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Metal-free carbon dioxide reduction and acidic C–H activations using a frustrated Lewis pair

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ABSTRACT

Activation of CO_2 and acidic C–H bonds by the lutidine-tris(pentafluorophenyl)borane [Lut/B(C_6F_5)$_3$] frustrated Lewis pair (FLP) are described (lutidine = 2,6-dimethylpyridine). Lut/B(C_6F_5)$_3$ reacts with CO_2 and H_2 at ambient temperature and 4 atm of pressure to form the lutidinium boro-formate salt [LutH$^+$][HC(=O)OB(C_6F_5)$_3^-$]. This salt has been fully characterized including an X-ray crystal structure and independent synthesis from formic acid and Lut/B(C_6F_5)$_3$. Attempts to activate a C–H bond in methane by Lut/B(C_6F_5)$_3$, analogous to its heterolytic cleavage of H_2, were unsuccessful, which are consistent with published calculations showing significant barriers to this reaction. Lut/B(C_6F_5)$_3$ does react with more acidic C–H bonds, including acetone and nitroalkanes. With nitromethane, the boro-nitrone anion $H_2C{=}NO_2B(C_6F_5)_3^-$ is formed, as indicated by NMR and mass spectral analyses.

1. Introduction

Chemical transformations of carbon dioxide (CO_2) and methane (CH_4) to produce useful chemical feedstocks are very attractive goals due to current concerns about climate change and decline of petroleum reserves [1]. The activation of these and related small molecules in solution has typically been accomplished by transition metal complexes [2]. CO_2 could be an attractive carbon feedstock [1,3], however current methods of CO_2 reduction to formic acid, formaldehyde, methanol, and their derivatives often involve expensive metal catalysts and extreme conditions [4]. Methane is the primary component of natural gas and is expensive to transport. It is also a potent and substantial greenhouse gas (CH_4 is 62 times more efficient than CO_2 as a greenhouse gas [5]). Because of interest in converting methane to a liquid such as methanol, and for related conversions of more complex organic molecules, catalytic C–H activation and functionalization has long been an attractive goal [6–8].

Recently, Stephan and coworkers have shown that frustrated Lewis pairs (FLPs) can accomplish a range of interesting bond activation and catalytic reactions [9–12]. FLPs involve a Lewis acid and base, typically fluorinated organoborane acids combined with bulky phosphine or pyridine bases, whose steric bulk prevents strong dative bond formation. The weak Lewis acid/base adduct thus retains much of the reactivity of the individual acid and base. FLPs have been reported to accomplish a variety of small molecule activations such as the heterolytic cleavage of H_2 [13,14], N_2O and CO_2 complexation [15,16], THF ring-opening [9], and more recently, the conversion of CO_2 to CH_4 via a FLP with triethylsilane as the reductant [17].

We set out to determine whether pyridine-based FLPs can reduce CO_2 using molecular hydrogen. The reported methods for metal-free CO_2 hydrogenation do not use hydrogen (H_2) as the hydrogen source [18]. As described below, facile formation of a boro-formate salt from an FLP, CO_2, and H_2 under mild conditions was observed [19]. While this work was in progress, Ashley, Thompson, and O'Hare reported similar reactivity using a bulky piperidine base, albeit at higher temperatures [20]. They also showed that methanol can be produced under harsher conditions and with destruction of their FLP. Our focus then shifted towards C–H activation reactions, starting with methane to compare with the calculations by Wang and co-workers [21], and concluding with FLP reactions of acidic C–H bonds.

2. Results and discussion

2.1. CO_2 reduction by H_2 using 2,6-lutidine/B(C_6F_5)$_3$

The FLP formed from 2,6-lutidine (Lut = 2,6-dimethylpyridine) and B(C_6F_5)$_3$ heterolytically cleaves H_2 to yield the borohydride salt [LutH$^+$][HB(C_6F_5)$_3^-$] as a white solid, as reported by Geier and Stephan [9]. This hydrogen product was treated with 4 atm of CO_2 in toluene-d_8 in a flame-sealed NMR tube. Over the course of hours at room temperature, monitoring by ^{1}H NMR spectroscopy revealed

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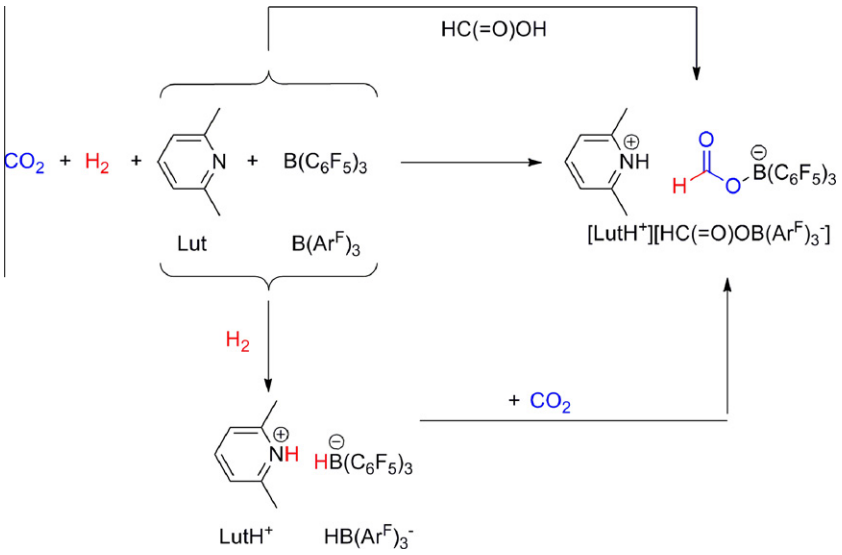
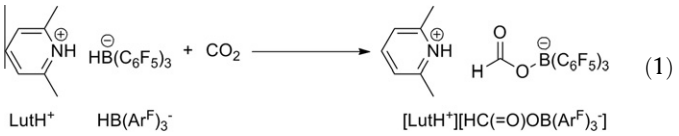


