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# Sustainable hydrogen production *via* CO<sub>2</sub>-assisted BH<sub>3</sub> + BH<sub>3</sub> reaction: a computational analysis†

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The activation and utilization of carbon dioxide (CO<sub>2</sub>) for hydrogen production represents a central challenge in the development of sustainable and carbon-neutral energy systems. Borane (BH<sub>3</sub>), a potent Lewis acid with high reactivity toward small molecules, has emerged as a promising candidate for CO<sub>2</sub> activation and hydrogen release. However, the mechanistic effects of incorporating multiple CO<sub>2</sub> molecules into BH<sub>3</sub>-based systems remain poorly understood. In this study, density functional theory (DFT) calculations were conducted to explore the reaction mechanisms of a dimeric BH<sub>3</sub> system in the presence of zero to three CO<sub>2</sub> molecules. Potential energy surfaces were constructed at the M06-2X/6-311++G(3df,2p) level to identify key intermediates, transition states, reaction energies, and activation barriers. The computational results reveal a stepwise mechanism involving BH<sub>3</sub>-CO<sub>2</sub> adduct formation and distinct transition states, with CO<sub>2</sub> playing a significant role in modulating both thermodynamic stability and kinetic accessibility. Notably, the inclusion of CO<sub>2</sub> stabilizes multi-component complexes and lowers activation barriers, thereby facilitating hydrogen release. These findings underscore the dual function of CO<sub>2</sub> as both a structural stabilizer and an energetic facilitator, offering valuable insights into CO<sub>2</sub> valorization and hydrogen generation in the context of sustainable energy applications.

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## 1 Introduction

One of the key areas of interest in organoboron chemistry<sup>1</sup> is the reactivity of boron hydrides, especially the interaction of borane (BH<sub>3</sub>) and its derivatives with small molecules.<sup>2–4</sup> Borane, a strong Lewis acid,<sup>5</sup> readily participates in a variety of chemical transformations, including hydroboration,<sup>6</sup> coordination with Lewis bases, and activation of small molecules.<sup>7</sup> Among these, the reaction between borane and carbon dioxide (CO<sub>2</sub>)<sup>8,9</sup> has attracted considerable attention due to its potential implications in CO<sub>2</sub> fixation, catalysis, and hydrogen storage applications.<sup>10–16</sup> Borane-based reagents offer a promising strategy for CO<sub>2</sub> utilization through chemical-physical transformation. Borane, a strong electrophile, can react with CO<sub>2</sub> directly or in the presence of additional reactants, leading to various reduction and activation pathways.<sup>17</sup> However, a comprehensive mechanistic understanding of this reaction remains incomplete in some experimental and computational studies in some experimental and computational studies.<sup>9,10</sup> Theoretical methods, particularly density functional theory (DFT), are valuable tools for elucidating reaction mechanisms, providing insight into electronic structures, energy landscapes,

and dynamics of intermediate and transition states. The borane-CO<sub>2</sub> interaction involves initial adduct formation and subsequent structural rearrangements that determine the reaction pathway. Intermediate stability is influenced by electronic effects, solvation, and CO<sub>2</sub> stoichiometry. Experimental and computational studies show borane can reduce CO<sub>2</sub> under suitable conditions, yielding formate, carbonate, or methane derivatives, depending on the reaction environment and mechanism.<sup>10,17</sup>

A fundamental question regarding this reaction is why two borane molecules are required instead of a single BH<sub>3</sub> reacting with multiple CO<sub>2</sub> molecules. This requirement arises could be from several key factors: Although BH<sub>3</sub> is a strong Lewis acid, a single molecule has limited capacity to coordinate with multiple CO<sub>2</sub> molecules, whereas the presence of two BH<sub>3</sub> molecules enables more efficient cooperative activation of CO<sub>2</sub>. Additionally, the formation of multinuclear boron species plays a crucial role in stabilizing transition states and lowering reaction barriers, thereby facilitating CO<sub>2</sub> conversion. The interaction between two BH<sub>3</sub> molecules also increases the likelihood of forming cyclic of B-H atoms,<sup>18–20</sup> which are more stable. Furthermore, theoretical studies indicate that intermediates involving two BH<sub>3</sub> molecules exhibit higher stability due to boron-boron interactions,<sup>21,22</sup> leading to more favorable reaction pathways.

To effectively address these challenges, a comprehensive investigation into the electronic and structural changes

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occurring throughout the reaction is essential. In particular, the competition between a concerted single-step CO<sub>2</sub> insertion and stepwise, radical-mediated pathways highlights the need for in-depth theoretical analysis. Recent advancements in DFT methodologies offer a powerful framework for accurately predicting transition states, activation barriers, and the thermodynamic viability of proposed mechanisms. In this study, we utilize state-of-the-art computational techniques to systematically explore the borane–CO<sub>2</sub> reaction, with a focus on identifying key intermediates and transition states, as well as elucidating structure–reactivity relationships that underpin CO<sub>2</sub> activation. Furthermore, recent DFT-based investigations on boron hydride species such as BH<sub>4</sub><sup>−</sup> reacting with radical HO<sup>•</sup><sup>23</sup> provide valuable complementary insights into hydrogen evolution mechanisms and radical reactivity within boron chemistry.

To gain deeper insights into the electronic nature of the reaction, we incorporated quantum chemical analyses, such as the electron localization function (ELF) to examine the bonding characteristics of critical species, offering valuable insights into the electronic rearrangements governing the reaction. Additionally, potential energy surface (PES) calculations were performed to delineate viable reaction pathways and characterize transition states, providing a comprehensive picture of borane–CO<sub>2</sub> interactions at the molecular level.

Infrared (IR) spectral simulations were also conducted to compare theoretical vibrational frequencies with experimental data, aiding in the identification of reaction intermediates and key transition states.

Kinetic modeling complemented our mechanistic investigation by estimating reaction rate constants and activation parameters along the preferred reaction pathways. By integrating PES mapping with kinetic analysis, we constructed a detailed reaction model that accounts for both thermodynamic and kinetic considerations, ultimately providing a predictive framework for borane-mediated CO<sub>2</sub> activation. The findings of this study contributed to a more profound understanding of boron-based CO<sub>2</sub> transformation processes, paving the way for the rational design of boron-containing catalysts and reagents. A deeper comprehension of these fundamental reaction mechanisms facilitated the development of efficient CO<sub>2</sub> conversion strategies, thereby supporting broader efforts in sustainable carbon utilization. Furthermore, the insights gained from this research extended to other borane-mediated small molecule activations, expanding the scope of organoboron chemistry beyond traditional hydroboration and synthetic applications. The computational methodology employed in this work served as a valuable reference for future experimental validation and further advancements in borane–CO<sub>2</sub> chemistry.

## 2 Computational methods

All electronic structure calculations were carried out using the Gaussian 09 (ref. 24) suite of programs. The geometries of reactants, products, intermediates, and transition states involved in the reactions of BH<sub>3</sub> + BH<sub>3</sub> + *n*CO<sub>2</sub> (*n* = 0–3) were

optimized by employing the Minnesota functional (M06-2X) in combination with the 6-311++G(3df,2p) basis set.<sup>25</sup> This methodological framework enabled the precise optimization of BH<sub>3</sub> structure in the presence of CO<sub>2</sub>, providing valuable insights into molecular interactions and structural characteristics.

