Establishing the Role of Triflate Anions in H₂ Activation by a Cationic Triorganotin(IV) Lewis Acid

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ABSTRACT: Cationic Lewis acids (LAs) are gaining interest as targets for frustrated Lewis pair (FLP)-mediated catalysis. Unlike neutral boranes, which are the most prevalent LAs for FLP hydrogenations, the Lewis acidity of cations can be tuned through modulation of the counteranion; however, detailed studies on such anion effects are currently lacking in the literature. Herein, we present experimental and computational studies which probe the mechanism of H₂ activation using iPr₃SnOTf (1-OTf) in conjunction with a coordinating (quinuclidine; qui) and non-coordinating (2,4,6-collidine; col) base and compare its reactivity with {iPr₃Sn·base}{Al[OC(CF₃)₃]₄} (base = qui/col) systems which lack a coordinating anion to investigate the active species responsible for H₂ activation and hence resolve any mechanistic roles for OTf⁻ in the iPr₃SnOTf-mediated pathway.

KEYWORDS: frustrated Lewis pair, hydrogen activation, anion, tin, stannylium

INTRODUCTION

Frustrated Lewis pairs (FLPs), where bulky Lewis acid (LA) and Lewis base (LB) partners are sterically precluded from forming strong classical adducts, are now well-established systems for small-molecule activation with main group compounds.⁷ Perhaps most notably, H₂ heterolysis can be effected by FLPs to form H⁺ and H⁻ equivalents, which can be delivered to unsaturated bonds to form a reduced compound and the original FLP. Accordingly, FLP-catalyzed hydrogenations of organic compounds containing the C=–X (X=C, N, and O) bonds have received widespread attention and have been thoroughly studied.⁷ The LAs used in these reactions are predominantly triarylboranes BAr₃, particularly B(C₆F₅)₃ and similar derivatives⁴ thereof, where the electronic and steric profiles have been tuned by the variation of aryl substituents (although these are predominantly confined to H, F, and Cl),⁸ which can afford a systematic manipulation of BAr₃ Lewis acidity. Accordingly, novel BAr₃ have recently been developed that can catalyze the hydrogenations of substrate classes previously inaccessible by FLPs or display the catalytic activity in the presence of alcohols/moisture, yet accessing such heteroleptic boranes requires laborious multistep syntheses.⁵,⁶ Although some aspects of the H₂ activation mechanism between the BAr₃ and N- or P-centered bases are still being debated,⁷ it is generally assumed that facile H₂ heterolysis is associated with the initial formation of a noncovalent LA–LB “encounter complex”, which subsequently reacts with H₂ in a cooperative manner (i.e., a concerted mechanism via a single transition state).⁸ Important exceptions are “frustrated radical pairs”, which activate substrates via single electron pathways.⁹ Recently, the range of LAs displaying FLP-like reactivity has expanded to encompass a number of cationic species (or neutral species that act as surrogates for the active cationic LA) based on B(III),¹⁰ Si(IV),¹¹ C(IV),¹² N(III),¹³ P(V),¹⁴ and Sb(V).¹⁵,¹⁶

Tuning the LA strength, and hence the reactivity, of these LAs may also be achieved through ligand design within the formally cationic fragment, akin to BAr₃ compounds; however, their anions also provide an additional locus for variation and hence a comparatively simple route to optimize the Lewis acidity of the cationic species. For instance, replacement of [TfO]⁻ for [B(C₆F₅)₄]⁻ in phosphonium or stibonium LAs can switch on otherwise absent reactivity (see Figure 1), which has been rationalized only by reference to the relative sequestration of the cation by more strongly coordinating anions, resulting in weaker LAs. A detailed analysis of any intimate effects the anion may exert during a reaction (e.g. by its coordination within a transition state, which could perturb...
its energy) have not been previously undertaken for cationic LAs. We reported previously that iPr$_3$SnOTf (1-OTf; Tf = O$_2$SCF$_3$), which acts as a surrogate for the stannylium ion [iPr$_3$Sn]$^+$ ([1]$^+$), activates H$_2$ in conjunction with LBs (e.g., 2,4,6-collidine; col) and catalyzes the hydrogenation of imines and ketones and the reductive amination of carbamates.$^{17}$ Despite the diversity of hydrogenation substrates accessible by 1-OTf, which can operate in the presence of moisture and strong LBs, productive hydrogenation using 1-OTf/coll is rather slow and requires forcing conditions (>120 °C, 10 bar H$_2$). A thorough understanding of the factors affecting 1-OTf/LB catalytic hydrogenations would clearly aid the development of superior R$_2$SnX LA hydrogenation catalysts, although it should be borne in mind that this will require a more complicated treatment, cf. B-based FLPs. This is predominantly due to the presence of the (hemi-labile) TfO anion and the fact that the [R$_2$Sn]$^+$ species are known to readily bind two anionic-neutral donors (as opposed to only one for BAr$_3$); such five-coordinate adducts may also be important off-cycle entities in catalysis. A previous computational study by Pati et al. suggested that the weakly associated complexes of 1-OTf and either DABCO (1,4-diazabicyclo[2.2.2]octane) or col cove H$_2$ via an FLP-type concerted mechanism$^{18}$ analogous to that seen in the FLP reactivity of the electrophilic [(C$_6$F$_5$)$_3$P-X]$^+$ species. Pati et al. assumed that 1-OTf was the only active LA despite the experimental evidence for the formation of [1-(LB)]$^+$ adducts (e.g.,$^{19}$Sn NMR shifts) in 1-OTf/LB mixtures.$^{17a}$ Accordingly, any role of [1-(LB)]$^+$ species was not investigated, nor the potential impact of charged hypervalent Sn species upon reductions mediated by 1-OTf, all of which could arise from the displacement of labile [TfO]$^-$ during the reaction pathway (see Scheme 1). Clearly, ascertaining the correct catalytic speciation in these more complex systems is crucial if targeted improvements in activity/selectivity are to proceed in a logical and predictive manner. Herein, we report a comprehensive study into the mechanism of H$_2$ activation using 1-OTf/LB pairs, using complementary experimental and theoretical methods, which reveal the noninnocent nature of [TfO]$^-$ in influencing both kinetic and thermodynamic factors. These results provide fundamental insight into how heavier-element cationic Lewis pairs activate H$_2$, which will help guide the design of new cationic p-block LA catalysts by encouraging further research into the role and tunability of the anion in reactions featuring such LAs.

