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Investigation of main group promoted carbon dioxide reduction

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Abstract

The reduction of carbon dioxide (CO_2) is of interest to the chemical industry, as many synthetic materials can be derived from CO_2 . To help determine the reagents needed for the functionalization of carbon dioxide this experimental and computational study describes the reduction of CO_2 to formate and CO with hydride, electron, and proton sources in the presence of sterically bulky Lewis acids and bases. The insertion of carbon dioxide into a main group hydride, generating a main group formate, was computed to be more thermodynamically favorable for more hydridic (reducing) main group hydrides. A ten kcal/mol increase in hydricity (more reducing) of a main group hydride resulted in a 35% increase in the main group hydride's ability to insert CO_2 into the main group hydride bond. The resulting main group formate exhibited a hydricity (reducing ability) about 10% less than the respective main group hydride prior to CO_2 insertion. Coordination of a second identical Lewis acid to a main group formate complex further reduced the hydricity by about another 20%. The addition of electrons to the CO adduct of $t\text{Bu}_3\text{P}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ resulted in converting the sequestered CO_2 molecule to CO. Reduction of the CO_2 adduct of $t\text{Bu}_3\text{P}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ with both electrons and protons resulted in only proton reduction.

1. Introduction

The utilization of carbon dioxide (CO_2) as a carbon source in synthetic chemistry has been a topic of interest since the late 19th century.¹ Interest in the functionalization of CO_2 has increased over the last 20–25 years, with the recognition that CO_2 acts as a greenhouse gas in the earth's atmosphere and attributes to global warming.² Although many materials and molecular compounds have been found to sequester CO_2 ,³ a recent United States Department of Energy report states: “The major obstacle preventing efficient conversion of carbon dioxide into energy-bearing products is the lack of catalysts.”⁴

With the recent discovery of the sequestration of CO_2 with frustrated Lewis pairs (FLPs), the possibility of the catalytic functionalization of CO_2 without a metal can be realized.^{5–6} Stephan and coworkers have pioneered this field, showing that boron and aluminum-based Lewis acids can be utilized for the sequestration of CO_2 .^{7–8} A major advance, in the field of main group-mediated CO_2 activation, occurred when Ménard and Stephan reported the utilization of aluminum halides in tandem with $\text{P}(\text{Mes})_3$ to not only sequester CO_2 , but also to functionalize CO_2 into methanol⁹ or carbon monoxide.¹⁰ These discoveries prompted many other groups to develop main group complexes capable of similar transformations.^{11–12} Although the reduction of CO_2 to methanol is targeted, not all reductions of a CO_2 molecule sequestered by a FLP result in methanol or CO. The most common reduction product in the reduction of CO_2 sequestered by FLPs is formate.¹¹ For example, the

treatment of solutions of [2,6-lutidinium][HB(C₆F₅)₃] with CO₂ result in a formate complex.¹³ Although, the 2,6-lutidine-CO₂-B(C₆F₅)₃ adduct was not observed,¹³ the reduction of CO₂ to formate occurs when a H₂ and CO₂ atmosphere are exposed to a 1:1 ratio of 2,6-lutidine and B(C₆F₅)₃. In a similar way, the CO₂ adduct of the FLP of 2,2,6,6-tetramethylpiperidine (TMP) and B(C₆F₅)₃ can be reduced to methanol (17–25% conversion) under very forcing conditions (temperatures of 160°C for 6 days) in the presence of a hydrogen atmosphere.¹⁴ The ability to reduce CO₂ with an FLP and H₂ suggests that equivalents of H₂ (protons and electrons) may also be utilized in the reduction of a sequestered CO₂ molecule.

The utilization of FLPs in the electrocatalytic activation of small molecules provides a unique approach to molecule activation, as catalytic molecular transformations void of a metal are possible. With this possibility, it is a surprise that the electrochemical analysis of frustrated Lewis pair small molecule adducts is virtually non-existent. Only recently has Ashley and coworkers described the use of FLPs in the electrochemical oxidation of H₂.^{15–16} Although these reports suggest the use of electrochemistry to functionalize small molecules coordinated to FLPs is possible, analysis of the electrochemistry of small molecule adducts of FLPs beyond H₂ have yet to be reported.

