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Low pK_a Phosphido-Boranes Capture Carbon Dioxide with Exceptional Strength: DFT Predictions Followed by Experimental Validation

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basicity. A few notable exceptions are extremely electron-rich phosphines studied by Dielmann et al.,[6] as well as phosphide metal salts,[7] all of which are exceptionally strong bases. Frustrated Lewis pairs (FLPs), first synthesized by Douglas et al.,[8] have also been analyzed for CO_2 capture,[9] itself. Furthermore, analysis of the basicity of these complexes, completed by Dornhaus et al., indicates that the anionic motif of the phosphido-borane salt is more Lewis basic toward the [BH_3] compared to its neutral analogues, making these compounds ripe for usage in CO_2 capture.[11]

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with these compounds using a frustrated lone pair induced by steric

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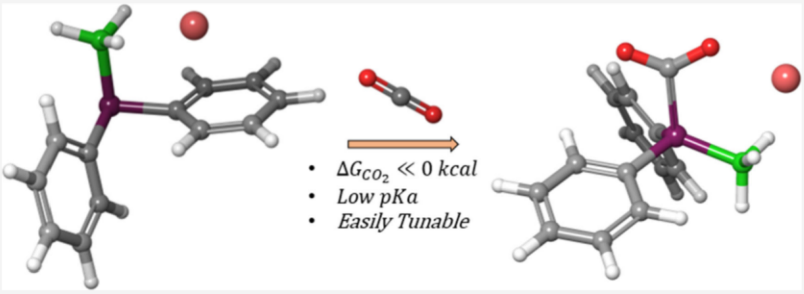

ABSTRACT: We have developed a class of phosphido-boranes (BoPh's) with formula $X^+[R_2PBH_3^-]$ that bind CO_2 with exceptional strength ($\Delta G = -8.2$ to -24.0 kcal/mol) at ambient conditions. We use quantum mechanics (QM) to determine how the choice of electron-donating versus electron-withdrawing ligand impacts the CO_2 binding strength, in the presence of a donating borane moiety. We also examine the role of the cation in CO_2 binding, finding that the ion position relative to the bound CO_2 dramatically alters binding strength. We find that the BoPh with two ethyl ligands $Li[Et_2PBH_3]$ leads to $\Delta G = -24.0$ kcal/mol upon CO_2 binding while $Li[Ph_2PBH_3]$ leads to $\Delta G = -12.8$ kcal/mol. We synthesized the BoPh with two phenyl ligands $Li[Ph_2PBH_3]$ to validate the QM-predicted stability and predicted pK_a.

[redacted]

simple phosphide complexes are well-established for binding CO_2 and serve as the basis for state-of-the-art CO_2 extraction technologies.[3,4] In contrast phosphines generally do

[5]

hindrance to drive CO_2 binding. These compounds do not include a P−B bond and instead use steric hindrance to drive binding. While previous analyses have examined various frustrated lewis pairs for CO_2 activation, we find that direct formation of the P−B bond allows for the borane moiety to donate charge to the phosphorus. This allows for these compounds to have extensively different properties than those

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Herein, we report a combined computational−experimental study that examines several phosphido-boranes (BoPh) for the efficient capture of CO_2. We used quantum mechanics (QM) to predict CO_2 binding for a number of BoPh's followed by NMR experimental validation in d_8-THF solution. Our deprotonated secondary phosphido-boranes complexes exhibit CO_2 binding free energies of −8.2 to −24.0 kcal/mol at 300 K despite having only moderate Brønsted basicity, comparable to that of the *tert*-butoxide anion. Formation of the Lewis acid− base complex between BH_3 and secondary phosphines (R_2P− H) leads to a substantial increase in the P−H Brønsted acidity of the H-PR_2-BH_3^- adduct compared to the free phosphine. This observation has been exploited widely in the synthesis of tertiary phosphines, since PR_2-BH_3^- anions serve as excellent P nucleophiles, bear a built-in BH_3 protecting group for the P atom, and offer significant experimental advantages compared to the parent R_2P^- phosphide counterpart.[12] These phosphideborane salts have excellent CO_2 binding in comparison to other P-based systems as a result of their acidity. Instead of a strong base needed for deprotonation and subsequent activation, only mild conditions are needed. While these phosphido-borane complexes have some ditopic character, with dual reactivity at both the P and H centers, the use of these phosphide-borane complexes as hydride sources has not been reported. As shown by Consiglio et al.,[12] the introduction of various carbonyl derivatives led to the formation of multiple products due to the inclusion at both the P site and H site in the compounds under investigation. This ditopic behavior indicates the complexity of the reaction mechanisms associated with reduction induced by various phosphide-borane compounds.[13] What has so far remained unnoticed is that the $PR_2BH_3^-$ anions possess remarkably strong CO_2 binding affinity for P-based compounds with Brønsted basicity between that of bulky trialkylphosphines (e.g.., PCy_3) and the weakest of the P superbases, such as Verkade's base, neither of which form stable CO_2 adducts. Furthermore, the CO_2 binding motif in the form of a single P−C bond in the resulting carboxylate ion rather than a cyclic lactone is likely to benefit subsequent activation to form stable CO_2-based compounds.

We report here density functional theory (DFT) studies examining several subclasses of phosphido-boranes (BoPh) candidates for use in CO_2 capture. We found that the ΔG of CO_2 binding ranges from −8.2 to −24.0 kcal/mol. Of the molecules studied, the BoPh with two phenyl ligands Li[Ph_2PBH_3] led to a predicted ΔG = −12.8 kcal/mol, which we have now validated experimentally.

We first evaluated the influence of electron-withdrawing and electron-donating groups on CO_2 capture and their interplay with the anionic borane motif. We also investigated the countercation effect on CO_2 capture, revealing how the position of the cation relative to the BoPh dramatically alters CO_2 binding strength. We propose several BoPh's with varying functionalities that may affect CO_2 binding. BoPh's 1, 2, and 3 contain electron-donating groups, and BoPh 4 contains an electron-withdrawing group. Phosphines 5 and 6 do not contain the borane moiety, serving as references for comparison with BoPh's 1 through 4. While it is known that simple phosphide salts form CO_2 complexes, we included example phosphines as reference to explore the effect of the borane unit on CO_2 binding energies. This is shown in the case of phosphine 5.