Subsequent to geometry optimization, a detailed vibrational frequency analysis was conducted to characterize each stationary point. These computed vibrational frequencies were instrumental in confirming the nature of stationary points and applying zero-point energy (ZPE) corrections. Such calculations were essential for evaluating the stability and energetic properties of molecular species, thereby deepening our comprehension of their fundamental behavior. For open-shell species, the restricted formalism (M06-2X) was adopted to ensure accuracy.

Transition states were located using the Synchronous Transit-Guided Quasi-Newton (STQN) methodology, specifically employing the Quadratic Synchronous Transit (QST2 & QST3) approach when necessary. To validate the connectivity between transition states and their respective reactants and products, intrinsic reaction coordinate (IRC) analyses were performed.

The influence of CO<sub>2</sub> was systematically explored by progressively varying the number of CO<sub>2</sub> molecules (*n* = 0–3) within the system. For each configuration, geometry optimization, vibrational analysis, and electronic energy calculations were performed to evaluate the influence of CO<sub>2</sub> on reaction mechanisms, energy barriers, and product distribution. The Electron Localization Function (ELF)<sup>26</sup> approach was employed to determine the localization of excess electrons by partitioning the total electron density into distinct basins. Complementary to ELF analysis, the Atoms-in-Molecule (AIM) framework<sup>27</sup> utilized to investigate electron density distribution, with both analyses were conducted using the Multiwfn program.<sup>28</sup>

A crucial aspect of this study was the determination of the rate constant (*k*), which serves as a key parameter in quantifying reaction kinetics. Using transition state theory (TST) under standard conditions (1 M concentration at 298.15 K), rate constants were computed *via* eqn (1).<sup>29–36</sup> All kinetic parameters were estimated in the gas phase using conventional TST, incorporating the partition functions of the reactants (BH<sub>3</sub>, BH<sub>3</sub>, CO<sub>2</sub>) and transition states. The ChemRate software<sup>37</sup> was employed for all kinetic calculations.

$$k = \sigma \kappa \frac{k_B T}{h} e^{-\frac{(\Delta G^\ddagger)}{RT}} \quad (1)$$

In this expression,  $\sigma$  denotes the reaction symmetry number,<sup>38,39</sup> while  $\kappa$  accounts for tunneling corrections,<sup>40</sup> determined using the Eckart barrier. The constants  $k_B$  and  $h$  correspond to the Boltzmann and Planck constants, respectively, whereas,  $\Delta G^\ddagger$  represents the Gibbs free energy of activation.

## 3 Results and discussions

### 3.1 Gas-phase hydrogen release: the BH<sub>3</sub> + BH<sub>3</sub> → BH<sub>2</sub>BH<sub>2</sub> + H<sub>2</sub> reaction

The BH<sub>3</sub> + BH<sub>3</sub> dehydrogenation mechanism was re-examined using M06-2X/6-311++G(3df,2p), with a focus on benchmarking against existing literature.



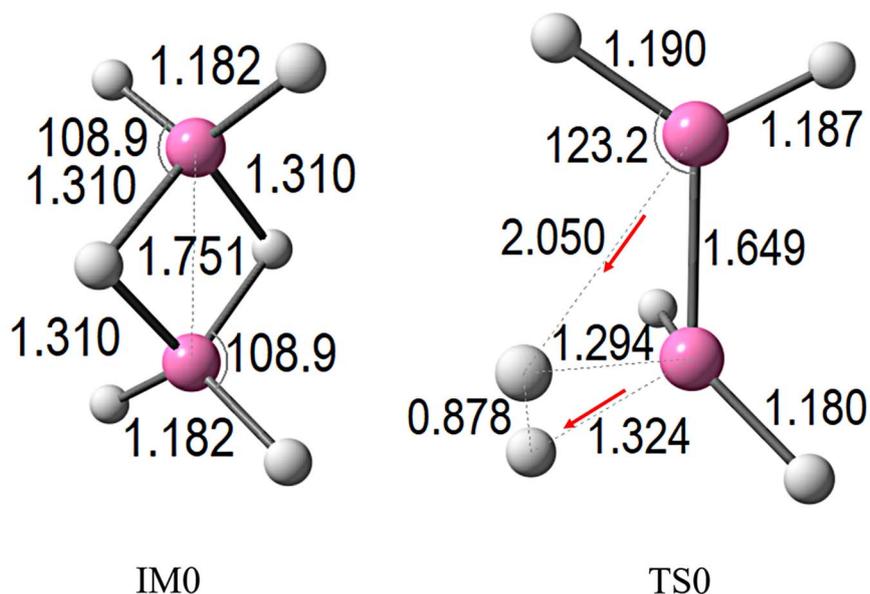


Fig. 1 Presents the optimized geometries of all species participating in the  $\text{BH}_3 + \text{BH}_3$  reaction in the gas phase, including selected bond lengths (in Å) and bond angles (in degrees), obtained at the M06-2X/6-311++G(3df,2p) level of theory.

In the initial stage,  $\text{BH}_3$  interacts with  $\text{BH}_3$ , leading to the formation of an intermediate complex, designated as IM0. This species subsequently progresses to a transition state, TS0, which corresponds to the highest energy point along the reaction coordinate, where hydrogen dissociation is actively occurring. The optimized structures of IM0 and TS0, along with key

geometric parameters, are illustrated in Fig. 1. The corresponding relative energies, referenced to the isolated reactants, are depicted in the potential energy surface shown in Fig. 2 (green curve, where  $n = 0$  denotes the absence of  $\text{CO}_2$  molecules).

The interaction between two  $\text{BH}_3$  molecules leads to the formation of diborane(6) ( $\text{B}_2\text{H}_6$ ). Structural parameters shown

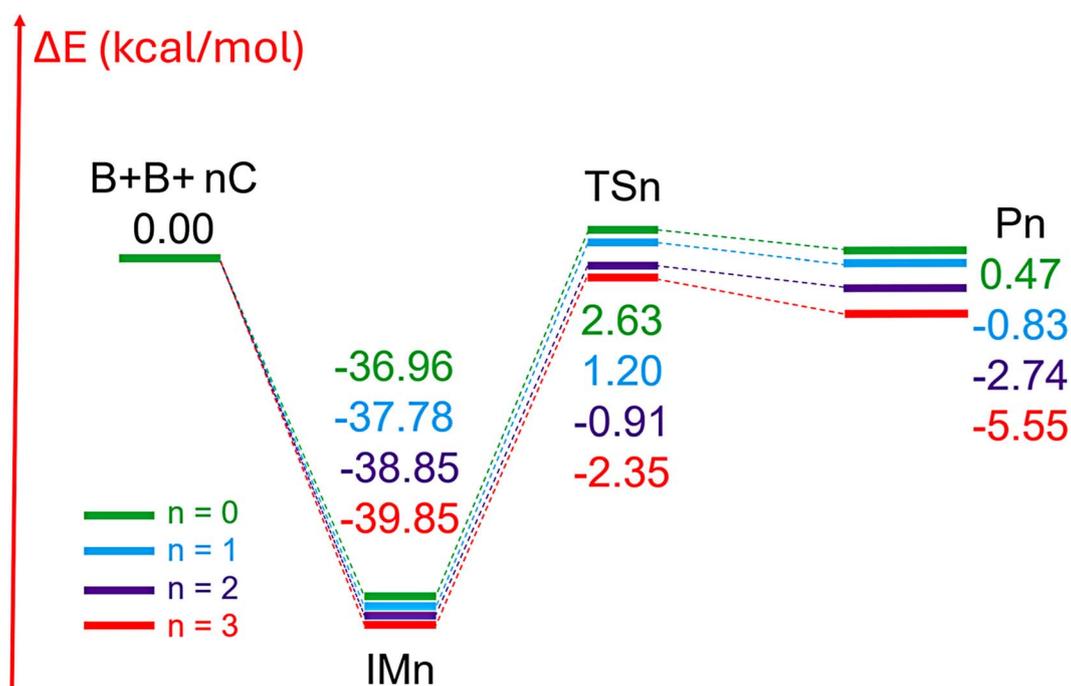


Fig. 2 The reaction energy profile for  $\text{BH}_3 + \text{BH}_3 + n\text{CO}_2$  (denoted as  $\text{B} + \text{B} + n\text{C}$ ) in the gas phase, presented as relative electronic energies ( $\Delta E + \text{ZPE}$ ) in  $\text{kcal mol}^{-1}$ , computed at the M06-2X/6-311++G(3df,2p) level.



