

Catalytic Hydrogenation of Carbon Dioxide with Ammonia–Borane by Pincer-Type Phosphorus Compounds: Theoretical Prediction

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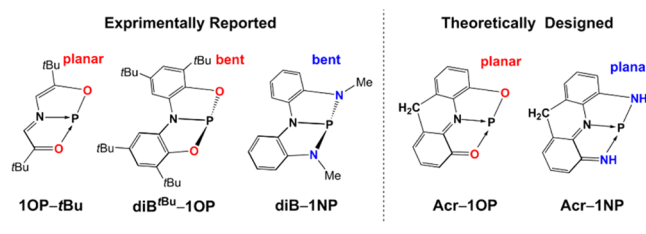
S Supporting Information

ABSTRACT: Two theoretically designed and one experimentally reported pincer-type phosphorus compounds are found to be active for the hydrogenation of carbon dioxide with ammonia–borane. DFT, ONIOM(CCSD-(T):MP2), and CCSD(T) computational results demonstrated that the reaction occurs through phosphorus–ligand cooperative catalysis, which provides an unprecedented protocol for metal-free CO₂ conversion. The phosphorus compounds with the NNN ligand are more active than those with the ONO ligand. The planar conjugate ligand considerably improves the efficiency of the catalyst.

The chemical conversion of carbon dioxide to value-added chemicals and renewable energy is an appealing strategy to address both the greenhouse effect and energy crisis issues. However, CO₂ conversion is challenging due to the inherent thermodynamic and kinetic stabilities of CO₂. Therefore, the process is usually associated with precious-metal catalysts, for which the toxicity of the catalyst brings new environmental issues.¹ In this regard, photocatalytic² and electrocatalytic³ reductions of CO₂, which are friendly to environment, have experienced a robust development in the past few decades. In recent years, the use of main-group element compounds, which are abundant, cheap, and green, in CO₂ conversion has started to emerge. For instance, several Frustrated Lewis Pairs (FLPs) have been applied to the conversion of CO₂ to CH₃OH,⁴ CH₄,⁵ and CO.⁶ A series of N-heterocyclic carbenes and ethynyl dithiocarbamate species have also been reported for CO₂ conversion and/or activation.⁷ However, the catalytic transformation of CO₂ by main-group element compounds is still in its infancy, with limited catalysts. Hence, developing new metal-free catalysts for CO₂ transformation is essential for the utilization of CO₂ in an environmentally friendly manner.

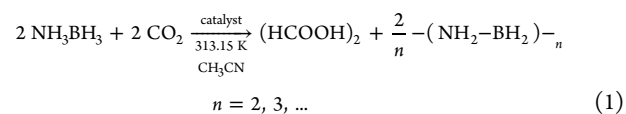
In 2012, a pincer-type phosphorus compound, **1OP-*t*Bu**⁸ (Chart 1), was found to be active for the transfer hydrogenation of azobenzene with ammonia–borane (NH₃BH₃).⁹ The mechanistic study showed that this reaction occurs through phosphorus–ligand cooperative catalysis,¹⁰ which resembles metal–ligand cooperative catalysis that is powerful in chemical transformations by transition-metal complexes. Since then, several other pincer-type phosphorus catalysts have been experimentally reported, which are capable of activations of small molecules (H₂O and NH₃).¹¹ These results suggest that pincer-type phosphorus compounds offer a new and promising

Chart 1. Phosphorus Catalysts Investigated in This Work



way to achieve metal-free cooperative catalysis, as an alternative to the use of FLPs. It is of great interest to apply pincer-type phosphorus compounds to the transformation of CO₂, which may provide a new protocol for CO₂ conversion. Note that a variety of pincer metal complexes have been employed in the CO₂ transformation reaction.¹²

Here, we report the first computational investigation on hydrogenation of CO₂ with NH₃BH₃ by pincer-type phosphorus compounds (Chart 1); see eq 1. The use of NH₃BH₃ as the hydrogen source is not unreasonable, because it has been employed in the hydrogenation of CO₂ by FLPs recently.^{4b,c}



Possible reaction pathways were first explored using the AFIR method¹³ implemented in the GRRM program,¹⁴ like in our previous study.¹⁰ Full geometry optimization was then carried out by the DFT method with the B3PW91 functional, considering the solvent effect of acetonitrile with the CPCM model.¹⁵ Each transition state was verified by IRC calculation.¹⁶ Electronic energies were evaluated by ONIOM(CCSD-(T):MP2)¹⁷ or CCSD(T).¹⁸ The Gibbs energy was calculated at 313.15 K like in the transfer hydrogenation of azobenzene catalyzed by **1OP-*t*Bu**.^{9a} These calculations were performed by Gaussian09;¹⁹ see the Supporting Information (SI) for computational details. Hereafter, the ligand moiety that coordinates with the phosphorus center is named ONO or NNN, depending on the coordinating atoms.