**RESULTS AND DISCUSSION**

### Identifying Ground-State Speciation in 1-OTf/Quinuclidine Lewis Pairs

Because DABCO contains two donor atoms, which in theory could both interact with LAs and accordingly complicate the identification of equilibria speciation in 1-OTf/LB pairs, we chose instead to study the interaction of 1-OTf with quinuclidine (qui) because of its similar basicity [pK$_a$(MeCN): [DABCO-H]$^+$ 18.3, [qui-H]$^+$ 19.5]$^{20}$ and steric profile. 1-OTf exhibits a broad peak in its $^{119}$Sn$^1$(H) NMR spectrum at $\delta$ = 166 ppm in 1,2-difluorobenzene (DFB),$^{21}$ which moves to 34 ppm and sharpens upon addition of 1 equiv of qui at room temperature (RT), suggesting a spontaneous association to form [qui]-1-OTf and/or formation of the ion pair [1-(qui)]$^+$[OTf]$^-$.

Gratifyingly, slow cooling of this solution yielded single crystals that were analyzed by X-ray diffraction; the solved structure (Figure 2) reveals the former species: a five-coordinate adduct in which OTf$^-$ and the qui coordinate trans across the [1]$^+$ core, with a trigonal pyramidal geometry for the Sn atom [bond angles ($^\circ$): C-Sn-N = 91.41(9), 93.73(9), and 93.76(9); O1-Sn-N = 177.40(7)]. Although this (qui)-1-OTf adduct represents the ground-state structure in the solid phase, it is possible that [1-(qui)]$^+$(OTf)$^-$ is accessible at RT in solution. In order to spectroscopically identify [1-(qui)]$^+$ as a distinct moiety, it was necessary to characterize it in the absence of any exchange equilibria, which was achieved by exchanging [OTf]$^-$ for the much more weakly coordinating aluminate [Al(OC(CF$_3$)$_3$)$_4$]$^-$ ([Al(OR)$_3$)$_4$]$^-$; this was chosen because it is particularly robust to strongly Lewis and Bronsted acidic media.$^{22}$ Thus, the reaction of K[Al(OR)$_3$)$_4$], 1-OTf, and qui (1:1:1) in DFB
resulted in the precipitation of KOTf, with the $^{19}$F NMR spectrum of the filtrate showing only a single signal for the aluminic anion, demonstrating clean anion metathesis (Scheme 2). Layering this solution with pentane yielded crystals suitable for X-ray diffraction studies; the structural solution to these data is represented in Figure 3 and corresponds to the salt $[1·(qui)]\text{[Al(OR$_5$)$_4$]}^-$.\textsuperscript{23}

As anticipated, the $[\text{Al(OR$_5$)$_4$}]^-$ ion does not display any close contacts to the $[1]^+$ unit and therefore does not coordinate to the LA Sn atom. Consequently, the $[1·(qui)]^+$ assembly adopts a distorted tetrahedral geometry around the Sn center [N-Sn=C bond angles ($\delta$) = 103.7(2), 102.8(2), 102.9(3)]. The Sn=N bond distance is considerably shorter than that observed for the qui-1-OTf adduct [2.448(2) Å], which is consistent with a Sn=N weakening in the latter because of a trans-labilizing effect of the OTf$^-$ and/or increased steric encumbrance. The $^1$H NMR spectroscopic analysis of the DFB solutions of $[1·(qui)]\text{[Al(OR$_5$)$_4$]}^-$ showed that the observed chemical shifts and couplings for the $i$Pr groups are similar to those for 1-OTf in DFB; the relative integration of these with the signals for qui confirms a 1:1 ratio between $[i$Pr$_2$Sn]$^+$ and qui. The $^{119}$Sn$[^1]$H NMR spectrum, however, conclusively shows the formation of a new stannylium adduct with a sharp resonance at $\delta$ = 113 ppm, which is upfield from 1-OTf ($\delta$ = 166 ppm), but notably downfield of that seen for 1-OTf/qui mixtures ($\delta$ = 34 ppm). Taken together, these spectroscopic data confirm that the gross solid-state structure of $[1·(qui)]\text{[Al(OR$_5$)$_4$]}^-$ is retained in the solution. Curiously, the $^{119}$Sn$[^1]$H NMR spectroscopic data for the adduct formed from 1-OTf and qui in situ, or by redissolution of (qui)-1-OTf crystals obtained thereof, are inconsistent with those of either authentic 1-OTf or $[1·(qui)]^+$. This suggests that neither compound is present exclusively. It is plausible that a rapid equilibrium containing 1-OTf, (qui)-1-OTf, and $[1·(qui)]^+$ exists in the solution. To understand better the speciation, we assessed the relative energies of these species computationally (Scheme 3), with our density functional theory (DFT) calculations\textsuperscript{5,4} predicting the formation of a ternary complex (qui)-1-OTf to be clearly favored thermodynamically with respect to qui + 1-OTf, in contrast with the previously obtained results for the related DABCO + 1-OTf system.\textsuperscript{18,25} Additionally, dissociation of the adduct (qui)-1-OTf into $[1·(qui)]^+$ + [OTf]$^-$ is also found to be thermodynamically feasible, with the latter computed to be 4.8 kcal/mol more stable than the original qui + 1-OTf reference state.

We also probed two other possible adducts: one where the qui molecule coordinates to $[1·(qui)]^+$, and another where a further qui molecule coordinates to $[1·(qui)]^+$; of these two ternary adducts, $[1(OTf)_2]^-$ is stabilized notably with respect...
to the dissociated form, whereas \([1\text{-}(\text{qui})_2]^+\) is predicted to be an unstable species (see Scheme 3). The optimized structures of possible binary and ternary adducts are depicted in Figure 4, and the computed bond distances suggest considerably weakened Sn–ligand bonds in the ternary species. The notable difference between the computationally and X-ray crystallographically determined Sn–N/O bond lengths in the (qui)-1-OTf complex is likely due to the intermolecular forces in the crystal structure, which appreciably influences the character of the Sn–N/O dative bonds. Of note, one of the Sn–N bonds in \([1\text{-}(\text{qui})_2]^+\) is particularly elongated, which results in asymmetry across the equatorial plane and is likely due to steric effects.\(^{26}\) Having predicted that 1-OTf, (qui)-1-OTf, and \([1\text{-}(\text{qui})]^+\) are thermally accessible in a solution at RT, we sought to identify each species experimentally by manipulating the equilibria between them. Upon portion-wise addition of qui to 1-OTf in DFB, the \(^1H\) NMR iPr methine resonance (\(\delta = 2.15\) ppm) moves upfield to a limiting value of \(\delta = 1.94\) ppm (5.5 equiv qui), after which further qui results in no further change. Similarly, the \(^{119}\text{Sn}\{^1H\}\) NMR resonance moves upfield from that observed for pure 1-OTf (\(\delta = 166 \rightarrow 0\) ppm; see the Supporting Information). Only a single resonance attributable to the \([1]^+\) fragment was observed for any qui:1-OTf ratio in the \(^{119}\text{Sn}\{^1H\}\) NMR spectra (the same is true for the iPr resonances in the \(^1H\) NMR spectra), indicating that the observed shifts are weighted averages of the multiple species, all of which are in rapid exchange.

