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Roles of the Lewis Acid and Base in the Chemical Reduction of CO_2 Catalyzed by Frustrated Lewis Pairs

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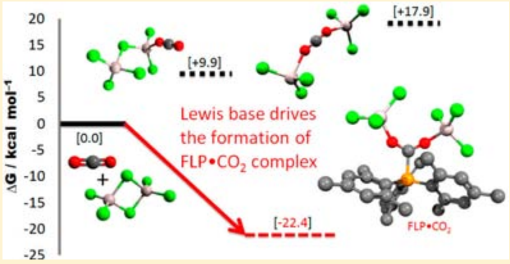
Supporting Information



ABSTRACT: We employ quantum chemical calculations to discover how frustrated Lewis pairs (FLP) catalyze the reduction of CO_2 by ammonia borane (AB); specifically, we examine how the Lewis acid (LA) and Lewis base (LB) of an FLP activate CO_2 for reduction. We find that the LA (trichloroaluminum, $AlCl_3$) alone catalyzes hydride transfer (HT) to CO_2 while the LB (trimesitylenephosphine, $PMes_3$) actually hinders HT; inclusion of the LB increases the HT barrier by ~8 kcal/mol relative to the reaction catalyzed by LAs only. The LB hinders HT by donating its lone pair to the LUMO of CO_2, increasing the electron density on the C atom and thus lowering its hydride affinity. Although the LB hinders HT, it nonetheless plays a crucial role by stabilizing the active FLP·CO_2 complex relative to the LA dimer, free CO_2, and free LB. This greatly increases the concentration of the reactive complex in the form FLP·CO_2 and thus increases the rate of reaction. We expect that the principles we describe will aid in understanding other catalytic CO_2 reductions.

The rising concentration of atmospheric carbon dioxide (CO_2) and its potential to impact global climate has motivated a growing effort to lower atmospheric CO_2 levels.[1] One approach that has gained significant attention is the capture and sequestration of CO_2. However, among the many obstacles to this approach is the significant challenge of long-term, stable storage of CO_2 in vast quantities.[2] An alternative approach that has received less attention and avoids the issue of long-term CO_2 sequestration is the chemical reduction of CO_2 into valuable materials such as methanol (CH_3OH) or its dehydrated form dimethyl ether[3] or possibly C_n ($n \geq 2$) products. The conversion of CO_2 into CH_3OH or other fuels using renewable energy input would enable a carbon-neutral energy cycle that could have a dramatic effect on atmospheric CO_2 levels. The successful conversion of CO_2 to CH_3OH by various homogeneous catalysts and reducing agents has been reported elsewhere;[4−8] here we use quantum chemistry to discover the underlying principles that govern CO_2 conversion by frustrated Lewis pair (FLP) catalysts.

Experimentally, an FLP was first used to activate CO_2 by irreversibly complexing with it to catalyze CO_2 reduction via hydride transfer (HT) from ammonia borane (NH_3BH_3, AB), which acts as a sacrificial hydride donor;[9,10] each HT is equivalent to a two-electron reduction. A 37−51% yield of CH_3OH was observed after 15 min at ambient conditions. The FLP consists of a Lewis acid (LA) and a Lewis base (LB) with bulky ligands that prevent these species from neutralizing each other.[11] In particular, the FLP used to activate CO_2 for reduction (and our focus in this work) consists of two trichloroaluminum ($AlCl_3$) LAs and the trimesitylenephosphine ($PMes_3$, Mes = 2,4,6-$C_6H_2Me_3$) LB, where the LAs and LB datively bond to the oxygens and carbon of CO_2, respectively, to form an FLP·CO_2 complex (Figure 1b).

