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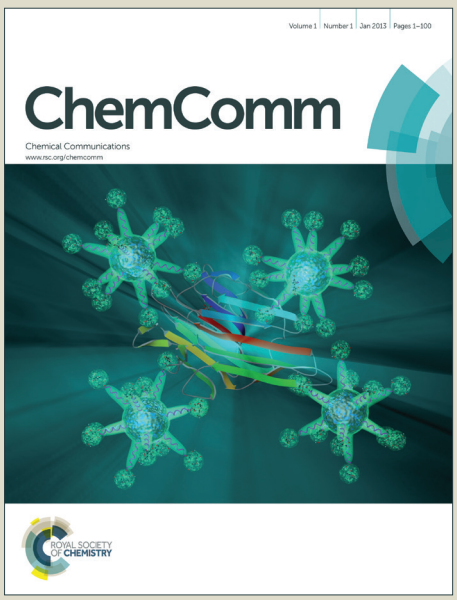





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# Bio-inspired computational design of iron catalysts for hydrogenation of carbon dioxide

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**Inspired by the active site structure of monoiron hydrogenase, a series of iron complexes are built by experimentally ready-made acylmethylpyridinol and aliphatic PNP pincer ligands. Density functional theory calculations indicate that the newly designed iron complexes are very promising to catalyze the formation of formic acid from $H_2$ and $CO_2$.**

The utilization of carbon dioxide as an abundant, inexpensive and non-toxic $C_1$ building block for the synthesis of valuable chemicals is attracting increasing attention. Steady progress has been achieved in developing transition metal catalysts for the reduction of $CO_2$.[1] The most active catalyst to date is Nozaki's aromatic PNP pincer iridium trihydride complex, which achieved TOF and TON values of 150000 $h^{-1}$ and 3500000, respectively, for hydrogenation of $CO_2$ to formate in aqueous solution with base.[2] Hazari and co-workers reported an aliphatic PNP pincer iridium trihydride catalyst and achieved TOF and TON values of 18780 $h^{-1}$ and 348000, respectively, for $CO_2$ reduction.[3] Hull and co-workers reported high efficiency Cp* iridium bipyrimidine catalysts for reversible hydrogenation of $CO_2$ and dehydrogenation of formic acid.[4]

The development of high efficiency base metal catalyst for $CO_2$ reduction is more challenging. Beller and co-workers reported a tetradentate iron hydride complex for catalytic hydrogenation of $CO_2$.[5] Yang computationally designed a pincer iron complex, *trans*-($^{iPr}$PNP)Fe(H)$_2$CO, and predicted its catalytic activity for hydrogenation of $CO_2$ and ketones.[6] Milstein and co-workers synthesized a similar iron complex, *trans*-($^{tBu}$PNP)Fe(H)$_2$CO, which achieved a TOF value of 156 $h^{-1}$ for catalytic hydrogenation of $CO_2$ under mild condition.[7] Linehan and co-workers reported a cobalt-based catalyst for hydrogenation of $CO_2$ and achieved 3400 $h^{-1}$ TOF at room temperature and 1 atm.[8] Although significant progress has been achieved in homogeneous hydrogenation of $CO_2$, most of the reported catalytic systems either contain expensive noble metals, or require rigid reaction conditions with basic environment. A base usually plays a critical role in the reaction by participating the cleavage of molecular hydrogen, or making the formation formic acid thermodynamically favourable. In addition, the efficiencies of those reported base metal catalysts are still rather low. Therefore, the design of low-cost, high efficiency catalysts using abundant first-row transition metal for hydrogenation of $CO_2$, while challenging, remains highly attractive.

In our previous theoretical study of $H_2$ activation catalyzed by monoiron hydrogenase ([Fe]-hydrogenase),[9] we found that the pyridone ligand in its active center assists $H_2$ cleavage through the formation of a strong dihydrogen, Fe–$H^{\delta-}\cdots H^{\delta+}$–O, bond. If we could build a five coordinated iron complex that contains a pyridone type ligand, we may be able to utilize the specialties of metal dihydrogen bond and mimic the hydrogen activation property of [Fe]-hydrogenase. We are glad to see Hu and co-workers have recently reported the synthesis of a series of active site models of [Fe]-hydrogenase with a mono-iron center ligated by an acylmethylpyridinol ligand.[10] In addition to the pyridinol type ligand, tridentate pincer ligands have excellent redox-activities and have been widely used to build iron catalysts for hydrogenation and dehydrogenation reactions.[11] Therefore, the combination of a bidentate acylmethylpyridinol ligand and a tridentate pincer ligand and seems promising to build low-cost iron catalysts for hydrogen activation.