A variable temperature \(^{119}\text{Sn}\{^1H\}\) NMR experiment of a 1:1 mixture of 1-OTf and qui (CD\(_2\)Cl\(_2\))\(^{27}\) was undertaken to slow the exchange between the adducts (Figure 5, spectra A1 and A2),\(^{28}\) which revealed the broad RT resonance (\(\delta = 45\) ppm) to split into three distinct peaks (i–iii) below 263 K. Resonance i (\(\delta = 119\) ppm, 233 K) is very similar to that seen for authentic \([1\text{-}(\text{qui})]^{+}[\text{Al}(\text{ORF})_4]^-\) (\(\delta = 113\) ppm, 293 K; Figure 5, spectrum B), and accordingly, it is assigned to the cation fragment therein. The existence of the latter implies that dissociation of [OTf]\(^-\) from qui-1-OTf has occurred, which is computationally predicted to bind spontaneously to 1-OTf and form \([1\text{-}(\text{OTf})_2]^-\) (\(\Delta G = -3.2\) kcal/mol).\(^{29}\) To verify this, an equimolar solution of [nBu\(_4\text{N}\)] [OTf] and 1-OTf (DFB, 293 K) was prepared, which displayed a broad peak at \(\delta = 62.5\) ppm in the \(^{119}\text{Sn}\{^1H\}\) spectrum (Figure 5, spectrum C); this is significantly upfield from the chemical shift of either 1-OTf or \([1\text{-}(\text{qui})]^+\) and is almost identical to that observed for \(\delta = 62.9\) ppm, 233 K), so it is attributed to \([1\text{-}(\text{OTf})_2]^-\). Notably at temperatures below 203 K, only one peak at \(\delta = 14\) ppm is observed (Figure 5, spectrum A3); DFT calculations predict the 1:1 adduct between qui and 1-OTf to be the most stable species at low temperatures (for details, see the Supporting Information, Section 6.1), and accordingly, we ascribe resonance iii to (qui)-1-OTf.

### Mechanism for the Activation of H\(_2\). Admission of 4 bar H\(_2\) to \([1\text{-}(\text{qui})][\text{Al}(\text{ORF})_4]\) in DFB led to no reaction by \(^1H\) or \(^{119}\text{Sn}\{^1H\}\) NMR spectroscopy at RT after several days, nor after heating at 100 °C for 10 h. Furthermore, this salt did not scramble HD to H\(_2\), D\(_2\), and HD, which would detect rapidly reversible heterolysis. These results exclude a simple mechanism by which the Sn–N bond can elongate (with or without complete cleavage) to activate H\(_2\) in a manner akin to that reported for the related classical adduct \([\text{Pr}_3\text{Si–P}]{\text{Bu}_3}][\text{B}(\text{CF}_3)_4]\).\(^{11}\) In support of this conclusion, computations predict the activation energy for H\(_2\) cleavage via this mechanism to be prohibitively high (\(\Delta G = 36.4\) kcal/mol; see Supporting Information Section 6.4 for the transition-state structure).

Because 1-OTf and \([1\text{-}(\text{qui})]\) are both present at RT in solutions of 1-OTf/qui LP, either could feasibly engage with qui to mediate H\(_2\) cleavage; accordingly, we sought to elucidate whether they could act as LAs for the FLP-mediated H\(_2\) activation. \([1\text{-}(\text{qui})][\text{Al}(\text{ORF})_4]\) is a valid model compound to study the reactivity of \([1\text{-}(\text{qui})]\) as a LA fragment, so using \([1\text{-}(\text{qui})][\text{Al}(\text{ORF})_4] + \text{qui}\) (hereafter referred to as the “\([1\text{-}(\text{qui})]\)/qui” LP) allows the investigation of H\(_2\) activation, where [OTf]\(^-\) cannot be involved at any point in the reaction.

When one equivalent of qui is added to \([1\text{-}(\text{qui})][\text{Al}(\text{ORF})_4]\), the evidence of H\(_2\) activation is observed immediately after H\(_2\) admission by the appearance of NMR spectroscopic resonances attributable to 1-H (SnH; \(\delta (\text{H}) = 5.10\) ppm, \(J(\text{H}–\text{Sn}) = 1404\) Hz, \(J(\text{H}–\text{Sn}) = 1470\) Hz; \(\delta (^{119}\text{Sn}\{^1H\}) = -47.3\) ppm) and [qui-H]\(^+\) (\(\delta (\text{H}) =

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**Figure 4.** Optimized structures of possible binary and ternary adducts in the solution phase for the 1-OTf + qui Lewis pair. Selected bond distances are given in Å. All hydrogen atoms are omitted for clarity.

**Figure 5.** (A1–A3): Stacked \(^{119}\text{Sn}\{^1H\}\) NMR spectra of a 1:1 mixture of 1-OTf + qui in CD\(_2\)Cl\(_2\) at selected temperatures. (B) \(^{119}\text{Sn}\{^1H\}\) NMR spectrum of authentic \([1\text{-}(\text{qui})][\text{Al}(\text{ORF})_4]\) in DFB. (C) \(^{119}\text{Sn}\{^1H\}\) NMR spectrum of 1-OTf + [nBu\(_4\text{N}\)] [OTf] in DFB.
The $^{27}$Al and $^{19}$F NMR spectra remain unchanged, indicating that $[\text{Al(OR})_3]^{-}$ remains intact and does not participate in H$_2$ activation, as expected. Based on these observations, we propose the mechanism shown in Scheme 5, which is supported computationally.

**Scheme 4. H$_2$ Activation by $[1\cdot(\text{qui})]^+$ Only Occurs When Free qui LB Is Present; $R^2 = \text{C(CF}_3)_3$**

and does not participate in H$_2$ activation, as expected. Based on these observations, we propose the mechanism shown in Scheme 5, which is supported computationally. $^{19}$H$_2$ is cleaved

**Scheme 5. Proposed Mechanism for H$_2$ Activation with the $[1\cdot(\text{qui})]^+/\text{qui Lewis Pair via a Ternary TS; [Al(OR})_3]_4$ Counteranion Omitted; $R^2 = \text{C(CF}_3)_3$**

shows the time evolution of the respective $^1$H NMR spectra for these reactions to illustrate their differing rates. Initially, as H$_2$ activation by 1-OTf/qui proceeds, the $^{119}$Sn-{$^1$H} NMR spectra show the expected resonance at $\delta = -47$ ppm for 1-H growing in intensity and a peak at $\delta = 40$ ppm corresponding to the aforementioned fast equilibrium between 1-OTf, (qui)-1-OTf, $[1\cdot(\text{qui})]^{-}[\text{OTf}]^{-}$, and $[\text{OTf}_2]^{-}$ species; the latter moves upfield and sharpens as the reaction approaches completion, reaching a limiting value of $\delta = 19$ ppm, which we attribute to the generation of $[1\cdot(\text{OTf})_2]^{-}$.

