

Enabling Catalytic Ketone Hydrogenation by Frustrated Lewis Pairs

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S Supporting Information

ABSTRACT: Hydrogenation of alkyl and aryl ketones using H₂ is catalytically achieved in 18 examples using 5 mol % B(C₆F₅)₃ in an ethereal solvent. In these cases the borane and ether behave as a frustrated Lewis pair to activate H₂ and effect the reduction.

Catalytic hydrogenation of unsaturated substrates is one of the most fundamental transformations in chemistry. It is pertinent to biological systems and employed in a plethora of industrial chemical processes.¹ Our ability to effect such reductions has its genesis in the seminal discovery by Sabatier in the early 1900s.² Subsequently the emergence of organometallic chemistry in the 1960s led to the development of numerous homogeneous catalysts for this transformation³ as well as designed systems for asymmetric hydrogenations.⁴ More recent work has focused on catalysts derived from Earth-abundant metals such as Fe.⁵

The ability of main group systems to catalyze hydrogenations has also emerged in recent years with the discovery of frustrated Lewis pairs (FLPs). These combinations of sterically encumbered main group Lewis acids and bases⁶ have been shown to be uniquely reactive. Perhaps most striking is their ability to effect the catalytic hydrogenation of a variety of unsaturated organic substrates. For example, the metal-free catalytic hydrogenation of imines,⁷ protected nitriles, aziridines,^{7,8} enamines,⁹ silyl enol ethers,¹⁰ *N*-heterocycles,¹¹ olefins,¹² and poly arenes,¹³ have been achieved while most recently alkynes have been reduced to *cis*-alkenes.¹⁴ Further, stoichiometric reductions of anilines to cyclohexylammonium derivatives¹⁵ have been described and extended to pyridines and other *N*-heterocycles.^{11b}

Noticeably absent from these substrates are oxygen-based species such as ketones. This is perhaps surprising given the precedent of catalytic hydrosilylation of ketones established by Piers.¹⁶ Moreover, a number of groups have demonstrated the ability of FLPs to effect the reduction of CO₂ using silanes,¹⁷ boranes,¹⁸ or ammonia-borane¹⁹ as sources of the reducing equivalents. The limited attention given to hydrogenation of ketones might be attributed to the high oxophilicity of electrophilic boranes. Indeed, in an earlier report, Erker et al. described the irreversible capture of benzaldehyde by the intramolecular FLP, Mes₂PCH₂CH₂B(C₆F₅)₂.^{6c} Similarly, Erker's group has also demonstrated 1,4-addition of FLPs to conjugated ynones.²⁰ Nonetheless, the group of Privalov has generated a proposed mechanism for ketone reduction using B(C₆F₅)₃ as the catalyst which is computed to be energetically viable.²¹ Subsequently Repo et al. described the stoichiometric

reactions of aromatic carbonyls with B(C₆F₅)₃ effecting deoxygenation of the ketone, affording (C₆F₅)₂BOH, HC₆F₅, and arylalkane.²² Similar degradation of B(C₆F₅)₃ via B–C bond cleavage, affording (C₆F₅)₂BOMe, was reported by Ashley and O'Hare in their efforts to reduce CO₂ in the presence of H₂.²³ More recently, Wang et al. approached the notion of catalytic ketone hydrogenation computationally, suggesting that a bifunctional amine-borane FLP catalyst would be viable.²⁴ In the communication herein a simple and elegant solution to the metal-free ketone hydrogenation is achieved by the judicious choice of the FLP catalyst.