To reduce CO₂ by one electron, very negative potentials are required (Equations 1 and 2, potentials are vs. Cp₂Fe/Cp₂Fe⁺). The harsh reducing conditions are needed due to the energy required for the structural change from linear CO₂ to bent CO₂^{•−}.³ Due to the harsh reducing conditions needed to reduce CO₂, we hypothesized that a CO₂ adduct of a FLP, where the CO₂ molecule was already bent, would result in more facile reduction reactions.

Although several groups have shown that the chemical reduction of CO₂ sequestered between a Lewis acid and a Lewis base to methanol and CO,^{9, 17} implementation of electrochemistry in the reduction of CO₂ sequestered by an FLP has not yet been reported. In this computational and experimental study, we describe the thermodynamics for the insertion of CO₂ into a main group hydride bond and also investigate the use of electrochemistry to reduce a CO₂ molecule sequestered by an FLP.

2. Results and Discussion

2.1. Computational Analysis of the Generation and Hydricity of Main Group Formate Complexes

The insertion of CO₂ into the boron-hydride bond of borohydride has been known since the late 1950's.^{18–20} Based on these results and the recent report by Knopf and Cummins, we

hypothesized that the strength of a Lewis acid and the reducing capacity (hydricity) of a main group hydride would influence the thermodynamics of CO₂ insertion into a main group hydride bond, generating a main group formate (Equation 3). This hypothesis is based on the recent reports describing the influence of Lewis acid strength on the resulting Brønsted acidity of a coordinated protogenic Lewis base²¹ or the ability to accept a hydride of a coordinated unsaturated substrate molecule.²²

To probe the influence of Lewis acid strength on the reactivity of CO₂ with main group hydrides, we employed a Lewis acidity scale probing seven Lewis acids ([PhSiH₂]⁺, [SiEt₃]⁺, B(C₆F₅)₃, B(C₆F₅)₂Ph, B(C₆F₅)Ph₂, BPh₃, and BEt₃), allowing for examination of Lewis acidity over 70 kcal/mol (Figure 1). The strength of the Lewis acids was ranked according to the computationally determined hydricity of the respective main group hydride (Equation 4).²³ As expected, a stronger Lewis acid (e.g. B(C₆F₅)₃) resulted in a poorer hydride donor (e.g. [HB(C₆F₅)₃][−] in Figure 2), and a weaker Lewis acid (e.g. BEt₃) resulted in a better hydride donor (e.g. [HBEt₃][−] in Figure 2).

To determine the ability to insert CO₂ into the main group-hydride bond, computational analysis using Density Functional Theory (DFT) was undertaken (see experimental section for more details). Utilizing the seven main group hydrides seen in Figure 1, the thermodynamics for the insertion of CO₂ into the main group-hydride bond, generating the main group formate complex, was computed (Equation 3). Insertion of CO₂ into the B-H bond of [HB(C₆F₅)₃][−] was computed to be exergonic by about 3.6 kcal/mol. As hypothesized, insertion of CO₂ into better hydride donors (weaker B-H bond) revealed a more favorable insertion reaction. For example, the insertion of CO₂ into the B-H bond of [HBEt₃][−] was computed to be exergonic by 13.6 kcal/mol. To further probe this effect, the hydricity of the boron hydride vs. the free energy of CO₂ insertion (−ΔG_{CO2}) was plotted (Figure 2). From Figure 2, a linear correlation between the hydricity of a B-H bond and the ability to insert a CO₂ molecule was observed. An increase in hydricity of the B-H bond by 10 kcal/mol resulted in a 3.5 kcal/mol increase in the ability to insert CO₂ into the B-H bond. Plotting −ΔG_{CO2} as a function of ΔG_{H[−]} (Figure 2) also revealed the insertion of CO₂ into the B-H bond was not thermodynamically favorable for weak hydride donors (ΔG_{H[−]} > 74.3). Whereas a hydridic B-H bond is favorable for CO₂ insertion, hydridic B-H bonds (generated from weak Lewis acids) have recently been shown to promote the catalytic hydrogenation of ketones in the presence of a strong Lewis base.²⁴