This result implies that as H$_2$ activation proceeds, $[\text{qui}]^{-}[\text{OTf}]^{-}$ accumulates, and $[\text{OTf}]^{-}$ is concomitantly sequestered by 1-OTf to produce inactive $[1\cdot(\text{OTf})_2]^{-}$ (Scheme 3); this association quenches the electrophilicity of 1-OTf because the five-coordinate anionic adduct is not Lewis acidic enough to participate in H$_2$ heterolysis. Therefore, the attainable conversion of H$_2$ cleavage is impaired by the increasing concentration of $[1\cdot(\text{OTf})_2]^{-}$. In support of this hypothesis, the incremental addition of [nBuN]$^+\cdot[\text{OTf}]^{-}$ to 1-OTf in DFB reproduces the upfield movement of the $^{119}$Sn-$^1$H NMR shift for the 1-OTf/qui/H$_2$ reaction exactly, confirming that the binding of $[\text{OTf}]^{-}$ to 1-OTf occurs in situ during H$_2$ activation (see the Supporting Information). Conversely, during H$_2$ activation by $[1\cdot(\text{qui})]^+/\text{qui}$, the noninteracting counteranion in the $[\text{qui-H}]^{-}[\text{Al(OR})_3]_4$ product cannot coordinate and quench the $[1\cdot(\text{qui})]^+$ LA, so the reaction can proceed to quantitative conversion.

It is notable that for this latter LP system, the concentration of uncoordinated qui should remain constant throughout the...
reaction with H₂ (Scheme 5); indeed, it is found that the \([1\cdot(\text{qui})]^+/\text{qui LP}\) is actually catalytic with respect to qui, and H₂ activation proceeds with substoichiometric amounts of added qui, albeit at correspondingly reduced rates. For the \(1\cdot\text{OTf}/\text{qui}\) LP, however, the concentration of free qui is reduced by its association with \(1\cdot\text{OTf}\) and decreases further as the reaction proceeds. The concentration of free qui is therefore expected to be lower at all times for H₂ cleavage reactions employing \(1\cdot\text{OTf}/\text{qui}\) versus \([1\cdot(\text{qui})]^+/\text{qui}\); this difference makes a direct quantitative kinetic comparison extremely difficult. Nevertheless, the initial H₂ activation rate is clearly higher for the \(1\cdot\text{OTf}/\text{qui}\) LP in spite of the lower concentration of free qui available, which supports the conclusion that H₂ activation is inherently faster at the beginning of the reaction for \(1\cdot\text{OTf}/\text{qui}\) than \([1\cdot(\text{qui})]^+/\text{qui}\). In order to rationalize our observations regarding the rates and yields of H₂ heterolysis induced by these two qui-dependent systems, we additionally examined the basic mechanistic features of the latter reaction, computationally (Figure 8).

![Figure 8](https://example.com/figure8.png)

**Figure 8.** Transition-state TS\(_{\text{OTf-qui}}\) identified computationally for H₂ activation with \(1\cdot\text{OTf}/\text{qui}\) and the species corresponding to the most stable product state \((1\cdot\text{H} + [\text{qui-H}]^+[\text{OTf}]^-)\). Relative stabilities (in kcal/mol) are shown in parentheses, and selected bond distances are given in Å.35

Consistent with our experimental results, the transition state identified for the H₂ splitting process \(\text{TS}\(_{\text{OTf-qui}}\)\) possesses a significantly lower barrier with respect to the \(1\cdot\text{OTf} + \text{qui} + \text{H}_2\) state \(^{31}\) (13.5 kcal/mol) when compared to that obtained for the \([1\cdot(\text{qui})]^+ + \text{qui} + \text{H}_2\) reaction (19.5 kcal/mol). When the ground state of the reactants in the former case is factored in, corresponding to \([1\cdot(\text{qui})]^+ + [\text{OTf}]^- + \text{H}_2\), the overall kinetic barrier is actually 18.3 kcal/mol (see Scheme 3 and Figure 8). These computed barriers are in agreement with the measured reaction times.\(^{32}\) Our computational analysis suggests that the differing energies of TS\(_{\text{OTf-qui}}\) and TS\(_{\text{K-qui}}\) relative to their corresponding reactant states could be associated with solvent effects (for a more detailed analysis of solvation effects, see Supporting Information Section 6.6). The reactant state of \(1\cdot\text{OTf} + \text{qui} + \text{H}_2 \rightarrow 1\cdot\text{H} + [\text{qui-H}]^+ + [\text{OTf}]^-\)

involves only neutral components, whereas the \(\text{H}_2\) heterolysis yields two ionic species. The charge separation is notable already in TS\(_{\text{OTf-qui}}\) which has a relatively late character, so it is stabilized more by solvent polarity than the reactant state. On the other hand, no charge variation occurs in the reaction

\[ [1\cdot(\text{qui})]^+ + \text{qui} + \text{H}_2 \rightarrow 1\cdot\text{H} + [\text{qui-H}]^+ + \text{qui} \]

Interestingly, on the product side of the reaction with the \(1\cdot\text{OTf}/\text{qui}\) Lewis pair, the \(1\cdot\text{H} + [\text{qui-H}]^+ + [\text{OTf}]^-\) state is predicted to be the most stable form lying at \(-4.9\) kcal/mol in free energy, which is close to that of the reactant state (\(-4.8\) kcal/mol) and suggests that, even in the absence of subsequent capture of \([\text{OTf}]^-\) by \(1\cdot\text{OTf}\) to form \([1\cdot(\text{OTf})]^+\) (predicted to be exergonic by 3.2 kcal/mol; vide supra), the reaction would in fact still only reach approximately 50% conversion.

