Frustrated Lewis Pairs

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Facile Protocol for Catalytic Frustrated Lewis Pair Hydrogenation and Reductive Deoxygenation of Ketones and Aldehydes**

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Abstract: *A series of ketones and aldehydes are reduced in toluene under H_2 in the presence of 5 mol% $B(C_6F_5)_3$ and either cyclodextrin or molecular sieves affording a facile metal-free protocol for reduction to alcohols. Similar treatment of aryl ketones resulted in metal-free deoxygenation yielding aromatic hydrocarbons.*

In the latter part of the 19th and early 20th centuries, Sabatier[1] uncovered the ability of amorphous metals to catalyze the hydrogenation of organic substrates. About 60 years later, Wilkinson[2] discovered the ability of homogeneous transition metal complexes to catalyze the hydrogenation of olefins. Since these two seminal findings, hydrogenation catalysis has found use in a myriad of products for modern society. Among the outstanding developments are the remarkably selective asymmetric hydrogenation catalysts developed by Noyori[3] and Knowles.[4] Despite the power of these technologies, research efforts prompted by cost, toxicity and low abundance have focused on the development of first-row transition metal-based catalysts.[5] An alternative strategy to hydrogenation catalysis based on main-group compounds has emerged in the last decade.[6] These systems known as frustrated Lewis pairs (FLPs) are derived from combinations of main-group Lewis acids and bases in which steric or electronic features preclude quenching of the acidic and basic components allowing the two reagents to act concurrently effecting the heterolytic cleavage of H_2. Moreover, these FLP systems were first shown to effect the catalytic hydrogenation of imines, protected nitriles, aziridines[7] and subsequently extended to other catalysts[8] and substrates including enamines,[9] silyl enol ethers,[10] N-heterocycles,[11] olefins,[12] polyarenes,[13] fulvenes,[14] and alkynes.[15] In related work, the aromatic hydrogenation of *N*-phenyl amines to give cyclohexylammonium derivatives was demonstrated[16] and this concept was extended to effect the reduction of pyridines[17] and a variety of N-heterocycles.[18]

In the case of carbonyl substrates, there are well established main-group routes to ketone reductions. For example, transfer hydrogenation from a sacrificial alcohol can be mediated by an aluminum alkoxide catalyst through the Meerwein, Ponndorf and Verley (MPV) mechanism.[19] Alternatively, $NaBH_4$ and $LiAlH_4$ can be used as stoichiometric reagents to hydrogenate unsaturated functional groups.[20] Berkessel and co-workers[21] reported the first metal-free reduction of benzophenone using H_2 and *t*BuOK as the catalyst at 100 atm of H_2 and 200 °C. However, the emergence of FLPs allowed catalytic metal-free hydrogenations under more mild conditions. In 2009, the group of Privalov[22] computationally predicted that catalytic ketone hydrogenation should be possible using $B(C_6F_5)_3$ as the catalyst. Although in assessing this prediction, Repo et al.[23] found only stoichiometric deoxygenation of aromatic carbonyls. Wang et al.[24] approached the catalytic ketone hydrogenation challenge computationally, suggesting that a bifunctional amine-borane FLP catalyst would be viable. In our own attempts to effect ketone reduction we found that treatment of dialkylketones with $B(C_6F_5)_3$ and H_2 in toluene led to the stoichiometric formation of C_6F_5H and borinic esters of the form $RR'CHOB(C_6F_5)_2$.[25] In addition, the stoichiometric reduction of carbonyl groups by N/B[26] and P/B[27] FLPs, including regioselectivity studies using deuterium and tritium labeling experiments have been reported.[28]

In rather dramatic recent findings, our group[29] and that of Ashley[30] simultaneously found that the use of ethereal solvents for FLP-catalyzed reductions of ketones and aldehydes resulted in effective hydrogenations. In these cases, the role of the solvent was proposed to hydrogen bond to the transient protonated ketone precluding protonation of the B–C bond, thus allowing catalysis to proceed effectively. In the present study, we further FLP based hydrogenations of ketones and aldehydes, exploring reductions in toluene with the addition of an oxygen containing material such as α-cyclodextrin (α-CD) or molecular sieves (MS). Use of these materials provides a heterogeneous Lewis base for H_2 activation and hydrogen bonding, thus yielding a facile catalytic protocol for ketone and aldehyde reduction and the reductive deoxygenation of aryl ketones using H_2.