Recent experimental efforts have aimed at modifying the original $AlCl_3$−$PMes_3$ FLP system,[12,13] e.g., by varying the LA bound to CO_2[14] and employing geminal P/Al-based FLPs,[15] but those systems afforded weaker complexation to CO_2 than the $AlCl_3$−$PMes_3$ FLP. Additionally, recent theoretical studies identify the mechanistic steps for conversion of CO_2 to CH_3OH catalyzed by the FLP[16] and provide insights into the effect of explicit C_6H_5Br solvent in FLP·CO_2 formation.[17] However, these experimental and theoretical efforts have not examined several key issues of CO_2 reduction by FLPs, namely, the mode of CO_2 activation, the roles of the LA and LB in CO_2 reduction, the effect of LA dimerization, and the possible need for prebending CO_2 prior to its reduction. The use of an expensive FLP and AB as a sacrificial hydride source will unlikely be pragmatic for CO_2 reduction; however, we examine the basic aspects of CO_2 reduction by FLPs and LAs to further the fundamental understanding of CO_2 activation that may provide insight into developing improved CO_2 reduction catalysts.

■ LB HINDERS HT: AN ANTICATALYTIC ROLE

One might expect both members of the FLP to assist in catalysis. However, close inspection of the FLP·CO_2 complex shown in Figure 1b reveals a striking chemical contradiction in

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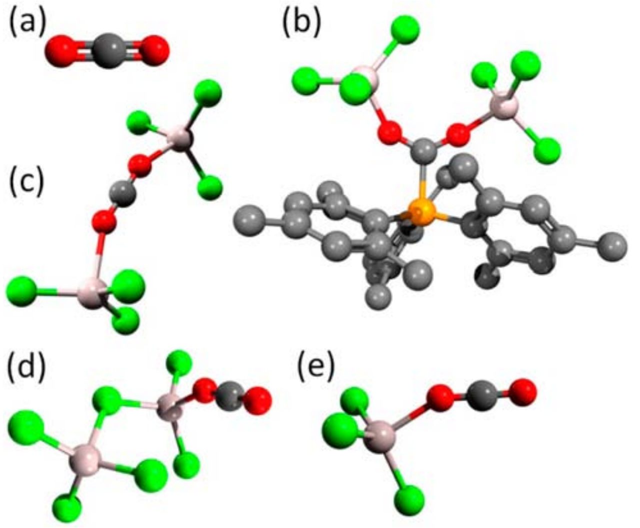

Figure 1. Reactive complexes of CO_2 considered: (a) free CO_2 molecule; (b) FLP·CO_2, composed of CO_2, two LAs, and one LB; (c) LA—O=C=O—LA; (d) CO_2·$(LA)_2$; and (e) CO_2·(LA). H atoms in part b omitted for clarity. Al, light gray; C, gray; Cl, green; O, red; and P, orange.

the role of the LB in FLP activation of CO_2 for its chemical reduction; in the complex, the LB donates its lone pair to the carbon of CO_2, which should decrease the electrophilicity of the CO_2 carbon and hence lower its tendency to accept a hydride. We thus hypothesize that (1) the LB in FLP·CO_2 actually hinders HT, and consequently (2) the LA must act as the catalyst that both activates CO_2 for reduction and overcomes the hindrance to HT caused by the LB.

To test these hypotheses, we have calculated the reaction barrier (activation enthalpy, $\Delta H^{\ddagger}_{\text{hydride}}$) for HT from AB to CO_2 using $AlCl_3$ as the LA and $PMes_3$ as the LB for the following five cases: (a) the reference uncatalyzed reduction (Figure 2a) where AB reduces CO_2 in the absence of the FLP, (b) catalyzed reduction by the FLP (Figure 2b), (c and d) catalyzed reduction by two LAs (isomer 1, Figure 2c and isomer 2, Figure 2d), and (e) catalyzed reduction by a single LA (Figure 2e). Cases c—e involve only LAs and thus allow us to determine whether LAs alone catalyze CO_2 reduction and, if so, which arrangement is most effective, and by comparison with the FLP-catalyzed reaction (case b), whether the LB hinders HT.