in Fig. 1 indicate that the two  $\text{BH}_3$  units are bridged *via* B–H bonds with calculated bond lengths of 1.310 Å, and a B–B distance of 1.751 Å, obtained at the M06-2X/6-311++G(3df,2p) level. These values are in close agreement with the data reported by D. Sethio *et al.*,<sup>20</sup> who employed the CCSD(T)/cc-pVTZ method, reporting 1.315 Å and 1.763 Å, respectively. Moreover, the computed bond lengths also show strong consistency with the experimental values of 1.314 Å and 1.747 Å obtained by J. L. Duncan,<sup>41</sup> further demonstrating the reliability and accuracy of the selected computational model. As shown in Fig. 2, the binding energy for dimer formation leading to  $\text{B}_2\text{H}_6$  (IM0) is calculated to be  $-36.96 \text{ kcal mol}^{-1}$ , representing a pre-

transition state complex. This process proceeds *via* the transition state TS0, which features an activation barrier of  $2.63 \text{ kcal mol}^{-1}$  relative to the isolated reactants. Analysis of the vibrational modes at TS0 reveals a key imaginary frequency of  $-340.19 \text{ cm}^{-1}$ , corresponding to a concerted  $\text{H}_2$  elimination mechanism. In this step, each  $\text{BH}_3$  unit contributes a single hydrogen atom to form the  $\text{H}_2$  molecule, while the two  $\text{BH}_3$  units move closer together, shortening the B–B distance to 1.649 Å. In the TS0, the hydrogen atom from the upper  $\text{BH}_3$  (in Fig. 2) separates, with a  $\text{B}\cdots\text{H}$  distance of 2.050 Å, while the lower  $\text{BH}_3$  provides a hydrogen atom with a  $\text{B}\cdots\text{H}$  distance of 1.324 Å. These two hydrogen atoms combine to form molecular  $\text{H}_2$ ,

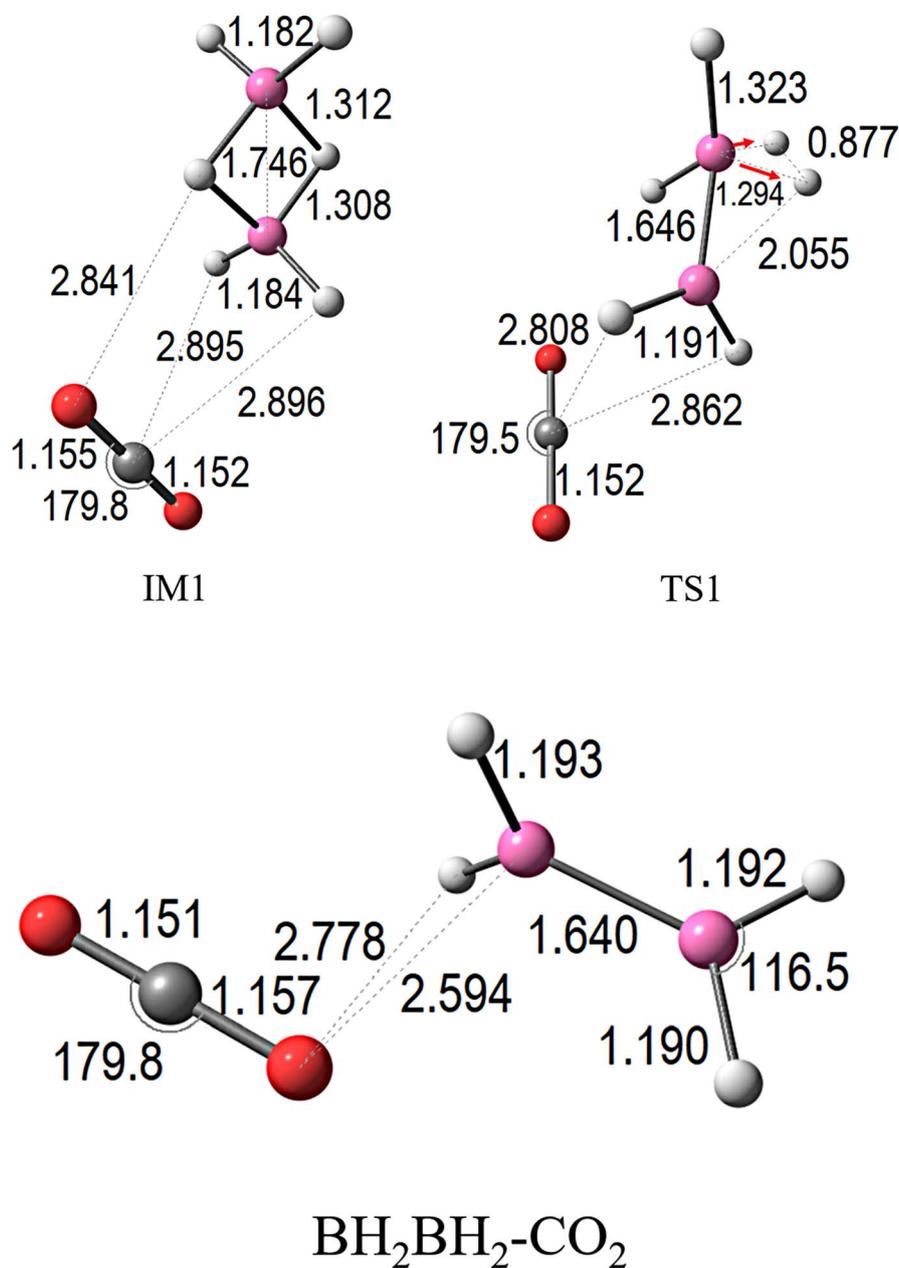


Fig. 3 Calculated molecular structures of species along the gas-phase  $\text{BH}_3 + \text{BH}_3 + 3\text{CO}_2$  reaction pathway, optimized at M06-2X/6-311++G(3df,2p), displaying key bond lengths (Å) and bond angles ( $^\circ$ ).



which dissociates from the remaining  $B_2H_4$  fragment. The final relative energy of this product is  $0.47 \text{ kcal mol}^{-1}$ . This mechanism highlights that the  $H_2$  release from  $B_2H_6$  proceeds *via* a much lower activation energy pathway compared to direct cleavage of two hydrogen atoms from a single  $BH_3$  unit, which requires a significantly higher energy input of  $89.14 \text{ kcal mol}^{-1}$ , as reported by Q. Ge *et al.*<sup>42</sup> This finding underscores the cooperative role of the  $BH_3$  dimer in facilitating efficient  $H_2$  evolution, offering valuable insight into borane-based hydrogen storage and release processes.