- 1 [$(CH_3)_2PBH_3$] contains two −CH_3 (Me) groups which should function as weak electron-donating groups. • 2 [$(CH_3CH_2)_2PBH_3$] contains two −CH_2CH_3 (Et) groups, as an extension to 1.
- 3 [(Butyl)$_2$PBH$_3$] contains the BoPh anion (P−BH_3^-) accompanied by two *n*-butyl units bound to the central P. Butyl is used here because we previously found that both Me and Et groups had extremely exergonic CO_2 binding strength (−23.1 and −24.0 kcal/mol). Moreover, we can directly compare the butyl groups to the Me and Et groups for CO_2 binding, in the context of altering the chain lengths of unsubstituted alkyl groups to an electron-rich substrate such as the BoPh.
- 4 [$(Ph)_2PBH_3$] has two −C_6H_5 (Ph) units, which should operate as electron-withdrawing groups bonded to the central, electron-rich P.
- 5 [$(Ph)_2P$] also has two Ph units but lacks the borane, such that the third ligand position becomes occupied by the countercation.
- 6 [Ph_3P] also lacks the borane and should therefore serve nicely for elucidating the effect of the borane moiety on CO_2 binding affinity.

The reactant conformer was selected by varying the position of the counterion across multiple local pockets in the reactant complex. From there, the ion position that led to the lowestenergy conformation was selected. CO_2 binding free energies for the lowest-energy reactant and product conformers with Li^+ counterions are shown in Figure 1. It was observed that the

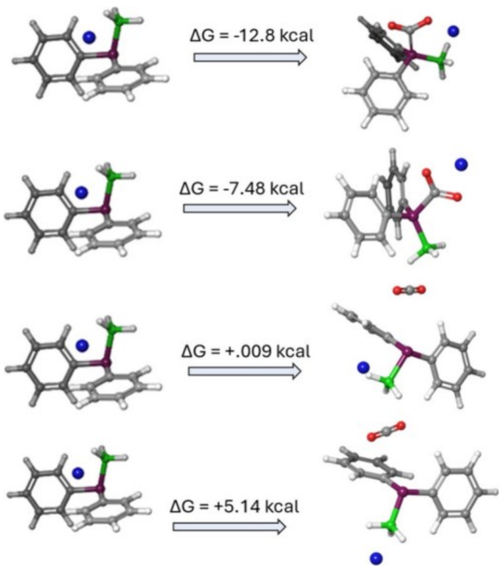

Figure 1. Effect of the counterion on overall Δ*G*. The most stable of the counterion is in-between the CO_2 and P-BH_3 groups. Moving the counterion to other groups, such as near the $-BH_3$ or the $-CO_2^-$ groups, drives Δ*G* significantly, to −7.5 and +5.1 kcal, respectively.

closer the counterion was to the P-BH_3 unit, the more able it was to stabilize charge and thus the more effectively it was able to substantially increase reactant stability.

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The overall ΔG of binding CO_2 is based on the stability of the product complex. The counterion plays a significant role in stabilizing the CO_2^- moiety upon binding, balancing charge distribution throughout the entire system. Altering the placement of the counterion in different pockets throughout the system dramatically changes binding energies. Here, the closer the counterion is to the bounded CO_2 and the electronrich moieties of the system, including the electron-donating $-BH_3$ unit, the more able it is to stabilize effective charge. Shown in the following, a summary of the effect of the counterion in terms of overall binding energies is presented by changing the pocket where each counterion is coordinated to the system. As shown in the image, the pocket where the counterion is coordinated to the system dramatically affects binding energy.

Absolute distance also affects binding energy. In the first case, where the Li^+ counterion is positioned between the terminal oxygen and the $-BH_3$ group, increasing the distance by merely 0.35 Å increases binding energy by +5.9 kcal. This is shown in Figure 2.

For the case of Li^+ counterions, the most stable product BoPh conformer has the Li^+ seated between an oxygen of the bound CO_2 and two hydrides of the anionic $-BH_3^-$. Increases in the thermodynamic driving force as a result of this can be attributed to charge stabilization in the product structure, as well as charge transfer from P to the CO_2 unit upon binding.[14] In these structures, binding CO_2 leads the borane moiety to donate a charge of +0.09 to the P−C single bond (P is now formally +1). We generally find that bulkier ligands increase steric crowding which in turn limits the availability of the nucleophilic P for binding CO_2.

As shown for compound 4, the coupled effect of having both weak electron-withdrawing groups and steric crowding around the nucleophilic site of the phosphorus lone pair decreases the magnitude of ΔG, although the anionic borane offsets this effect due to charge transfer into the newly formed P−C bond. In compounds 1, 2, and 3, alkyl groups act as weak electron donors to the nucleophilic P binding site, leading to ΔG from −24 to −19 kcal/mol (Figure 3).

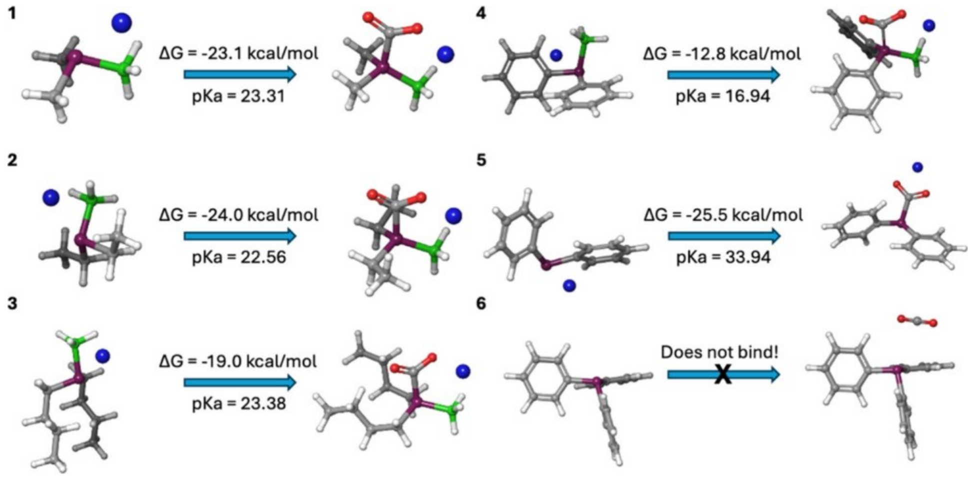

Figure 3. DFT-predicted CO_2 binding energies (kcal/mol) in THF solvent with Li counterions for various BoPh's. Here P is purple, B is green, C is gray, H is white, and Li is blue. pK_a values were tabulated in water solvent, following the equation $pK_a = \frac{1}{2.3RT}D$, where D is the free energy change associated with dissociation of BH^+ to B^- and H^+ in water solvent. The value of H^+ is determined to be −259.5 kcal/mol for the solvation free energy change of a proton.