The ketone 3-methyl-2-butanone was combined with an equivalent of α-CD and 5 mol% $B(C_6F_5)_3$ in toluene and heated at 60 °C under H_2 (60 atm). After 12 h, quantitative reduction to the product 3-methyl-2-butanol was evidenced by ^{1}H NMR spectroscopy, revealing a diagnostic multiplet at 3.27 ppm corresponding to the presently formed CH group and broad singlet at 1.82 ppm assignable to the OH group (Table 1, entry 1). Under similar conditions, a series of methyl alkyl ketones (entries 2–6), dialkyl ketones (entries 7–9), aryl (entries 10–14), benzyl (entries 15–19) and cyclic ketones (entries 20–22) were hydrogenated in high yields. In addition, the catalytic reduction of aldehydes was similarly performed

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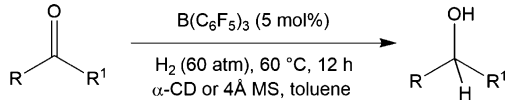
Table 1: Catalytic hydrogenation of ketones and aldehydes in toluene.



Entry	R	R^1	α-CD[c]	MS[c]
1	Me	*i*Pr	>99	(94)
2	Me	2-butyl	>99	>99
3	Me	CH_2tBu	>99	(95)
4	Me	CH_2Cl	>99	80
5	Me	Cy	>99	>99
6	Me	*n*-C_5H_{11}	>99	(87)
7	Et	*i*Pr	>99	>99
8	Et	*n*-C_4H_9	95	(83)
9	*n*-C_3H_7	*n*-C_3H_7	>99	(83)
10[a]	Me	Ph	30	trace
11	CH_2CH_2Cl	Ph	54	(48)
12	CF_3	Ph	20	20
13	Me	*o*-$CF_3C_6H_4$	trace	25
14	Me	*p*-$MeSO_2C_6H_4$	60	(94)
15	Me	*n*-CH_2CH_2Ph	>99	(86)
16	Me	CH_2(*o*-FC_6H_4)	75	>99
17	Me	CH_2(*p*-FC_6H_4)	>99	>99
18	Me	CH_2(*m*-$CF_3C_6H_4$)	>99	>99
19	Et	CH_2Ph	>68	(92)
20		$-(CH_2)_5-$	>99	(78)
21[b]		$-(CH_2)_3CH{=}CH-$	67	82
22		$-$(2-*i*Pr-5-Me)C_5H_8-	>99	>99
23	Cy	H	10	(44)
24	Ph_2CH	H	47	(86)
25	PhCH(Me)	H	20	35

[a] Reported yields are for phenylethanol. [b] Product is cyclohexanol. [c] Conversions in % as determined by ^{1}H NMR spectroscopy. Yields of isolated products are in brackets.

to give the corresponding primary alcohols (entries 23–25). The ^{1}H NMR spectra for all products displayed a characteristic resonance at approximately 4 ppm diagnostic of CH and CH_2 protons for ketone and aldehyde reductions, respectively. The $^{13}C\{^1H\}$ resonance of the reduced carbonyl group is observed at about 70 ppm. Mass spectroscopy was also used to characterize the products. It is noteworthy that use of α-CD gave only racemic mixtures of chiral alcohols.

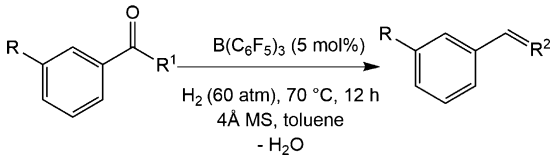
The efficient nature of these catalytic reactions infer that $B(C_6F_5)_3$ and the oxygen atoms of α-CD act as a FLP to activate H_2 initiating the hydrogenation catalysis. In a similar fashion α-CD could be conveniently replaced with molecular sieves (MS) for the catalytic hydrogenation of ketones and aldehydes (Table 1). It is important to note that HD isotope equilibration reactions of $B(C_6F_5)_3$ and MS or α-CD in toluene showed isotope scrambling yielding H_2 and D_2 (see Supporting Information (SI)), demonstrating FLP cleavage of dihydrogen.

These catalytic hydrogenations could also be performed on an increased scale as 1.00 g of 4-heptanone in toluene, 5 mol% of $B(C_6F_5)_3$ and MS gave 4-heptanol quantitatively (95% isolated yield). The sieves could be reused in successive hydrogenations without loss of activity although addition of $B(C_6F_5)_3$ was required suggesting physisorption of borane onto MS is insufficient for hydrogenation catalysis.