Initially, B(C₆F₅)₃ was added to excess 4-heptanol (10 equiv) and heated to 80 °C for 12 h. This resulted in no reaction beyond formation of the alcohol-borane adduct (Pr₂CHOH)–(B(C₆F₅)₃), as evidenced by the ¹¹B and ¹⁹F NMR spectra (¹¹B δ 1.97 ppm; ¹⁹F δ –132.6, –155.2, –162.8 ppm). In contrast, heating a toluene solution of 5 mol % B(C₆F₅)₃ and 4-heptanone under H₂ (60 atm) at 70 °C yielded complete conversion of the borane catalyst to Pr₂CHOB(C₆F₅)₂ with concurrent liberation of HC₆F₅. The remaining 95% of the initial ketone was unaltered. This observation has recently been generalized to provide a stoichiometric route to a number of borinic esters²⁵ and illustrates that the borane/ketone acts as an FLP to heterolytically cleave H₂ affording nominally [Pr₂COH][HB(C₆F₅)₃]. However, the acidity of the protonated ketone apparently prompts B–C bond cleavage.

To avoid this degradation pathway, an alternative FLP is required, one that is active enough to effect H₂ activation and yet not so acidic as to react with the B–C bond. In this regard, we have previously reported that the ethereal oxygen of the borane-oxborate (C₆F₅)₂BCH(C₆F₅)OB(C₆F₅)₃, derived from the reaction of an FLP with syn-gas, is sufficiently Lewis basic to activate H₂.²⁶ Further, we subsequently showed that the combination of Lewis bases such as Et₂O, electron-deficient triarylphosphines, and diaryl amines^{12b,d} are sufficiently basic for both H₂ activation and yet not so acidic to degrade the borane, permitting catalytic reduction of olefins.

To probe the viability of this approach, a *d*₈-toluene solution of 5 mol % B(C₆F₅)₃ was combined with a 1:1 ratio of Et₂O/4-heptanone and heated at 70 °C under 4 atm of H₂. Monitoring this reaction by ¹H NMR spectroscopy at 70 °C revealed the gradual hydrogenation of the ketone yielding approximately 30% of 4-heptanol after 12 h. This was evidenced by the diagnostic ¹H NMR quintet at 3.45 ppm, the multiplet at 1.30–1.38 ppm, and triplet at 0.87 ppm. Increasing the H₂ pressure to

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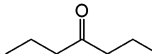
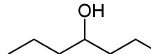
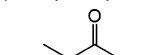
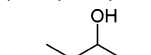
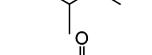
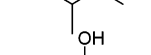
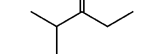
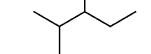
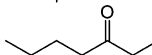
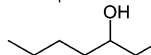
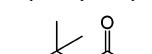
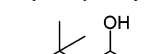
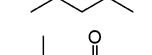
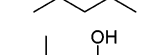
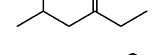
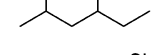
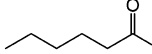
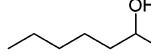
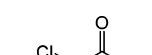
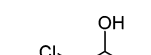
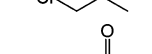
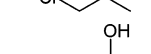
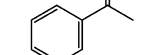
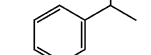
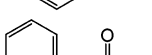
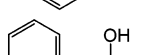
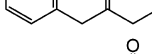
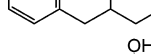
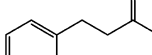
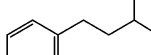
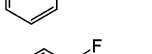
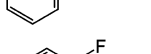
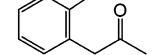
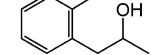
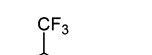
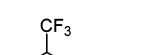
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60 atm improved the yield of 4-heptanol to 50%. Alternatively, incrementing the ratio of Et₂O/4-heptanone resulted in increased yields. Ultimately, a Et₂O/4-heptanone ratio of 8:1 in toluene at 70 °C under 60 atm of H₂ gave a 97% yield of 4-heptanol after 12 h (see Supporting Information (SI)). Employing identical conditions but using Et₂O as the solvent resulted in the quantitative formation of 4-heptanol after 12 h (Table 1, entry 1). Similarly, employing ⁱPr₂O as the solvent in analogous hydrogenations gave quantitative yields of 4-heptanol (Table 1, entry 1). The corresponding use of Ph₂O and (Me₃Si)₂O resulted in yields of 44% and 42% in the same time frame (see SI).