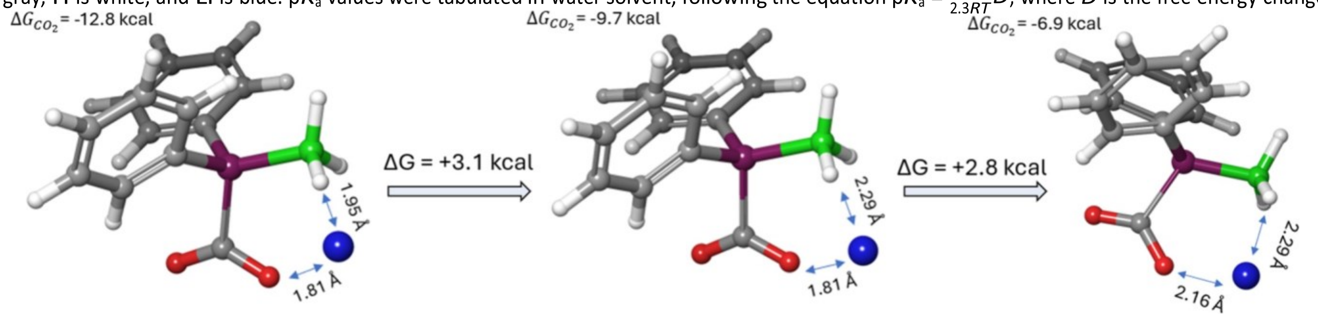

Figure 2. Effect of distance on ΔG. Increasing the counterion distance from the O-BH_3 pocket by 0.35 Å increases binding energy by +5.9 kcal. ΔG_{CO_2} increases for the biphenyl case from −12.8 kcal/mol to −6.9 kcal/mol.

In BoPh 4, the reactant P charge is much higher than those of BoPh 1−3. The larger cationic character of the phosphorus in the reactant complex limits the ability for nucleophilic attack on the electrophilic carbon of the CO_2, decreasing the Δ*G* to −13 kcal/mol. Compared to other conformers in which the counterion was placed in less stable sites, Li^+ coordination to the oxygen of the CO_2 unit and the hydrides of the borane (Figure 1) yielded O−C−O bond angles close to sp^2 hybridization (120°). Strong deviation from the linear bond angle of 180° for CO_2 also indicates increased thermodynamic driving force for CO_2 binding, with more negative Δ*G* values arising from species able to accommodate CO_2 near 120°. As the Li^+ moves closer to the oxygens, the O−C−O bond angle decreases to near the sp^2 hybridization angle of 120°.

Li^+, along with its role in adjusting the CO_2 bond angle, acts as a soft Lewis acid in the THF solvent, making Δ*G* more negative. The naked biphenyl phosphide-borane has an incredibly downhill binding energy of almost −12 kcal/mol for CO_2 binding. Other analogues have even stronger binding energies, some in the −20 to −30 kcal/mol range. This result can be used as a baseline for further alternations to the ligands bound to phosphorus to increase overall Δ*G* for conversion to a value-added product. For the creation of a value-added product, Δ*G* for CO_2 binding must be increased in order to ensure that the bound CO_2 can be released upon formation of the product. This can be done in a variety of different ways, including the following:

- decreasing the nucleophilicity of the phosphorus by increasing the electron-withdrawing nature of the ligands, e.g., by introducing −F substituents on the aryl withdrawing group or otherwise;
- decreasing the electron-donating ability of the $-BH_3$ group by replacing the hydrides with other substituents;
- altering reaction conditions to make conditions more acidic; or
- changing the counterion involved in stabilizing the bound CO_2 product, such as replacing Li^+ with K^+.

This would ultimately balance adsorption and collection Δ*G*s for capture and subsequent conversion.

Explicit solvent inclusion in the reactant conformers indicates that, in addition to stabilizing effects from both the phosphorus (P) and boron (B) atoms due to the counterion being placed between them, the electron-donating tetrahydrofuran (THF) molecules also contribute to stabilization. The oxygens of each THF group are oriented toward the counterion, enhancing the overall stability of the system. This has been validated through X-ray crystallography of the reactant structures and is in direct agreement with previous analyses of these phosphido-borane complexes in THF and other electron-donating solvents.[10,12] However, while inclusion of these stabilization effects is necessary for understanding the system, they are minimal in their effect on CO_2 capture. The additional stability provided by the THF groups only increases Δ*G* of CO_2 binding by 3.0 kcal/mol. This has been elucidated in comparing CO_2 binding in $[(Ph)_2PBH_3]$ using DFT. This is shown in Figure 4.

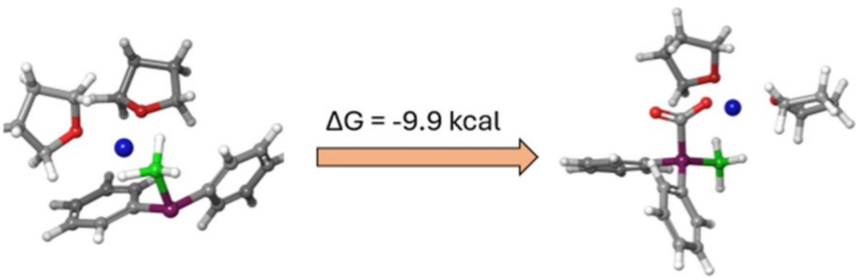

Figure 4. Explicit solvation of the $[(Ph)_2PBH_3]$ phosphido-borane. Explicit solvation increases overall Δ*G* by +2.9 kcal/mol, but it is still bound by 9.9 kcal/mol.