**Employing Collidine as the LB Partner.** To provide further context, we also studied the analogous system using col as a LB partner for \([1]^\text{-based LAs because it was found to be the optimally performing base surveyed for catalytic hydrogenations using 1-OTf and also to resolve any reactivity effects because of its different steric profile versus qui.\(^{33,\text{ab}}\) All attempts to isolate samples \((\text{col})\cdot1\cdot\text{OTf}\) or \([1\cdot(\text{col})]^+\cdot[\text{OTf}]^-\), from mixtures of the LPs by analogy with qui experiments, were unsuccessful. This indicates that the association between 1-OTf and col is weaker compared with qui, which is consistent given that col exhibits a lower basicity \(\log pK_a = 12.6\) \(^{34}\) and that its N center is hindered by the flanking 2,6-Me substituents. The dative bound adduct \((\text{col})\cdot1\cdot\text{OTf}, analogous to \((\text{qui})\cdot1\cdot\text{OTf}, could be identified computationally; however, an appreciable Sn-N bonding interaction is sterically prevented with only a weak col\cdot1\cdot\text{OTf} association evident from DFT calculations (see Supporting Information Section 6.7 for a ternary complex structure). A mixture of 1-OTf and col \((1:1, \text{DFB})\) displays a broad signal in the RT \(^{119}\text{Sn}\{^1\text{H}\} \text{NMR spectrum at } \delta = 142 \text{ ppm, which is significantly downfield from that observed for 1-OTf/qui } (\delta = 34 \text{ ppm}) \text{ and moves upon warming to a limiting value at 353 K that is identical to authentic 1-OTf. When the solution is cooled, the peak moves upfield } (\delta = 116 \text{ ppm at 243 K, indicating that col is binding to 1-OTf more strongly.}^{35}\) Our computations suggest that the small change in chemical shift (24 ppm) can be ascribed to the \([1\cdot(\text{col})]^+\) complex formed in low concentrations. Although several different species might be contributing to the observed average chemical shift, these could not be resolved; nonetheless, it is clear that the association between 1-OTf and col is significantly less favored than for qui.

Fortunately, \([1\cdot(\text{col})]^+[\text{Al(OR)}^3]^\text{-}\) can be prepared by an analogous route to \([1\cdot(\text{qui})]^+[\text{Al(OR)}^3]^-\) (Scheme 2), as a yellow oil that unfortunately resisted attempts at crystallization. Its \(^{119}\text{Sn}\{^1\text{H}\} \text{NMR spectrum exhibits a broad resonance at } \delta = 128 \text{ ppm, which is slightly downfield from the qui counterpart } (\delta = 113 \text{ ppm). Similar to [1\cdot(\text{qui})]^+, [1\cdot(\text{col})]^+[\text{Al(OR)}^3]^-\) does not react with \(\text{H}_2\) unless additional col is added, resulting in the appearance of resonances attributable to 1-H + [col-H]^+ by \(^1\text{H}\) and \(^{119}\text{Sn}\{^1\text{H}\} \text{NMR spectroscopy. This strongly suggests that [1\cdot(\text{qui}/\text{col})]^+ LAs activate H}_2 with their corresponding LB partners via the same mechanism. Notably, however, an elevated pressure (10 bar \(\text{H}_2\)) is required for \(\text{H}_2\) activation to proceed effectively by [1\cdot(\text{col})]^+/col, and the rate to reach quantitative conversion is considerably slower (28 days) under analogous equimolar conditions. These latter results are consistent with previous observations\(^{17,\text{ab}}\) and are commensurate with the lower basicity of col relative to qui. For \(\text{H}_2\) activation with the \(1\cdot\text{OTf}/\text{col LP}, once only partial conversion to 1-H and [col-H]^+ is observed (ca. 50% in 4 days.}
at RT) by $^1$H NMR spectroscopy because of the formation of $[1(\text{OTf})_2]$; however, the initial reaction rate is faster when 1-OTf is the LA compared with $[1(\text{col})]$.

To shed light on the similarities and differences between the qui and col systems thus far, the energetics of H$_2$ activation for the $[1(\text{col})]^{+}/\text{col}$ and 1-OTf/col LPs were assessed computationally; the key structures and their relative stabilities are shown in Figures 9 and 10. The principal mechanistic features of these reactions are quite similar to those of the analogous reactions with qui as the LB (concerted asynchronous H$_2$ splitting and base dissociation processes, formation of H-bonded species with the protonated base), yet there are profound differences in the computed energetics. For instance, H$_2$ activation with $[1(\text{col})]^{+}/\text{col}$ is predicted to be more favored thermodynamically as compared to $[1(\text{qui})]^{+}/\text{qui}$, which appears counterintuitive in light of the relative basicities; the computed proton affinities (kcal/mol) are $-160.9$ and $-155.4$ for qui and col, respectively.

However, the strained nature of the $[1(\text{col})]^{+}$ binary complex implies substantial reactant-state destabilization with a dissociation free energy into $[1]^{+} + \text{col}$ of only $17.6$ kcal/mol, so the reaction becomes more exergonic versus qui (for a detailed energy decomposition analysis, see Supporting Information Section 6.8). Destabilizing steric effects are even more enhanced in the transition state for H$_2$ splitting (TS$_{\text{K-col}}$ in Figure 9), which in combination with the reduced basicity of col results in a higher barrier compared to that obtained for $[1(\text{qui})]^{+}/\text{qui} + \text{H}_2$ (25.7 vs 19.5 kcal/mol, respectively).

For the 1-OTf/col system, the computational results predict the 1-OTf + col state to be clearly favored over the ionic $[1(\text{col})][\text{OTf}]^{-}$ alternative (Figure 10), and the H$_2$ activation reaction is found to be less favored (both kinetically and thermodynamically) than the analogous reaction with 1-OTF/qui. The latter trend for the predicted energetics of these two reactions follows the difference in the proton affinity of the two bases, which is also in line with our experimental observations. Importantly, H$_2$ activation by 1-OTf/col is predicted to have a much lower activation energy (20.2 kcal/mol) than the $[1(\text{col})][\text{col}]^{+}$ LP (25.7 kcal/mol), which is consistent with the observed reaction rates. We attribute this to the stabilization of TS$_{\text{OTf-col}}$ by the polar solvent relative to the neutral ground state (1-OTf + col + H$_2$), and the destabilizing steric effects in TS$_{\text{K-col}}$ which are weaker in TS$_{\text{OTf-col}}$.