In addition to observing that a better hydride donor results in the insertion of CO₂ into a B-H bond, CO₂ reduction can also occur with silanes.²⁵ We computed the insertion of CO₂ into HSiEt₃ and HSiPhH₂ to be exergonic by 11.4 and 5.7 kcal/mol, respectively. The ability of HSiPhH₂ to insert CO₂ into the Si-H bond exhibited similar energetics to the insertion of CO₂ into the B-H bond of [HB(C₆F₅)₂Ph][−], which is more hydridic than HSiPhH₂ by about 40 kcal/mol. A similar result is observed for HSiEt₃, where the generation of (HCO₂)SiEt₃ exhibits similar energetics to [HB(C₆F₅)Ph₂][−], which is also more hydridic than HSiEt₃ by about 40 kcal/mol. The ability of less hydridic silanes to insert CO₂ to the same extent as the more hydridic borohydrides is attributed to the greater thermodynamic stabilization from the generation of a Si-O bond from a Si-H bond, when compared to the generation of a B-O bond from a B-H bond.²⁶ Okuda and coworkers have recently shown that the insertion of CO₂ into a Si-H bond can be catalyzed by BPh₃.²⁷

Whereas a more hydridic main group hydride is more capable of inserting CO₂ into the main group-hydride bond, the hydricity of the resulting main group formate complex can be determined (Equation 5). Plotting the computed hydricity of the main group formate complex vs. the hydricity of the respective main group hydride (Figure 3), resulted in a linear correlation. From the observed linear correlation, the hydricity of a main group hydride complex is about 10% more reducing than the respective main group formate complex. For example, the formate complex of B(C₆F₅)₃, [(HCO₂)(BC₆F₅)₃][−], has a hydricity of 69.7 kcal/mol and [HB(C₆F₅)₃][−] has a hydricity of 66.1 kcal/mol. Figure 3 also revealed that the coordination of a Lewis acid weaker than BEt₃ does not bind to formate, thus will not influence the hydricity of formate.

Upon coordination of a second identical Lewis acid to a Lewis acid-formate complex, hydride transfer from the resulting complex became less favorable (less hydridic). For example, the addition of a second equivalent of B(C₆F₅)₃ to [(HCO₂)B(C₆F₅)₃][−], resulting in [(HCO₂)(B(C₆F₅)₃)₂][−], became about 13 kcal/mol less hydridic (Equation 6). Plotting the hydricity of [(HCO₂)(Lewis acid)₂][−] vs. the hydricity of the respective main group hydride revealed that the coordination of a second Lewis acid will not occur for Lewis acids weaker than BPh₃. Coordination of a second Lewis acid to a Lewis acid-formate complex revealed a hydride donor that was about 30% less hydridic than the respective main group hydride, and about 20% less hydridic than the respective main group formate complex.

2.2. Electrochemical Analysis of $t\text{Bu}_3\text{P-CO}_2\text{-B(C}_6\text{F}_5)_3$ (**1**)

There are many literature examples of the reduction of FLP bound CO_2 complexes.^{10–11, 28–33} Although many examples of FLP promoted CO_2 activation can promote the reduction of the sequestered CO_2 molecule,¹¹ we were more interested in understanding why some CO_2 -containing FLP adducts, primarily focusing on $t\text{Bu}_3\text{P-CO}_2\text{-B(C}_6\text{F}_5)_3$ (**1**), do not undergo reduction as readily as other FLP- CO_2 adducts. To benchmark our level of theory, we computed the formation of **1** to be exergonic by 12.3 kcal/mol, which matches well with previously computed values.⁵ Computational analysis of the ability to transfer a hydride to **1** to generate $[\text{HCO}_2\text{-B(C}_6\text{F}_5)_3]^-$ and $t\text{Bu}_3\text{P}$ revealed that any hydride donor more hydridic than $[\text{HB(C}_6\text{F}_5)_2\text{Ph}]^-$ should be thermodynamically (not considering kinetic limitations) capable of reducing **1**. To test this hypothesis, we prepared **1**, as reported by Stephan and coworkers. Treatment of **1** with Bu_4NBH_4 resulted in no reaction at 23 °C, suggesting that the steric bulk surrounding the sequestered CO_2 molecule in **1** is too great for a hydride (cone angle = 75°)³⁴ or $[\text{BH}_4]^-$ (cone angle = 83°)³⁵ to attack the sequestered CO_2 molecule and that more forcing conditions are needed to overcome the kinetic barrier of this reaction.