In regard to the effect of the counterion on CO_2 stability, while the charge of the Li^+ counterion remains unchanged in compounds 1 through 5, Li^+ polarizes the oxygens of the CO_2 unit in the product, slightly disrupting otherwise perfect resonance among both O atoms of the CO_2-bound complex.

The pK_a of the phosphido-borane conjugate acid is correlated to the binding affinity of CO_2 to the central phosphorus, with higher pK_a values indicating a greater Lewis basicity and hence greater reactivity to the Lewis acidity of the CO_2. This can be seen in differences between phosphines 1, 2, and 3, with pK_a = 23, and 4, with pK_a = 17. The relative acidity of the $H\text{-}P^+R_2BH_3^-$ complex compared to the naked $H\text{-}PPh_2$ requires only a mild base to form the active lone pair site on the phosphorus. Here, the borane moiety increases the acidity of the hydrogen on the $H\text{-}P^+R_2BH_3^-$ zwitterionic complex acting as a source of electron charge upon CO_2 binding, effectively making Δ*G* less negative and increasing synthetic ease.

Along with the correlation of the O−C−O bond angle with Δ*G* values, the zwitterion character changes. While no conclusions can be made about the correlation between zwitterionic character and the thermodynamic driving force of CO_2 binding, zwitterion formation may provide insight as to the mechanism of binding and the origin of such high Δ*G* values. The BH_3^- group present in each BoPh complex acts as a source of electron density upon CO_2 binding, with the Lewis basicity of each P atom increasing upon binding due to the donation of charge from the BH_3^- moiety. Replacing the BH_3^- moiety with the −R group ligand decreases the Δ*G* values for all tested species. Replacing BH_3^- with −Ph, as shown for 6, increased Δ*G* of CO_2 binding significantly, to the point where CO_2 binding was no longer favorable.

For comparison, we also computed CO_2 binding strengths in the presence of a Na^+ counterion. Reactant and product structures along with their respective CO_2 binding energies are depicted in Figure S1 of the Supporting Information.

Na^+ is a softer ion than Li^+ in terms of its cationic character. As a result, charge stabilization in the Na^+ product complex is not as pronounced as for the Li^+ case. Lack of stabilization in the product conformer reduces the stability of the product complex, making Δ*G* less negative, as illustrated in Figure S1. Decreased charge stabilization in the product complex also increases the transition state barrier ($\Delta G^\ddagger$) for CO_2 binding. In both the Na- and Li-containing transition states, the counterion is positioned between the approaching CO_2 and the BH_3^- moiety of the phosphido-boranes. The counterion forms an ion pair with the negatively charged BH_3^- subunit, simultaneously accepting charge from the partially charged oxygens of the now-binding CO_2. In addition, the decreased polarization in the transition state reduces the overall energy of the system, reducing the large differences in polarization in the activated complex. Decreased charge polarization subsequently reduces the transition state energy and thus the overall activation barrier.

The transition state and binding free energies for $[(Ph)_2PBH_3]$ with Li^+ and Na^+ are depicted in Figure 5; here, the position of the counterion is of critical importance. In Figure 5, we observe that Li^+ coordinated to a CO_2 oxygen and the hydrides of the BH_3^- reduces $\Delta G^\ddagger$ by ∼2 kcal/mol relative to Na^+. The overall CO_2 binding $\Delta G^\ddagger$ values for the Li^+- and Na^+-containing phosphido-boranes are +2.43 and +4.43 kcal/ mol, respectively. The $\Delta G^\ddagger$ values of CO_2 binding for the parent Li-PPh_2 and Na-PPh_2 which lack the borane are +0.7 and +1.5 kcal/mol, respectively.

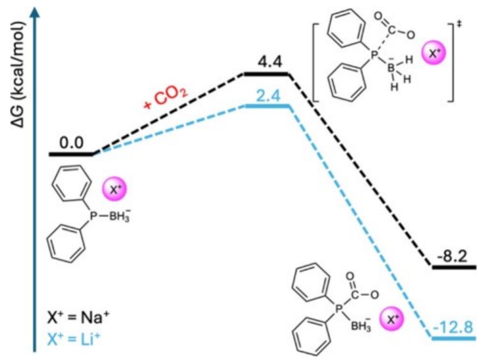

Figure 5. DFT-predicted binding and transition state energies at 300 K for the Li and Na-containing diphenylphosphido-boranes in THF solvent. The pink X^+ indicates the counterion. The blue and black paths indicate the potential energy surfaces for Li^+ and Na^+, respectively.

While direct pathways of CO_2 binding are almost instantaneous, competing BH_3 transfer reactions must also be considered. BH_3^- transfer from THF-BH_3 to PPh_2BH_3 for the formation of $Na^+PPh_2(BH_3)_2$ is unfavorable in comparison to CO_2 binding, with a $\Delta G^\ddagger$ of +9.6 kcal/mol. Formation of $Na^+PPh_2BH_3^-$ via BH_3 transfer from BH_3THF to $Na^+PPh_2^-$ in the absence of CO_2 occurs with a barrier of +10.9 kcal/mol; this reaction occurs instantaneously in experiment (see below).

In addition to Na^+ and Li^+, PPh_4^+ was also used as a counterion in our experiments. Because of the bulky and rigid nature of PPh_4^+, CO_2 was unable to bind to the phosphidoboranes complex, with PPh_4^+ forming a salt complex with the reactant phosphine instead. This, alongside Figure 1 and Tables 1 and S1, highlights the significance of the counterion in binding. To separately control the transition barrier and adsorption energy, alterations to the counterion and the system can be done separately to alter one or the other. As shown in the figure, substituting Li^+ for Na^+ increases Δ*G* of adsorption while only slightly increasing the transition state barrier. This decreases the stability of the product complex without necessarily affecting the transition state barrier significantly. Similarly, if one were to use a sterically hindered counterion, such as a quaternary carbon or nitrogen, one could raise the transition state barrier while keeping the binding energy unchanged. The phosphorus would be unavailable to attack the Lewis acidic CO_2, and thus, the activation energy would increase without necessarily altering the binding energy if an equivalently stabilizing counterion were to be used. Adjusting either the ligand or the counterion in regard to steric control and counterion alterations could selectively adjust either the transition state barrier or the adsorption energy, respectively. To shed further insight on the role of the

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counterion and electron-donating and electron-withdrawing groups in CO_2 binding, we examined additional phosphine complexes with other donating and withdrawing ligands, as shown in Figure 3 and Table 2.