Analogous treatment of acetophenone using the above protocol and α-CD for 12 h at 70 °C under H_2 resulted in ca. 60% consumption of acetophenone and the formation of two products in equal proportion (see SI). The ^{1}H NMR spectrum gave a distinct quartet at 4.24 ppm, broad singlet at 3.42 ppm and a doublet at 1.02 ppm, consistent with the hydrogenated product phenylethanol. The ^{1}H NMR spectrum of the second product gave three separate doublet of doublets with olefinic chemical shifts observed at 6.52, 5.56 and 5.04 ppm, with each signal integrating to one proton. Mass spectroscopy confirmed this product to be styrene, derived from reductive deoxygenation of acetophenone.

To probe this catalytic deoxygenation further, the ketone 3′-(trifluoromethyl)acetophenone was treated with 5 mol% $B(C_6F_5)_3$ in toluene and added to a suspension of MS and heated for 12 h at 70 °C under H_2 (60 atm). This resulted in formation of the deoxygenated product 3-(trifluoromethyl)-styrene in 95% yield (Table 2, entry 2). Similar treatment of

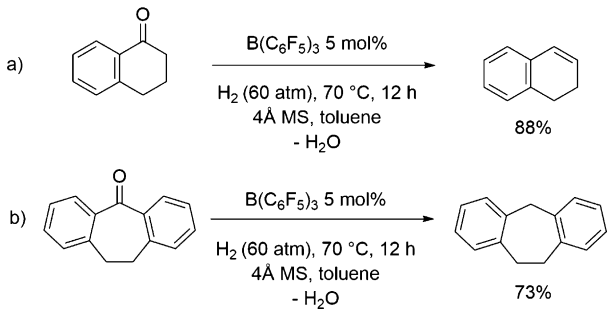
Table 2: Deoxygenation of aryl alkyl ketones.



Entry	R	R^1	R^2	Yield [%][a]
1	H	Me	CH_2	92
2	CF_3	Me	CH_2	95[b]
3	H	Et	$CHCH_3$	*trans* 96, *cis* 4
4	H	*i*Pr	$C(CH_3)_2$	75[b]

[a] Yield of isolated product. [b] Conversion in % as determined by ^{1}H NMR spectroscopy.

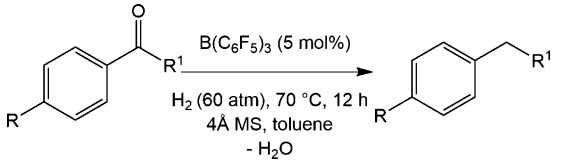
propiophenone gave *trans*-β-methylstyrene in 96% yield (entry 3) while the deoxygenation of isobutyrophenone was performed giving 75% of the hydrocarbon 2-methyl-1-phenyl-propene (entry 4). In this case, the marginally lower reaction rate is presumably due to increased steric hindrance about the carbonyl functionality. Indeed, this effect is more pronounced with 2,2,2-trimethylacetophenone as no reaction was observed. Finally, the bicyclic ketone 1-tetralone gave 1,2-dihydronaphthalene in 88% yield (Scheme 1 a).



Scheme 1. Hydrogenation and deoxygenation of a) 1-tetralone and b) dibenzosuberone.

In light of the established tandem hydrogenation and deoxygenation protocol, under analogous conditions benzophenone is deoxygenated to give diphenylmethane in 81% yield (Table 3, entry 1). Similarly, diaryl ketones with substituents including CH_3O, Br, *t*Bu, and CH_3 groups were successfully reduced affording the corresponding diarylmethane products in yields ranging from 67–99% (entries 2–5). In the case of *p*-CF_3 substituted benzophenone, the reaction gave 10% deoxygenation and 50% of the alcohol products (entry 6). Analogous treatment of 2-methylbenzophenone resulted in 20% conversion to the aromatic hydrocarbon (entry 7). This example, including the result for 2′-(trifluoromethyl)acetophenone (25% yield) (entry 13) certainly infer that increased steric hindrance about the carbonyl group has an impact on reactivity. Finally, the tricyclic ketone dibenzosuberone afforded the reduced arylalkane dibenzocycloheptene in 73% yield (Scheme 1b). It is noteworthy that Repo et al.[23] have previously reported $B(C_6F_5)_3$ mediated reductive deoxygenation of acetophenone in CD_2Cl_2, however in their case, concurrent hydration of the borane affords $(C_6F_5)_2BOH$ and HC_6F_5. In the present system, MS precludes this degradation allowing deoxygenation to proceed catalytically.

Table 3: Deoxygenation of diaryl ketones.

