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Frustrated Lewis Pairs

Combinations of Ethers and $B(C_6F_5)_3$ Function as Hydrogenation Catalysts**

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Since its discovery in the 1960s, the electrophilic borane $B(C_6F_5)_3$[1,2] has been used extensively in catalysis. Perhaps best-known as a co-catalyst or activator for ethylene polymerization,[3–7] this highly electrophilic species has also found applications within a variety of Lewis acid-catalyzed transformations. For example, in the early 2000s, Piers, Gevorgyan, and co-workers pioneered its use in hydrosilylation chemistry.[8–13] Since then, others have developed applications in hydrostannylation,[14,15] silane dehydrocoupling, and silicone production and derivatization.[16–25] More recently, this electrophile has been exploited in "frustrated Lewis pair" (FLP) chemistry, acting as the Lewis acid partner in conjunction with bases to activate a wide variety of small molecules, including H_2, CO_2, olefins,[26] alkynes,[27] N_2O,[28,29] and NO,[30] among others.[31] The application of this borane in FLP or "metal-free" hydrogenation catalysis[32] has drawn much attention. Initially, the substrates were limited to imines, protected nitriles, and aziridines. Subsequently, enamines and silylenol ethers were also shown to be viable substrates for FLP reductions. More recently, combinations of $B(C_6F_5)_3$ with weakly basic triaryl phosphines or triaryl amines were shown to be capable of catalyzing hydrogenations of olefins[33] and polyaromatic systems.[34] $B(C_6F_5)_3$ was then shown to effect reductions of N-substituted anilines,[35] pyridines, and N-heteroatomic species.[36] At the same time, Nikonov et al.[37] provided experimental and theoretical evidence that $B(C_6F_5)_3$ alone does not activate H_2. Interestingly, however, these authors and others[38] showed that $C_4H_8O{-}BD_3$ undergoes H/D exchange under pressures of H_2 to produce $C_4H_8O{-}BH_3$. In very recent work, we described the reaction of H_2 with the epoxyborate salt, $[t\mathrm{Bu}_3\mathrm{PH}]\,[(C_6F_5)_2BCH(C_6F_5)OB(C_6F_5)_3]$, affording the borane–borate salt, $[t\mathrm{Bu}_3\mathrm{PH}][(C_6F_5)BCH_2(C_6F_5)OB(C_6F_5)_3]$.[31] This observation suggested the possibility that simple oxygen donors might also act in concert with $B(C_6F_5)_3$ to effect H_2 activation, thereby affording a remarkably simple and inexpensive hydrogenation catalyst. Indeed, herein we describe such reactivity. Labile dialkyl ether/$B(C_6F_5)_3$ combinations are shown to effect H_2 activation to catalyze hydrogenations of 1,1-diphenylethylene and anthracene.

The combination of $B(C_6F_5)_3$ with 2 equiv of Et_2O in CD_2Cl_2 exhibits two distinct chemical exchange processes by ^1H NMR spectroscopy at reduced temperatures. Analysis of a 2:1 mixture of $Et_2O/B(C_6F_5)_3$ between 25 and −90 °C[39] reveals coalescing Et_2O methylene signals at −55 °C that are consistent with lone pair inversion at oxygen in the adduct $Et_2O{-}B(C_6F_5)_3$ of $\Delta G^{\neq} = 10.3\ \mathrm{kcal\,mol^{-1}}$. A similar coalescence is also observed at −30 °C, corresponding to the rapid exchange of free and coordinated Et_2O with a $\Delta G^{\neq} = 10.5\ \mathrm{kcal\,mol^{-1}}$.[40] In a subsequent experiment, a 1:1 mixture of $Et_2O/B(C_6F_5)_3$ in CD_2Cl_2 (0.14 M) was exposed to 4 atm of HD gas in a J-Young tube at ambient temperature. ^1H NMR analysis of the mixture after 15 min showed equal intensity signals for H_2 and HD. Integrations were also consistent with the catalytic isotope equilibration of HD to a 2:1:1 statistical mixture of $HD/H_2/D_2$ (Figure 1 B). It is noteworthy that such equilibration was not observed employing solutions of $B(C_6F_5)_3$ alone (Figure 1 A).