Since the steric bulk surrounding **1** is too great to be reduced by a hydride, we hypothesized that the addition of an electron could be utilized to get around the steric bulk of **1** and promote the reduction of the sequestered CO_2 molecule in **1**. To investigate the ability to electrochemically reduce $t\text{Bu}_3\text{P-CO}_2\text{-B(C}_6\text{F}_5)_3$ (**1**), generating $[t\text{Bu}_3\text{P-CO}_2\text{-B(C}_6\text{F}_5)_3]^-$ (**[1]**[−]), we computationally examined the electronic structure of **[1]**[−]. Analysis of the unpaired spin density of **[1]**[−] revealed 40% of the unpaired spin density resided on the phosphorus center of $t\text{Bu}_3\text{P}$ and 16% of the unpaired spin density resided on the carbonyl carbon of CO_2 (Figure 4). Only 1–2% of the unpaired spin density resided on the CO_2 oxygen atoms. Surprisingly, about 10% of the unpaired spin density resided on one of the ipso carbons of the tert-butyl group of $t\text{Bu}_3\text{P}$. Analysis of the structure of **[1]**[−], when compared to **1**, revealed that the reduction of **1** resulted in a lengthening of the carbon oxygen bonds by 0.05 and 0.03 Å for the C=O and C-O bonds, respectively. The B-O and P-C bonds contracted by 0.06 and 0.01 Å, respectively.

To gain further insight into the reduction and functionalization chemistry of CO_2 bound to a FLP, we examined the electrochemistry of $t\text{Bu}_3\text{P-CO}_2\text{-B(C}_6\text{F}_5)_3$ (**1**). To our surprise, cyclic voltammetry experiments of dichloromethane solutions of **1** showed no reduction events down to −2.58 V vs. $\text{Cp}_2\text{Fe/Cp}_2\text{Fe}^+$, where potentials below −2.58 V resulted in the reduction of CH_2Cl_2 . To determine whether the absence of a reduction was due to the limited potential window of CH_2Cl_2 ,³⁶ or no reduction events are present in **1**, cyclic voltammetry experiments in acetonitrile and THF were also tried. Cyclic voltammetry experiments of **1** in both THF and acetonitrile revealed an irreversible reduction of **1** at −2.56 V and −2.61 V, respectively. A similar result was observed in the electrochemical analysis of $t\text{Bu}_3\text{P-C}_2\text{H}_4\text{-B(C}_6\text{F}_5)_3$, see supporting information. The presence of a reduction event for **1** at very reducing potentials suggests that **1** can be reduced chemically,³⁷ but harsh reagents are needed and solvent choice is important.³⁶

In an attempt to further probe the reduction product of **1**, **1** was treated with 1.5 equivalents of KC_8 in the presence of 18-crown-6, resulting in a colorless solution. To our surprise, NMR spectroscopic analysis of the reaction product revealed only the presence of multiple diamagnetic products. One of the products, which was washed out with THF, was assigned to free ${}^t\text{Bu}_3\text{P}$. The generation of free ${}^t\text{Bu}_3\text{P}$ was verified by the presence of a doublet at 1.36 ppm in the ${}^1\text{H}$ NMR spectrum and a singlet at 66 ppm in the ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR spectrum. The other product contained 18-crown-6 and one tetrahydrofuran molecule as evidenced by the ${}^1\text{H}$ NMR spectrum (see Supporting Information). The other reduction product also showed the presence of a singlet in the ${}^{11}\text{B}$ NMR spectrum at -4.59 ppm, and three signals (-136.41 , -162.69 , and -166.26 ppm) in the ${}^{19}\text{F}$ NMR spectrum, suggesting the presence of a four coordinate borane. To determine the ligand attached to $\text{B}(\text{C}_6\text{F}_5)_3$, x-ray quality crystals were grown from THF and pentane. Molecular structure analysis of the borane product revealed the presence of an ionic compound containing a potassium cation coordinated to 18-crown-6, a THF molecule, and a hydroxide coordinated to $\text{B}(\text{C}_6\text{F}_5)_3$ (Figure 5). The bond distances of the anion, $[(\text{HO})\text{B}(\text{C}_6\text{F}_5)_3]^-$, were similar to previously reported structures containing a $[(\text{HO})\text{B}(\text{C}_6\text{F}_5)_3]^-$ fragment.^{38–43} The formation of $[\text{HO}-\text{B}(\text{C}_6\text{F}_5)_3]^-$ and ${}^t\text{Bu}_3\text{P}$ from the reduction of **1** suggests that the addition of an electron to a sequestered CO_2 molecule may result in the generation of CO. To examine this hypothesis, the reduction of **1** with KC_8 and 18-crown-6 under an argon atmosphere was attempted. Analysis of the headspace of the reaction mixture by GC-MS revealed the production of CO.