First, we investigated the CO₂ hydrogenation with NH₃BH₃ catalyzed by **1OP-*t*Bu**, **diB^{*t*Bu}-1OP**, and **Acr-1OP** (Chart 1), because these compounds were used experimentally and/or

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investigated theoretically in the transfer hydrogenation of azobenzene with NH_3BH_3 .¹⁰ Here, we employed the model compounds **1OP-Me** and **diB-1OP** in the calculations to save computational cost.²⁰ The dehydrogenation of NH_3BH_3 mediated by these compounds, producing an intermediate **4OP** (containing P–H and O–H bonds), has been investigated in previous works;^{10,21} this step is not discussed here. In this work, we focus on the hydrogenation of CO_2 with **4OP**; see **Figures 1** and **2**. The detailed geometry changes are shown in

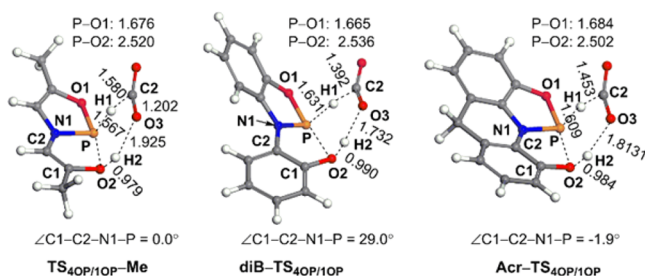


Figure 1. Geometries of transition states in the hydrogenation step of CO_2 by the phosphorus catalysts with the ONO ligand. Distances are in Å.

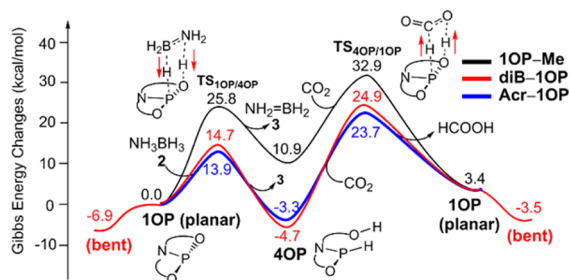


Figure 2. Gibbs energy (313.15 K) profiles of the hydrogenation reaction of CO_2 with NH_3BH_3 by **1OP-Me**, **diB-1OP**, and **Acr-1OP**.

Figures S1–S6 in the **SI**. As shown in **Figure 2**, the CO_2 hydrogenation occurs through phosphorus–ligand cooperative catalysis in a concerted manner. The Gibbs activation energies (ΔG^{\ddagger}) are 32.9, 31.8, and 27.0 kcal/mol for the hydrogenation

of CO_2 by **4OP-Me**, **diB-4OP**, and **Acr-4OP**, respectively (**Figure 2**). These results clearly show that theoretically designed **Acr-1OP** is more active than the experimentally reported **1OP-Me** and **diB-4OP** for the CO_2 hydrogenation with NH_3BH_3 . As shown in **Figure 2**, the CO_2 hydrogenation reaction (**eq 1**) is endothermic by 3.4 kcal/mol. However, it becomes exergonic by 7.2 kcal/mol when the dimerization energies of both $\text{NH}_2=\text{BH}_2$ (-7.0 kcal/mol calculated by CCSD(T)/BSII)²² and formic acid (-14.2 kcal/mol)²³ are considered, indicating that the reaction of **eq 1** is thermodynamically feasible. However, the ΔG^{\ddagger} value (27.0 kcal/mol) of the **Acr-1OP**-catalyzed reaction is not small. One reason for this high energy barrier is that both of the P–H and O–H bonds of **Acr-4OP** are cleaved in **Acr-TS_{4OP/1OP}**.

One can expect that if two bonds are not cleaved in one transition state but cleaved in a stepwise manner, the energy barrier would decrease. With this expectation, we employed **diB-1NP** (**Chart 1**) in the CO_2 hydrogenation with NH_3BH_3 , because the N–H bond of *N*-methylaniline is stronger than the O–H bond of phenol;²⁴ note that a large difference in bond energies between the P–H bond and the E–H bond (E = O or N) would be necessary for the stepwise reaction. Actually, the N–H bond energy (95.0 kcal/mol)²⁵ is much larger than the P–H bond (71.0 kcal/mol) in **diB-4NP**, whereas the O–H bond (84.1 kcal/mol)²⁵ is moderately larger in energy than the P–H bond (71.8 kcal/mol) in **diB-4OP**.

