Be\textsubscript{12}O\textsubscript{12} Nano-cage as a Promising Catalyst for CO\textsubscript{2} Hydrogenation

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An efficient conversion of CO\textsubscript{2} into valuable fuels and chemicals has been hotly pursued recently. Here, for the first time, we have explored a series of M\textsubscript{12}X\textsubscript{12} nano-cages (M = B, Al, Be, Mg; X = N, P, O) for catalysis of CO\textsubscript{2} to HCOOH. Two steps are identified in the hydrogenation process, namely, H\textsubscript{2} activation to 2H\textsuperscript{+}, and then 2H\textsuperscript{+} transfer to CO\textsubscript{2}, forming HCOOH, where the barriers of two H\textsuperscript{+} transfer are lower than that of the H\textsubscript{2} activation reaction. Among the studied cages, Be\textsubscript{12}O\textsubscript{12} is found to have the lowest barrier in the whole reaction process, showing two kinds of reaction mechanisms for 2H\textsuperscript{+} (simultaneous transfer and a step-wise transfer with a quite low barrier). Moreover, the H\textsubscript{2} activation energy barrier can be further reduced by introducing Al, Ga, Li, and Na to Be\textsubscript{12}N\textsubscript{12} cage. This study would provide some new ideas for the design of efficient cluster catalysts for CO\textsubscript{2} reduction.

The energy crisis and greenhouse effect caused by the emission of carbon dioxide (CO\textsubscript{2}) are the two serious global problems at the present day and even remain in the next 50 years\textsuperscript{1}, which stimulated the current research interest in efficient conversion of CO\textsubscript{2} into valuable fuels and chemicals\textsuperscript{2-4}. However, due to the negative adiabatic electron affinity (EA) and large ionization potential (IP), the CO\textsubscript{2} molecule is thermodynamically stable and kinetically inert, thus making the conversion difficult under normal conditions\textsuperscript{5}. To overcome these challenges, we need to understand the basic chemical processes of the conversion and seek for highly efficient, cost-effective, and environmentally sound catalysts. Since formic acid (FA) has been widely used as a medium for hydrogen storage and an industrial chemical, catalytic hydrogenation of CO\textsubscript{2} to FA becomes one of the most common and promising way to utilize CO\textsubscript{2}.

Recently, systems containing frustrated Lewis pairs (FLPs) have been found as effective catalysts for H\textsubscript{2} activation\textsuperscript{6-8}, CO\textsubscript{2} reduction\textsuperscript{9-11} and hydrogenation\textsuperscript{12-14} for the production of CI fuels. As we know that a FLP and CO\textsubscript{2} further hydrogenation?

In the past few years, experiment and theoretical research efforts have been devoted to (XY)n (M = B, Al, Be, Mg; X = N, P, O) nanostructures such as nanocages, nanohorns, nanotubes, and nanowires\textsuperscript{12-14}. Theoretical studies found that the fullerene-like cages (XY)\textsubscript{12} with $T_h$ symmetry were the most stable geometry\textsuperscript{16,17}. Moreover, Be\textsubscript{12}N\textsubscript{12} has been synthesized and detected by laser desorption time-of-flight mass spectrometry\textsuperscript{18}. Al-, Ga-doped\textsuperscript{19} and Li-, Na- decorated\textsuperscript{20} stable Be\textsubscript{12}N\textsubscript{12} clusters have been also theoretically studied. In addition, previous studies indicated that BN\textsubscript{35}, AlN\textsubscript{36,37} and BeO\textsubscript{38,39} clusters can absorb H\textsubscript{2} molecularly due to the polar bond between B and N, Al and N, Be and O with different electron affinities. Moreover BN clusters can also capture CO\textsubscript{2}\textsuperscript{40,41}. In fact, the most special point for cluster catalyst is that the addition or removal of a single atom can have a substantial influence on the activity and selectivity of reaction, which provides us the basis for converting
CO₂ to different products with different efficiencies by introducing different atoms to the cluster surface or inside the cluster with more flexibilities and diversities. Based on these points, in the present work we systematically study H₂ dissociation (2H*) and CO₂ hydrogenation using M₁₂X₁₂ (M = B, Al, Be, Mg; X = N, P, O) cage clusters, and explore the involved mechanisms.