Scheme 1.

that the initial signals characteristic of the lutidinium borohydride decrease, including the broad singlet for the N–H proton at δ 9.82 ppm[2] and the borohydride four line pattern at δ 3.85 ppm (J_{BH} = 83 Hz). These resonances are replaced by a sharp singlet at δ 8.31 ppm, assigned as the formate proton *H*C(=O)O of a boroformate anion (Eq. (1), Fig. S1). The chemical shift for the formyl hydrogen in free formic acid is δ 7.78 ppm in toluene-d_8. When ^{13}C-labeled CO_2 is used, the singlet is replaced by a doublet with J_{CH} = 216 Hz at the same chemical shift, and a resonance is observed at δ 153 ppm in the $^{13}C\{^1H\}$ NMR spectrum (Fig. S3). These data confirm that a formate C–H bond has been formed.



(1)

To further probe the production of the proposed boro-formate product, ESI-MS of the reaction mixture, diluted in acetonitrile, show a peak with m/z = 557 in the negative ion mode, with the appropriate isotope pattern for $HC(=O)OB(C_6F_5)_3^-$. ^{19}F NMR spectra of the reaction mixture show growth of a set of three resonances for the boroformate anion, in addition to two sets of resonances for $HB(C_6F_5)_3^-$ and hydroxy-borate ($HOB(C_6F_5)_3^-$) (Fig. S2). $HOB(C_6F_5)_3^-$ is almost always present in small amounts despite subliming the $B(C_6F_5)_3$ reactant, drying the solvents, and flame-drying the glassware. The hydroxy-borate appears to arise at least in part from the water adduct H_2O–$B(C_6F_5)_3$ in samples purchased from Strem Chemical, as indicated by ^{19}F NMR spectra that are broad at room temperature and show both H_2O–$B(C_6F_5)_3$ and free $B(C_6F_5)_3$ resonances at low temperatures [22].

$[LutH^+][HC(=O)OB(C_6F_5)_3^-]$ is formed directly from CO_2 and H_2 by the Lut/$B(C_6F_5)_3$, as shown in Scheme 1. It has also been independently synthesized from Lut, $B(C_6F_5)_3$, and formic acid. The air-stable white solid obtained is spectroscopically identical to that obtained from CO_2 via Eq. (1), and has also been characterized by elemental analysis. Crystals of $[LutH^+][HC(=O)OB(C_6F_5)_3^-]$ suitable for X-ray crystallography were grown from a dichloromethane solution by vapor diffusion of heptanes. The X-ray crystal structure (Fig. 1) has two independent lutidinium–boroformate ion pairs in the asymmetric unit with the unit cell containing in total eight pairs. In each pair, the acidic lutidinium proton forms a hydrogen bond to the carbonyl oxygen of the formate, with an N···O distance of 2.78 ± 0.01 Å. The values reported are the averages of the values in the two independent ion pairs. The formate anion has an OCO bond angle of 122.29 ± 0.20° and is bound to the borane with a d(B–O) of 1.53 ± 0.01 Å.

While these results were being prepared for publication, Ashley, Thompson and O'Hare reported a similar reaction using the FLP containing 2,2,6,6-tetramethylpiperidine (TMP) and $B(C_6F_5)_3$ [20]. They reported that at 100 °C, CO_2 reacts with $[TMPH^+][HB(C_6F_5)_3^-]$ to give a boro-formate salt with a $[TMPH]^+$ counterion analogous to our lutidinium salt, as revealed by spectroscopic and crystallographic analyses. Upon heating $[TMPH^+][HC(=O)OB(C_6F_5)_3^-]$ in toluene to 80 °C under N_2, they observed loss of CO_2 and regener-

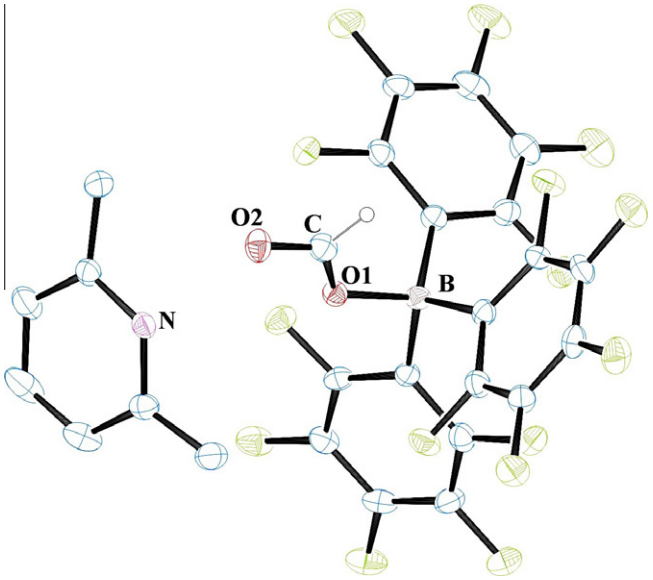


Fig. 1. ORTEP [23] drawing of $[LutH^+][HC(=O)B(C_6F_5)_3^-]$ with thermal ellipsoids at their 50% probability level.