- $(CH_3O)_2PBH_3$ (Figure 6, 1) contains two $-CH_2OH$ units, which should operate as weak electron-withdrawing groups. The position of the oxygen atoms in the methoxy groups stabilize the counterion, decreasing CO_2 binding.
- F_2PBH_3 (Figure 6, 2) has two −F groups. The F explores the effects of an inductive electron-withdrawing group. The −F R-group withdraws electron density away from the nucleophilic phosphorus atom. This makes Δ*G* significantly less negative.
- $(F_5C_6)_2PBH_3$ (Figure 6, 3) has two $-C_6F_5$ groups, acting as electron-withdrawing aryl groups, again removing charge from the P and leading to much less favorable Δ*G*.
- $(TMG)_2PBH_3$ (Figure 6, 4) contains the phosphidoBorane anion ($P-BH_3^-$) accompanied by two monodentate tetramethyl guanidium (TMG) ligands bound to the central P. TMG is used here because we previously found that $P(TMG)_3$[15] had a very exergonic CO_2 binding strength (−13.5 kcal/mol); however, here Δ*G* = −7.4 kcal/mol.
- $[(H_3C)_2N]_2PBH_3$ (Figure 6, 5) contains two $-N(CH_3)_2$ ligands which act as electron-donating groups to the nucleophilic phosphorus, leading to Δ*G* = −14.3 kcal/mol.

As found in the alkyl BoPh's, Δ*G* is correlated to Δ*Q* on P. Cases with the more negative Δ*G* have larger Δ*Q* values, regardless of whether the ligand type present is electrondonating or electron-withdrawing. However, electron-donating groups on the phosphine did yield lower Δ*G* values than electron-withdrawing groups, highlighting the significance of ligand choice in BoPh synthesis. Higher negative charge on the CO_2 moiety is correlated with a lower Δ*G*. Interestingly, smaller values of Δ*Q* on BH_3^- are correlated with lower Δ*G* values. $(F_5C_6)_2PBH_3$, with two electron-withdrawing C_6F_5 groups, exhibits a large change in Δ*Q* upon CO_2 binding. Contrasted with $[(H_3C)_2N]_2PBH_3$ containing two electrondonating $-N(CH_3)_2$, Δ*Q* on BH_3^- in $(F_5C_6)_2PBH_3$ was significantly higher, by +0.08. This trend is not observed in the alkyl and aryl BoPh's, indicating that electron-donating and electron-withdrawing ligand groups drastically impact the ability of BH_3^- to donate charge and stabilize the +1 charge on phosphorus. Δ*Q* is the change in the charge on the phosphorus and $-BH_3$ moieties, upon formation of the (+1) tetravalent phosphorus upon binding of the CO_2. A higher Δ*Q* is indicative of the relative nucleophilicity of the phosphorus in context of a potent Lewis acid such as CO_2. In the case of CO_2 binding, if Δ*Q* is larger, then the reactant is very nucleophilic and is able to bind CO_2 easier as compared to compounds where Δ*Q* is far smaller. For BH_3, upon binding CO_2, charge is

Table 1. Properties of Various BoPh's[a]

Phosphido-borane	Δ*G* of CO_2 binding	Δ*Q* on P	Δ*Q* on BH_3^-	CO_2 Charge	Change in P−B Bond Order	P−C Bond Order
$[(CH_3)_2PBH_3]$	−23.1	+0.73	+0.088	−0.992	−0.067	+0.82
$[(CH_3CH_2)_2PBH_3]$	−24.0	+0.74	+0.086	−0.970	−0.074	+0.81
$[(Butyl)_2PBH_3]$	−19.0	+0.72	+0.082	−0.987	−0.079	+0.84
$[(Ph)_2PBH_3]$	−12.8	+0.57	+0.082	−0.942	−0.061	+0.84

[a]For the case of a Li^+ counterion in THF. CO_2 binding free energy (kcal/mol), charges on the P atom and BH_3^- moiety in both reactant and product complexes, O−C−O bond angle after binding, and P−B and P−C bond orders (BO) and bond lengths (Å).

Table 2. Binding Energy of CO_2 Binding and Respective Charges on the P Atom and BH_3^- Moiety or the Li^+ Counterion in THF in Both Reactant and Product Complexes P−B and P−C Bond Orders[a]

Phosphido-borane	Δ*G* of CO_2 binding	Δ*Q* on P	Δ*Q* on BH_3^-	CO_2 Charge	Change in P−B Bond Order	P−C Bond Order
$(CH_3O)_2PBH_3$	−7.6	+0.74	+0.06	−1.03	−0.09	+0.78
F_2PBH_3	−1.3	+0.65	+0.02	−0.96	−0.11	+0.82
$(F_5C_6)_2PBH_3$	−0.4	+0.49	+0.11	−0.85	−0.07	+0.84
$(TMG)_2PBH_3$	−7.4	+0.78	+0.01	−1.09	−0.02	+0.73
$[(H_3C)_2N]_2PBH_3$	−14.3	+0.77	+0.03	−1.03	−0.05	+0.78