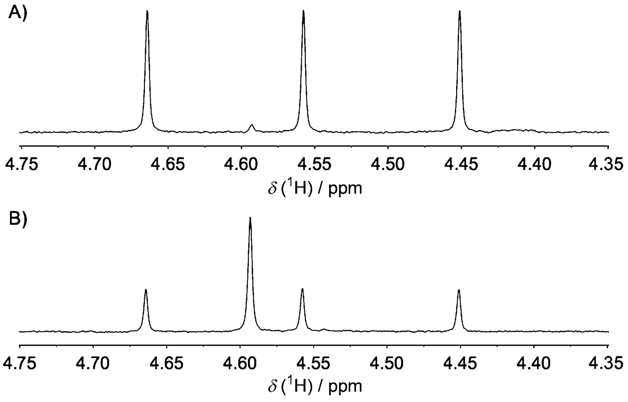

Figure 1. ^1H NMR spectra showing A) HD in the presence of $B(C_6F_5)_3$ after 60 min and B) complete isotope scrambling of HD by 1:1 $Et_2O/B(C_6F_5)_3$ after 15 min in CD_2Cl_2.

These observations clearly indicate the ability of $Et_2O{-}B(C_6F_5)_3$ to activate dihydrogen, thus suggesting the ability of this species to act as a hydrogenation catalyst. To assess this inference, a 0.4 M solution of 1,1-diphenylethylene containing 20 mol % $B(C_6F_5)_3$ and 30 mol % ether in CD_2Cl_2 was pressurized with 4 atm of H_2. Heating to 50 °C for 48 h

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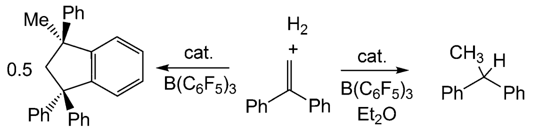


Scheme 1. Reaction of 1,1-diphenylethylene in presence of $B(C_6F_5)_3$ with (right) and without (left) diethyl ether.

resulted in 95% conversion of the olefin to the alkane, $Ph_2C(H)CH_3$ (Scheme 1; Table 1). Interestingly, the same reaction carried out in C_6D_5Br at 150°C resulted in slower hydrogenation of the olefin, although increasing the concentration of Et_2O to 160 mol% afforded faster and higher conversion. Increasing the pressure of H_2 also enhances the reduction rate. Using 10 mol% $B(C_6F_5)_3$ and 20 mol% Et_2O under 100 atm of H_2 pressure at 20°C, the reduction of $Ph_2C{=}CH_2$ is essentially quantitative in 24 h, whereas at 4 atm, heating to 50°C for 96 h is required for complete reduction.

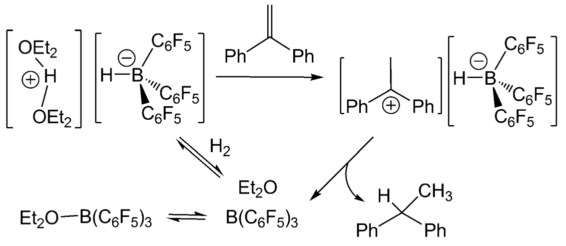
Table 1: Ether/$B(C_6F_5)_3$-catalyzed hydrogenation.[a]

Substrate	$B(C_6F_5)_3$ [mol%]	Ether (mol%)	T [°C]	t [h]	Conv. [%]
$Ph_2C{=}CH_2$	20	–	20	24	65[f]
$Ph_2C{=}CH_2$	20	Et_2O (30)	50	48	95
$Ph_2C{=}CH_2$[c]	20	Et_2O (30)	150	24	35
$Ph_2C{=}CH_2$[c]	20	Et_2O (160)	120	18	60
$Ph_2C{=}CH_2$	10	Et_2O (30)	50	96	96
$Ph_2C{=}CH_2$[b]	10	Et_2O (20)	20	24	>99
$Ph_2C{=}CH_2$	20	12C4 (20)	25	48	56
$Ph_2C{=}CH_2$	20	12C4 (20)	50	72	>99
$Ph_2C{=}CH_2$	20	DB24C8 (20)	25	48	57
$Ph_2C{=}CH_2$	20	DB24C8 (20)	50	72	>99
$C_{14}H_{10}$[b]	10	Et_2O (20)	20	24	34
$C_{14}H_{10}$[b,d]	20	DB24C8 (20)	80	24	59

[a] 0.4 M Solutions of substrate in CD_2Cl_2, 4 atm of H_2. [b] 0.1 M Substrate, 100 atm of H_2. [c] Solvent C_6D_5Br. [d] Solvent $C_2H_4Cl_2$. [e] Conversion [%] calculated with respect to substrate. [f] Major product: olefin dimer.