In this Communication, we report a bio-inspired catalyst design. A series of aliphatic PNP iron pincer complexes are built based on the active site structure of [Fe]-hydrogenase. Their catalytic activities for base free hydrogenation of carbon dioxide are predicted through density functional theory (DFT) calculations by using the Gaussian 09 suite of programs[12] for the M06 density functional[13] in conjugation with the all-electron 6-31++G(d,p) basis set for all atoms.[14] Unless otherwise noted, the energies reported in the text are Gibbs free energies with the solvent effect corrections for THF. Further computational details and the evaluation of density functionals are provided in the Supporting Information.

Figure 1 shows our newly proposed iron complexes (**E**) and several structures closely related to our design, including the crystal structure of the active site of [Fe]-hydrogenase (**A**),[15] the model structure of the active site of [Fe]-hydrogenase synthesized by H...

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and co-workers (**B**),[10] the structure model in the computational study of Yang and Hall (**C**),[9] and the structures of recently reported aliphatic PNP iron complexes (**D**).[11] As shown in Figure 1A, the iron in the active site of [Fe]-hydrogenase is ligated by two *cis*-carbonyls, a Cys176-sulfur and an acylmethylpyridinol group. According to our previously catalytic mechanism study, acylmethylpyridinol group plays an essential role in $H_2$ activation. Therefore, we keep it coordinated to Fe and use a tridentate aliphatic PNP pincer ligand to replace the thiol group and two carbonyls in the newly complex. The vacant position in the newly designed five-coordinated iron complex could be filled by a $H_2$ molecule for further activations.

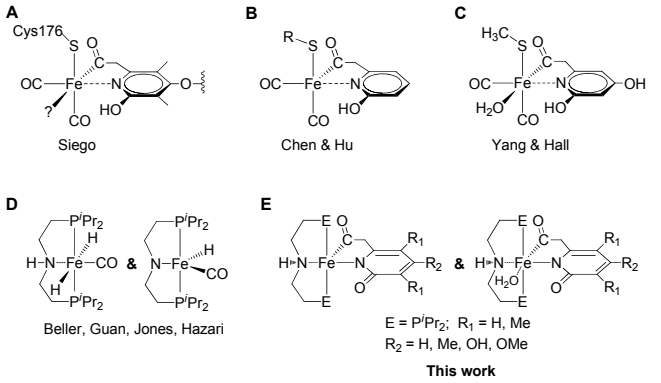



**Fig. 1** (**A**) Observed crystal structure of the active site of [Fe]-hydrogenase. (**B**) Synthesized structure model of the active site of [Fe]-hydrogenase with an acylmethylpyridinol ligand. (**C**) Structure model of the active site of [Fe]-hydrogenase in computational study. (**D**) Aliphatic PNP iron catalysts. (**E**) Newly designed iron complexes.

We first examined the iron complexes with the simplest acylmethylpyridinol ligand ($R_1$ = $R_2$ = H, **1** and **1′**). The optimized structures of **1** and its isomer **1′** are shown in Figure 2. They are neutral complexes with singlet ground states. The primary difference between **1** and **1′** is the directions of the N2-H1 and Fe−C1 bonds, which have the same direction in **1**, but reversed directions in **1′**. Calculation results indicate that **1** is 2.4 kcal/mol more stable than **1′**. We believe the higher stability of **1** comes from the interaction between H1 and O1 with a distance of 2.006 Å in **1**.