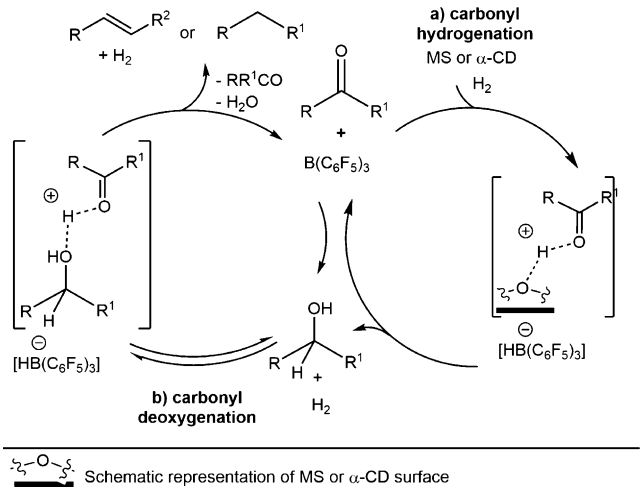


Entry	R	R^1	Yield [%][a]
1	H	Ph	81
2	CH_3O	Ph	85
3	Br	Ph	67[c]
4	*t*Bu	Ph	>99
5	CH_3	*p*-$CH_3C_6H_4$	75
6[b]	CF_3	Ph	10[c]
7	H	*o*-$CH_3C_6H_4$	20

[a] Yield of isolated product. [b] Resulting product is 10% hydrocarbon and 50% alcohol. [c] Conversion in % as determined by ^{1}H NMR spectroscopy.

The mechanism of these reductions is thought to be analogous to the FLP reductions previously described for ketone hydrogenations using $B(C_6F_5)_3$ in ethereal solvents. In the present case, the FLP initiating heterolytic H_2 activation is believed to be the Lewis basic oxygen atoms on the surface of the α-CD or MS and the Lewis acid $B(C_6F_5)_3$ (Scheme 2). The protonated surface hydrogen bonds to the carbonyl fragment inducing nucleophilic attack by hydride from the $[HB(C_6F_5)_3]$ anion. The generated alkoxide anion is then sufficiently basic to accept proton thus liberating alcohol.

In the case of benzylic alcohols deoxygenation is observed. It is proposed that hydrogen bonding of the protonated aryl ketone and alcohol prompt C–O bond cleavage, with hydride delivery and loss of H_2O to give either the alkane or alkene product. It is interesting to note that the independent treatment of benzylic alcohols with



Scheme 2. Proposed mechanism for a) hydrogenation of ketones and aldehydes and b) reductive deoxygenation of aryl ketones.

$B(C_6F_5)_3$, H_2 and MS alone does not prompt deoxygenation. However addition of a small amount of ketone initiates the reaction (see SI). This is consistent with the suggested role of the protonated ketone in the further activation of the C–O bond (Scheme 2).

Reductive deoxygenation of carbonyl groups by FLP systems has been previously achieved using silanes, boranes[31] or ammonia borane as sacrificial reducing agents. The Piers group demonstrated $B(C_6F_5)_3$-catalyzed deoxygenative hydrosilylation of CO_2 to CH_4 using 2,2,6,6-tetramethylpiperidine, $B(C_6F_5)_3$ and excess Et_3SiH.[32] Such transformations have also been reported using N-heterocyclic carbenes and hydrosilane.[31,33] Fontaine and co-workers[34] have effected the catalytic hydroboration of CO_2 to methanol using FLPs. Reductive deoxygenation using H_2 as the reducing agent was reported for CO_2 by Ashley[35] using the stoichiometric combination of $B(C_6F_5)_3$ and 2,2,6,6-tetramethylpiperidine at 160 °C to give methanol in 17–25% yield.

In the results presented herein, α-CD or MS acts as the Lewis base component of the FLP facilitating both H_2 activation and hydrogen bonding. In the case of reductive deoxygenation, MS also serve to adsorb the by-product water. The insolubility of these materials allows them to be easily recycled. Indeed, α-CD was filtered, washed and reused in five successive hydrogenations without impact on the product yield. This did however require renewal of the borane for each successive catalytic run.

In summary, the catalytic hydrogenation of ketones and aldehydes, generating the corresponding alcohols in a non-polar solvent is achieved using cyclodextrin or molecular sieves in the presence of a catalytic amount of $B(C_6F_5)_3$. This combination of soluble borane and insoluble materials mediates the reductions avoiding protodeborylation and providing a facile protocol for such reductions. In the case of aryl ketones, further reaction results in deoxygenation of the carbonyl group affording either the alkane or related alkene product. We are continuing to study the utility and potential applicability of these and other heterogeneous FLP catalysts for a variety of important transformations.[36]

Keywords: boranes · deoxygenation · frustrated Lewis pairs · hydrogenation

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