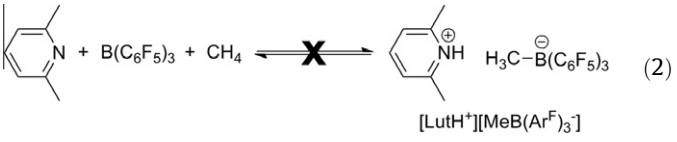
[2] Depending on the water concentration in the solvent, this N-H proton signal can shift and broaden out into the baseline due to exchange.

ation of $[TMPH^+][HB(C_6F_5)_3^-]$, indicating that formation of the formate is reversible. More forcing conditions (144 h at 160 °C in benzene) yielded a number of species including $B(C_6F_5)_3$, TMP, C_6F_5H, and $CH_3OB(C_6F_5)_3$, and that vacuum distillation of this solution at 100 °C yielded CH_3OH in 17–25% yield. In contrast, we find that heating our lutidinium salt at 80 °C results only in decomposition.

The apparently greater reactivity of the lutidine FLP than the piperidine analog – room temperature versus 100 °C – is surprising in light of calculations reported by Pápai et al. [24]. They find that heterolytic cleavage of H_2 is thermodynamically less favorable for $Lut/B(C_6F_5)_3$ than for $TMP/B(C_6F_5)_3$ by approximately 10 kcal mol^{-1}. Perhaps the higher reactivity of $Lut/B(C_6F_5)_3$ for CO_2 reduction is due to a mechanism involving both hydride donation from $HB(C_6F_5)_3^-$ and Lewis-acid activation of CO_2 by free $B(C_6F_5)_3$. However, preliminary studies show that the addition of excess $B(C_6F_5)_3$ to Eq. (1) does not significantly accelerate the reaction. Similarly, the addition of excess lutidine does not cause a substantial change in rate.

2.2. Hydrocarbons plus 2,6-lutidine/$B(C_6F_5)_3$

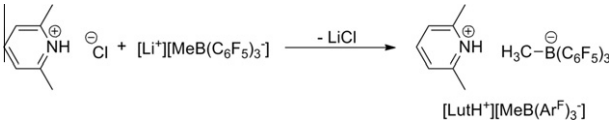
Since $Lut/B(C_6F_5)_3$ activates H_2 under very mild conditions, we have explored the activation of methane by this FLP. An NMR tube was charged with $Lut/B(C_6F_5)_3$, 3 atm $^{13}CH_4$, and toluene-d_8 and flame sealed. The reaction was monitored by 1-D Heteronuclear Multiple Quantum Coherence spectroscopy (HMQC), which observes ^1H–^{13}C coupling [25]. After heating at 80 °C for approximately 3 days, several new resonances were observed, including peaks at δ 5.54 ppm and δ 3.07 ppm, and a weak doublet at δ 2.2 ppm by HMQC (this signal was observed only with difficulty in the ^1H NMR spectra due to overlap with the lutidine and toluene methyl groups being in the same region; Figs. S6 and S7). However, similar peaks are observed in reactions of $Lut/B(C_6F_5)_3$ with unlabeled CH_4 and upon heating $Lut/B(C_6F_5)_3$ in toluene-d_8 at 80 °C in the absence of methane (Fig. S11). On the basis of this and other experiments, we have no evidence for methane activation (Eq. (2)).



(2)

The possible activation of the toluene was probed by treating stoichiometric amounts of FLP and protio-toluene in benzene-d_6 in a flame-sealed NMR tube. After heating to 80 °C for 4 days, the aforementioned signals at δ 5.5 and δ 3.1 ppm were observed in the ^1H NMR spectrum. Also, 1-D HMQC of FLP + toluene in benzene-d_6 shows the same doublet centered at δ 2.2 ppm. Heating the FLP alone in C_6D_6 resulted in the same resonances in the ^1H NMR spectrum as when heated in the presence of toluene. ^{19}F NMR spectra of these reactions showed multiple species in solution. Thus the FLP decomposes under these reaction conditions and there is no evidence for toluene activation. In contrast, Chakraborty and Chen have suggested, based on partial NMR spectra, that the FLP of 2,6-di-*t*-butylpyridine and the aluminum Lewis acid $Al(C_6F_5)_3$ react with toluene to give pyridinium aryl-aluminate salts [26].

To determine whether the lack of reaction with methane is due to kinetic or thermodynamic factors, we independently prepared the possible product of methane activation, the lutidinium-methylborate salt. $Li[MeB(C_6F_5)_3]$ was prepared from halide-free methyl lithium (MeLi) and $B(C_6F_5)_3$ [27] and reacted with lutidinium chloride (from HCl gas + lutidine). Combining $Li[MeB(C_6F_5)_3]$ and [LutH]Cl in chloroform gave a precipitate of LiCl and $[LutH^+][MeB(C_6F_5)_3^-]$, as indicated by ^1H NMR spectroscopy (Eq. (3)). In toluene-d_8, $[LutH^+][MeB(C_6F_5)_3^-]$ has a ^1H NMR signal for the methylborate at δ 0.8 ppm (Fig. S8). Heating this lutidinium-methylborate salt at 80 °C for 4 days resulted in decomposition of the reagents without formation of methane. There thus appears to be a significant kinetic barrier to interconvert $Lut/B(C_6F_5)_3 + CH_4$ with $[LutH^+][MeB(C_6F_5)_3^-]$ (Eq. (2)).



(3)

The free energy barrier for the activation of methane by the $^tBu_3P/B(C_6F_5)_3$ FLP has been calculated by Wang et al. to be $\Delta G^‡ = 38.3$ kcal mol^{-1} [21]. $^tBu_3P/B(C_6F_5)_3$ is thermodynamically a more reactive FLP than $Lut/B(C_6F_5)_3$, according to calculations of Pápai et al. by approximately 8 kcal mol^{-1} [24], so the barrier for $Lut/B(C_6F_5)_3$ should be higher than 38 kcal mol^{-1}. The observation that $Lut/B(C_6F_5)_3$ does not react with CH_4 over 9 days at 80 °C (by ^1H NMR spectroscopy) implies, using a pseudo-first order model, that the minimum free energy barrier is $\Delta G^‡ > 27.1$ kcal mol^{-1}. Thus the lack of reaction of methane with the $Lut/B(C_6F_5)_3$ FLP is consistent with the computational studies.