Results and Discussions

Geometry structures. For M₁₂X₁₂ type cluster with T₆ symmetry as B₁₂N₁₂, Al₁₂N₁₂, B₁₂P₁₂, Al₁₂P₁₂, Be₁₂O₁₂ and Mg₁₂O₁₂, they all consist of eight 6-membered rings (6-MR) and six 4-membered rings (4-MR), as was shown on Fig. 1(a). To improve the binding with CO₂ and H₂, Al, Ga [Fig. 1(b)] and Li, Na [Fig. 1(c)] are introduced to B₁₂N₁₂ cage, the geometry parameters can be found in Table S1 of Supporting Information, where there are two types of M-X bonds: the bond shared by two 6-MRs (labelled MX-66), and the other one shared between a 4-MR and 6-MR (labelled MX-64), the former is longer than the latter for all studied nano-cages.

H₂ and CO₂ Activation. In order to determine the configuration with the lowest energy for H₂ and CO₂ adsorption on the surface of the cluster, a number of different initial structures have been used for optimization. The results of stable H₂/M₁₂X₁₂, CO₂/M₁₂X₁₂ complexes as well as their corresponding transition state (TS) structures are shown in Fig. 2. For the convenience of discussions, we distinguish the physisorption (P) from the chemical functionalization (C) for the molecules on the cages. As seen from Fig. 2, in the process of physisorption, H₂ and CO₂ molecules are weakly adsorbed on the clusters with minor changes in geometry. While in the chemical adsorption, H₂ is dissociated forming 2H* and CO₂ is chemically activated forming CO₂*. The corresponding geometry parameters as well as their TSs are shown in Tables S2 and S3, and the interaction energies of H₂ and CO₂ physisorption and chemical absorption are given in Table S4 of Supporting Information.

The activation energies of H₂ on MX-64 and MX-66 are labeled as ΔG²H and ΔG₁H, respectively, while the activation energies of CO₂ on MX-64 and MX-66 are labeled as ΔG²C and ΔG₁C respectively. The energy barriers

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**Figure 1. Geometry sketches.** (a) MX clusters (M₁ = B, Al, Be, Mg; X = N, P or O); (b) AlB₁₁N₁₂ and GaB₁₁N₁₂ (M₂ = Al, Ga); (c) LiB₁₁N₁₂ and NaB₁₁N₁₂ (M₃ = Li, Na).

**Figure 2. Geometry sketches for H₂ and CO₂ physisorption (P), chemisorption (C) and the transition states (TS) in MX-64 and MX-66 configurations.**
for $H_2$ activation ($\Delta G^H$) are calculated as the Gibbs energy difference between the $TS^H$ (the TS for $H_2$ activation) and the initial state of $H_2$ adsorption:

$$\Delta G^H = G^H_{TS} - G^H_p$$

(1)

Similarly, the energy barriers for the $CO_2$ activation ($\Delta G^C$) are calculated as the Gibbs energy difference between the $TS^C$ (the TS for $CO_2$ activation) and the initial state of $CO_2$ adsorption:

$$\Delta G^C = G^C_{TS} - G^C_p$$

(2)

The calculated results are listed in Table 1, and typical structures with $H_2$ and $CO_2$ either in physisorption, or chemisorption as well as their transition states are given in the Fig. 2. All the Gibbs energy barrier for $H_2$ activation on MX-64 are all lower than which of the MX-66. When the activation barrier is overcome, $H_2$ can be dissociated generating hydridic ($H_a$) and protic ($H_b$) hydrogens.

Instead for $CO_2$ activation, the Gibbs energy barrier on MX-64 are all higher than that of the MX-66 except for $Al_{12}P_{12}$ and $Be_{12}O_{12}$ clusters. The activation barriers of $CO_2$ are lower than that of $H_2$ for the studied systems except for $B_{12}P_{12}$. The $Al$, $Ga$ doped and $Li$, $Na$ decorated $B_{12}N_{12}$ cages have lower activation energy barriers for $H_2$ and $CO_2$ than those of the pristine $B_{12}N_{12}$. This illustrates that the doping with $Al$ and $Ga$ as well as decoration with $Li$ and $Na$ can increase the activity of $B_{12}N_{12}$ cluster.

To clarify the effect of $H_2$ and $CO_2$ adsorptions on the electronic structures of nano-cages, natural bond orbital (NBO) analyses are performed and the results are listed in Table S5, from which one can see that upon the adsorption, charges on the cages are redistributed due to the geometry change and charge transfer. For example, in all the cases $CO_2$ received electrons from cages resulting in the activation. The charges on $M$ sites in all clusters are decreased upon the $H_2$ adsorption, while increased upon the $CO_2$ adsorption.