[a] Δ*G* of CO_2 binding and Δ*Q*'s are shown here as well. The

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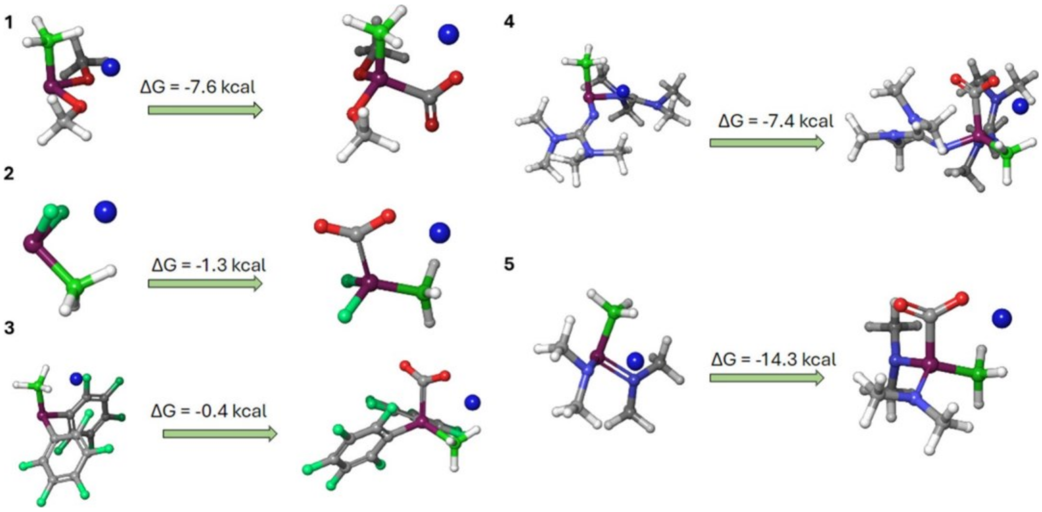

Figure 6. DFT-predicted CO_2 binding energies (kcal/mol) in THF solvent with Li counterions for various BoPh's. Here P is purple, B is green, C is gray, H is white, Li is dark blue, N is light blue, O is red, and F is turquoise.

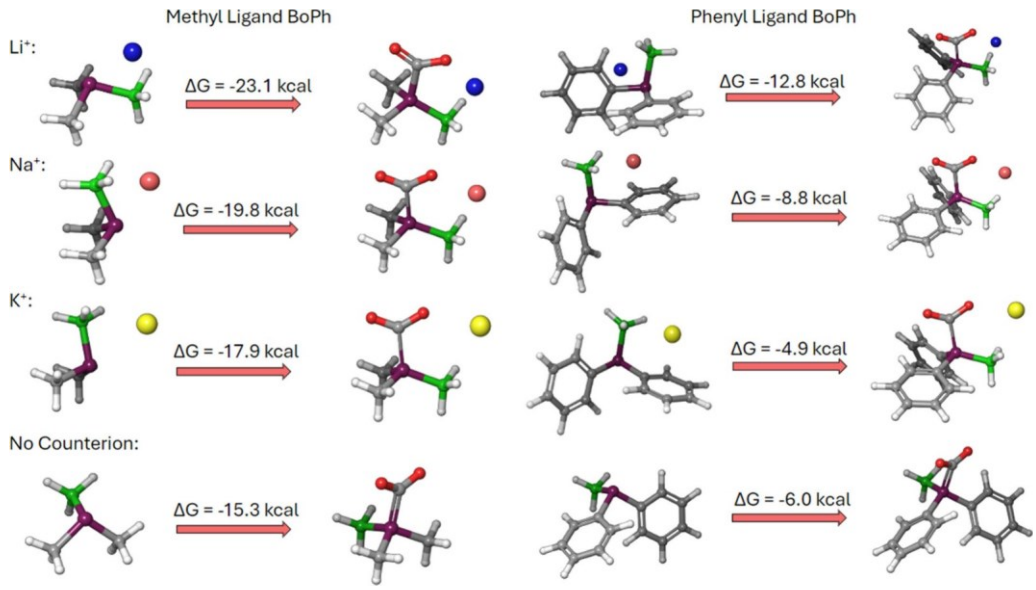

Figure 7. DFT-predicted CO_2 binding energies (kcal/mol) in THF solvent with methyl and phenyl BoPh's with no counterion, and with Li^+, Na^+, and K^+. Here P is purple, B is green, C is gray, H is white, Li is dark blue, Na is pink, K is yellow, and O is red.

donated from the BH_3 to the P−C bond. This increases Δ*G* and is what is responsible for the incredibly high Δ*G* values shown here.

Electron-donating groups increase the nucleophilicity and electron density on the phosphorus, increasing its ability of nucleophilic attack on the electrophilic carbon center of CO_2. This then decreases Δ*G*. Electron-withdrawing groups decrease the electron density at phosphorus and hence its nucleophilicity. This then decreases the magnitude of Δ*Q* on P, resulting in smaller overall change in electron density between product and reactant structures. In addition to charge density, there is a correlation between bond order and Δ*G*. BoPh's with little to no difference in reactant and product P−B bond orders have more negative Δ*G* values, as opposed to BoPh's with larger differences in P−B bond orders. The resulting difference between the product and reactant conformers is also responsible for increased Δ*G* values. As a result of the increased stability of the Li^+ counterion in the $(TMG)_2PBH_3$ complex from the nitrogens, the reactant complex is more stable than it otherwise would be without the nitrogens. This then decreases overall reactivity and increases Δ*G*.

The counterion stabilizes effective charge buildup in both the product and transition state, resulting in more negative overall Δ*G* values. Furthermore, changes in the relative size of the counterion drastically affect Δ*G*, as shown for the Li^+, Na^+, and K^+ cases in Figure 7. As shown below, increasing counterion size increases ΔG of binding.

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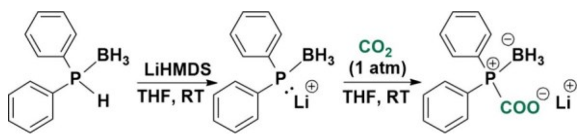
The counterion stabilizes charge in the product and transition state, making ΔG more negative. Here, we see that due to the larger size of Na^+, it is unable to stabilize charge as well as Li^+. This is also seen for K^+. In addition, for the no counterion cases with methyl and phenyl R-groups, there is no stabilization of charge in the entire anionic complex, with ΔG hence being the most positive. Between Li^+ and the cases with no counterion, we see a large difference in ΔG. Thus, between the methyl and phenyl cases, ΔG increases by an average of +7.3 kcal.