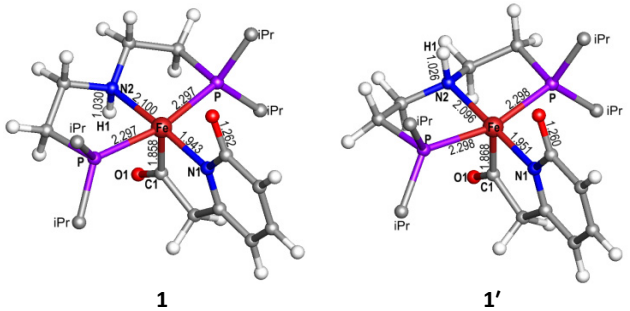
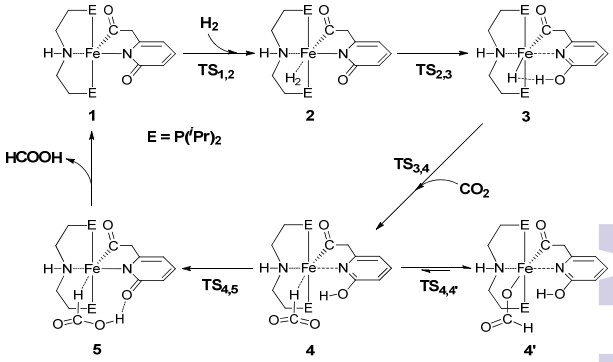



**Fig. 2** Optimized structures of **1** and **1′**. Isopropyl groups are omitted for clarity. Bond lengths are in Å.

The distances between Fe and two P atoms in **1** are both 2.297 Å, which is almost the same as the observed Fe−P distances of 2.3 Å in the crystal structures of ($^{i\text{Pr}}$PNP)Fe(CO) complexes.[11a, 11d] The Fe−N1 distance in **1** is 1.943 Å, which is significantly shorter than the Fe−N distance of 2.0−2.1 Å in the crystal structures of [Fe]-hydrogenase,[15a] and is almost the same as the Fe−N distance of 1.953 Å in the synthesized model structure of [Fe]-hydrogenase reported by Hu et al.[10c] The Fe−N2 distance in **1** is 2.100 Å, slightly longer than the Fe−N distances of 2.07 Å in the crystal structures of ($^{i\text{Pr}}$PNP)Fe(CO) complexes.[11] Such short Fe−P, Fe−N and Fe−C bond lengths indicate that **1** is a stable five-coordinated iron complex.




**Scheme 1** Mechanism of hydrogenation of $CO_2$ catalyzed by newly designed pincer iron complexes features the formation of a strong Fe−H$^{\delta-}$···H$^{\delta+}$−O dihydrogen bond for $H_2$ cleavage.

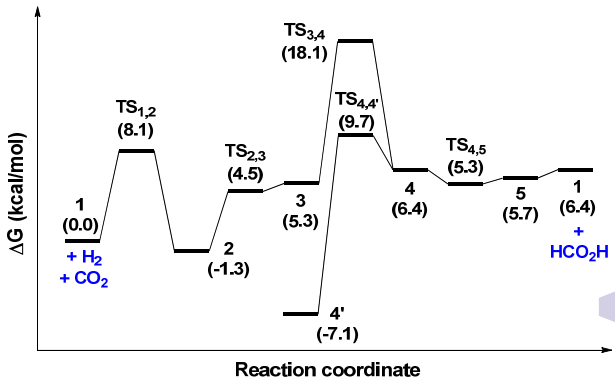



**Fig. 3** Free energy profile for the formation of formic acid from $H_2$ and $CO_2$ catalyzed by **1**.

Scheme 1 shows the reaction mechanism of the formation of formic acid from $H_2$ and $CO_2$ catalyzed by the newly designed iron complexes. Figure 3 shows the corresponding free energy profile. Figure 4 shows the optimized structures of key intermediates and transition states. At the beginning of the reaction, a $H_2$ molecule fills the vacant position in **1** through transition state **TS$_{1,2}$** and forms a slightly more stable intermediate **2** (Figure 4). The $H_2$ molecule in **2** is easily split by Fe and the oxygen of the acylmethylpyridone ligand in a fashion of frustrated Lewis pairs (FLP) with a free energy barrier of only 5.8 kcal/mol (**2** → **TS$_{2,3}$**). Intermediate **3** (Figure 4) is 6.6 kcal/mol less stable than **2** and has a strong dihydrogen Fe−H$^{\delta-}$···H$^{\delta+}$−O, bond in it. The calculated H$^{\delta-}$···H$^{\delta+}$ distance in **3** is 1.411 Å, much shorter than the H···H distances range of 1.7–2.2 Å in most metal dihydrogen bonds reported so far.[16] The Fe−H$^{\delta-}$···H$^{\delta+}$ and H$^{\delta-}$···H$^{\delta+}$−O angles in **3** are 99.0° and 175.5°, respectively, which are consistent with the typical M–H σ-bond interactions in

most of the observed metal dihydrogen bonds. The existence of a similar Fe−H$^{\delta-}\cdots$H$^{\delta+}$−N dihydrogen bond had been theoretical predicted by Hall and co-workers[17] in their computational study of [FeFe]-hydrogenase, and experimentally observed in a structure model of [Fe]-hydrogenase by Liu et al.[18]