**Relevance to Catalytic Hydrogenations Using 1-OTf/col.** Our previous observations in the catalytic hydrogenation of imine and carbonyl compounds by 1-OTF + col (our optimum LB for catalysis) showed that the reduction steps involved the reaction of 1-H with protonated imines and (carbonyl)-1-OTF species (i.e., activated substrates), respectively. These were more rapid than H$_2$ activation, and notably, 1-H was observed neither by $^1$H NMR nor by $^{119}$Sn-$^1$H NMR spectroscopy at any point during catalysis; hence, it was proposed that the H$_2$ cleavage was the rate-determining step.\(^{17a,b}\) The current results show that $[1(\text{OTf})_2]^{3-}$ forms as H$_2$ heterolysis by 1-OTF/col proceeds and because of the sequestration of active LA 1-OTF, it would therefore be expected to affect the reaction rate deleteriously in catalytic reactions. It should be noted, however, that in catalytic reactions, the direct H$_2$ cleavage products 1-H and [col-H][col-H][OTf]$^{-}$ are almost immediately consumed during proton and hydride transfers to the substrate; because H$_2$ cleavage is the rate-determining step, the accumulation of $[1(\text{OTf})_2]^{3-}$ will be suppressed and/or it will form reversibly (Scheme 6). The latter postulate is reinforced by the calculated small free energy difference between the formation of 1-H + [col-H][OTf] from 1-OTF + col + H$_2$ (+1.7 kcal/mol) and binding of 1-OTF with [col-H][OTf]$^{-}$ (−3.2 kcal/mol); this implies that all of these species would coexist in a readily perturbed equilibrium, as 1-H + [col-H][OTf]$^{-}$ is consumed in substrate hydrogenation. Indeed, $[1(\text{OTf})_2]^{3-}$ is not observed by $^{119}$Sn-$^1$H NMR spectroscopy during catalytic reactions, verifying that this species plays an insignificant role under the conditions of hydrogenation catalysis. Taking the results together, we propose that lowering the activation energy of H$_2$ cleavage is the most important factor to improve the rate of hydrogenation by triorganotannylium-based catalysts. Because [OTf]$^{-}$ explicitly interacts with [1]$^{+}$ in the reactants and the lowest energy TS possible for H$_2$ heterolysis by 1-OTF/col, this anion affects their stabilities; variation of this anion should consequently affect the activation energy as long as it remains associated in such a manner.
Scheme 6. Simplified Catalytic Cycle for Hydrogenations Mediated by 1-OTf/col. The Reduction Step Is Rapid Relative to the \( \text{H}_2 \) Cleaveage, Making 1-OTf + Col the Resting State under Catalytic Conditions; Because [OTf]− Does Not Accumulate in Situ, 1-OTf Is Not Sequestered (as [1(OTf)]2−) during the Catalytic Hydrogenations; X = NR, O

**CONCLUSIONS**

In conclusion, we have elucidated that 1-OTf is the LA involved in the lowest energy TS for \( \text{H}_2 \) activation with both coordinating (qui) and noncoordinating (col) LBs. 1-OTf and qui associate to form the dative adduct (qui)-1-OTf, which was characterized by single-crystal X-ray crystallography; solution-qui associate to form the dative adduct (qui) which is subsequently sequestered by DFB, and hence a lower barrier to the \( \text{H}_2 \) cleavage. The activation energies for \( \text{H}_2 \) cleavage for both 

| System                  | Activation Energy (kcal/mol) |
|------------------------|-----------------------------|
| [OTf]−/LB              | 50                           |
| [1(OTf)]2−/LB          | 25                           |


Resting State under Catalytic Conditions; Because [OTf]− Does Not Accumulate in Situ, 1-OTf Is Not Sequestered (as [1(OTf)]2−) during the Catalytic Hydrogenations; X = NR, O

ability to vary the anion partner of LA cations offers a design principle unavailable to neutral LAs. We expect that this will encourage further research into anion tunability for the tailoring of LA reactivity, especially toward the reactions of important small molecules.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c02023.

Full synthetic and computational details, NMR spectra of the reported reactions, and crystallographic data are contained therein (PDF)

X-ray structure for (qui)-1-OSO₂CF₃ (CIF)

X-ray structure for [1-(qui)]{[Al([OC(CF₃)]₄)₄]}− (CIF)