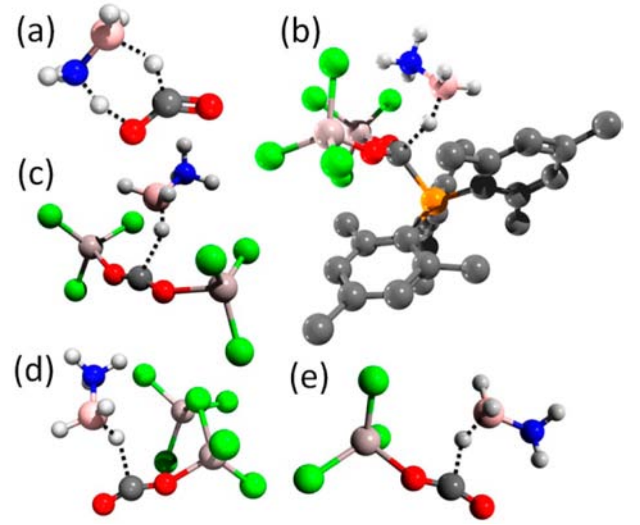

Figure 2. Transition state structures of CO_2 complexes with AB. (a) CO_2 + AB, (b) FLP·CO_2 + AB, (c) LA—O=C=O—LA + AB, (d) CO_2·$(LA)_2$ + AB, and (e) CO_2·(LA) + AB. The H atoms of $PMes_3$ ligands in part b are omitted for clarity. Al, light gray; B, pink; C, gray; Cl, green; H, white; N, blue; O, red; P, orange.

One of us previously published a detailed mechanistic study using the accurate CCSD(T) method for the uncatalyzed conversion of CO_2 to CH_3OH by AB where complete conversion to CH_3OH requires three HTs.[18] Here, we instead examine the first catalyzed HT in order to focus on the roles of the LA and LB in CO_2 activation. It is important to note in this connection that, in the uncatalyzed case a, the hydride and proton transfer concomitantly occur to produce formic acid,[18] whereas in the catalyzed (vide infra) cases b—e our calculations predict HT occurs to produce (complexed) formate ($HCOO^-$). Table 1 reports the predicted $\Delta H^{\ddagger}_{\text{hydride}}$ for the aforementioned five cases in C_6H_5Cl solvent, described by the implicit polarizable continuum model (CPCM).[19,20]

Table 1. HT Barrier ($\Delta H^{\ddagger}_{\text{hydride}}$) and Hydride Affinity (HA) of CO_2 Complexes at T = 298 K and P = 1 atm

system	$\Delta H^{\ddagger}_{\text{hydride}}$[a]	HA[b]
(a) CO_2	25.3	40.5
(b) FLP·CO_2	7.9	79.9
(c) LA—O=C=O—LA	−0.2	131.9
(d) CO_2·$(LA)_2$	4.1	99.1
(e) CO_2·(LA)	3.8	91.7

[a] HT (from AB) enthalpic barriers, in kcal/mol, referenced to the reactant complex. [b] Hydride affinity, in kcal/mol. All calculations performed using MP2/6-311++G(d,p)//B97-D/6-311G(d,p) [MP2//B97-D], except $\Delta H^{\ddagger}_{\text{hydride}}$ of case c, which was calculated using CCSD(T)/6-311++G(d,p)//MP2/6-311G(d,p) [CCSD(T)//MP2]. All enthalpies include zero-point energies (ZPEs) and thermal corrections at 298 K. Solvation in C_6H_5Cl was treated with the CPCM solvent model.

Before discussing the results in Table 1, an important computation issue requires comment. The FLP system involves significant dispersion interactions that affect complexation energies and thus HT barriers. Therefore, we employed the B97-D exchange-correlation functional to obtain TS and equilibrium geometries as this method accounts for dispersion effects important in complex formation.[21] Grimme et al. previously used this functional to describe the heterolytic cleavage of H_2 by an FLP catalyst for which the popular B3LYP functional gave erroneous results due to its neglect of dispersion.[22] For accurate energies, we performed MP2 single-point energy calculations at the B97-D identified stationary point geometries, which we found differ from high-level CCSD(T)//MP2 energies by less than 1 kcal/mol for both HT barriers and complexation energies (see Supporting Information for additional computational details).