To examine the stability of $[\mathbf{1}]^-$, and investigate the thermodynamics of the generation of CO, ${}^t\text{Bu}_3\text{P}$, and $[\text{HO}-\text{B}(\text{C}_6\text{F}_5)_3]^-$, computational analysis was undertaken. Upon generation of $[\mathbf{1}]^-$, decomposition of $[\mathbf{1}]^-$ into ${}^t\text{Bu}_3\text{P}$, CO, and $[\text{O}-\text{B}(\text{C}_6\text{F}_5)_3]^-$ was computed to be endergonic by 4.6 kcal/mol. Although the decomposition of $[\mathbf{1}]^-$ is endergonic, $[\text{O}-\text{B}(\text{C}_6\text{F}_5)_3]^-$ is a very good H-atom acceptor, where the abstraction of H-atoms from solvent molecules (e.g. toluene, THF, MeCN, Et_2O , CH_2Cl_2) is exergonic by 10–15 kcal/mol (see Supporting Information, Table S1). The bond dissociation free energy (BDFE) of the OH bond of $[\text{HO}-\text{B}(\text{C}_6\text{F}_5)_3]^-$ was computed to be 106.6 kcal/mol, which is about 25 kcal/mol higher than the average BDFE for the OH bond of a phenol.⁴⁴ The generation of the paramagnetic $[\text{O}-\text{B}(\text{C}_6\text{F}_5)_3]^-$, was computed to be capable of abstracting a H-atom from THF, exergonic by 14.3 kcal/mol. The resulting THF-radical was capable of dimerization, which was computed to be exergonic by 33.1 kcal/mol. A similar result has been seen by Szymczak and coworkers.⁴⁵ From the computed reactions, decomposition of $[\mathbf{1}]^-$ to ${}^t\text{Bu}_3\text{P}$, CO, $[(\text{HO})\text{B}(\text{C}_6\text{F}_5)_3]^-$, and THF-dimer was found to be exergonic by 42.9 kcal/mol (Scheme 1).

The formation of CO from the reduction of **1** is not a surprise, as Saveant and coworkers have described the electrochemical reduction of free CO_2 , resulting in the reductive disproportionation of CO_2 to CO and CO_3^{2-} .^{46–47} A similar result has been observed when CO_2 is coordinated to transition metal complexes, where the conversion of a metal- CO_2 complex to metal-CO has been shown to occur in the presence of an oxide acceptor.⁴⁸

Wildgoose and coworkers have shown that the chemical reduction of $\text{B}(\text{C}_6\text{F}_5)_3$ in CH_2Cl_2 results in the generation of the $[\text{B}(\text{C}_6\text{F}_5)_3]^{\bullet-}$ radical anion, which rapidly decomposes into $[\text{ClB}(\text{C}_6\text{F}_5)_3]^-$ (39%), $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (14%), $[\text{Cl}_2\text{B}(\text{C}_6\text{F}_5)_2]^-$ (21%), $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (6%), and

[HClB(C₆F₅)₂][−] (20 %).⁴⁹ They also have been able to show that the cyclic voltammogram of B(C₆F₅)₃ in CH₂Cl₂ only exhibits a small degree of reversibility at scan rates greater than 2000 mV/s.⁴⁹ The fact that there is some reversibility in the reduction wave of B(C₆F₅)₃, suggests that the generated [B(C₆F₅)₃]^{•−} radical anion may be intercepted by CO₂ to generate a CO₂ adduct of [B(C₆F₅)₃]^{•−}, which may allow for further reduction of the coordinated CO₂ molecule prior to the decomposition of [B(C₆F₅)₃]^{•−}. Examination of the electrochemistry of B(C₆F₅)₃ under a CO₂ atmosphere showed two reduction waves at −1.93 and −2.16 V vs. Cp₂Fe/Cp₂Fe⁺ that were only marginally visible at a scan rate of 5000 mV/s (see Supporting Information, Figure S18). No reduction waves could be deconvoluted at slower scan rates. Attempts at isolating reduced CO₂ products through chemical reductions of B(C₆F₅)₃ under a CO₂ atmosphere were unsuccessful.