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**Author Contributions**

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(1) For key publications see: (a) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. Reversible, Metal-Free Hydrogen Activation. Science 2006, 314, 1124–1126. (b) Welch, G. C.; Stephan, D. W. Facile heterolytic cleavage of dihydrogen by phosphines and boranes. J. Am. Chem. Soc. 2007, 129, 1880–1881. (c) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. Metal-Free Catalytic Hydrogenation. Angew. Chem., Int. Ed. 2007, 46, 8050–8053. (d) Chase, P. A.; Jurca, T.; Stephan, D. W. Lewis acid-catalyzed hydrogenation: B(C6F5)3-mediated reduction of imines and nitriles with H2. Chem. Commun. 2008, 1701–1703. (e) Chen, D.; Klankermayer, J. Metal-free catalytic hydrogenation of imines with tris(perfluorophenyl)borane. J. Org. Chem. 2008, 73, 5689–5693. (f) Cao, L. L.; Zhu, D.; Zhou, J.; Stephan, D. W. Homolytic cleavage of CO2 to CH2OH. Angew. Chem., Int. Ed. 2009, 48, 9839–9843. (g) Cherchneiko, K.; Madarasz, A.; Pápai, N.; Sieger, M.; Leskelä, M.; Repo, T. A. Frustrated-Lewis-pair approach to catalytic reduction of alkenes to cis-alkenes. Nat. Chem. 2013, 5, 718–723. (h) Légare, M.-A.; Courtemanche, M.-A.; Rochette, E.; Fontaine, F.-G. Metal-free catalytic C−H bond activation and borylation of heteroarenes. Science 2015, 349, 513–516. (2) For overviews of FLPs see: (a) Erker, G.; Stephan, D. W. Frustrated Lewis pairs: From borenium ion catalysis to catalytic reduction of alkynes to −alkenes. Angew. Chem., Int. Ed. 2017, 56, 9512–9516. (b) Cao, L. M.; Gyo, S.; Szabo, M.; Kita, B.; Pápai, I.; Domján, A.; Soós, T. Moisture-Tolerant Frustrated Lewis Pair Catalyst for Hydrogenation of Aldehydes and Ketones. ACS Catal. 2015, 5, 5366–5372. (c) Dorko, E.; Szabo, M.; Kita, B.; Pápai, I.; Domján, A.; Soós, T. Expanding the Boundaries of Water-Tolerant Frustrated Lewis Pair Hydrogenation: Enhanced Back Strain in the Lewis Acid Enables the Reductive Amination of Carboxyls. Angew. Chem., Int. Ed. 2017, 56, 5217–5221. (e) Sitte, N. A.; Bursch, M.; Grimm, S.; Paradies, J. Lewis Acid Enables the Reductive Amination of Amides: Halides as Active Lewis Base in the Metal-Free Hydrogen Activation. J. Am. Chem. Soc. 2019, 141, 159–162. (f) Hoshimoto, Y.; Kinoshita, T.; Hazra, S.; Ohashi, M.; Ogoshi, S. Main-Group-Catalyzed Reductive Alkylation of Multiply Substituted Amines with Aldehydes Using H2. J. Am. Chem. Soc. 2018, 140, 7292–7300. (7) For a recent overview of unmetallated mechanistic issues, see: Daru, J.; Bakó, I.; Stirling, A.; Pápai, I. Mechanism of Heterolytic Hydrogen Splitting by Frustrated Lewis Pairs: Comparison of Static and Dynamic Models. ACS Catal. 2019, 9, 6049–6057. (8) For a review on relevant computational studies, see: Rokob, T. A.; Pápai, I. Hydrogen Activation by Frustrated Lewis Pairs: Insights from Computational Studies. Top. Curr. Chem. 2013, 332, 157–211. (9) We excluded the possibility of radical-mediated H2 cleavage by Lewis pairs comprising [Pr3Sn]7− fragments in our previous studies; see ref 17. For examples of “frustrated radical pairs” see: (a) Liu, L.; Cao, L. L.; Shao, Y.; Stephan, D. W. Single Electron Delivery to Lewis Pairs: An Avenue to Anions by Small Molecule Activation. J. Am. Chem. Soc. 2017, 139, 10062–10071. (b) Liu, L.; Cao, L. L.; Shao, Y.; Ménard, G.; Stephan, D. W. A Radical Mechanism for Frustrated Lewis Pair Reactivity. Inorg. Chem. 2017, 3, 259–267. (c) Liu, L. L.; Cao, L. L.; Zhu, D.; Zhou, J.; Stephan, D. W. Homolytic cleavage of peroxide bonds via a single electron transfer of a frustrated Lewis pair. Chem. Commun. 2018, 54, 7431–7434. (d) Merk, A.; Große-Kaempfgen, H.; Schmidt-Mann, M.; Luecke, M. P.; Lorent, C.; Driess, M.; Oestreich, M.; Klare, H. F. T.; Müller, T. Single-Electron Transfer Reactions in Frustrated and Conventional Silylum Ion/Phosphate Lewis Pairs. Angew. Chem., Int. Ed. 2018, 57, 15267–15271. (e) Liu, L. L.; Stephan, D. W. Radicals derived from Lewis acid/base pairs. Chem. Soc. Rev. 2019, 48, 3454–3463. (f) Bennett, E. L.; Lawrence, E. J.; Blagg, R. J.; Mullens, A. S.; MacMillan, F.; Ehlers, A. W.; Scott, D. J.; Sapsford, J. S.; Ashley, A. E.; Wildgoose, G. G.; Sloatweg, J. C. A New Mode of Chemical Reactivity for Metal-Free Hydrogen Activation by Lewis Acid Boranes. Angew. Chem., Int. Ed. 2019, 58, 8362–8366. (g) Soltani, Y.; Dasgupta, A.; Gasz, T. A.; Ould, D. M. C.; Richards, E.; Slater, B.; Stekova, K.; Vladimirov, V. Y.; Wilkins, L. C.; Wilcox, D.; Melen, R. L. Radical Reactivity of Frustrated Lewis Pairs with Diaryl Esters. Cell Reports Phys. Sci. 2020, 1, 100016. (10) (a) Eisenberger, P.; Bailey, A. M.; Cruden, C. M. Taking the F out of FLP: Simple Lewis acid-base pairs for mild reductions with neutral boranes via borenium ion catalysis. J. Am. Chem. Soc. 2012, 134, 17384–17387. (b) Farrell, J. M.; Hatnean, J. A.; Stephan, D. W.
Activation of Hydrogen and Hydrogenation Catalysis by a Borenium Cation. J. Am. Chem. Soc. 2012, 134, 15728–15731. (c) Eisenberger, P.; Bestvater, B. P.; Keske, E. C.; Cruden, C. M. Hydrogenations at Room Temperature and Atmospheric Pressure with Mesionic Carbene-Stabilized Borenium Catalysts. Angew. Chem., Int. Ed. 2015, 54, 2467–2471. (d) Clark, E. R.; Grosso, A. D.; Ingleson, M. J. The Hydride-Ion Affinity of Borenium Cations and Their Propensity to Activate H2 in Frustrated Lewis Pairs. Chem.—Eur. J. 2013, 19, 2462–2466. (e) Lam, J. J.; Günther, B. A. R.; Farrell, J. M.; Eisenberger, P.; Bestvater, B. P.; Newman, P. D.; Melen, R. L.; Cruden, C. M.; Stephan, D. W. Chiral carbone—borane adducts: precursors for borenium catalysts for asymmetric FLP hydrogenations. Dalton Trans. 2016, 45, 15303–15316. (f) Mercea, D. M.; Howlett, M. G.; Pisacik, A. D.; Scott, D. J.; Steven, A.; Ashley, A. E.; Fuchter, M. J. Enantioselective reduction of N-alkyl ketimines with frustrated Lewis pair catalysis using chiral borenium ions. Chem. Commun. 2019, 55, 7077–7080.

(11) (a) Herrington, T. J.; Ward, B. J.; Doyle, L. R.; McDermott, J.; White, A. J. P.; Hunt, P. A.; Ashley, A. E. Bypassing a highly unstable frustrated Lewis pair: dihydrogen cleavage by a thermally robust silylum—phosphine aduct. Chem. Commun. 2014, 50, 12753–12756. (b) Oestreich, M.; Hermeke, J.; Mohr, J. A unified survey of Si–H and H–H bond activation catalysed by electron-deficient boranes. Chem. Soc. Rev. 2015, 44, 2202–2220. (c) Weicker, S. A.; Stephan, D. W. Activation of Carbon Dioxide by Silyl Trimflate-Based Frustrated Lewis Pairs. Chem.—Eur. J. 2015, 21, 13027–13034. (d) Mållöf, I.; Ruddy, A. J.; Zhu, H.; Grimmme, S.; Stephan, D. W. Carbon–F Bond Activation by Silyle Cation/Phosphine Frustrated Lewis Pairs: Mono-Hydrodefluorination of PhCF5, PhCF2H and PhCF2F. Chem.—Eur. J. 2017, 23, 17692–17696.

(12) (a) Clark, E. R.; Ingleson, M. J. N-Methylcarbazolium Salts: Carbon Lewis Acids in Frustrated Lewis Pairs for σ-Bond Activation and Catalytic Reductions. Angew. Chem., Int. Ed. 2014, 53, 11306–11309. (b) Mosafari, E.; Ripsman, D.; Stephan, D. W. The air-stable carbocation salt [(MeO2C6H4)CPh2][BF4] in Lewis acid activated hydrolysis of alkenes. Chem. Commun. 2016, 52, 8291–8293. (c) Fasano, V.; Radcliffe, J. E.; Curless, L. D.; Ingleson, M. J. N-Methyl-Benzothiazolium Salts as Carbon Lewis Acids for Si–H Sigma-Bond Activation and Catalytic (De)hydroxylation. Chem.—Eur. J. 2017, 23, 187–193.