### 3.2 Influence of single $CO_2$ molecule on the $BH_3 + BH_3$ dehydrogenation mechanism

As above discussed, the  $H_2$  release process from  $B_2H_6$  is thermodynamically unfavorable, owing to its endothermic nature ( $\Delta H > 0$ ). This highlights the importance of identifying suitable co-reactants that could drive the reaction toward thermodynamic feasibility. Although species such as  $SiH_4$ ,  $NH_3$ ,  $H_2O$ , and  $CO$  have been investigated,<sup>43–46</sup> the potential influence of  $CO_2$  has not been thoroughly explored. This motivates the present investigation into the  $B_2H_6 + nCO_2$  reaction, aimed at understanding how  $CO_2$  interacts with electron-deficient boranes. Such interactions are directly relevant to  $CO_2$  activation and conversion, both of which are crucial challenges in carbon management. Furthermore, exploring the chemical behavior of  $B_2H_6$  under  $CO_2$  atmosphere provides valuable insight into how small molecules, particularly  $CO_2$ , influence hydrogen release from boron hydrides, ultimately linking to clean hydrogen production and carbon recycling technologies.

To assess the effect of  $CO_2$  on the dehydrogenation pathway of  $BH_3 + BH_3$ , we conducted a computational investigation of the  $BH_3 + BH_3 + CO_2$  reaction at the same theoretical level (Fig. 3).

As presented in Fig. 2 (blue line,  $n = 1$ ), the initial interaction between  $BH_3-BH_3$  and  $CO_2$  forms a stable complex, serving as the reference point with a relative electronic energy ( $\Delta E + ZPE$ ) set at  $0.0 \text{ kcal mol}^{-1}$ . Progressing along the reaction coordinate, this interaction leads to the formation of intermediate IM1, which exhibits considerable stabilization at  $-37.78 \text{ kcal mol}^{-1}$ , highlighting the strong association between the reactants, particularly through the participation of  $CO_2$ . The conversion from IM1 to the corresponding transition state (TS1) requires surpassing an activation barrier of only  $1.2 \text{ kcal mol}^{-1}$ , markedly lower than the  $2.63 \text{ kcal mol}^{-1}$  required in the absence of  $CO_2$  (TS0). This clear reduction in barrier height underscores the catalytic-like influence of  $CO_2$  in promoting the process.

At TS1 (see Fig. 3), notable structural rearrangements are observed: two B–H bonds within  $BH_3$  extend to  $1.323 \text{ \AA}$  and  $2.055 \text{ \AA}$ , indicating partial bond cleavage during  $H_2$  evolution. Simultaneously, the B–B bond contracts slightly to  $1.646 \text{ \AA}$ . The  $CO_2$  fragment interacts strongly within the complex, maintaining C=O bond lengths near  $1.15 \text{ \AA}$  and a nearly linear O=C=O angle of  $179.5^\circ$ . These structural changes correspond to an imaginary frequency of  $-332.32 \text{ cm}^{-1}$ , associated with a vibrational mode representing the concerted  $H_2$  release and atomic rearrangement. Beyond this transition state, the pathway leads

to the exergonic formation of  $BH_2BH_2-CO_2$  and  $H_2$ , with a final relative energy of  $-0.83 \text{ kcal mol}^{-1}$ . The presence of  $CO_2$  not only lowers the activation barrier but also enhances both  $CO_2$  capture and  $H_2$  generation, offering a dual benefit relevant to clean energy production and carbon management.

### 3.3 Influence of double $CO_2$ molecules on the $BH_3 + BH_3$ dehydrogenation mechanism

In this section, the influence of two  $CO_2$  molecules on the dehydrogenation pathway of the  $BH_3BH_3$  complex is investigated. Calculations were conducted using the M06-2X/6-311++G(3df,2p) level of theory. The initial interaction among  $BH_3 + BH_3 + 2CO_2$  establishes a reference electronic energy (including ZPE) of  $0.0 \text{ kcal mol}^{-1}$ . As the reaction proceeds, this interaction leads to the formation of an intermediate complex (IM2, Fig. 4) with a significantly lower energy of  $-38.85 \text{ kcal mol}^{-1}$  (see Fig. 2), indicating strong stabilization due to cooperative binding by the two  $CO_2$  molecules. The subsequent transformation from IM2 to the product state requires overcoming a remarkably low activation barrier of  $-0.91 \text{ kcal mol}^{-1}$ , which is considerably reduced compared to the barriers for TS0 ( $2.63 \text{ kcal mol}^{-1}$ ) and TS1 ( $1.20 \text{ kcal mol}^{-1}$ ). This substantial reduction highlights the pronounced catalytic effect arising from the second  $CO_2$ , further accelerating the dehydrogenation process. At the TS2 structure, significant geometric rearrangement is observed: the B–H bond contracts to  $1.309 \text{ \AA}$ , while the opposite B–H bond within the lower  $BH_3$  unit elongates to  $2.013 \text{ \AA}$ , marking the onset of  $H_2$  release. Simultaneously, the B–B bond contracts slightly to  $1.646 \text{ \AA}$ . Both  $CO_2$  molecules exhibit strong interactions with the evolving product complex, with C=O bond lengths of approximately  $1.155 \text{ \AA}$  and nearly linear O=C=O angles of  $179.6^\circ$ . The imaginary frequency associated with TS2 is calculated as  $-445.71 \text{ cm}^{-1}$ , corresponding to a vibrational mode coordinating the concerted release of  $H_2$  and the structural adjustment of the  $CO_2$  framework.

As the reaction progresses, the final products  $BH_2BH_2-2CO_2$  and  $H_2$  form with an overall exergonicity of  $-2.74 \text{ kcal mol}^{-1}$ , demonstrating that the incorporation of a second  $CO_2$  not only further reduces the activation energy but also enhances the efficiency of both dehydrogenation and  $CO_2$  capture, underscoring its potential significance in combined hydrogen production and carbon utilization strategies.

### 3.4 Influence of triple $CO_2$ molecules on the $BH_3 + BH_3$ dehydrogenation mechanism

To gain deeper insight into the  $CO_2$ -assisted dehydrogenation process, we examined the pathway involving  $BH_3 + BH_3$  in the presence of three  $CO_2$  molecules. The optimized structures of the intermediate and transition state are illustrated in Fig. 5

The corresponding potential energy profile, including ZPE corrections, indicates that the initial  $BH_3 + BH_3 + 3CO_2$  complex starts at  $0.0 \text{ kcal mol}^{-1}$  (Fig. 2). The reaction proceeds through the formation of an intermediate species, IM3, which is significantly stabilized at  $-39.85 \text{ kcal mol}^{-1}$  (Fig. 5). Notably, the introduction of three  $CO_2$  molecules further reduces the activation energy required for dehydrogenation. The computed