Experiments. Very few studies have been published on phosphine-based systems that bind CO_2.[16−18] These systems either exhibit very strong basicity or create electron density on the P atom, making it electron-rich. For instance, the work of Buß et al. showcases electron-rich phosphines that bind CO_2, where their most stable adducts or best phosphines have predicted pK_a value of ∼33.7 and free binding energy at room temperature of −10.3 kcal/mol.[16] In contrast, our BoPh's have predicted binding free energies up to 23 kcal/mol with pK_a as low as 17. To validate our computational studies, we synthesized the anionic diphenylphosphido-borane, 4, since it had the lowest pK_a and a good binding energy (Scheme 1).

Scheme 1



First we synthesized the diphenylphosphine Li[Ph_2PBH_3] borane complex by following the synthetic route described by Stankevic et al.[19] Here 0.2218 g of the resulting phosphidoborane was dissolved in 3 mL of tetrahydrofuran (THF) in a 10 mL valve. Here 2 mL of THF was used to dissolve 0.1856 g of lithium bis(trimethylsilyl)amide (LiHMDS). The solution of LiHMDS was added dropwise to the solution of

Li[Ph_2PBH_3] to minimize side reactions. An aliquot of the resulting solution was taken to confirm the structure using NMR spectroscopy with the results in Figure 8b, confirming complete deprotonation Li[Ph_2PBH_3] to form Li[Ph_2PBH_3] salt. We then bubbled CO_2 gas through lithiated anionic phosphido-borane salt at 1 atm and room temperature for about 10 min to saturate it with CO_2. NMR analysis on an aliquot of the sample revealed formation of P-CO_2 adducts as shown in Figure 8c. For confirmation of the predicted pK_a of the P Li[Ph_2PBH_3], we used lithium tertbutoxide to deprotonate the Li[Ph_2PBH_3] in butanol which resulted in the lithiated anionic phosphido-borane salt. This leads to a pK_a of 19.2, in good agreement with the predicted pK_a of 21.3 for

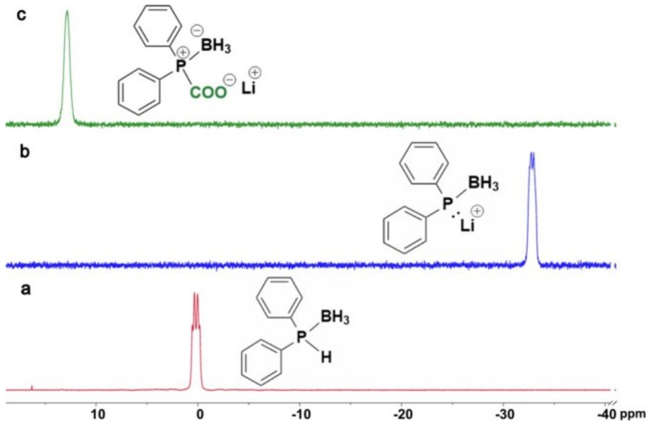


Figure 8. (a) ^{31}P NMR of Li[Ph_2PBH_3] (red spectrum) (162 MHz, THF-d_8) δ 1.16 to −0.79 (m). (b) ^{31}P NMR of $LiPh_2PBH_3$ (blue spectrum), (162 MHz, THF-d_8) δ −32.87 (d, J = 60.7 Hz). (c) ^{31}P NMR of $LiPh_2PBH_3$−CO_2 (green spectrum) (162 MHz, THF-d_8) δ 12.86.

lithium tert-butoxide, which is consistent with the lower pK_a of 17 for Ph_2BoPh.

Figure 8 shows the ^{31}P NMR resonance spectra of Ph_2BoPh (Figure 8a), Li[Ph_2PBH_3] salt (Figure 8b), and the Li[Ph_2PBH_3]−CO_2 adduct (Figure 8c). The spectra in Figure 8a,b show a quartet resonance signal due to ^{31}P−^{11}B coupling. The upfield chemical shift from 0.19 ppm to −32.87 ppm indicates successful deprotonation of the phosphido-borane complex to form its lithiated salt. This upfield shift is expected as a result of the shielding effect of the lone pair on the phosphorus atom, which is very much in accordance with the works by Jaska et al.[20] The downfield chemical shift from −32.87 ppm to 12.86 ppm in Figure 8c due to the CO_2 molecule bound to the phosphorus atom results from deshielding of the phosphorus nuclei by the Lewis acid, which in this case is the CO_2 gas molecule. The broad characteristic peak feature of the ^{31}P NMR of the Li[Ph_2PBH_3]−CO_2 adduct is likely the result of an exchanging of the CO_2 from one phosphorus atom to another.

Figures 9 and 10 depict the ^{1}H and ^{13}C NMR of the Ph_2PHBH_3 (red spectrum), $LiPh_2PBH_3$ (blue), and $LiPh_2PBH_3$−CO_2 (green spectrum) respectively. The disappearance of the P−H bond at 6.83 and 5.88 ppm in Figure 8 (blue spectrum) shows the complete formation of $LiPh_2PBH_3$ which serves as the nucleophilic material that reacts with CO_2 to form the $LiPh_2PBH_3$−CO_2 (green spectrum). As shown in Figure 8 (green spectrum), the P atom does not steal any H from the BH_3 unit but rather binds successfully with the CO_2 molecule to form the adduct. This is further confirmed by the ^{13}C NMR in Figure 10 (green spectrum), where the appearance of the signals at 172.95

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and 172.11 ppm shows the coupling of the P atom to the CO_2 molecule from the
$LiPh_2PBH_3$–CO_2 complex.

In conclusion, ithis work, we propose novel, easily synthesized borane-phosphines for CO_2 capture and sequestration. Along with extremely favorable ΔG values of −13 to −23 kcal/mol for CO_2 binding, only mildly basic conditions are needed for reduction and subsequent deprotonation of Li[Ph_2PBH_3]. This, along with the inexpensive reagents needed for their synthesis, makes use of these BoPh's for CO_2 sequestration very appealing.