Using this FLP hydrogenation protocol, a range of ketone substrates were treated with 5 mol % B(C₆F₅)₃ in Et₂O or ⁱPr₂O and heated for 12 h at 70 °C under H₂ (60 atm). The substrates investigated included several alkyl ketones (Table 1, entries 1–8), an aryl ketone (Table 1, entry 9), and benzyl substituted ketones with substituents including F and CF₃ groups (Table 1, entries 10–14), and cyclic carbonyl substrates including cyclohexanone and L-menthone as well as cyclohexylmethyl ketone and cyclohexylaldehyde (Table 1, entries 15–18). The ¹H NMR spectra of the alcohol products displayed the characteristic multiplets at about 4 ppm assignable to the distinctive methine protons while the OH group gave only broad signals. The corresponding ¹³C{¹H} resonances for the reduced carbonyl fragment were observed at ca. 70 ppm as expected. Mass spectroscopy was used to characterize the product alcohols, and it is noted that L-menthone gave L-menthol (see SI). These reactions gave generally excellent conversions to the corresponding alcohol products (Table 1). Evaluating these reductions by ¹H NMR spectroscopy showed yields ranging between 32 and >99% and isolated yields ranging from 43% to 91% (Table 1) with reduction of cyclohexylaldehyde being the least efficient. This latter observation suggests the steric nature of the substrate impacts on reduction efficiency. Further attempts to reduce esters, beta-diketones, or ketones incorporating functional groups such as amines, thiophene, and thioethers were not successful (see SI). Nonetheless, for the viable substrates, these reactions could also be performed on a comparatively large scale. For example, 1.00 g of 4-heptanone was converted completely to 4-heptanol using 5 mol % B(C₆F₅)₃ as the catalyst in Et₂O and isolated in 87% yield.

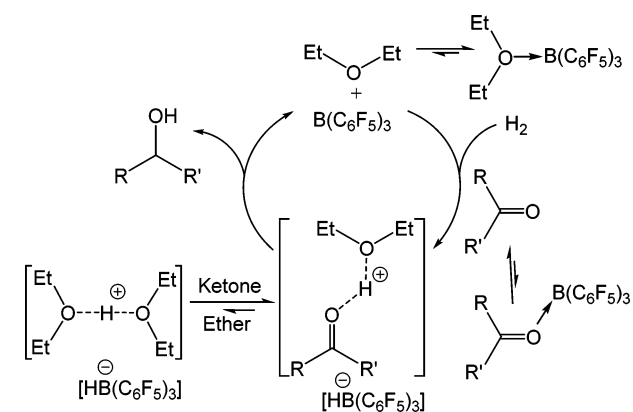
The mechanism of these reactions is thought to be analogous to that previously described for imine hydrogenations.⁷ In the present case, ether combines with the borane in equilibrium between the classical Lewis acid–base adduct and the corresponding FLP (Scheme 1). This latter combination effects the heterolytic cleavage of H₂. The resulting protonated ether then associates with ketone via a hydrogen-bonding interaction. This activates the carbonyl fragment to accept hydride from the [HB(C₆F₅)₃][−] anion. The generated basic alkoxide anion is then protonated yielding the product alcohol and liberating borane and ether to further activate H₂. The possibility of initial H₂ activation by ketone/borane combinations cannot be dismissed; however, the above-mentioned concept is based on the overwhelming abundance of ether in comparison to ketone. In support of this proposed mechanism we note that the activation of H₂ by Et₂O/B(C₆F₅)₃ has been previously described. The generated salt [(Et₂O)₂H][HB(C₆F₅)₃] has been shown to protonate imine²⁷ and alkene²⁸ en route to the corresponding hydrogenation products, so the proposed interaction with ketone is reasonable.