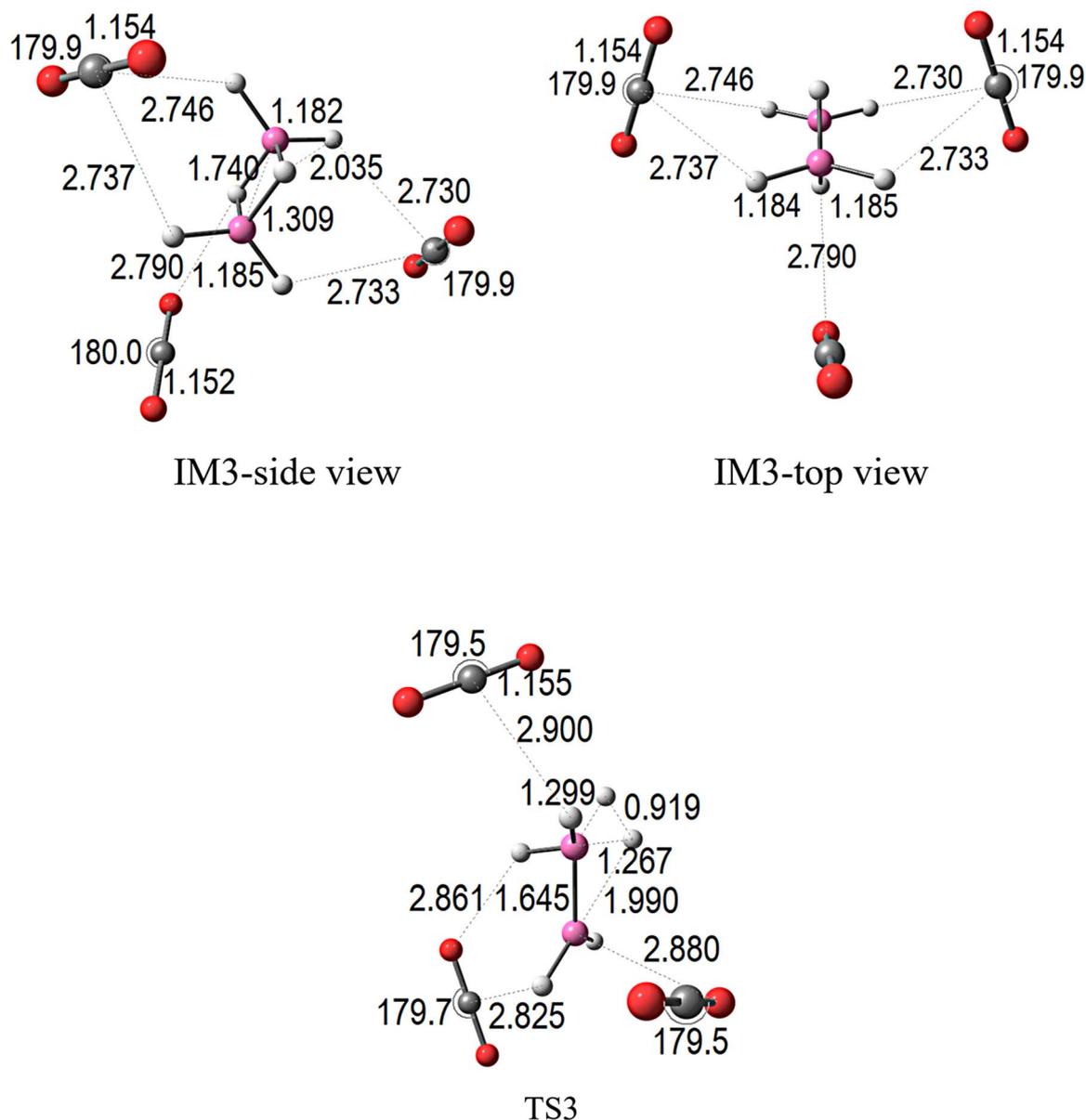


Fig. 5 M06-2X/6-311++G(3df,2p) optimized geometries of species along the  $\text{BH}_3 + \text{BH}_3 + 3\text{CO}_2$  gas-phase reaction pathway, with key bond lengths (Å) and bond angles ( $^\circ$ ).

borane-based systems in future catalytic and energy storage applications, aligning with global efforts toward sustainable energy and environmental remediation.

### 3.5 IR spectra and vibrational features of $\text{BH}_3\text{BH}_3-n(\text{CO}_2)$ complexes ( $n = 0$ to 3)

Fig. 6 presents the infrared (IR) spectra of four species:  $\text{BH}_3\text{BH}_3$  (a),  $\text{BH}_3\text{BH}_3\text{-CO}_2$  (b),  $\text{BH}_3\text{BH}_3\text{-2CO}_2$  (c), and  $\text{BH}_3\text{BH}_3\text{-3CO}_2$  (d) which generated based on vibrational frequency results obtained from quantum chemical calculations performed at the M06-2X/6-311++G(3df,2p) level of theory (Table S2<sup>†</sup>). These spectra reveal distinct shifts in the low-frequency region (0–

$500\text{ cm}^{-1}$ ) upon sequential incorporation of  $\text{CO}_2$  molecules into the  $\text{BH}_3\text{BH}_3$  framework. For pristine  $\text{BH}_3\text{BH}_3$  (spectrum a), no prominent absorption bands are observed within this range, indicating the absence of external molecular interactions. However, after coordination with a single  $\text{CO}_2$  molecule (spectrum b), new vibrational peaks emerge, attributable to modes induced by  $\text{CO}_2$  binding. With the addition of a second  $\text{CO}_2$  molecule (spectrum c), these features become more prominent, reflecting enhanced interaction strength. In the case of  $\text{BH}_3\text{BH}_3\text{-3CO}_2$  (spectrum d), the intensities of these peaks further increase, signaling more complex vibrational coupling arising from multiple  $\text{CO}_2$  incorporations. Collectively, these spectral changes provide clear evidence of progressive  $\text{CO}_2$