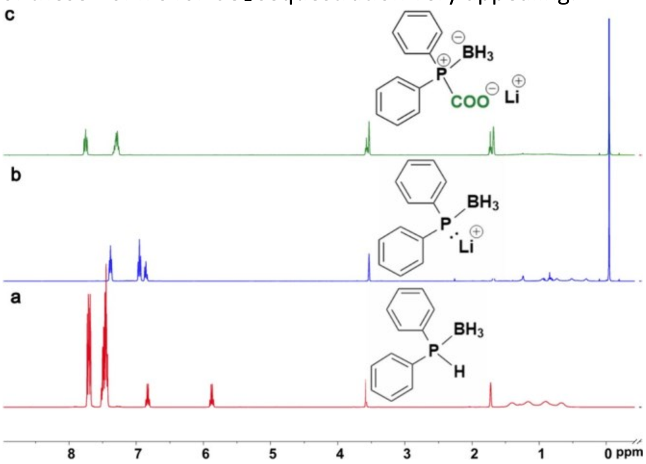

Figure 9. ^{1}H NMR of (a) Ph_2PHBH_3 (red), (b) $LiPh_2PBH_3$(blue), and (c) $LiPh_2PBH_3$–CO_2(green). (a)^{1}H NMR of Ph_2PHBH_3(red spectrum) (400 MHz, THF-d_8) δ 7.75–7.65 (m, 5H), 7.53–7.40 (m, 7H), 6.83 (q, J = 7.1 Hz, 1H), 5.88 (q, J = 7.1 Hz, 1H), 1.04 (dd, J = 199.4, 94.5 Hz, 4H). (b)^{1}H NMR of $LiPh_2PBH_3$ (blue spectrum) (400 MHz, THF-d_8) δ 7.43 (ddd, J = 8.0, 6.1, 1.5 Hz, 5H), 7.00 (td, J = 7.2, 1.3 Hz, 5H), 6.93–6.85 (m, 2H), 0.67 (dd, J = 174.9, 86.6 Hz, 5H). (c)^{1}H NMR of $LiPh_2PBH_3$–CO_2 (green spectrum) (400 MHz, THF-d_8) δ 7.80 (ddt, J = 9.9, 6.7, 1.6 Hz, 5H), 7.41–7.28 (m, 7H), 1.42–0.60 (m, 4H).

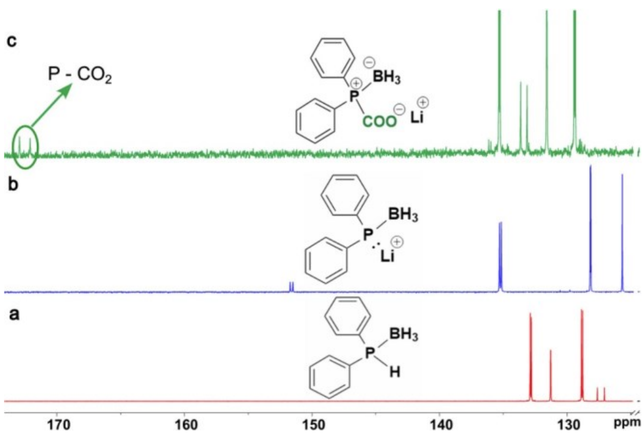

Figure 10. ^{13}C NMR of (a) Ph_2PHBH_3 (red), (b) $LiPh_2PBH_3$(blue), and (c) $LiPh_2PBH_3$–CO_2(green). (a)^{13}C NMR of Ph_2PHBH_3 (red spectrum) (101 MHz, THF-d_8) δ 132.88, 132.79, 131.29, 131.27, 128.87, 128.76, 66.22, 66.00, 24.15, 23.95. (b) ^{13}C NMR of $LiPh_2PBH_3$ (blue) (101 MHz, THF-d_8) δ 135.32, 135.17, 128.21, 128.16, 125.68, 68.87, 68.73, 68.51, 26.73, 26.61, 26.53, 26.41, 26.33. (c) ^{13}C NMR of $LiPh_2PBH_3$–CO_2 (green spectrum) (101 MHz, THF-d_8) δ 172.95, 172.11, 135.36, 135.28, 131.62, 131.60, 129.47, 129.37, 68.86, 68.73, 68.64, 68.51, 26.74, 26.61, 26.54, 26.41, 26.33.

Counterion effects also play a significant role in binding, with Li^+ encouraging stronger CO_2 binding compared to Na^+ and K^+.

In the context of these highly polarized phosphido-borane species, the cationic counterion provides charge stabilization for the product, increasing the magnitude of the negative ΔG. Based on the large negative magnitude of the ΔG values predicted, experimental studies in CO_2 activation to form hydrocarbon products from these phosphido-boranes are warranted.

COMPUTATIONAL METHODS

All density functional theory calculations were performed using the Jaguar v10.9 software from Schrodinger Inc. All calculations utilized the M06-2X meta-GGA functional with the D3 empirical correction for London dispersion forces.[21,22] All atoms were described by the 6-311G**++ Pople basis set,[23] augmented with polarization and diffuse functions.

All calculations included a continuum solvent treatment described by the Polarizable Continuum Model (CPCM).[24]

Unless otherwise noted, we used solvent parameters matching tetrahydrofuran (dielectric constant = 7.6, probe radius = 2.52).

Vibrational frequency calculations were performed to confirm that all geometries are true minima (no negative eigenmodes of the Hessian) and to compute thermochemical properties such as enthalpy (H), entropy (S), and free energies (G) at 298.15 K. Because librational modes are hindered in solvent media, we corrected our free energies by reducing translational and rotational entropy modes by 50%.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.4c02484.

Figure S1: DFT-predicted binding energies at 300 K in THF solvent with Na counterions; Table S1: For the Na^+ counterion in THF–Binding energies of CO_2 binding and respective charges on the P atom and BH_3^- moiety in both reactant and product complexes (P–B and P–C bond orders are also displayed); Figure

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S2: Thermogravimetric analysis of $LiPh_2PBH_3-CO_2$ adducts computationally predicted NMR shifts using GIAO of $X[PPh_2BH_3]$ reactant and product complexes coordinate geometries of all DFT-computed geometries
(PDF)

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Notes

The authors declare no competing financial interest.

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