The different behaviors in $H_2$ activation on MX-64 and MX-66 are due to the different activities between them. As seen from Table S5, more charges are on $M$ and $X$ sites in MX-64 than those in MX-66, which makes the former more active with a lower $H_2$ activation barrier as compared with the latter one.

2$H^*$ transfer mechanism. Two reaction pathways for $CO_2$ hydrogenation on Lewis pair moiety have been identified, one involves the physisorped $CO_2$ reacting with the chemisorbed $2H^*$, and the other one involves the physisorped $H_2$ reacting with $CO_2^*$. For the latter, the reaction barrier for hydrogenation of the activated $CO_2^*$ is usually very high as found by Ye12 (2.65 eV in UiO-66-P-BF$_2$ catalyst) and by us (2.84 eV for MX-64 and 2.97 eV for MX-66 of $B_{12}N_{12}$), and this pathway leads to the formation of chemisorbed $HCO$ and $OH$ ([HCO + OH$^*$]) instead of HCOOH as shown in Supporting Information (Fig. S1). Consequently, in the following discussions, we only focused on the first path way for HCOOH formation.

According to the first pathway, $CO_2$ is firstly physisorbed on MX-2$H^*$(P), and then forms HCOOH (C) via the transition state (TS) (Fig. 3). For $B_{12}N_{12}$ nano cage, the reaction barrier for $H_2$ activation on MX-64 (1.19 eV) is lower than that on MX-66 (1.27 eV), while the $2H^*$ transfer barrier on MX-64 (1.28 eV) is higher than that on MX-66 (1.19 eV). The IRC calculations show that the hydride and protons are transferred to $CO_2$ simultaneously.

Table 1. Gibbs energy barrier for $H_2$ ($\Delta G^H$), and $CO_2$ activation ($\Delta G^C$), All values are in eV.

| Clusters        | $B_{12}N_{12}$ | $Al_{12}N_{12}$ | $B_{12}P_{12}$ | $Al_{12}P_{12}$ | $Be_{12}O_{12}$ | $Mg_{12}O_{12}$ | $LiB_{12}N_{12}$ | $NaB_{12}N_{12}$ | $AlB_{12}N_{12}$ | $GaB_{12}N_{12}$ |
|-----------------|----------------|-----------------|---------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| $\Delta G^H_1$ | 1.19           | 0.61            | 0.74          | 1.25           | 1.04           | 0.90           | 0.76           | 0.76           | 0.83           | 0.83           |
| $\Delta G^H_2$ | 1.27           | 0.68            | 1.06          | 1.46           | 1.33           | 0.92           | 0.92           | 0.84           | 0.94           | 0.94           |
| $\Delta G^C_1$ | 0.56           | 0.12            | 1.11          | 0.61           | 0.44           | 0.04           | 0.50           | 0.39           | 0.46           | 0.46           |
| $\Delta G^C_2$ | 0.51           | 0.11            | 1.06          | 0.63           | 0.47           | 0.03           | 0.33           | 0.26           | 0.36           | 0.43           |

Figure 3. Geometry sketches for $2H^*$ transfer from MX cluster to $CO_2$ in physisorption (P), chemisorption (C) and the transition states (TS) on MX-64 (a) and MX-66 (b) of the MX-2$H^*$ clusters.
In other words, the H transfer step is essentially the donation of a hydride and a proton from the ion-pair products to CO$_2$ via a concerted mechanism. Tables S6 and S7 list the corresponding geometry parameters, transition states, and interaction energies for CO$_2$ and HCOOH.

When attempting to bind CO$_2$ with Mg$_{12}$O$_{12}$−2H* in a way shown in Fig. 3(P), we cannot find any stable structures from our calculations. While CO$_2$ can directly bond at Mg and O sites (as shown in Fig. 4a) with a stronger binding energy of $-0.5$ eV (Table S4). Similarly, when introducing HCOOH to Mg$_{12}$O$_{12}$ shown in Fig. 3(C), one H atom of HCOOH was taken away by the O atom in Mg$_{12}$O$_{12}$ nano-cage (Fig. 4b). This suggests that Mg$_{12}$O$_{12}$ is not competent to be the catalyst for CO$_2$ hydrogenation to HCOOH.

The activation energies of H$_2$ transfer on MX-64 and MX-66 are labeled as $\Delta G_{HT}^1$ and $\Delta G_{HT}^2$ respectively.