Although somewhat less effective than Et_2O, the crown ethers [12]crown-4 (12C4) or dibenzo[24]crown-8 (DB24C8) also enabled the hydrogenation of $Ph_2C{=}CH_2$ in the presence of $B(C_6F_5)_3$. Anthracene could also be hydrogenated to 9,10-dihydroanthracene using DB24C8/$B(C_6F_5)_3$ in up to about 60% yield, although more forcing conditions (heating to 80°C under 100 atm of H_2 in 1,2-dichloroethane) were required. Using $(Me_3Si)_2O$ or Ph_2O instead of Et_2O only resulted in the previously reported Friedel–Crafts-type dimer of the olefin (Scheme 1).[41] It is also noted that this same dimer is formed on treatment of $Ph_2C{=}CH_2$ with 20 mol% $B(C_6F_5)_3$ alone, under H_2. Thus, it appears that the decreased basicity of $(Me_3Si)_2O$ or Ph_2O preclude H_2 activation, thus permitting the dimerization pathway to prevail in the absence of a donor. An attempt to hydrogenate a series of olefins, including *cis*-stilbene, 1-hexene, cyclohexene, methylenecyclohexane, and *tert*-butylethylene as well as 1,2-diphenylacetylene using $Et_2O/B(C_6F_5)_3$ gave no reduction after 24 h. Efforts to reductively open *cis/trans*-1,2-diphenylcyclopropane was also ineffective. These observations are consistent with the lower Brønsted basicity of terminal olefins and suggest the formation of a relatively stable tertiary carbocation by protonation is required for reduction to proceed. In the case of α-methylstyrene, *p*-methoxy-α-methylstyrene, and α,*p*-dimethylstyrene, the reactions proceed to more than 99% consumption of the olefin; however, the major products are the Friedel–Crafts dimers with a minor product being the hydrogenated alkane, demonstrating that Lewis acid catalyzed dimerization is kinetically favored over hydrogenation.

The mechanism of hydrogenation (Scheme 2) is presumably analogous to that reported for FLP hydrogenations of olefins by phosphine/$B(C_6F_5)_3$ combinations in which heterolytic cleavage of hydrogen allows for protonation of the olefin and hydride delivery to the resulting carbocation.[33] Comparing the experimental rates of H/D-exchange and hydrogenation demonstrates that the activation of H_2, and thus the equilibrium concentration of the ion pair, $[Et_2O\cdots H\cdots OEt_2][HB(C_6F_5)_3]$, is not rate-determining for the olefin reduction. The somewhat accelerated conversions observed when phosphines were employed as bases could be attributed to the simultaneous use of a J-Young NMR tube rotation technique (that we did not employ), which was found to increase the effective concentration of H_2 in solution.[33]



Scheme 2. Proposed mechanism of the hydrogenation of 1,1-diphenylethylene by $Et_2O/B(C_6F_5)_3$. (The addition and removal of Et_2O molecules is not depicted.)

It is indeed surprising that ether and borane act as an FLP to effect the activation of H_2 with such ease. To understand the mechanism of this remarkably facile H_2 activation process, a DFT study using state-of-the-art quantum chemical methods was conducted[42–46] (see the Supporting Information for details). First, gas-phase structure optimizations at the dispersion-corrected DFT level, using large triple-zeta AO basis sets (TPSS-D3/def2-TZVP), followed by single-point energy calculations at the high double-hybrid level (B2PLYP-D3/def2-QZVP), were performed. On top of that, thermostatistical corrections from ZPVE-exclusive energy (ΔE) to free energy (at $T = 298.15$ K, 1 atm pressure) and corrections for solvation free energy by the accurate (DFT-based) COSMO-RS model were applied.[47–50] Various H_2 activated structures were investigated and the most likely candidates selected (Figure 2). Consideration of all corrections from gas-phase energy to ΔG in solution (ΔG_R) is essential for an understanding of the mechanism. Previous results[51,52] have showed that the barrier to H_2-splitting is only a few kcal mol^{-1} higher than the zwitterionic intermediate. Thus, only the