■ HYDRIDE TRANSFER BARRIERS AND AFFINITIES REVEAL THE CATALYTIC ROLE OF THE LA

We now return to the main focus of this Article and observe that the $\Delta H^{\ddagger}_{\text{hydride}}$ values reported in Table 1 indicate that although the FLP does indeed catalyze CO_2 reduction by lowering $\Delta H^{\ddagger}_{\text{hydride}}$ from 25.3 kcal/mol for the uncatalyzed case a to 7.9 kcal/mol for the FLP-catalyzed case b, the barriers are even lower for cases c−e that exclude the LB and only involve the LAs. This confirms our hypothesis that the LB impedes HT and that the LAs alone activate CO_2 for reduction (see SI, section 3 for additional TS properties). The previously reported $\Delta H^{\ddagger}_{\text{hydride}}$ using B3LYP for case b is ~7 kcal/mol higher than our calculated barrier,[16] which we attribute to B3LYP's neglect of dispersion (see SI, section 4). Furthermore, in contradiction to the suggestion that "prebending" of CO_2 is necessary to assist its reduction, we show that LAs catalyze the reduction of the linear form of CO_2 resulting in low HT barriers (see Figure 1c−e). For example, at the transition state (TS) for case c ∠O−C−O is 178° (Figure 1c), and HT is barrierless. In addition, in case b where CO_2 is prebent (Figure 1b, ∠O−C−O = 126°), the LB raises $\Delta H^{\ddagger}_{\text{hydride}}$ by ~8 kcal/mol compared to case c; this is due to the nucleophilic competition between the donating lone pairs of the LB and the transferring hydride from AB to the LUMO of CO_2.

We now examine the relative roles of the LB and LA moieties in further detail. We start with the case of two LAs (case c), obtained by elimination of the $PMes_3$ LB from the FLP case b. We could not locate a TS for this step with B97-D, but were able to determine a TS using MP2 (single imaginary frequency of 182*i* cm^{-1}). A CCSD(T) energy at the MP2 TS geometry predicts a barrierless reaction after addition of ZPE and thermal contributions. Thus, the two LAs catalyze CO_2 reduction, and adding the LB increases the barrier. With the catalytic importance of the two LAs of case c thus established, we ask if a different arrangement of the LAs would be more effective. The alternate arrangement $CO_2{\cdot}(AlCl_3)_2$ was suggested by Olah et al. as one of the reactive complexes in the addition of CO_2 to C_6H_6 to produce benzoic acid.[23] We examine this type of complex involving a $(LA)_2$ dimer in case d. We find that $\Delta H^{\ddagger}_{\text{hydride}}$ = 4.1 kcal/mol, showing that this dimer also catalyzes HT to CO_2. These results suggest examination of the single LA (case e). Also, here we calculate a HT barrier of 3.8 kcal/mol. Thus, as we have previously noted, all three LA configurations c−e have HT barriers substantially below that of the FLP case b involving two LAs and the LB.

What is the key property of the LAs for catalytic CO_2 reduction efficacy? For Friedel−Crafts acylation where CO_2 adds to C_6H_6 to produce benzoic acid, Olah et al. concluded that the reaction was catalyzed by $AlCl_3$'s superelectrophilic activation of CO_2.[23] Also, Ren et al. observed a notable increase in the electrophilicity of simple aldehydes and ketones (carbonyl-containing species, like CO_2) when complexed to the LA BF_3.[24] These observations are consistent with our results, which show that the LAs lower the HT barriers by electrophilic activation of CO_2. We elaborate upon this explanation via hydride affinity (HA) calculations, reported in Table 1. HA is here defined as the negative of the change of enthalpy when CO_2's carbon (in complexes a−e) accepts a hydride. HA quantifies the electrophilicity of the carbon of CO_2 to accept a hydride, and as we now discuss, the fact that complexes a−e are more electrophilic with increasing HA is key for understanding the trends in Table 1's HT barriers.