2.3. Influence of Protons on the Reduction of **1**

Since the reduction of **1** leads to rapid decomposition (see Section 2.2), we hypothesized that if the reduction of **1** was undertaken in the presence of acid, the protonation of [**1**][−] could occur prior to decomposition, leading to the electrochemical generation of [(HCO₂)-B(C₆F₅)₃][−]. This hypothesis is validated by the fact that the Mulliken charge analysis of [**1**][−] revealed that the oxygen atoms of the carbon dioxide ligand contained the greatest negative charge, suggesting that they would be the location of protonation. To examine the acid strength needed to protonate **1**, the basicity of **1** was examined computationally. Although **1** is about 28 p*K*_a units more basic than free CO₂ (p*K*_a = −40.8 in MeCN), a superacid would be required to protonate **1** (p*K*_a of −12.5 in MeCN). To test this hypothesis, a strong acid, [H(OEt₂)₂][B(C₆F₅)₄],⁵⁰ was added to a CD₃CN solution of **1** without an external reductant. The addition of one equivalent of [H(OEt₂)₂][B(C₆F₅)₄], in the absence of electrons, to **1** resulted in [^tBu₃PH][B(C₆F₅)₄], CO₂, and CD₃CN-B(C₆F₅)₃ (see Supporting Information). The fact that the formation of **1** is weakly reversible also shifts the equilibrium towards the generation of [^tBu₃PH][B(C₆F₅)₄], CO₂, and CD₃CN-B(C₆F₅)₃ in the presence of a strong acid. These results suggest that the addition of a weaker acid in combination with an electron source is needed to promote the reduction of the sequestered CO₂ molecule in **1**.

To examine the influence of acid strength on the electrochemical reduction of **1**, cyclic voltammetry experiments employing **1** in the presence of acids in MeCN were undertaken. To investigate the influence of acid strength on the electrochemical reduction of **1**, acids ranging in p*K*_a's from 7–18 (p-cyano-anilinium tetrafluoroborate, anilinium tetrafluoroborate, trifluoroacetic acid, pyridinium tetrafluoroborate, and triethylammonium tetrafluoroborate) were utilized. Acids with a p*K*_a greater than 10 resulted in only the reduction of the acid to H₂ (see Supporting Information). Electrochemical experiments employing 1–4 equivalents of p-cyano-anilinium tetrafluoroborate (p*K*_a = 7.0 in MeCN)⁵¹ to **1** resulted in two irreversible reduction events (E° = −1.43 and −2.17 V) that increased with each subsequent addition of acid (Figure 6). To determine the nature of the reduction events of **1** with acid, **1** was treated with three equivalents of p-cyanoanilinium tetrafluoroborate, resulting in about 30% decomposition of **1** to [^tBu₃PH][B(C₆F₅)₄], CO₂, p-cyano-aniline, and CD₃CN-B(C₆F₅)₃. Upon addition of five equivalents of KC₈ to the reaction mixture, no generation of formate, only H₂ production, was observed, suggesting that more efficient proton-coupled-electron-transfer needs to occur to promote the reduction of the CO₂

molecule in **1** to formate. From the chemical experiments, and an independent cyclic voltammetry experiment (see supporting information, Figure S18), the reduction event at -1.43 V is attributed to the reduction of $[^t\text{Bu}_3\text{PH}]^+$ (reduction of H^+ to H_2), and the second irreversible reduction ($E^\circ = -2.17$ V) is attributed to the reduction of [p-cyanoanilinium] $[\text{BF}_4]$ to H_2 on the glassy carbon electrode.⁵¹