(13) (a) Zhou, J.; Liu, L. L.; Cao, L. L.; Stephan, D. W. An unpairing of Lewis acidity/basis at nitrogen by deprotonation of a cyclic (azon)-aryl)nitrenium cation. Chem. Commun. 2018, 54, 4390–4393. (b) Zhou, J.; Liu, L. L.; Cao, L. L.; Stephan, D. W. Nitrogen-Based Lewis Acids: Synthesis and Reactivity of a Cyclic (Azo)-Nitrenium Cation. Angew. Chem., Int. Ed. 2018, 57, 3322–3326. (c) Waked, A. E.; Ostadasharf Memar, R.; Stephan, D. W. Nitrogen-Based Lewis Acids Derived from Phosphonium Diazoc Cations. Angew. Chem., Int. Ed. 2018, 57, 11934–11938.

(14) (a) Caputo, C. B.; Hounjet, L. J.; Dobrovetsky, R.; Stephan, D. W. Lewis Acidity of Organofluorophosphonium Salts: Hydrodefluorination by a Saturated Accepter. Science 2013, 341, 1374–1377. (b) Pérez, M.; Hounjet, L. J.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W. Olefin Isomerization and Hydroxylation Catalysis by Lewis Acidic Organofluorophosphonium Salts. J. Am. Chem. Soc. 2013, 135, 18308–18310. (c) Stein, T. V.; Peréz, M.; Dobrovetsky, R.; Winkelhaus, D.; Caputo, C. B.; Stephan, D. W. Electrophilic Fluorophosphonium Cations in Frustrated Lewis Pair Hydrogen Activation and Catalytic Hydrogenation of Olefins. Angew. Chem., Int. Ed. 2015, 54, 10178–10182. (d) Fasano, V.; LaFortune, J. H. W.; Bayne, J. M.; Ingleson, M. J.; Stephan, D. W. Air- and water-stable Lewis acids: synthesis and reactivity of P-trifluoromethyl electrophilic phosphonium cations. Chem. Commun. 2018, 54, 662–665. (e) Postle, S.; Podgoryn, V.; Stephan, D. W. Electrophilic phosphonium cations (EPCs) with perchlorinated-aryl substituents: towards air-stable phosphorus-based Lewis acid catalysts. Dalton Trans. 2016, 45, 14651–14657. (f) Barrado, A. G.; Bayne, J. M.; Johnstone, T. C.; Lehmann, C. W.; Stephan, D. W.; Alcarazo, M. Dicationic phosphonium salts: Lewis acid initiators for the Mukaiyama-aldol reaction. Dalton Trans. 2017, 46, 16216–16227. (g) Bayne, J. M.; Fasano, V.; Szkop, K. M.; Ingleson, M. J.; Stephan, D. W. Phosphorous(V) Lewis acids: water/base tolerant P₃-trimethylated trications. Chem. Commun. 2018, 54, 12467–12470.
(24) The DFT calculations were carried out using the \( \omega \text{B97X-D} \) functional along with the Def2SVP and Def2TZVPP basis sets. The reported relative stabilities were obtained from solution phase Gibbs free energies. To model the global solvation effects, the SMD implicit solvation model was employed. For further computational details, see the Supporting Information Section S5.

(25) This seems to contradict the results obtained previously for DABCO/1-OTf.\(^{18} \) Pati et al. found the formation of the datively bound (DABCO)·1-OTf complex to be only marginally exergonic with respect to the 1-OTf + DABCO state. The orientation of the \( \text{iPr} \) groups in the most stable form of (qui)·1-OTf is different from that reported for the analogous (DABCO)·1-OTf complex (ref 18a), which may explain the difference found in the relative stabilities of the two complexes.

(26) Only one set of (unobscured) qui resonances are observed in the \( \text{\textsuperscript{1}H} \) NMR spectrum (\( \delta = 2.98 \) and \( 1.67 \) ppm) for a 1:1 mixture of [1·(qui)][Al(OR\(^{\text{3}}\))\(_{4}\)] and qui, in DFB. The corresponding resonances in [1·(qui)]\(^{+}\) are appreciably downfield at \( \delta = 3.16 \) and \( 1.86 \) ppm, respectively. This is consistent with qui being bound to the electron deficient [1]\(^{+}\) fragment in the former, while in the mixture a weighted average of chemical shifts between coordinated and uncoordinated qui is seen, implying a fast exchange equilibrium. Although [1·(qui)]\(^{+}\) is calculated to be unstable relative to [1·(qui)]\(^{+}\) + qui (4.7 kcal/mol), this could be considered as an activation energy to degenerate exchange between bound and unbound qui, which will be readily surmountable at room temperature.

(27) The melting point of DFB (−35 °C; 239 K) limits the utility of this solvent for low-temperature NMR studies. Accordingly CD\(_{2}\)Cl\(_{2}\) was used instead.

(28) Although broadening of the \( \text{\textsuperscript{119}Sn} \{\text{\textsuperscript{1}H}\} \) NMR resonance is observed at 243 K in DFB, the solvent freezes below this temperature (mp = 239 K). The data are included in the Supporting Information.

(29) Spontaneous dissociation of [OTf\(^{−}\)] from 1-OTf to form [1]\(^{+}\) is thought to be highly unlikely due to the very reactive and unstable nature of stannylium ions, especially in weak donor solvents such as DFB or CH\(_{2}\)Cl\(_{2}\).

(30) [1·(qui)]\(^{+}\) and [Al(OR\(^{\text{3}}\))\(_{4}\)]\(^{−}\) are predicted to be separated in DFB (dissociation energy = −11.1 kcal/mol); [Al(OR\(^{\text{3}}\))\(_{4}\)]\(^{−}\) was therefore omitted from mechanistic calculations (for more details see Supporting Information Section S6.3).

(31) In principle, the [1·(qui)]\(^{+}/[\text{OTf}^{−}]\) pair may also induce FLP-type \( \text{H}_2 \) activation, however, the barrier of this process is predicted to be much higher (31.2 kcal/mol) than that of the 1-OTf/qui pair (see Supporting Information, Section S6.5 for transition state structure).

(32) We note, however, that the level of agreement we find here should not be considered as a measure for the accuracy of the applied methodology.

(33) A direct comparison between the two systems [1·qui]\(^{+}/qui\) and 1-OTf/qui is not straightforward because there is neither a common reference state, nor common reaction coordinate. We have attempted to make the best comparison possible using the two free energy profiles starting with their own reference states, including the \( \text{H}_2 \) activation transition states, and product states.

(34) Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. Extension of the Self-Consistent Spectrophotometric Basicity Scale in Acetonitrile to a Full Span of 28 pK\(_{a}\) Units: Unification of Different Basicity Scales. J. Org. Chem. 2005, 70, 1019–1028.

(35) Further cooling of CD\(_{2}\)Cl\(_{2}\) solutions beyond this temperature was uninformative due to precipitation of 1-OTf.