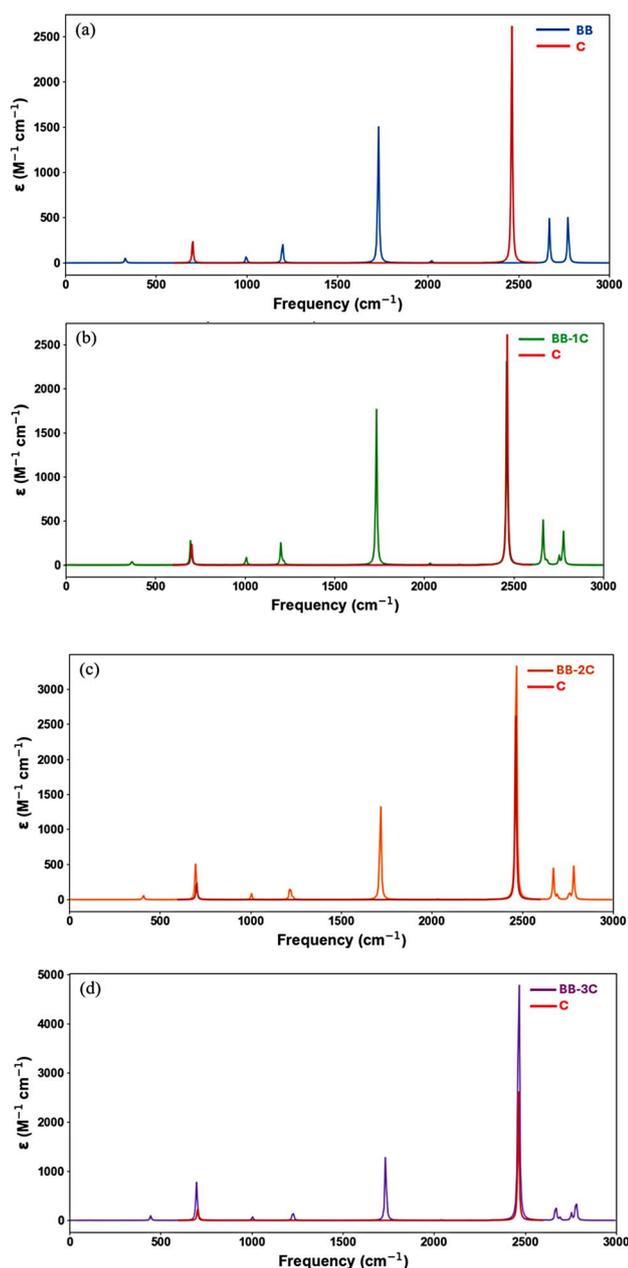


Fig. 6 Calculated IR spectra of: (a)  $\text{BH}_3\text{-BH}_3$ , (b)  $\text{BH}_3\text{-BH}_3\text{-CO}_2$ , (c)  $\text{BH}_3\text{-BH}_3\text{-2CO}_2$ , and (d)  $\text{BH}_3\text{-BH}_3\text{-3CO}_2$ , obtained at the M06-2X/6-311++G(3df,2p) level of theory.

integration, which profoundly modifies the vibrational signature of the parent  $\text{BH}_3\text{BH}_3$  species.

### 3.6 Analysis of electrostatic interactions in the $\text{BH}_3\text{BH}_3\text{-nCO}_2$ system

Analysis of the electron localization function (ELF)<sup>26</sup> maps for the  $\text{BH}_3\text{BH}_3\text{-nCO}_2$  complexes (shown in Fig. 7a-c) provides clear evidence of direct contact between the hydrogen atoms from the boron hydride framework and oxygen atoms from the  $\text{CO}_2$  molecules. These interactions primarily take place at the interface between the boron-containing fragment and the

adsorbed  $\text{CO}_2$  units, where increased electron density suggests partial covalent character. Supporting this interpretation, topological analysis using atoms-in-molecules (AIM)<sup>27</sup> theory (Fig. 7d-f) reveals the presence of distinct bond critical points (BCPs) that correspond to these interaction sites. Such findings indicate that the bonding mechanism is consistent with a Lewis acid-base interaction, where the boron centers function as electron acceptors, while the oxygen atoms of  $\text{CO}_2$  act as electron donors. Together, the ELF and AIM data provide strong confirmation that stable and cooperative bonding occurs when  $\text{CO}_2$  interacts with the  $\text{BH}_3\text{BH}_3$  system. To further clarify the stabilizing role of  $\text{CO}_2$ , we calculated the interaction energies ( $E_{\text{bd}}$ ) for the formation of the  $\text{BH}_3\text{BH}_3 \cdot n\text{CO}_2$  adducts using the expression:

$$E_{\text{bd}} = E[\text{BH}_3\text{BH}_3 \cdot n\text{CO}_2] - E[\text{BH}_3\text{BH}_3] - nE[\text{CO}_2] \text{ (kcal mol}^{-1}\text{)}$$

The resulting interaction energies are  $-0.81 \text{ kcal mol}^{-1}$  ( $n = 1$ ),  $-1.89 \text{ kcal mol}^{-1}$  ( $n = 2$ ), and  $-2.89 \text{ kcal mol}^{-1}$  ( $n = 3$ ), confirming a progressively stronger stabilization effect as more  $\text{CO}_2$  molecules are introduced. This trend indicates not only additive but also cooperative binding interactions between the  $\text{BH}_3$  dimer and  $\text{CO}_2$  molecules. Additionally, structural analysis reveals that the B-B bond length decreases from  $1.751 \text{ \AA}$  (in  $\text{IM}_0$ ) to  $1.645 \text{ \AA}$  (in  $\text{TS}_3$ ), while the B-H bonds involved in  $\text{H}_2$  formation show slight elongation. These trends, consistent across the reaction coordinate, indicate that  $\text{CO}_2$  not only stabilizes the complex electronically but also induces favorable geometric changes that facilitate hydrogen release. This quantitative structural and energetic evidence reinforces the dual role of  $\text{CO}_2$  as both a structural stabilizer and a reactivity modulator in the  $\text{BH}_3$  dimer system.

### 3.7 $\text{CO}_2$ adsorption capacity of the $\text{BH}_3 + \text{BH}_3$ complex and comparison with conventional adsorbents

To evaluate the  $\text{CO}_2$  capture potential of the  $\text{BH}_3 + \text{BH}_3$  complex, we computed its  $\text{CO}_2$  adsorption capacity under conditions where one, two, and three  $\text{CO}_2$  molecules are incorporated into the structure. The adsorption capacity, expressed in mmol  $\text{CO}_2$  per gram of  $\text{BH}_3$ , was determined based on the molecular weight of the system and the stoichiometry of  $\text{CO}_2$  binding. The calculated adsorption capacities were subsequently compared with values reported for conventional hybrid sorbents, including graphene oxide (GO)-based composites, metal-organic frameworks (MOFs), and hydrogen boride (HB) sheets. These materials, summarized in Table 1.

Notably, the  $\text{CO}_2$  adsorption capacity of the  $\text{BH}_3 + \text{BH}_3$  complex far exceeds those of conventional sorbents, such as  $\text{Fe}_3\text{O}_4\text{-rGO}$  ( $2.50 \text{ mmol g}^{-1}$ ),  $\text{GO-UiO-66}$  ( $3.37 \text{ mmol g}^{-1}$ ),  $\text{GO-ZnO}$  ( $1.94 \text{ mmol g}^{-1}$ ), and  $\text{N-doped rGO-Zn}$  ( $3.31 \text{ mmol g}^{-1}$ ). This striking enhancement can be attributed to the strong chemisorptive interactions between  $\text{CO}_2$  and the electron-deficient boron centers within the  $\text{BH}_3\text{-BH}_3$  system, further stabilized through cooperative binding effects arising from the flexible, adaptive nature of the dimeric boron hydride framework. In contrast, most conventional hybrid sorbents primarily rely on physisorption mechanisms, which are inherently weaker