As can be seen in Table 1, the FLP catalyst increases the HA of CO_2 from 40.5 (a) to 79.9 (b) kcal/mol, a result consistent with the increase in CO_2 electrophilicity and thus the lowering of the HT barrier from 25.3 to 7.9 kcal/mol. When CO_2 is complexed with LAs only, as in cases c−e, the HA markedly increases to greater than 90 kcal/mol, consistent with the low HT barriers of c−e. This is especially true for c, where the HA is 131.9 kcal/mol and HT is barrierless. Thus, the role of the LAs is to render CO_2 more electrophilic (high HA), and as a result lower the barrier to HT. These results also support Stephan et al.'s very recent proposal that coordination of LAs to the oxygens of formate promotes HT.[25] The hindering role of the LB that we have emphasized is evident when the HAs of cases b and c are compared: removing the LB from b to create c results in a significant increase in HA from 79.9 to 131.9 kcal/mol.

■ POSITIVE ROLE OF THE LB: ESTABLISHING HIGH CONCENTRATIONS OF REACTIVE CO_2 COMPLEXES

We have already established that the role of the LB in the key CO_2 reduction step is a negative one: to hinder HT. We now ask if the LB might play any positive role in the FLP activation of CO_2; we will find that the answer is yes, but its origin lies in the formation of reactive CO_2 complexes rather than in their activation for reduction. Table 2 shows the calculated thermochemistry for several complexes (shown in bold and defined in eq 1; see SI, section 5) referenced to the starting reactants in case 1: two free CO_2, $(LA)_2$ dimer $[(AlCl_3)_2]$, two free LB ($PMes_3$), and two free AB. Ammonia borane has been included here because, even though it was added to function as a reducing agent, it also complexes with the electrophilic LA through its hydridic hydrogens.[25] Dimeric $(AlCl_3)_2$ was chosen as the reference for Table 2 because $AlCl_3$ is known to predominantly form dimers[23] at various conditions;[26−28] the dimerization enthalpy of the LAs must be considered in determining the relative concentrations of reactive CO_2 complexes (vide infra).

Table 2. Thermodynamics of Complex Formation Relative to the Reactants Two Free CO_2, $(LA)_2$ Dimer, Two Free LB, and Two Free AB at T = 298 K and P = 1 atm

complexes	ΔH^a	$T\Delta S^a$	$K_{eq}{}^b$
(1) $2CO_2 + (LA)_2 + 2LB + 2AB$	0.0	0.0	1.0
(2) **FLP·CO_2** + CO_2 + LB + 2AB	−49.0	−26.5	2.8×10^{16}
(3) **LA—O=C=O—LA** + CO_2 + 2LB + 2AB	12.9	−5.1	7.3×10^{-14}
(4) **$CO_2{\cdot}(LA)_2$** + CO_2 + 2LB + 2AB	0.8	−9.1	5.4×10^{-8}
(5) 2[**$CO_2{\cdot}(LA)$**] + 2LB + 2AB	4.9	−5.6	2.1×10^{-8}
(6) **$CO_2{\cdot}(LA)$** + CO_2 + **LA·LB** + LB + 2AB	−20.9	−12.6	1.2×10^{6}
(7) **$CO_2{\cdot}(LA)$** + CO_2 + **LA·AB** + 2LB + AB	−9.8	−8.0	2.1×10^{1}
(8) **$CO_2{\cdot}NH_3BH_2{}^+$** + **$AlCl_3H^-$** + CO_2 + **LA·AB** + 2LB	24.3	−7.5	4.7×10^{-24}
(9) $2CO_2$ + 2[**LA·LB**] + 2AB	−46.7	−19.6	7.1×10^{19}
(10) $2CO_2$ + 2[**LA·AB**] + 2LB	−24.5	−10.4	2.1×10^{10}
(11) $2CO_2$ + **LA·LB** + **LA·AB** + LB + AB	−35.6	−15.0	1.21×10^{15}