2.3. Activation of acidic C–H bonds

A number of organic molecules with heteroatoms and acidic C–H bonds have been reacted with $Lut/B(C_6F_5)_3$. The molecules tested and their corresponding pK_a values are listed in Table 1. The oxygen or nitrogen atoms in these molecules can bind to the Lewis acid, which makes their C–H bonds more acidic and facilitate deprotonation by the Lewis base.

2.3.1. Nitrotoluenes

Addition of one equivalent of 3-nitrotoluene or 4-nitrotoluene to a toluene-d_8 solution of $Lut/B(C_6F_5)_3$ caused an immediate color change to bright yellow in a J. Young NMR tube. In both cases, ^1H NMR spectra showed small upfield shifts of the nitrotoluene resonances (Figs. S12 and S13). The same yellow color and upfield shift were observed in a reaction of substrate and Lewis acid without the lutidine. Combining the Lewis base with nitrotoluene, however, resulted in no color change or shift in the ^1H spectrum. Dissolution of 4-nitrotoluene in oleum also forms a yellow species [29]. These data indicate complexation between the nitrotoluenes and $B(C_6F_5)_3$, presumably through one or more of the oxygen atoms of the nitro group, but the resulting adduct is not sufficiently acidic to be deprotonated by the lutidine base. This contrasts with the report of C–H activation of toluene by an alane/lutidine FLP [26].

2.3.2. Acetonitrile

Stoichiometric amounts of acetonitrile and $Lut/B(C_6F_5)_3$ were dissolved in toluene-d_8 in an NMR tube. A ^1H NMR spectrum collected after a few minutes showed a new signal at δ 0.4 ppm (Fig. S14). It has been reported that nitriles bind tightly to $B(C_6F_5)_3$ and the B–N adducts have been characterized by NMR, IR, and X-ray crystallography [30]. For $MeCN–B(C_6F_5)_3$, the re-

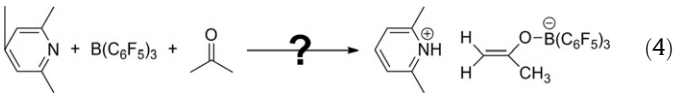
Table 1
pK_a values (in DMSO [28]) of C–H bonds studied.

Substrate	pK_a
Methane	56
3-Nitro- and 4-Nitro-toluenes	not available
Acetonitrile	31.3
Acetone	26.5
Nitromethane	17.2

ported data include NMR spectra in benzene-d_6, 1H: δ 0.32 and 11B: δ −10.3, and a CN stretching frequency at 2367 cm^{-1}. Our reaction in toluene-d_8 has a ^{11}B NMR resonance at δ −11.3 ppm, and the derived white solid obtained in KBr has νCN = 2370 cm^{-1}. The adduct is unreactive with lutidine in toluene even after heating to 80 °C over a day, as indicated by no change in the ^1H NMR spectrum. Thus acetonitrile binds to the Lewis acid to form an adduct but is not deprotonated, even under forcing conditions.

2.3.3. Acetone

Lut/$B(C_6F_5)_3$ was treated with a stoichiometric amount of acetone in toluene-d_8. Within minutes the ^1H NMR spectrum showed two new singlets at δ 1.8 ppm and δ 3.7 ppm (br), integrating in a 3:2 ratio (Fig. S16). After 12 h, ^1H NMR spectra showed additional peaks indicating decomposition of the initial product. To avoid any further reactions such as aldol condensations, half an equivalent of acetone was reacted with the FLP. However, ^1H NMR spectra of this reaction still showed free acetone, possibly indicating that an equilibrium with incomplete conversion may be reached. ^{19}F NMR spectra of both reactions showed multiple products. Attempts to isolate solids from the reaction have been unsuccessful.

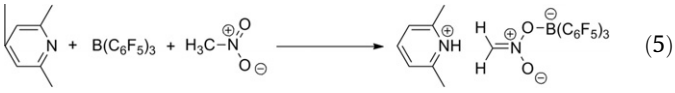


(4)

We tentatively assign the initial acetone product as a boro-enolate salt, analogous to the boro-formate described above (Eq. (4)). The ^1H NMR spectrum is consistent with this formulation if the two downfield enolate protons are coincidentally degenerate at δ 3.7 ppm. The peak at δ 1.8 ppm is then due to the methyl group. The ^{11}B NMR spectrum showing a sharp singlet at δ −13.6 ppm indicates a four-coordinate boron atom, consistent with this assignment [31].

2.3.4. Reactions of nitroalkanes

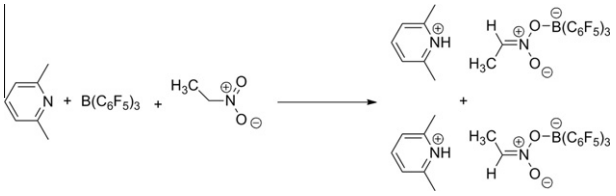
Nitromethane ($MeNO_2$) reacts rapidly with a stoichiometric amount of Lut/$B(C_6F_5)_3$ in toluene-d_8 in a sealed NMR tube. The first ^1H NMR spectrum obtained at ambient temperatures showed a new signal at δ 5.8 ppm (Fig. S18). A ^{11}B NMR spectrum of this solution showed a broad singlet at δ −4.5 ppm, which is within the normal range for four-coordinate boron species [31]. The ^{19}F NMR spectrum has one major species in solution, with ca. 6% hydroxy-borate ($HOB(C_6F_5)_3^-$). Cross peaks in a 2-D HMQC spectrum were suggestive of a C–H activated nitromethane product. The δ 5.8 ^1H NMR signal correlates with a ^{13}C NMR signal at δ 121 ppm, with a ^{13}C–^1H coupling constant of 194 Hz, indicating the presence of an sp^2 hybridized carbon bound to an electron withdrawing group (Fig. S21). On the basis of these data and those below, the product is assigned as a boro-nitrone anion, as illustrated in Eq. (5). This assignment requires that the two nitrone proton signals in the ^1H NMR are coincidentally degenerate at δ 5.8. Alternatively, the $B(C_6F_5)_3$ group could be moving between the two oxygen atoms rapidly with respect to the NMR timescale, although there is no evidence for such fluxionality from studies of the nitroethane product described below.