Table 1. FLP Mediated Catalytic Ketone Hydrogenation

Entry	Substrate	Product	Alcohol	
			% Conversion (Yield) Et ₂ O	ⁱ Pr ₂ O
1			>99 (91)	>99
2			>99 (76)	>99
3			>99	>99 (89)
4			>99 (87)	95
5			>99	>99 (90)
6			40	47
7			93 (85)	50 (43)
8			>99 (85)	>99
9			90	69 (52)
10			>99 (84)	97
11			>99 (84)	69
12			97	>99 (90)
13			>99	>99 (88)
14			>99	>99 (90)
15			>99 (88)	89
16			53	41
17			77	-
18			32	-

^a% Conversions were determined by ¹H NMR spectroscopy; isolated yields are in parentheses; reactions marked as - were not performed

Scheme 1. Proposed Mechanism of Catalytic Ketone Hydrogenation in Etheral Solvents



This notion was further probed by the stoichiometric reaction of a toluene solution of Jutzi's acid $[(Et_2O)_2H][B(C_6F_5)_4]$ ²⁹ with 1-phenyl-2-butanone and iPr_2O . After heating to 70 °C for 2 h, a white crystalline solid **1** was isolated in 87% yield. The 1H NMR spectrum of **1** showed a broad singlet at 11.52 ppm suggesting a proton involved in hydrogen bonding. Resonances attributable to both 1-phenyl-2-butanone and iPr_2O were unambiguously present, although these shifts were deshielded in comparison to the individual components. These data in addition to the definite presence of $[B(C_6F_5)_4]$ were evidenced by the ^{11}B and ^{19}F NMR spectra, leading to the formulation of **1** as $[(^iPr_2O)H(O=C(CH_2Ph)CH_2CH_3)][B(C_6F_5)_4]$. This was unambiguously confirmed by single crystal X-ray crystallography. The molecular structure (Figure 1) of

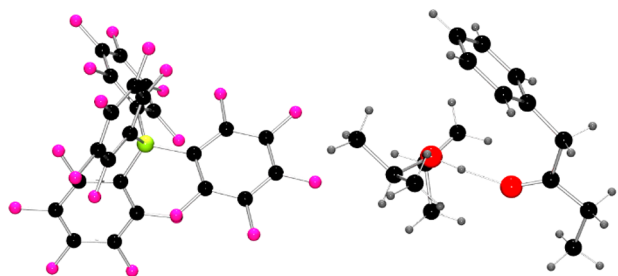


Figure 1. POV-Ray depiction of **1**. C, black; O, red; H, gray; B, yellow-green; F, pink.

this salt shows the proximity of the ketone and ether in the cation with an O–O separation of 2.53 Å. Location and complete refinement of the proton in the cation shows it is associated with the ether oxygen and hydrogen-bonded to the ketone with O–H distances of 1.04(2) and 1.54(2) Å. The resulting angle at H is 158.1°, consistent with that typically seen for hydrogen-bonding situations.³⁰ The closer proximity of the proton to ether in this hydrogen-bonded cation is consistent with the predicted pK_a values of protonated ether and ketone, respectively.³¹ Moreover, the isolation of **1** provides a direct structural analog of the proposed intermediate in the above ketone hydrogenation mechanism.

Current protocols for the catalytic reduction of ketones are typically based on transition metal catalysts including Ru, Rh,⁴ and more recently Fe complexes.⁵ On the other hand, main group reductions of carbonyl groups have been limited to stoichiometric reactions often employing large excesses of the

classic boron or aluminum hydrides or their derivatives.³² Herein, we have uncovered a remarkably simple approach to a metal-free hydrogenation of ketones to alcohols. This method exploits FLPs derived from ether and the electrophilic borane $B(C_6F_5)_3$ and the participation of etheral solvent in hydrogen bonding, affording an efficient catalyst for these atom-economic transformations. We are continuing to explore modifications and applications of this new metal-free reduction protocol as well as the impact of intermolecular interactions on the utility of FLPs in catalysis.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and crystallographic details. CCDC No. 1020848. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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