3. Conclusions

Whether it be the insertion of carbon dioxide into main group hydride bonds or the coordination of carbon dioxide to frustrated Lewis pairs, the sequestration and reduction of carbon dioxide has received much attention from main group chemists. We have found that the insertion of carbon dioxide into a main group hydride, generating a main group formate, became more favorable for more hydridic (reducing) main group hydrides. An increase in hydricity of a main group hydride results in a 35% increase in the main group hydride's ability to insert CO_2 into the main group hydride bond. The resulting main group formate exhibited a hydricity (reducing ability) about 10% less than the respective main group hydride prior to CO_2 insertion. Coordination of a second identical Lewis acid to a main group formate complex further reduced the hydricity by about another 20%. The ability to adjust the hydricity of a main group formate complex through the coordination of an additional Lewis acid alludes to a new route for the control of the reducing capability of main group hydride sources. Although the reduction of a CO_2 molecule sequestered by $^t\text{Bu}_3\text{P}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ with $[\text{BH}_4]^-$ was unsuccessful due to steric constraints of the FLP, reduction of the CO_2 adduct of $^t\text{Bu}_3\text{P}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ with a chemical reagent (KC_8) resulted in converting the sequestered CO_2 molecule to CO . Reduction of the CO_2 adduct of $^t\text{Bu}_3\text{P}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ with both electrons and protons only resulted in proton reduction, suggesting that more efficient proton-coupled-electron-transfer is needed to reduce CO_2 sequestered to FLPs electrochemically. The investigation of main group complexes in redox promoted reactions is a topic of interest of our laboratory.

4. Experimental section

4.1. General Experimental.

All preparations and manipulations were performed on a double manifold N_2 /vacuum line with Schlenk-type glassware or in a N_2 -filled VAC glovebox, unless indicated otherwise. Solvents were dried using an Innovative Technologies solvent system, and degassed before use. NMR spectra were obtained on a Varian 400 MHz spectrometer, and spectra were referenced to residual solvent (^1H , ^{13}C) or externally (^{11}B ; $\text{BF}_3\cdot\text{OEt}_2$, ^{19}F ; CCl_3F , ^{31}P ; H_3PO_4).⁵² Chemical shifts are reported in parts per million (ppm). NMR solvents were purchased from Cambridge Isotopes, and used as received. $^t\text{Bu}_3\text{P}\text{-CO}_2\text{-B}(\text{C}_6\text{F}_5)_3$ and $^t\text{Bu}_3\text{P}\text{-C}_2\text{H}_4\text{-B}(\text{C}_6\text{F}_5)_3$ were prepared according to the procedures reported by Stephan and coworkers.^{5,53} All remaining reagents were purchased from Sigma Aldrich, Acros Organics, or Alfa Aesar and were used without further purification.

4.2. Electrochemical Conditions.

Cyclic voltammetry (CV) experiments were carried out at room temperature in nitrogen-purged acetonitrile solutions using a CH Instruments Model CHI600E electrochemical workstation. All CV experiments were performed using a glassy carbon working electrode (3.0 mm diameter). The electrode surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use and in between runs. The counter electrode was a carbon rod and the pseudo reference electrode was an Ag/AgCl electrode. The concentration of the sample and supporting electrolyte, tetrabutylammonium hexafluorophosphate, were 1.0 mM and 0.1 M, respectively. The supporting electrolyte was recrystallized from acetonitrile and stored in a desiccator prior to use. To employ moisture free conditions, the CV cell was dried in an oven (140 $^{\circ}\text{C}$ for 24 hours) prior to use. Voltammograms were referenced to 1.0 mM ferrocene/ferrocenium.

4.3. $[\text{K}(\text{18-crown-6})(\text{THF})][\text{HO-B}(\text{C}_6\text{F}_5)_3]$.