The energy barriers for H$_2$ activation ($\Delta G_{HT}$) are calculated as the Gibbs energy difference between the TS$_{HT}$ (the TS for H$_2$ transfer) and the initial state of CO$_2$ physisorbed on MX-2H*:

$$\Delta G_{HT} = G_{TS}^{HT} - G_{P}^{HT}$$

The corresponding activation energies for H$_2$ transfer are listed in Table 2, where one can see that the activation energies of H transfer are all higher than 1.0 eV, except for Be$_{12}$O$_{12}$ cage. Just the opposite to the H$_2$ activation process in Table 1, all the Gibbs energy barriers for 2H* transfer on MX-64 are all higher than that of MX-66.

Based on the overall consideration of H$_2$ activation and 2H* transfer barriers as listed in Tables 1 and 2, one can find that introducing Al, Ga, Li, and Na to B$_{12}$N$_{12}$ cage has definitely decreased the H$_2$ activation energy barrier but increased the 2H transfer energy as compared to the pristine B$_{12}$N$_{12}$.

In order to be more intuitive, a potential energy surfaces of the reaction pathway are shown in Fig. 5 showing a balance between H$_2$ activation and H transfer. Thus, the interaction between the cluster and H$_2$ is extremely important, the stronger catalyst with more strength to activate the hydrogen molecule would promote a faster hydrogen activation process. On the other hand, a stronger catalyst has more strength to keep the hydrogen, thus would slow down the hydrogen transfer process. This is in accordance with the general Sabatier principle.

To understand the trend of protonation activation barriers for the studied nanocages, we analyze the charges on C site of CO$_2$. In the free standing state, C carries 1.069 e. When CO$_2$ is adsorbed with MX-66 configuration on B$_{12}$N$_{12}$−2H*, NaB$_{12}$N$_{12}$−2H* and LiB$_{12}$N$_{12}$−2H*, the charges increase to 1.086, 1.084, and 1.087 e, respectively. The increased charges on C site make it more active to easily bind H with smaller barriers. The similar mechanism can also be applied to other cages.

### 2H* transfer one by one with stepwise mechanism.

When checking the overall the activation energy barrier of H$_2$ transfer and transfer (seen from Tables 1 and 2), one can find that many clusters such as Al$_{12}$N$_{12}$, NaB$_{12}$N$_{12}$ and AlB$_{11}$N$_{12}$ etc. have lower H$_2$ activation but higher 2H* transfer barriers. To search for a lower barrier of H transfer, the other mechanism needs to be investigated further. We find that a new stepwise mechanism exists for CO$_2$ hydrogenation only on Be$_{12}$O$_{12}$ cage as shown in Fig. 6.

By following this reaction mechanism, the first H transfer is a rate-limiting step-with an activation energy of 0.22 eV on MX-64 bond (red line on Fig. 6) and 0.36 eV on the MX-66 bond (blue line on Fig. 6). In contrast, the 2H* transfer activation on MX-64 and MX-66 bonds is 0.45 eV and 0.24 eV, respectively. Then, we can conclude

| Clusters          | B$_{12}$N$_{12}$ | Al$_{12}$N$_{12}$ | B$_{12}$P$_{12}$ | Al$_{12}$P$_{12}$ | Be$_{12}$O$_{12}$ | LiB$_{12}$N$_{12}$ | NaB$_{12}$N$_{12}$ | AlB$_{11}$N$_{12}$ | GaB$_{12}$N$_{12}$ |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\Delta G_{HT}^1$| 1.45            | 1.43            | 2.02            | 1.41            | 0.45            | 2.16            | 1.75            | 2.05            | 2.25            |
| $\Delta G_{HT}^2$| 1.40            | 1.36            | 1.91            | 1.47            | 0.24            | 1.49            | 1.51            | 1.89            | 2.06            |

Table 2. Gibbs energy barrier for H$_2$ transfer ($\Delta G_{HT}$) to form HCOOH, all values are in eV.
that 2H* simultaneously transfer to CO2 on MX-66 bond has lower activation energy than that of the one H transfer stepwise, but on MX-64 bond the situation is opposite.

For practical applications of an efficient catalyst, both the H2 activation and transfer barriers should be comparable or lower than 1 eV\(^4\). Among all systems studied here, Be\(_{12}\)O\(_{12}\) is the most promising catalyst, where the H2 activation barrier is close to 1 eV (1.04 eV) on MX-64 bond, and the following H* transfer barriers are all lower than 1 eV (0.45 eV by the 2H* simultaneously transfer mechanism, while 0.22 eV by the H* stepwise transfer mechanism). Therefore, the reaction pathway on Be\(_{12}\)O\(_{12}\) MX-64 bond has the lowest barrier based on the overall consideration of the H2 activation (1.04 eV) and H* stepwise transfer (0.22 eV).