[a] ΔH and $T\Delta S$ in kcal/mol referenced to two free CO_2, $(LA)_2$ dimer, two free LB, and two free AB of case 1 (see eq 1). [b] Equilibrium constant of the complexes (unitless), defined as $K_{eq} = \exp(-\Delta G/RT)$. Calculations were performed using MP2//B97-D in CPCM modeled C_6H_5Cl solvent.

$$2CO_2 + (LA)_2 + 2LB + 2AB \xleftrightarrow{\Delta H;\ T\Delta S;\ K_{eq}} \text{complexes 1 to 11} \quad (1)$$

The thermodynamic variables reported in Table 2 allow us to predict the relative concentrations of a number of reactive CO_2 complexes. We calculate that K_{eq} for LA—O=C=O—LA (3) formation is 7.3×10^{-14}. This exceptionally low equilibrium constant is due to both the enthalpic and entropic costs of forming the complex from the $(AlCl_3)_2$ dimer and CO_2. The $CO_2{\cdot}(LA)_2$ complex (**4**), where the LA dimer complexes with CO_2, initially looks more promising. K_{eq} for this case is 5.4×10^{-8}, ~6 orders of magnitude higher than for LA—O=C=O—LA. But this is still low, mainly due to the entropic cost of complex formation, which for this case is approximately enthalpically neutral. This $CO_2{\cdot}(LA)_2$ complex should attain its equilibrium concentration with CO_2 and $(LA)_2$ dimer in the absence of LB and AB because the barriers for its formation (10.6 kcal/mol) from and dissociation (9.9 kcal/mol) to CO_2 + $(LA)_2$ are thermally accessible at room temperature (see SI, section 3b). However, its low K_{eq} suggests that it will not in fact be present in significant concentration. Thus, although complexes LA—O=C=O—LA and $CO_2{\cdot}(LA)_2$ both have low barriers to HT (Table 1, cases c and d), their equilibrium concentrations are too low to have a significant reaction rate in reducing CO_2.

We next analyze reactive CO_2 complexes involving monomeric LA (Table 2, cases 5−7). Case 5 results from dissociation of the $AlCl_3$ dimer to form two $CO_2{\cdot}(LA)$ complexes. Its K_{eq} is low (2.1×10^{-8}) because $CO_2{\cdot}(LA)$ complexation is less exothermic than $AlCl_3$ dimerization. However, this dimerization is suppressed and an effective concentration of $CO_2{\cdot}(LA)$ is established when LB or AB dissociates the $AlCl_3$ dimer by forming LA·LB (Figure 3a) or LA·AB (Figure 3b) complexes, Table 2, cases 6 and 7, where K_{eq} is 1.2×10^6 and 2.1×10^1, respectively. Thus, in addition to its key role as a hydride donor, AB complexes with the LA via its hydridic H and promotes LA·AB adduct formation that increases $CO_2{\cdot}(LA)$ concentration. Given that $CO_2{\cdot}(LA)$ forms in nonvanishing concentrations relative to the dominant cases (Table 2, cases 2 and 9), combined with the low HT barrier of 3.8 kcal/mol (Table 1, case e), CO_2 reduction via reactive $CO_2{\cdot}(LA)$ contributes to the CO_2 reduction rate. Case 8 in Table 2 is similar to CO_2 activation by one LA (Table 1, case e). Here, borenium cation $NH_3BH_2^+$ acts as an LA that activates CO_2 for HT from the $AlCl_3H^-$ counterion. Figure 3c shows the TS for this HT where $\Delta H^{\ddagger}_{hydride}$ = 3.0 kcal/mol. However, despite the low HT barrier, the endothermic formation of $CO_2{\cdot}NH_3BH_2^+$ and $AlCl_3H^-$ results in a vanishingly low K_{eq} value of 4.7×10^{-24}, thus making this pathway inactive.

