalytic cycle for hydrogenation over hexacoordinate tin(IV) complexes (Scheme 1).

In the initial phase (Scheme 1, **I**), a ligand X[–] (Cl[–] or OTf[–]) dissociates from the complex to reveal an LA site. Interaction with the imine then forms the active FLP catalyst (**II**) and splits H₂ yielding L₄SnHX and [imineH][X] (**III**). The protonation activates the imine towards hydride transfer from the metal centre to the iminium double bond (**IV**).⁴³ The produced amine reversibly binds the tin(IV) complex, which slows down the reaction as demonstrated by the addition of the product (1 mmol) to the reaction, which decreased the conversion of the starting imine from 85% to 30% in a 6-hour reaction. Eventual dissociation of the produced amine then regenerates the active LA with a free binding site (**V**).





Scheme 1 Catalytic cycle proposed for imine hydrogenation with H₂ catalysed by tin(IV)-Schiff base complexes.

In conclusion, hexacoordinated tin(IV) complexes with Schiff base and labile or hemi-labile axial ligands can be used as LA components of FLPs for H₂ activation and imine hydrogenation. H₂ activation takes place with bases as weak as THF at 25 °C and can be reversible, as shown by HD scrambling. Nevertheless, imine reduction only occurs at temperatures ≥ 150 °C and optimally at 180 °C, suggesting that hydride transfer hinders the reaction. The best catalyst is [Sn(Salen)Cl₂] (2-Cl₂) even though dichloride complexes have the lowest ability to activate H₂ among all complexes tested in this study. In effect, various imines are hydrogenated in yields ranging from 6 to 98% in toluene depending on substrate substitution and functionalization. The high variability of these complexes opens up opportunities for developing hydrogenation catalysts based on hexacoordinated compounds of main-group elements.

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Conflicts of interest

There are no conflicts to declare.

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