(5)

^{13}C-labeled $MeNO_2$ was reacted with one equivalent of the FLP in toluene-d_8 to confirm the product assignment. ^1H NMR spectra of this solution showed a doublet centered at δ 5.8 ppm with J_{CH} = 194 Hz, the same as seen in the HMQC spectrum described above. The ^{13}C NMR spectrum contained a triplet at the aforementioned chemical shift, confirming the presence of a CH_2 group. The ^2H NMR spectrum of a reaction of nitromethane-d_3 with the FLP in toluene also had a singlet as δ 5.8 ppm. These results confirm that the δ 5.8 ppm and δ 121 ppm resonances derive from $MeNO_2$. ESI-MS spectra were obtained of products derived from both CH_3NO_2 and CD_3NO_2, after dilution with acetonitrile. The protio sample showed a peak at m/z = 572 in the negative ion mode, and the deutero analog showed a peak two units higher. High resolution mass spectrometry confirmed the composition of the anion as $H_2C{=}NO_2B(C_6F_5)_3^-$.

The analogous reaction of nitroethane gave a new primary product with a quartet at δ 6.2 ppm and a doublet at δ 1.4 ppm in its ^1H NMR spectrum, as well as another set of quartet/doublet signals of smaller intensity (*ca.* 17%) 0.5 ppm downfield from the larger signal (Fig. S23). These suggested the formation of an α-carbon C–H activated nitrone product, as shown in Eq. (6). Low temperature studies showed no substantial change in the NMR spectra down to −80 °C, indicating that the nitrone isomers are not rapidly interconverting. The ^{19}F NMR spectrum shows a set of three major peaks, similar to the nitromethane case, and some minor peaks that are difficult to discern but could be due to the second isomer.



(6)

All of the experimental results indicate that nitromethane and nitroethane undergo C–H activation upon reaction with Lut/$B(C_6F_5)_3$. Presumably this occurs by coordination of the nitro group to the Lewis acid, analogous to what is observed with the nitrotoluenes. Coordination makes the α-C–H protons more acidic and susceptible to deprotonation by the base. An alternative mechanism would be initial tautomerization of the nitroalkane to the *aci* form (nitronic acid): $CH_3NO_2 \rightleftharpoons CH_2{=}N(O)(OH)$ [32]. The *aci* form is a weak acid and would certainly react with the FLP by O–H activation to give the boro-nitrone anion. This tautomerization to *aci*-nitromethane typically requires catalysis by base. To test whether it is occurring under the conditions of Eqs. (5) and (6), toluene-d_8 solutions of nitromethane, lutidine, and excess methanol-d_4 were prepared. After three days, no change in the nitromethane peak was observed, indicating that no tautomerization is occurring. Tautomerization would have led to H/D exchange via rapid exchange of the aci-O*H* with the CD_3OD. The presence of lutidine or lutidine/methanol, has no effect on the CH_3NO_2 chemical shift.

3. Conclusions

Carbon dioxide is rapidly reduced to a boroformate derivative by H_2 and the frustrated Lewis pair (FLP) 2,6-lutidine/tris(pentafluorophenyl)borane. This reaction is much faster than the related chemistry with 2,2,6,6-tetramethylpiperidine [20], despite computational results suggesting that the latter is a more reactive FLP [24] The product boro-formate salt was fully characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography.

No activation of methane reactant or toluene solvent has been observed. This is consistent with the large barrier to methane activation calculated by Wang et al. [21]. Acetonitrile and nitrotoluene only form adducts with the Lewis acid. These less acidic substrates do not undergo deprotonation/C–H activation. However, more acidic C–H bonds are readily activated by the Lut/$B(C_6F_5)_3$ FLP. Nitromethane and nitroethane are converted to boro-nitrone an-

ions, as indicated by NMR and mass spectral data, and NMR spectra tentatively suggest that acetone is converted to an enolate.

4. Experimental

4.1. General procedures

All experiments were conducted under inert atmosphere (nitrogen) using a glove box or double manifold N_2/vacuum line with Schlenk-like techniques and glassware, unless otherwise noted. Tris(perfluorophenyl)borane (Strem) was sublimed under dynamic vacuum in a 90 °C oil bath. Formic acid (99 + %, Acros Organics) was used as received. Deuterated NMR solvents and isotopically labeled reagents were purchased from Cambridge Isotopes. 2,6-Lutidine was stirred over KOH overnight under nitrogen, vacuum distilled and stored in a glove box. Toluene was dried over sodium/benzophenone. Toluene-d_8 was dried over Na/K and stored in a sealed vessel. Acetone was dried over $CaSO_4$ and kept in the glove box. Nitromethane was dried over $CaCl_2$ and kept in glove box. *Para*-nitrotoluene (Matheson Coleman & Bell) was pure by ^{1}H NMR, dried under vacuum for *ca.* 1 h and kept in glove box. *Meta*-nitrotoluene (Sigma–Aldrich) was dried with P_2O_5 and kept in glove box. Acetonitrile was purchased from Honeywell Burdick and Jackson, sparged with argon, and plumbed directly into a nitrogen filled glove box with stainless steel piping. CO_2 and H_2 purchased from Praxair were passed through a Drierite column. NMR spectra were recorded on 300 MHz or 500 MHz Bruker Avance spectrometers and referenced to the residual solvent signal (^{1}H and ^{13}C) or an external CF_3COOH standard (^{19}F: δ −76.55). ^{11}B NMR was calibrated by ^{1}H NMR, and a subtraction method was used to obtain spectra without the signal from the borosilicate NMR tubes. Coupling constants are reported in Hz. Mass spectra were collected using a Bruker Esquire Liquid Chromatograph-Ion Trap mass spectrometer. High resolution mass spectra were collected using a Sciex Qstar XL mass spectrometer. Infrared spectra was obtained on a Bruker Tensor 27 FTIR. Samples were prepared in air with dried KBr with a nut and bolt to press into a pellet.