**Conclusions**

In summary, based on the DFT and MP2 calculations, a series M\(_{12}\)X\(_{12}\) nano-cages have been studied for activating H2 and CO2 to form HCOOH. The hydrogenation process mainly consists of H2 activation to 2H*, and then 2H* further transfer to CO2 forming a HCOOH molecule. Two kinds of H* transfer mechanisms are found: one involves 2H* simultaneous transfer, and the other is a stepwise H* transfer to CO2. The two mechanisms result...
in the same product HCOOH. Moreover, Al, Ga doped and Li, Na decorated \( \text{B}_{12}\text{N}_{12} \) cages have lower \( \text{H}_2 \) activation energy barriers, but higher \( 2\text{H}^+ \) transfer activation barriers than that of the pristine \( \text{B}_{12}\text{N}_{12} \). For practical applications, in order to have an efficient catalyst to reduce \( \text{CO}_2 \), we should search for a catalyst that has a balance between the energy barriers for \( \text{H}_2 \) activation and the \( \text{H}^+ \) transferring. Among all the systems studied here, \( \text{B}_{12}\text{O}_3\text{F}_2 \) is found to be the most promising catalyst, its reaction pathway on MX-64 bond has the lowest barriers (1.04 eV for \( \text{H}_2 \) activation and 0.22 eV for \( \text{H}^+ \) transferring). This conclusion would motivate experimental work in the future.

**Methods**

Since many theoretical calculations have demonstrated that different DFT functions (e.g. B97D, \( \omega \)-B97X-D, and M06-2X) and basis sets (e.g. 6–31 G*, 6–31 + G**) led to very similar results for the systems only containing main group elements for \( \text{H}_2 \) activations\(^7,8,11 \). In this work, all the geometry optimizations are performed at the M06-2X/6–31 + G** level as implemented in Gaussian 09 package\(^45 \). Solvent effects are taken into account by using the polarizable continuum model (PCM) with toluene as a solvent. The highly parameterized, empirical exchange correlation functional, M06-2X, developed by Zhao and Truhlar, was shown to better describe the main-group thermochemistry and kinetics than other density functionals such as B3LYP\(^46 \). Moreover, this hybrid density M06-2X functional has been previously proved to have a good reliability in computing molecular binding energies of \( \text{H}_2 \) and \( \text{CO}_2 \) on FLPs\(^32 \). Frequency calculations are carried out at the same level to characterize the nature of the stationary points along the reaction coordinates. No imaginary frequencies were found for the local minima, and one and only one imaginary frequency was found for the transition state. The Natural Bond orbitals (NBO) second-order perturbation theory (MP2)\(^24,50 \) with the cc-pVTZ triple-\( \omega \) basis set was used to perform all the calculations.