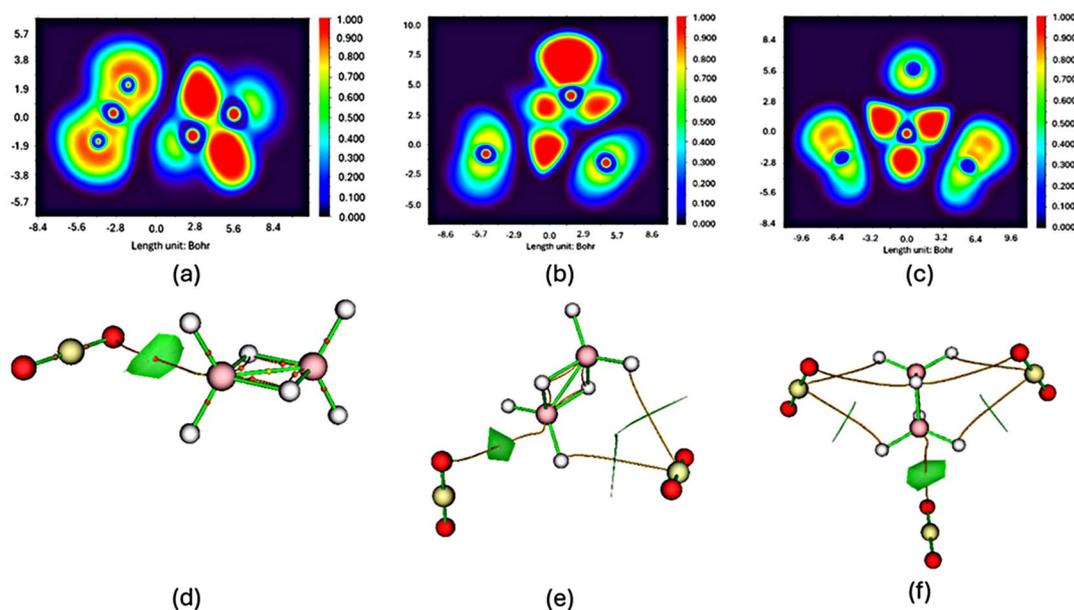


Fig. 7 ELF and AIM maps of the  $\text{BH}_3\text{BH}_3\text{-CO}_2$  (a and d);  $\text{BH}_3\text{BH}_3\text{-2CO}_2$  (b and e), and  $\text{BH}_3\text{BH}_3\text{-3CO}_2$  (c and f), calculated at M06-2X/6-311++G(3df,2p) level.

**Table 1** Comparison of  $\text{CO}_2$  adsorption capacities of the  $\text{BH}_3\text{-BH}_3$  complex with those of various conventional adsorbents

Adsorbent	$\text{CO}_2$ adsorbent capacity ( $\text{mmol g}^{-1}$ )
GO-ZnO	1.94 (ref. 47)
GO-UiO-66	3.37 (ref. 48)
$\text{Fe}_3\text{O}_4\text{-rGO}$	2.5 (ref. 49)
N-doped rGO-Zn	3.31 (ref. 50)
Hydrogen boride (HB) sheets	0.24 (ref. 51)
This work: $\text{BH}_3\text{-BH}_3\text{-}n\text{CO}_2$	36.14 ( $n = 1$ ); 72.28 ( $n = 2$ ); 108.42 ( $n = 3$ )

and less selective under ambient conditions. The extraordinarily high adsorption capacity observed for the  $\text{BH}_3\text{-BH}_3$  complex can, at least in part, be attributed to the fact that this system is evaluated at the molecular level, where individual interactions between  $\text{BH}_3$  units and  $\text{CO}_2$  molecules are fully resolved. At this scale, the inherent chemical reactivity of the boron centers and the flexibility of the B-H framework allow for highly efficient  $\text{CO}_2$  trapping. This result serves as a molecular-level signal indicating the strong intrinsic affinity of boron hydrides for  $\text{CO}_2$ , which could potentially be translated into larger-scale materials with engineered porosity and connectivity. This molecular insight is further supported by previous investigations into the  $\text{CO}_2$  adsorption properties of hydrogen boride (HB) sheets, a class of metal-free two-dimensional materials composed of boron and hydrogen in a 1 : 1 stoichiometric ratio. Recent studies<sup>51</sup> have demonstrated that pristine HB sheets exhibit negligible  $\text{CO}_2$  adsorption under ambient

conditions. However, hydrogen-deficient HB sheets in which some surface hydrogen atoms are removed demonstrate reproducible physisorption of  $\text{CO}_2$  at 297 K, with a saturation coverage of only  $2.4 \times 10^{-1} \text{ mmol g}^{-1}$ . The exceptional  $\text{CO}_2$  uptake of the  $\text{BH}_3\text{-BH}_3$  complex further reinforces its potential as a dual-functional platform, capable of simultaneously acting as a high-performance  $\text{CO}_2$  capture material and an efficient hydrogen storage medium. This combined functionality not only advances the development of integrated carbon capture and utilization (CCU) systems, but also provides a promising molecular design strategy for next-generation carbon management and clean hydrogen technologies. By leveraging its unique molecular structure and intrinsic reactivity, the  $\text{BH}_3\text{-BH}_3$  complex exemplifies how fundamental molecular chemistry can inspire the design of innovative materials for sustainable energy and environmental applications.

### 3.8 Kinetic study

This section investigates the hydrogen release kinetics from the  $\text{BH}_3$  dimer in the presence of increasing numbers of  $\text{CO}_2$  molecules. Key parameters, including equilibrium constants ( $K_{\text{eq}}$ ) and unimolecular rate constants ( $k_{\text{u}}$ ), were determined to assess how  $\text{CO}_2$  influences both thermodynamic and kinetic aspects of the process.

### 3.9 Equilibrium constants

The equilibrium constants for the association between  $\text{BH}_3 + \text{BH}_3$  and  $\text{BH}_3 + \text{BH}_3 + n\text{CO}_2$  (with  $n = 0, 1, 2, 3$ ) are summarized in Table 2. The data reveal a systematic decline in equilibrium



**Table 2** Equilibrium constants ( $K_{\text{eq}}$ ) for the reaction between  $\text{BH}_3$ ,  $\text{BH}_3$ , and varying numbers of  $\text{CO}_2$  molecules

Reaction	$K_{\text{eq}}$
$\text{BH}_3 + \text{BH}_3 \rightleftharpoons \text{BH}_3\text{-BH}_3$	$1.10 \times 10^{20}$
$\text{BH}_3 + \text{BH}_3 + \text{CO}_2 \rightleftharpoons \text{BH}_3\text{-BH}_3\text{-CO}_2$	$5.96 \times 10^{15}$
$\text{BH}_3 + \text{BH}_3 + 2\text{CO}_2 \rightleftharpoons \text{BH}_3\text{-BH}_3\text{-}2\text{CO}_2$	$3.17 \times 10^{10}$
$\text{BH}_3 + \text{BH}_3 + 3\text{CO}_2 \rightleftharpoons \text{BH}_3\text{-BH}_3\text{-}3\text{CO}_2$	$4.14 \times 10^5$

constants as more  $\text{CO}_2$  molecules are incorporated into the system. Without  $\text{CO}_2$ , the equilibrium constant reaches  $1.10 \times 10^{20}$ , indicative of an extremely favorable formation of the  $\text{BH}_3$  dimer. When a single  $\text{CO}_2$  is introduced, the equilibrium constant drops to  $5.96 \times 10^{15}$ , followed by  $3.17 \times 10^{10}$  for the two  $\text{CO}_2$  system, and finally  $4.14 \times 10^5$  when three  $\text{CO}_2$  molecules are present. This decreasing trend reflects the competitive stabilization provided by  $\text{CO}_2$  coordination, which shifts the equilibrium away from simple dimer formation toward the formation of  $\text{CO}_2$ -stabilized adducts. Despite this gradual reduction in  $K_{\text{eq}}$ , the values remain sufficiently large to indicate a strong thermodynamic driving force toward product formation in all cases. This implies that, while  $\text{CO}_2$  reduces the preference for direct  $\text{BH}_3$  dimerization, it promotes formation of more complex  $\text{BH}_3\text{-BH}_3\text{-CO}_2$  adducts, ensuring that  $\text{CO}_2$  incorporation does not hinder the overall hydrogen release process. Instead,  $\text{CO}_2$  contributes to restructuring the pathway to favor products where both hydrogen evolution and  $\text{CO}_2$  capture occur simultaneously.