A five mL, anhydrous THF solution of 85 mg (0.112 mmol) of $t\text{Bu}_3\text{P-CO}_2\text{-B}(\text{C}_6\text{F}_5)_3$, was added to a black slurry of 22.7 mg (0.168 mmol) KC_8 in five mL of anhydrous THF. The resulting black slurry was stirred under a N_2 atmosphere for five minutes. Then, two mL of anhydrous THF containing 29.6 mg (0.112 mmol) of 18-crown-6 was added to the reaction mixture, resulting in no visible changes. The black slurry was stirred at 25 $^{\circ}\text{C}$ for one hour and then filtered, resulting in a colorless solution. Removal of the solvent under reduced pressure yielded a colorless solid. The solid was recrystallized from the diffusion of pentane into an anhydrous THF solution, yielding a colorless crystalline solid. Yield: 57 mg (56 %). ^1H NMR (600 MHz, CDCl_3) δ = 1.85 (m, THF, 4H) 3.53 (s, 18-crown-6, 24H) 3.74 (m, THF, 4H). ^{11}B NMR (192 MHz, CDCl_3): δ = -4.59 (s). ^{19}F NMR (564 MHz, CDCl_3): δ = -136.34 (d, J = 24.34 Hz, 6F) -162.65 (t, J = 20.54 Hz, 3F) -166.26 (t, J = 19.76 Hz, 6F). The observed NMR spectra matched the reported spectra for the anion of [PPN] $[(\text{HO})\text{B}(\text{C}_6\text{F}_5)_3]$, where $[\text{PPN}]^+$ = bis(triphenylphosphoranylidene)-ammonium.⁴¹

4.4. Computational Methods.

All structures were fully optimized without symmetry constraints using the M06-2X⁵⁴ functional as implemented in Gaussian 09,⁵⁵ using the 6-31G(d,p) basis set.⁵⁶⁻⁵⁷ The exchange-correlation functional, M06-2X, was chosen for its good overall performance observed in the description of main group compounds.^{54, 58-59} In all calculations, the ultrafine integration grid was employed to ensure the stability of the optimization procedure for the molecules of interest. Each stationary point was confirmed by a frequency calculation at the same level of theory to be a real local minimum on the potential energy surface. The 6-311++G(d,p) basis set was used to compute more accurate electronic energies for the optimized geometries.⁶⁰⁻⁶¹ All reported $\text{p}K_a$'s are for acetonitrile solutions at the standard state (T = 298 K, P = 1 atm, 1 mol/L concentration of all species in acetonitrile) as modeled by a polarized continuum model.⁶² The reported $\text{p}K_a$'s utilized pyridine/pyridinium ($\text{p}K_a$ = 12.33 in MeCN) as an anchor.⁶³ An error of 1.3 $\text{p}K_a$ units is estimated for all computed $\text{p}K_a$ values. All reported bond dissociation free energies and free energies are for acetonitrile solutions at the standard state (T = 298 K, P = 1 atm, 1 mol/L concentration of all species in acetonitrile) as modeled by a polarized continuum model. The energies are purely

thermodynamic values, no examination of transition state energies were undertaken. TEMPO/TEMPOH ($G_{H\bullet} = 66.5$) was taken as the anchor for all bond dissociation free energy calculations.⁴⁴

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Ladder diagram showing the computationally determined hydride donor abilities (kcal/mol) of the Lewis acids and main group hydrides employed in this study. The smaller numbers indicate main group hydrides that are better hydride donors and the respective Lewis acid is a weaker Lewis acid.

Figure 2. Plot demonstrating the influence of Lewis acid strength on the ability to insert a CO₂ molecule into a boron-hydrogen bond.

Figure 3.

Plot showing the influence of Lewis acid strength on the computed hydricity of a main group formate complex (kcal/mol). The smaller numbers indicate main group hydrides that are better hydride donors. The blue circles indicate the presence of a single Lewis acid [(Lewis acid)(HCO₂)]⁻. The orange squares denote the computed hydricity of the coordination of a second Lewis acid [(Lewis acid)₂(HCO₂)]⁻.

Figure 4.
Computed unpaired spin density plot of $[1]^-$. Isovalue = 0.01 e-/a.u.

Figure 5. Molecular structure of K(18-crown-6)(THF)[HOB(C₆F₅)₃]. Thermal ellipsoids are drawn at 50% probability. Selected bond distances and angles: B(1)-O(1): 1.464(2) Å, K(1)-O(1): 2.693(1) Å, B(1)-O(1)-K(1): 146.79(8)°, B(1)-O(1)-OH: 111.45(8)°.

Figure 6.

Cyclic voltammogram showing the reduction of **1** in the presence of 0–4 equivalents of para-cyano-anilinium tetrafluoroborate. Solvent = acetonitrile, scan rate = 100 mV/s, electrolyte = Bu₄NPF₆. The reversible wave at 0 V is the ferrocene internal standard.

Scheme 1.

Proposed mechanism for the reduction of **1**. The free energy values are in units of kcal/mol.