The most favorable pathway for the reaction catalyzed by **diB-1NP** is shown in **Figure 3**. First, the bent **diB-1NP** transforms to a planar **diB-1NP'**, which is 7.4 kcal/mol above **diB-1NP**. The dehydrogenation reaction of NH_3BH_3 by **diB-1NP'** then occurs through the cooperative function of the phosphorus center and the NNN ligand to produce **diB-4NP** (containing P–H and N–H bonds). The ΔG^{\ddagger} and reaction energy (ΔG°) of this step are 26.4 and -0.4 kcal/mol, respectively. Next, the hydrogenation of CO_2 by **diB-4NP** occurs in a stepwise pathway, as expected above. The hydride-like H1 migrates from the phosphorus center to the carbon atom (C4) of CO_2 through a transition state, **diB-TS_{4NP/5NP}**, to afford **diB-5NP**, which contains a formate interacting with the phosphorus center with a P–O bond (1.835 Å). The ΔG^{\ddagger} and ΔG° values of this step are 19.9 and -0.5 kcal/mol,

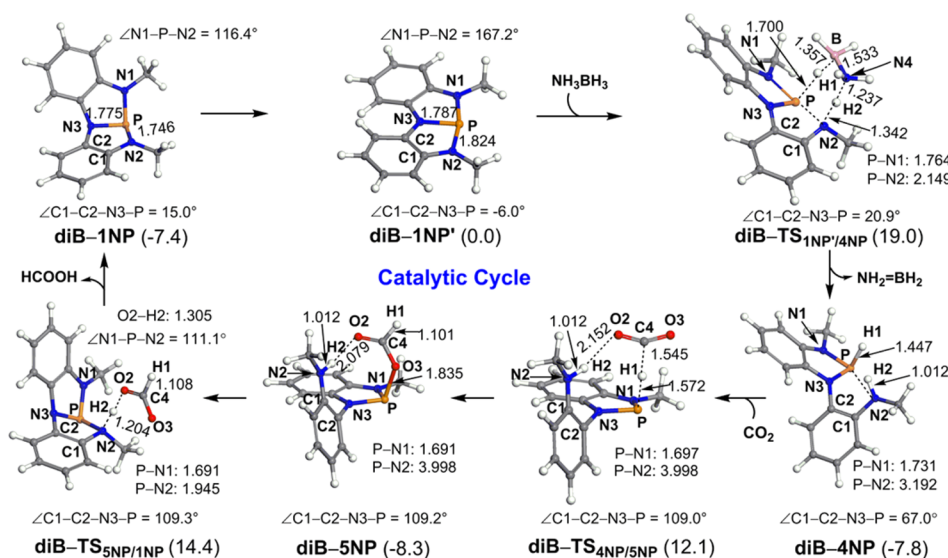
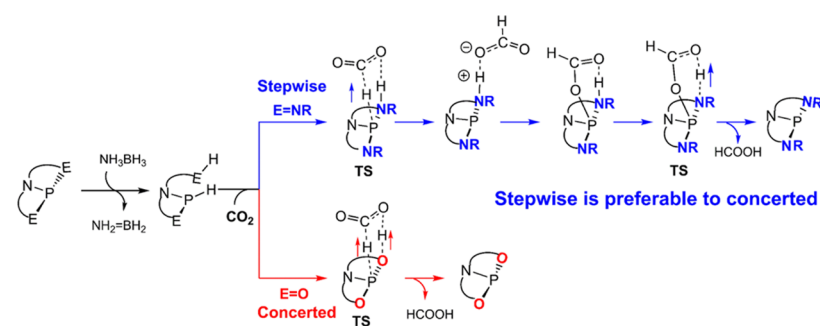


Figure 3. Geometry changes for the hydrogenation reaction of CO_2 with NH_3BH_3 by **diB-1NP**. Distances are in Å.

Scheme 1. Reaction Mechanism of the Transfer Hydrogenation of CO₂ with NH₃BH₃ by the Pincer-Type Phosphorus Compounds with the ONO and NNN Ligands

respectively. Finally, the proton-like H₂ is transferred from the coordinating N₂ atom of the NNN ligand to the formate group through a transition state, **diB-TS**_{5NP/1NP}, to afford formic acid and regenerate **diB-1NP**. The ΔG^{\ddagger} and ΔG° values of this step are 22.7 and 4.3 kcal/mol, respectively. Obviously, the ΔG^{\ddagger} value of the stepwise hydrogen transfer in the **diB-1NP**-catalyzed reaction is smaller than that (27.0 kcal/mol) of the concerted hydrogen transfer mediated by **Acr-1OP**; see Figures 2 and 4.