### 3.10 Rate constants for hydrogen release

The unimolecular rate constants ( $k_{\text{u}}$ ) associated with hydrogen release from each intermediate complex ( $\text{IM}_n$ ) to its corresponding transition state ( $\text{TS}_n$ ) are presented in Table 3. The results indicate a clear increasing trend in rate constants as the number of  $\text{CO}_2$  molecules rises. For the reaction involving only  $\text{BH}_3 + \text{BH}_3$ , the rate constant is  $3.3 \times 10^{-16} \text{ s}^{-1}$ . When one  $\text{CO}_2$  molecule is introduced, the rate decreases slightly to  $2.4 \times 10^{-16} \text{ s}^{-1}$ , while the system with two  $\text{CO}_2$  molecules accelerates to  $1.7 \times 10^{-15} \text{ s}^{-1}$ . The fastest hydrogen release occurs when three  $\text{CO}_2$  molecules are present, reaching  $1.2 \times 10^{-14} \text{ s}^{-1}$ . This enhancement in  $k_{\text{u}}$  highlights the catalytic role of  $\text{CO}_2$ , where increasing  $\text{CO}_2$  coordination stabilizes the intermediates through favorable electrostatic and Lewis acid–base interactions. This stabilization reduces activation barriers, enabling a more efficient transition to the hydrogen release step. This

**Table 3** Unimolecular rate constants ( $k_{\text{u}}$ ) for the hydrogen release process from intermediate complexes ( $\text{IM}_n$ ) to transition states ( $\text{TS}_n$ ) in the  $\text{BH}_3 + \text{BH}_3 + n\text{CO}_2$  system (where  $n = 0,1,2,3$ )

Reaction	$k_{\text{u}} (\text{s}^{-1})$
$\text{BH}_3 + \text{BH}_3 \rightarrow \text{BH}_2\text{BH}_2 + \text{H}_2$	$3.3 \times 10^{-16}$
$\text{BH}_3 + \text{BH}_3 + \text{CO}_2 \rightarrow \text{BH}_2\text{BH}_2\text{-CO}_2 + \text{H}_2$	$2.4 \times 10^{-16}$
$\text{BH}_3 + \text{BH}_3 + 2\text{CO}_2 \rightarrow \text{BH}_2\text{BH}_2\text{-}2\text{CO}_2 + \text{H}_2$	$1.7 \times 10^{-15}$
$\text{BH}_3 + \text{BH}_3 + 3\text{CO}_2 \rightarrow \text{BH}_2\text{BH}_2\text{-}3\text{CO}_2 + \text{H}_2$	$1.2 \times 10^{-14}$

trend reflects that  $\text{CO}_2$  coordination alters the reaction pathway, creating a smoother and more thermodynamically favored transition from reactants to products. Interestingly, the simultaneous decrease in equilibrium constants ( $K_{\text{eq}}$ ) and increase in rate constants ( $k_{\text{u}}$ ) with growing  $\text{CO}_2$  content reflects a mechanistic shift in the reaction. In the absence of  $\text{CO}_2$ , dimer formation is exceptionally favored thermodynamically, but hydrogen release is relatively slow. As more  $\text{CO}_2$  is incorporated, the system shifts from direct dimerization to forming multi-component adducts, which, while slightly less stable, allow for faster hydrogen evolution. This transition highlights a  $\text{CO}_2$ -induced catalytic enhancement, where  $\text{CO}_2$  plays a dual role: facilitating hydrogen release while simultaneously being captured into the product complex. This dual functionality makes the  $\text{BH}_3\text{-BH}_3\text{-CO}_2$  system particularly attractive for applications in clean energy and carbon management. It not only enables controlled hydrogen release, but also contributes to efficient  $\text{CO}_2$  capture, offering a promising integrated solution for hydrogen storage and carbon mitigation technologies.

## 4 Conclusions

This study employed Density Functional Theory (DFT) calculations and kinetic modeling to illuminate the reaction between  $\text{BH}_3$ ,  $\text{BH}_3$ , and  $\text{CO}_2$ , with a specific focus on hydrogen release and  $\text{CO}_2$  capture mechanisms. Our findings reveal a significant influence of  $\text{CO}_2$  on the  $\text{BH}_3\text{-BH}_3$  system:

(a)  $\text{CO}_2$  significantly alters the hydrogen evolution pathway: as the number of  $\text{CO}_2$  molecules increases, the reaction mechanism shifts, leading to reduced energy barriers and enhanced stabilization of intermediates.

(b) Strong  $\text{CO}_2\text{-BH}_3\text{-BH}_3$  interactions enhance  $\text{CO}_2$  adsorption and shift thermodynamic equilibrium: computed equilibrium constants and binding energies demonstrate a high affinity, favoring stable multi-molecular adduct formation, crucial for combined hydrogen storage and carbon capture.

(c) The  $\text{BH}_3\text{-BH}_3 + (\text{CO}_2)_n$  system functions as a dual-functional platform for clean energy: it simultaneously releases hydrogen and captures  $\text{CO}_2$ , offering a promising strategy to address both clean hydrogen generation and  $\text{CO}_2$  reduction. The system's tunability with varying  $\text{CO}_2$  amounts allows for optimization of both processes, showcasing its potential for energy storage and carbon management.

In essence, this work establishes the  $\text{BH}_3\text{-BH}_3 + n\text{CO}_2$  system as a highly promising candidate for integrated hydrogen storage and carbon capture. Future research should prioritize experimental validation and system optimization to fully realize its potential for sustainable energy solutions.

### 4.1 Influence of $\text{CO}_2$ on hydrogen evolution

The introduction of  $\text{CO}_2$  significantly reshapes the reaction pathway and modifies the energy profile of the  $\text{BH}_3\text{-BH}_3$  system. As the number of  $\text{CO}_2$  molecules increases from one to three, the reaction mechanism progressively shifts, reducing the energy barriers and enhancing the stabilization of intermediate species.



## 4.2 Equilibrium and interaction energies

The computed equilibrium constants ( $K_{\text{eq}}$ ) and binding energies reveal strong interactions between  $\text{CO}_2$  and the  $\text{BH}_3\text{-BH}_3$  complex. This strong affinity not only enhances  $\text{CO}_2$  adsorption but also impacts the thermodynamic equilibrium, with increasing  $\text{CO}_2$  concentration favoring the formation of stable multi-molecular adducts. Such robust binding further supports the feasibility of utilizing this system for combined hydrogen storage and carbon capture.

## 4.3 Dual-functional platform for clean energy

The ability to simultaneously release hydrogen and capture  $\text{CO}_2$  highlights the multifunctionality of the  $\text{BH}_3\text{-BH}_3$  complex. This dual capability offers a promising strategy to simultaneously address two pressing challenges: clean hydrogen generation and  $\text{CO}_2$  reduction. By adjusting the amount of available  $\text{CO}_2$ , the system can be tuned to optimize both processes, presenting valuable potential for energy storage and carbon management technologies.

In summary, this study identifies the  $\text{BH}_3\text{-BH}_3 + n\text{CO}_2$  system as a compelling candidate for integrated hydrogen storage and carbon capture applications. Future efforts should focus on experimental validation and further fine-tuning of system conditions to fully unlock its potential for sustainable energy solutions.

## Data availability

Data will be made available on request.

## Author contributions

Trinh Le Huyen: conceptualization, methodology, validation, data curation, formal analysis, visualization, writing – original draft, writing – review & editing. Tran Thi Thanh Huyen and Chi Nam Cao: data curation and visualization. Pham Cam Nam: supervision, software, writing – review & editing.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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