4.2. Synthesis of [2,6-$Me_2C_5H_3NH^+$] [$HC(=O)OB(C_6F_5)_3^-$] using formic acid

In a glove box, 0.49 g (0.97 mmol) $B(C_6F_5)_3$, 113 μL (0.98 mmol) 2,6-lutidine, approximately 20 mL dry toluene, and a Teflon magnetic stir bar was combined in a flask and capped with a rubber septum. The flask was removed from the glove box, uncapped and 36.8 μL formic acid was added to the flask, upon which the cloudy solution became clear. The septum was replaced and covered with parafilm. The reaction was left to stir for 1.5 h. The solution was pumped to dryness, pentane added, and the solid isolated by filtration. Yield: 0.625 g (97%). *Anal.* Calc. for $C_{26}H_{11}BF_{15}NO_2$: C, 46.95; H, 1.67; N, 2.11. Found: C, 46.82; H, 1.65; N, 2.14%. X-ray quality crystals were grown in dichloromethane by vapor diffusion of heptane. ^{1}H NMR (300 MHz, tol-d_8): 1.92 (s, 6H, C*H*$_3$), 5.92 (d, $^3J_{HH}$ = 8 Hz, 2H, *meta*-C*H*), 6.63 (t, $^3J_{HH}$ = 8 Hz, 1H, *para*-C*H*), 8.31 (s, 1H, *H*C(=O)), the N*H* peak is not visible most likely due to exchange with water in the sample; ^{19}F NMR (282 MHz, tol-d_8): −134.41 (dd, $^3J_{FF}$ = 23 Hz, $^4J_{FF}$ = 7 Hz, 6F, *ortho*-C_6F_5), −158.45 (t, $^3J_{FF}$ = 20 Hz, 3F, *para*-C_6F_5), −164.40 (m, 6F, *meta*-C_6F_5); ^{13}C{^{1}H} NMR (75 MHz, tol-d_8): 18.17 (s, *C*H$_3$), 123.60 (s, *meta*-*C*H), 137.47 (s, *para*-*C*H), 143.96 (s, *ortho*-*C*H), 153.27 (s, H*C*(=O)).

4.3. Reaction of [2,6-$Me_2C_5H_3NH^+$] [$HB(C_6F_5)_3^-$] with CO_2

[2,6-$Me_2C_5H_3NH^+$] [$HB(C_6F_5)_3^-$] was prepared following the reported synthesis [9]. In a glove box, 13.6 mg (0.02 mmol) [2,6-$Me_2C_5H_3NH^+$] [$HB(C_6F_5)_3^-$] was charged in a medium walled NMR tube with a 14/20 ground glass joint attached. A 180° adaptor was connected and the assembly was removed from the glove box and attached to a 7.2 mL volume bulb on a vacuum manifold. Toluene-d_8 was added via vacuum transfer, 4 atm CO_2 was condensed into the tube, and then the tube was flame sealed. The tube was stored at 77 K until just before the first NMR spectrum was obtained. ^{1}H (300 MHz): 1.83 (s, 6H, C*H*$_3$), 3.81 (q, 1H, $^1J_{BH}$ = 83 Hz, B*H*), 6.02 (d, 2H, $^3J_{HH}$ = 8 Hz, *meta*-C*H*), 6.72 (t, 1H, $^3J_{HH}$ = 7 Hz, *para*-C*H*), 8.31 (s, 1H, *H*C(=O)), 10.96 (br s, 1H, N*H*); ^{19}F NMR (282 MHz): −136.86 (br d, 6F, $^3J_{FF}$ = 19 Hz, *ortho*-C_6F_5), −161.67 (t, 3F, $^3J_{FF}$ = 21 Hz, *para*-C_6F_5), -166.53 (m, 6F, *meta*-C_6F_5); ^{13}C{^{1}H}NMR (126 MHz): 19.47 (s, *C*H$_3$), 122.92 (s, *meta*-*C*H), 137.53 (s, *para*-*C*H), 142.35 (s, *ortho*-*C*H), 154.33 (s, H*C*(=O)).

4.4. Reaction of $B(C_6F_5)_3$ and 2,6-$Me_2C_5H_3N$ with $^{13}CH_4$

In a glove box, 5.2 mg (10.1 μmol) $B(C_6F_5)_3$, 1.2 μL (10.1 μmol) 2,6-$Me_2C_5H_3N$, and 0.5 mL toluene-d_8 were combined in a medium walled NMR tube. A 180° adaptor fitted with a cajon was connected, taken out of the glove box, and attached to a 7.2 mL volume bulb on a vacuum manifold. $^{13}CH_4$ (3 atm) was condensed into the tube, and then the tube was flame sealed to a total volume of 2 mL. The tube was kept at 77 K until immediately before the first NMR spectrum was obtained. After recording an initial ^{1}H NMR spectrum, the tube was placed in an 80 °C oil bath and monitored by ^{1}H NMR spectroscopy.