**References**

1. Appel, A. M. et al. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of \( \text{CO}_2 \) Fixation. Chem. Rev. 113, 6621–6658 (2013).
2. Wang, W. H., Himeda, Y., Muckerman, J. T., Manbeck, G. F. & Fujita E. \( \text{CO}_2 \) Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical \( \text{CO}_2 \) Reduction. Chem. Rev. 115, 12936–12973 (2015).
3. Li, Y. W., Su, H. B., Chan, S. H. & Sun, Q. \( \text{CO}_2 \) Electrocatalysis on Transition Metal Diamines Supported on Graphene: A Theoretical Study. ACS Catal. 5, 6658–6664 (2015).
4. Li, Y. W. & Sun, Q. Recent Advances in Breaking Scaling Relations for Effective Electrochemical Conversion of \( \text{CO}_2 \). Adv. Energy Mater. 4, 16004631–19 (2016).
5. Li, Y. W., Chan, S. H. & Sun, Q. Heterogeneous Catalytic Conversion of \( \text{CO}_2 \): A Comprehensive Theoretical Review. Nanoscale. 7, 8663–8683 (2015).
6. Sun, X. Y., Li, B., Liu, T. F., Song, J. & Su, D. S. Designing Graphene as a New Frustrated Lewis Pair Catalyst for Hydrogen Activation by Co-doping. Phys. Chem. Chem. Phys. 18, 11120–11124 (2016).
7. Zeonjuk, L. L. Are Intramolecular Frustrated Lewis Pairs also Intramolecular Catalysts? A Theoretical Study on Hydrogen Activation. Phys. Chem. Chem. Phys. 17, 10687–10698 (2015).
8. Zeonjuk, L. L. et al. On the Mechanism of Hydrogen Activation by Frustrated Lewis Pairs. Chem. Eur. J. 19(51), 17413–17424 (2013).
9. Ghuman, K. K. et al. Photoexcited Surface Frustrated Lewis Pairs for Heterogeneous Photocatalytic \( \text{CO}_2 \) Reduction. J. Am. Chem. Soc. 138, 1206–1214 (2016).
10. Chen, J. W., Falivene, L., Caporaso, L., Cavallo, L. & Chen, E. Y.-X. Selective Reduction of \( \text{CO}_2 \) to \( \text{CH}_4 \) by Tandem Hydrosilylation: A Kinetic Study on the Reaction of \( \text{CO}_2 \) by Frustrated Lewis Pairs: from Understanding to Rational Design. Phys. Chem. Chem. Phys. 18, 3567–3574 (2016).
11. Ye, J. Y. & Johnson, J. Design of Lewis Pair–Functionalized Metal Organic Frameworks for \( \text{CO}_2 \) Hydrogenation. ACS Catal. 5, 2921–2928 (2015).
12. Courtemanche, M. A., Andrè-Légare, M., Maron, L. & Fontaine, F. G. Reducing \( \text{CO}_2 \) to Methanol Using Frustrated Lewis Pairs: The Interface between Phosphine–Borane-Mediated Hydroboration of \( \text{CO}_2 \). J. Am. Chem. Soc. 136, 10708–10717 (2014).
13. Stepah, D. W. & Erker, G. Frustrated Lewis Pair Chemistry: Development and Perspectives. Angew. Chem. Int. Ed. 54, 6400–6441 (2015).
14. Reisman, M., Schäfer, A., Jung, S. & Müller, T. Sillyium Ion/Phosphene Lewis Pairs. Organometallics 32, 6736–6744 (2013).
15. Herrington, T. J. et al. Bypassing a Highly Unstable Frustrated Lewis Pair: \( \text{H}_2 \) Activation and \( \text{H}^+ \) Transfer. J. Am. Chem. Soc. 136, 12573–12576 (2014).
16. Clark, E. R. & Ingleson, M. J. N-Methylacridinium Salts: Carbon Lewis Acids in Frustrated Lewis Pairs for Catalytic Reduction of \( \text{CO}_2 \). Angew. Chem. Int. Ed. 53, 11036–11039 (2014).
17. Xu, X., Zhao, G., Danilu, C. G. & Erker, G. Reactions of a Cationic Geminal Zr\( ^{+} \) with Small Molecules. J. Am. Chem. Soc. 135, 6465–6476 (2013).
18. Nomland, A. T. et al. Phosphido- and Amidozirconocene Cation-Based Frustrated Lewis Pair Chemistry. J. Am. Chem. Soc. 137, 10796–10808 (2015).
19. Chapman, A. M. & Wess, D. F. Cationic \( \text{Ti}(\text{IV}) \) and Neutral \( \text{Ti}(\text{III}) \) Titanocene-Phosphoryloxylic Frustrated Lewis Pairs: Hydrogen Activation and Catalytic Amine-Borane Dehydrogenation. Dalton Trans. 41, 9067–9072 (2012).
20. Chase, P. A., Gillette, T. M. & Stepah, D. W. Frustrated Lewis Pairs Derived from \( \text{N}^{2+} \)-Heterocyclic Carbines and Lewis Acids. Dalton Trans. 21, 7179–7188 (2009).
21. Hounjet, L. J. et al. Combinations of Ethers and \( \text{B}(\text{C}_6\text{F}_{13})_3 \): Function as Hydrogenation Catalysts. Angew. Chem. Int. Ed. 52, 7492–7495 (2013).
22. Longobardi, L. E., Tang, C. & Stephan, D. W. Stoichiometric Reductions of Alkyl-Substituted Ketones and Aldehydes to Borinate Esters. Dalton Trans. 43, 15723–15726 (2014).
23. Tanar, C. A. & Stephan, D. W. The Thiouther-Methyleneborane (\( \text{PhSC} \),\( \text{B}(\text{C}_6\text{F}_{13})_3 \)): Synthesis and Reactivity with Donors and Alkynes. Organometallics. 30, 3652–3657 (2011).
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Author Contributions
H.Z. carried out the theoretical calculations and wrote the manuscript. G.Z. and Y.L. analyzed the reaction mechanism. Q.S., H.S. and S.C. designed the study.

Additional Information
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