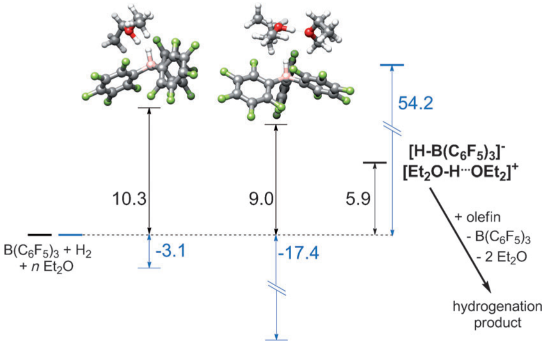


Figure 2. (Free) energy diagram with DFT-D3 optimized structures for hydrogen activation by $B(C_6F_5)_3$ and Et_2O ($n=1, 2$) leading to the ions $[Et_2OH\cdots OEt_2]^+[HB(C_6F_5)_3]^-$ (ΔG_R (kcal mol^{-1}): black; ΔE (kcal mol^{-1}): blue).

thermodynamics under equilibrium conditions were considered, and ΔG_R values were given relative to the separated reactants ($B(C_6F_5)_3$, Et_2O, and H_2). The Lewis acid–base adduct $(Et_2O)B(C_6F_5)_3$ forms with $\Delta G = -2.0$ kcal mol^{-1} ($\Delta E = -14.7$ kcal mol^{-1}), indicating that a significant concentration of the FLP is present in solution. Splitting of H_2 by $B(C_6F_5)_3$ and one Et_2O molecule is weakly exothermic ($\Delta E = -3.1$ kcal mol^{-1}) in the gas phase. The explicit "solvation" of the protonated ether by a second Et_2O yields a strong hydrogen bond and lowers the energy considerably to -17.4 kcal mol^{-1}. Adding a third molecule (not shown) lowers it further to -23.8 kcal mol^{-1}. However, compared to the corresponding FLP activation with $tBu_3P/B(C_6F_5)_3$, and in agreement with its lower efficiency, the present reaction is clearly less exothermic ($tBu_3P/B(C_6F_5)_3$: $\Delta E = -30.2$ kcal mol^{-1}), reflecting the lower basicity of Et_2O compared to the phosphine. Furthermore, the need of two or three molecules Et_2O leads to a large entropic penalty.

The calculated free energies ΔG_R were 10.3 and 9.0 kcal mol^{-1} for the computations involving one and two ether molecules, respectively, and thus such species are thermally accessible. Adding a third Et_2O to the ion pair complex seems less likely (increase of ΔG_R to 14.9 kcal mol^{-1}). Values of around 10–15 kcal mol^{-1} are our estimates of the effective free energy barrier to the splitting of H_2. The similar values for rather different structures indicate the flatness of the free energy hypersurface, and that the system is probably rather dynamic, an aspect that could not be treated adequately at present. Subsequently, the complex with two Et_2O dissociates exergonically to give the solvated ions $[Et_2O\cdots H\cdots OEt_2]^+$ and $[HB(C_6F_5)_3]^-$, which are only $\Delta G_R = 5.9$ kcal mol^{-1} above the reactants. Keeping in mind the theoretical error bars (2–3 kcal mol^{-1} for ΔG_R), this value is compatible with a significant equilibrium concentration of solvated proton and hydridoborate under ambient conditions. A large solvation energy and entropy release appear to be essential for formation of free ions, giving rise to the observed H/D exchange and hydrogenation catalysis.

In conclusion, the remarkable ability of ether/$B(C_6F_5)_3$ combinations to activate H_2 and effect catalytic hydrogenations of 1,1-diphenylethylene and anthracene has been demonstrated. A detailed theoretical study is consistent with an accessible barrier to the "encounter complex" in which H_2 is activated. Subsequent dissociation of this complex affords the ions $[Et_2O\cdots H\cdots OEt_2]^+$ and $[HB(C_6F_5)_3]^-$ in sufficient concentration to effect hydrogenation. The synthetic utility and variants of this remarkably simple hydrogenation catalyst are the subject of on-going efforts.

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