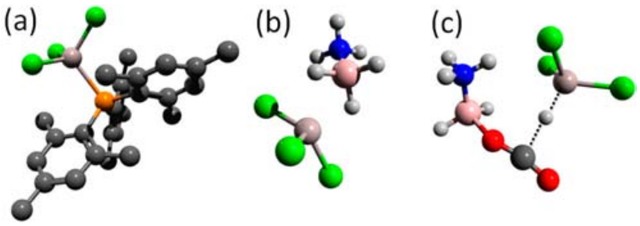

Figure 3. (a) LA·LB complex, (b) LA·AB complex, and (c) TS structure of $CO_2{\cdot}NH_3BH_2^+$ + $AlCl_3H^-$, calculated at MP2//B97-D. LA = $AlCl_3$, LB = $PMes_3$, and AB = NH_3BH_3. The H atoms in part a are omitted for clarity. Al, light gray; B, pink; C, gray; Cl, green; H, white; N, blue; O, red; and P, orange.

The single case that exhibits a positive role for the LB is case 2 of Table 2 in which CO_2 is activated in the FLP·CO_2 complex. FLP·CO_2 proves to be one of the most readily formed CO_2 complexes. The large formation constant of $K_{eq} = 2.8 \times 10^{16}$ results from a favorable −49.0 kcal/mol enthalpy of formation relative to the $(LA)_2$ dimer, free CO_2, and free LB; this enthalpic contribution is nearly double the unfavorable entropic contribution (see Table 2). We conclude that the role of the LB in FLP-catalyzed reduction of CO_2 by AB is to provide a sufficient enthalpic driving force for the formation of the reactive FLP·CO_2 complex. Thus, we predict that, given its large K_{eq} and relatively low 7.9 kcal/mol HT barrier (Table 1, case b), FLP-catalyzed CO_2 reduction via FLP·CO_2 complex will dominate the HT rate, with minor contributions from $CO_2{\cdot}(LA)$ formed through Table 2, cases 6 and 7.

In view of the above predictions, we now discuss the recent proposal by Stephan et al.[25] that, in the presence of AB, the FLP·CO_2 complex first dissociates to produce different reactive CO_2 complexes that can dominate the HT rate. For the specific LA and LB choices considered here, our results discussed above indicate that the dominant HT pathway proceeds through the undissociated FLP·CO_2 complex, with only minor contributions involving the AB-induced FLP·CO_2 dissociation product $CO_2{\cdot}(LA)$ (Table 2, case 7). On the other hand, when LA = $Al(C_6F_5)_3$, and LB = P(*o*-tol)$_3$, where *o*-tol =2-C_6H_4Me and AB = NMe_3BH_3,[25] the equilibrium of the analogues of 6 and 7 relative to 2 in Table 2 will be shifted due to the steric effects introduced by $Al(C_6F_5)_3$. This effect may increase the contribution to the HT rate by $CO_2{\cdot}(LA)$ in Table 2, cases 6 and 7, as proposed by Stephan et al.

In Table 2, cases 9−11, favorable LA·LB and LA·AB interactions lead to CO_2 not being complexed and thus not activated. In case 9, LA·LB exists in equilibrium ($K_{eq} = 7.1 \times 10^{19}$) with FLP·$CO_2$ ($K_{eq} = 2.8 \times 10^{16}$). In fact, LA·LB was isolated experimentally in the absence of CO_2. In contrast, FLP·CO_2 was isolated (as a solid) when the solvent was evaporated from mixtures containing LA, LB, and CO_2.[9] In the solid-state structure, the enthalpy of formation dominates K_{eq}; thus, FLP·CO_2 (ΔH = −49.0 kcal/mol) is predicted to exist in greater abundance than LA·LB (ΔH = −46.7 kcal/mol). In the presence of LB, 9 likely dominates over 10, although LA·AB can still coexist with LA·LB through 11. Interactions of the LB and AB with the LA in LA·LB and LA·AB complexes significantly shift the equilibrium concentrations and are key factors to consider in optimizing concentrations of reactive CO_2 complexes.