4.5. Synthesis of [2,6-$Me_2C_5H_3NH^+$] [$H_3CB(C_6F_5)_3^-$] using MeLi and HCl (g)

To obtain [$H_3CB(C_6F_5)_3$]Li following [27], in a glove box, 0.08 g $B(C_6F_5)_3$ (0.2 mmol) was placed in a 3-neck flask with two necks capped with septa, and the third capped with a 180° adaptor. The flask was evacuated on a high vacuum line. Dry diethyl ether (20 mL, Fischer Scientific, purged with argon) was transferred into the flask. The reaction flask was cooled to −78 °C and 0.1 mL 1.6 M halide-free MeLi in diethyl ether (Sigma–Aldrich) was added dropwise via syringe while stirring. The reaction was left to stir and warm to room temperature overnight. The solvent was removed *in vacuo* resulting in a colorless oil. [2,6-$Me_2C_5H_3NH$]Cl was synthesized by bubbling HCl (g) into an anhydrous solution of 0.2 mL 2,6-lutidine in 10 mL diethyl ether. The HCl was generated by dropwise addition of sulfuric acid to a separate flask loaded with sodium chloride, and passed from this flask to the lutidine solution using Teflon tubing. A white solid immediately precipitated. The solid was isolated by filtration over a glass frit. In a glove box, a small amount of [$H_3CB(C_6F_5)_3$]Li was combined with 2.8 mg of [2,6-$Me_2C_5H_3NH$]Cl (19 μmol) in $CHCl_3$. A white precipitate immediately formed. This solution was filtered through Celite and collected in an NMR tube. The solvent was removed and toluene-d_8 was added via vacuum transfer. ^{1}H NMR (300 MHz, tol-d_8): 0.83 (s, 3H, C*H*$_3$), 2.26 (s, 6H, lutidine-C*H*$_3$), 6.12 (d, 2H, $^3J_{HH}$ = 8 Hz, *meta*-C*H*), 6.73 (t, 1H, $^3J_{HH}$ = 8 Hz, *para*-C*H*); ^{19}F NMR (282 MHz, tol-d_8): −166.04 (t, 6F, $^3J_{FF}$ = 22 Hz, *meta*-C_6F_5), −163.50 (t, 3F, $^3J_{FF}$ = 20 Hz, *para*-C_6F_5), −130.92 (d, 6F, $^3J_{FF}$ = 22 Hz, *ortho*-C_6F_5); ^{11}B NMR (160 MHz, tol-d_8): −15.34 (s).

4.6. Reaction of $B(C_6F_5)_3$ and 2,6-$Me_2C_5H_3N$ with para-nitrotoluene

In a glove box, 0.5 mL of a freshly made 0.02 M solution of $B(C_6F_5)_3$ and 2,6-$Me_2C_5H_3N$ in toluene-d_8 was combined with 1.8 mg (13 μmol) *para*-nitrotoluene in a J. Young NMR tube. ^{1}H NMR (500 MHz): 1.76 (s, 3H, *p*-nitrotoluene-C*H*$_3$), 2.31 (br s, 6H, lutidine-C*H*$_3$), 6.44 (d, 2H, $^3J_{HH}$ = 9 Hz, *ortho*-C*H*, nitrotoluene), 6.56 (br s, 2H, *meta*-C*H*, nitrotoluene), 7.67 (d, 2H, $^3J_{HH}$ = 8 Hz,

meta-CH, lutidine), (the lutidine *para*-CH overlaps with the residual signals for the toluene-d_8 solvent).

4.7. Reaction of $B(C_6F_5)_3$ and 2,6-$Me_2C_5H_3N$ with meta-nitrotoluene

In a glove box, 5.3 mg (10.4 μmol) $B(C_6F_5)_3$, 1.2 μL (10 μmol) 2,6-$Me_2C_5H_3N$, 1.2 μL (10 μmol) *meta*-nitrotoluene, and 0.5 mL toluene-d_8 was combined in a J. Young NMR tube. ^{1}H NMR (500 MHz): 1.77 (s, *m*-nitrotoluene-CH_3), 2.34 (br s, lutidine-CH_3), 6.53 (br s), 6.65 (t, $^3J_{HH}$ = 9 Hz), 6.71 (br d), 7.64 (m) (all *m*-nitrotoluene–C*H* and lutidine C*H*; some signals overlap with the residual signals for the toluene-d_8 solvent).

4.8. Reaction of $B(C_6F_5)_3$ and 2,6-$Me_2C_5H_3N$ with acetonitrile

In a glove box, 51 mg (0.1 mmol) $B(C_6F_5)_3$, 11.4 μL (0.1 mmol) 2,6-$Me_2C_5H_3N$, 5.1 μL (0.1 mmol) acetonitrile, and 4.9 mL toluene was combined in a 25 mL flask with a magnetic stirbar. The reaction was capped and stirred for *ca.* 20 min. The volatiles were removed *in vacuo*, leaving a white solid. ^{1}H NMR (500 MHz, tol-d_8): 0.43 (s, CH_3), 1.64 (s, Lut–CH_3), 5.73 (d, $^3J_{HH}$ = 8 Hz, *meta*-CH), 6.42 (t, 1H, $^3J_{HH}$ = 9 Hz, *para*-CH); ^{11}B NMR (160 MHz, tol-d_8): −11.1 (br s); IR (KBr) $\tilde{\nu}_{C\equiv N}$ = 2370 cm^{-1}.