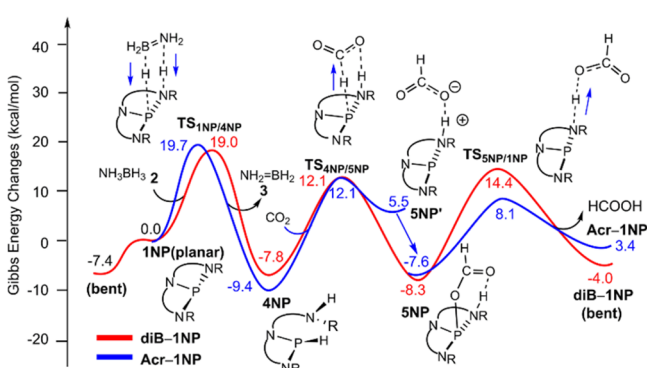


Figure 4. Gibbs energy (313.15 K) profiles of the hydrogenation reaction of CO₂ with NH₃BH₃ by **diB-1NP** and **Acr-1NP**.

Another possible reaction starting from **diB-4NP** is isomerization to dihydridophosphorane. However, this process is energetically unfavorable; see Figure S9 and discussion on page S16 in the SI.

According to the above discussion, **diB-1NP** is active for the CO₂ hydrogenation with NH₃BH₃ at 313.15 K in acetonitrile solution. The rate-determining step of this reaction is the dehydrogenation of NH₃BH₃, where the bent **diB-1NP** is a resting state and $\Delta G^{\ddagger} = 26.4$ kcal/mol relative to **diB-1NP** (Figure 4). If the planar **diB-1NP'** is taken as the energy reference, the rate-determining step shifts to the proton-transfer step, which has a much smaller $\Delta G^{\ddagger} = 22.7$ kcal/mol. One can expect that the planar ligand is favorable for the catalyst. Thus, compound **Acr-1NP**²⁶ was constructed by connecting the two phenyl groups in **diB-1NP** with a CH₂ linkage; see Chart 1.

As expected, **Acr-1NP** is planar, and the bent geometry was not located; see Figure S13 in the SI. The CO₂ reduction reaction catalyzed by **Acr-1NP** occurs through a pathway similar to that by **diB-1NP** (Figures S10–S14 in the SI).²⁷ As shown in Figure 4, the ΔG^{\ddagger} value for the dehydrogenation of NH₃BH₃ by **Acr-1NP** is 19.7 kcal/mol, which is much smaller than for the dehydrogenation of NH₃BH₃ by **diB-1NP**. The

hydride and proton then successively migrate from **Acr-4NP** to CO₂ to produce formic acid and regenerate the catalyst. It is noted that the hydride migration forms an unstable **Acr-5NP'** first, in which the formate interacts with the catalyst through a hydrogen bond. Next, **Acr-5NP'** transforms to a stable **Acr-5NP**, where the formate interacts with the phosphorus atom through a P–O bond (1.848 Å) like in **diB-5NP**. As shown in Figure 4, the hydride migration is the rate-determining step, where $\Delta G^{\ddagger} = 21.5$ kcal/mol. It is much smaller than the value $\Delta G^{\ddagger} = 26.4$ kcal/mol for the rate-determining step in the **diB-1NP**-catalyzed reaction. On the other hand, the isomerization of **Acr-4NP** to dihydridophosphorane has a larger energy barrier of 25.1 kcal/mol; see Figure S14 in the SI. All these results indicate that **Acr-1NP** is more active than **diB-1NP** for the CO₂ hydrogenation reaction with NH₃BH₃.

Because of the considerably smaller ΔG^{\ddagger} value for **Acr-TS**_{4NP/5NP} (rate-determining step) than for **Acr-TS**_{4OP/1OP}, **Acr-4NP** is much more active than **Acr-4OP**. Molecular orbital analysis²⁸ clearly shows that charge transfer (CT) from the HOMO of the phosphorus compound to the LUMO (π^* orbital) of CO₂ is crucial in both of these two transition states; see Scheme S1 in the SI. The significant difference in the CT arises from the fact that the HOMO (−4.57 eV) of **Acr-4NP** is at higher energy than that (−5.15 eV) of **Acr-4OP**. Therefore, CT stabilizes **Acr-TS**_{4NP/5NP} more than **Acr-TS**_{4OP/1OP}. This difference in HOMO energy comes from the larger electronegativity of the O-atom than the N-atom. This is one reason for high activity of **Acr-4NP**. In other words, the phosphorus compound which has the HOMO at a high energy is favorable for CO₂ hydrogenation.

In summary, several pincer-type phosphorus compounds were theoretically predicted to be active for the hydrogenation of CO₂ with NH₃BH₃. The reaction occurs through a phosphorus–ligand cooperation catalytic cycle; see Scheme 1. The phosphorus catalysts with the NNN ligand are more active than those with the ONO ligand, and **Acr-1NP** is the best catalyst theoretically designed here. The activity of the catalyst was greatly improved by introducing a planar conjugate ligand. These results clearly demonstrate that the pincer-type phosphorus compound is a promising new catalyst for the metal-free conversion of CO₂.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07274.

Additional comments and discussion of the findings in the manuscript, complete ref 19, and supplemental data as noted in the text (PDF)

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Notes

The authors declare no competing financial interest.

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