■ REACTIVE CO_2 COMPLEXES FORMED IN THE ABSENCE OF LB

In addition to revealing the roles of the LAs and LB in the FLP-catalyzed reaction, our results suggest an alternate approach to CO_2 reduction using only LAs. None of the cases 1, 3, 4, 5, 7, 8, and 10 in Table 2 involve the LB and are thus relevant for the LB-free situation. The comparison of their equilibrium constant values indicates that when LB is absent, the equilibrium established by 10 dominates in which AB dissociates the $AlCl_3$ LA dimer to form LA·AB in abundance. This conclusion agrees with the reported isolation of analogous LA·AB complexes (LA = $Al(C_6F_5)_3$ and AB = NMe_3BH_3) in high yield.[25] But, CO_2 is not activated by LA·AB. Our results suggest that reactive CO_2 species are instead formed as $CO_2{\cdot}(LA)$ by reaction 7 in equilibrium with 10. This proposal that CO_2 is activated in the $CO_2{\cdot}(LA)$ form is supported by isolation of $Al(C_6F_5)_3(HCO_2)$-H_2BNMe_3 formate species in the absence of LB;[25] the observed formate species is analogous to the HT product of the reaction of $CO_2{\cdot}(LA)$ with AB (Table 1, case e). We suggest that, in the absence of LB, the relative K_{eq} values for cases 1, 7, and 10 must be considered to optimize the concentration of $CO_2{\cdot}(LA)$ in order to lead to rapid CO_2 reduction. Ideally, the K_{eq} value for

7 should be high[29] relative to 1 and 10. In other words, a relatively high CO_2·(LA) complexation enthalpy and low binding affinities for LA·LA (dimer) and LA·AB formation will lead to significant concentrations of activated CO_2 complexes for CO_2 reduction. We propose that this can be achieved by employing LA and AB with bulky ligands[30,31] to weaken LA·LA and LA·AB interactions relative to CO_2·(LA).

In summary, we have determined a number of the underlying principles that govern CO_2 conversion by FLP catalysts. It is the LAs of the FLP that act as the catalyst by polarizing CO_2 to render it more electrophilic to accept a hydride at low barriers, which are strongly correlated with the hydride affinity of CO_2 in the complex. Furthermore, the LAs catalyze HT to CO_2 without prebending it from its linear geometry. Although we find that the LB hinders HT within the FLP·CO_2 complex by lowering the hydride affinity of CO_2, its role is to stabilize that complex relative to the $(LA)_2$ dimer, free CO_2, and free LB. This results in a high HT rate due to the high concentration of reactive CO_2 species in the FLP·CO_2 complex and a low HT barrier. In the presence of LB, and for the LA and LB considered here, we predict that the reactive CO_2 complex CO_2·(LA) is a minor pathway to HT relative to CO_2 reduction via the FLP·CO_2 complex. However, in the absence of LB, we predict that instead CO_2·(LA) will be the dominant reactive CO_2 complex responsible for forming HT products[25] such as formate and methoxide. We anticipate that the principles found here should prove useful in the understanding and discovery of other catalytic CO_2 reductions.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details, benchmarking studies, HT reactants and TS energies, formation of CO_2·$(LA)_2$ from free CO_2 and $(LA)_2$ dimer, thermochemistry energies, FLP·CO_2 + AB HT (B3LYP), thermodynamics of complex formation reported in Table 2, and coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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