4.9. Reaction of $B(C_6F_5)_3$ and 2,6-$Me_2C_5H_3N$ with acetone

In a glove box, 5.5 mg (10.7 μmol) $B(C_6F_5)_3$, 1.2 μL (10 μmol) 2,6-$Me_2C_5H_3N$, 0.7 μL (10 μmol) acetone, and 0.5 mL toluene-d_8 were combined in a J. Young NMR tube. ^{1}H NMR (500 MHz): 1.81 (s, 3H, CH_3), 2.26 (br, lutidine-CH_3), 3.73 (s, 2H, CH_2), 6.50 (br d, lutidine *meta*-CH) (the lutidine para-CH overlaps with the residual signals for the toluene-d_8 solvent); ^{11}B NMR (160 MHz, tol-d_8): −13.64 (s).

4.10. Reaction of $B(C_6F_5)_3$ and 2,6-$Me_2C_5H_3N$ with nitromethane

In a glove box, 0.05 g $B(C_6F_5)_3$ (0.1 mmol), 11.4 μL 2,6-$Me_2C_5H_3N$ (0.1 mmol), 5.2 μL nitromethane (0.1 mmol), and 5.2 mL toluene were combined in a 20 mL round bottom flask with magnetic stir bar. The reaction was capped with a 180° adaptor, removed from the glove box, and left to stir for 20 min. The flask was cooled with liquid nitrogen and lyophilized overnight, resulting in a white powder. ^{1}H NMR (300 MHz, tol-d_8): 1.96 (s, 6H, CH_3), 5.82 (s, 2H, CH_2), 6.20 (d, 2H, $^3J_{HH}$ = 8 Hz, *meta*-C*H*), 6.83 (t, 1H, $^3J_{HH}$ = 8 Hz, *para*-C*H*); ^{19}F NMR (282 MHz, tol-d_8): −162.37 (br t, 6F, $^3J_{FF}$ = 21 Hz, *meta*-C_6F_5), −155.42 (t, 3F, $^3J_{FF}$ = 21 Hz, *para*-C_6F_5), −132.20 (d, 6F, $^3J_{FF}$ = 20 Hz, *ortho*-C_6F_5); ^{11}B NMR (160 MHz, tol-d_8): −4.53 (s); ^{13}C NMR (75 MHz, tol-d_8, obtained using $^{13}CH_3NO_2$): 121 (J_{CH} = 194 Hz, CH_2NO_2). High resolution MS: 571.9957 *m*/*z* [$CH_2NO_2B(C_6F_5)_3^-$] and 528.9895 *m*/*z* [$HOB(C_6F_5)_3^-$].

4.11. Reaction of $B(C_6F_5)_3$ and 2,6-$Me_2C_5H_3N$ with nitroethane

In a glove box, 4.9 mg (9.6 μmol) $B(C_6F_5)_3$, 10 μL of 1 M 2,6-$Me_2C_5H_3N$ in toluene-d_8 (10 μmol), 0.8 μL (11.2 μmol) nitroethane, and 0.5 mL toluene-d_8 was combined in a J. Young NMR tube. ^{1}H (500 MHz): *major isomer:* 1.40 (d, 3H, $^3J_{HH}$ = 7 Hz, CH_3), 6.17 (q, 1H, $^3J_{HH}$ = 6 Hz, C*H*); *minor isomer:* 1.75 (d, $^3J_{HH}$ = 6 Hz, CH_3), 6.61 (q, $^3J_{HH}$ = 6.5 Hz, C*H*); *lutidinium:* 2.07 (s, 6H, CH_3), 6.09 (d, 2H, $^3J_{HH}$ = 7 Hz, *meta*-C*H*), 6.73 (t, 1H, $^3J_{HH}$ = 8 Hz, *para*-C*H*); ^{19}F NMR (282 MHz): -163.60 (br t, 6F, *meta*-C_6F_5), −157.72 (t, 3F, $^3J_{FF}$ = 20 Hz, *para*-C_6F_5), -132.16 (d, 6F, $^3J_{FF}$ = 19 Hz, *ortho*-C_6F_5).

4.12. X-ray structure of $[LutH^+][HC(=O)OB(C_6F_5)_3^-]$

The crystal structure of $[LutH^+][HC(=O)OB(C_6F_5)_3^-]$ was established with a Nonius Kappa CCD FR590 single crystal X-ray diffractometer. A colorless prism measuring 0.60 × 0.24 × 0.20 mm^3 was mounted on a glass capillary with paratone oil as adhesive. Data were collected at 130(3) K. The crystal-to-detector distance was set to 31.5 mm and the exposure time was 180 s for each collected frame. The scan width was 1.8°. Data collection was 99.3% complete to 25° in θ. A total of 58 919 partial and complete reflections were collected covering the indices, h = −47 to 47, k = −16 to 17, l = −24 to 24. 9314 symmetry independent reflections resulted from integration with *hkl*-SCALEPACK [33] which applies a multiplicative correction factor (S) to the observed intensities (I) and has the following form: $S = (e^{-2B(\sin^2\theta)/\lambda^2})/\text{scale}$. S is calculated from the scale and the B factor determined for each frame and is then applied to I to give the corrected intensity (I_{corr}). The data in monoclinic space group $C2/c$ was of average quality (R_{int} = 0.065). The structure was solved with direct methods within SIR97 [34] and refined with SHELXL97 [35]. Scattering factors are from Waasmaier and Kirfel [36]. All hydrogen atoms were located using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Crystallographic data are given in the Supporting Information. The asymmetric unit contains two symmetry-independent cations and anions. The fluorides tend to exhibit a larger thermal motion than the carbon ring atoms. Some fluorides are forced into close contact (F9–F18 F20–F20′). N2 forms a hydrogen bond to O4 within the asymmetric unit, and N1 forms a hydrogen bond to O2 of a symmetry related anion.

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Appendix A. Supplementary material

CCDC 788048 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.022.

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