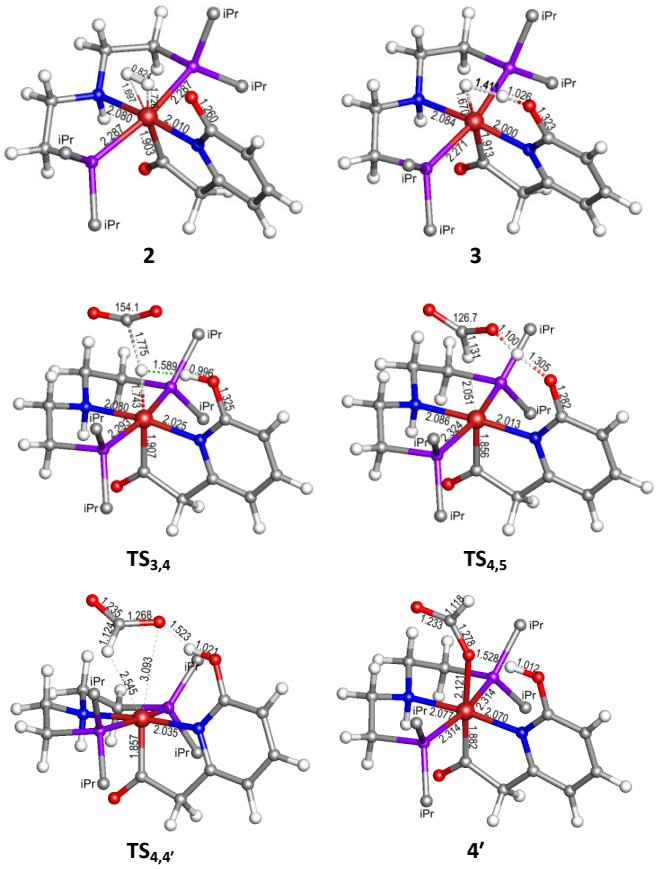



**Fig. 4** Optimized structures of **2**, **3**, **TS$_{3,4}$** (539*i* cm$^{-1}$), **TS$_{4,5}$** (300*i* cm$^{-1}$), **TS$_{4,4'}$** (159*i* cm$^{-1}$) and **4′**. Isopropyl groups are omitted for clarity.

Once the dihydrogen bond is formed, a $CO_2$ molecule attacks **3** and forms a formate anion by taking the hydride directly from the iron dihydrogen bond through transition state **TS$_{3,4}$**, which is the rate determining step with a free energy barrier of 19.4 kcal/mol (**2** → **TS$_{3,4}$**). After the formation of formate, the transfer of the hydroxyl proton to the formate oxygen (**TS$_{4,5}$**) for the formation of formic acid is fast. Although **TS$_{4,5}$** is slightly higher than **4** and **5** in electronic energy, its free energy at room temperature is even 1.1 kcal/mol lower than that of **4** after thermal correction. The similar situation happens between **TS$_{2,3}$** and **3**. The release of formic acid from **5** and the regeneration of **1** is only 0.7 kcal/mol uphill. The calculated free energy of formic acid is 6.4 kcal/mol higher than the free energy of separated $H_2$ and $CO_2$. This is in agreement with the free energy change of 7.9 kcal/mol from gaseous $H_2$ and $CO_2$ to liquid HCOOH.[19] The 6.4 kcal/mol difference in free energy is obtained by using THF as the solvent. Because of the more polar nature of formic acid, the calculated free energy of HCOOH in water is only 0.02 kcal/mol higher than the total free energy of $H_2$ and $CO_2$ in water. This result is very close to the free energy difference of −1 kcal/mol for the reaction happens in aqueous solution.[20] Therefore, the formation of formic acid could be accelerated by adding water to organic solution. Additional base could further expedite the hydrogenation of $CO_2$.

In addition to above direct formation and release of formic acid from **4**, the formate group in **4** could rotate easily through transition state **TS$_{4,4'}$** (Figure 4) and forms a much more stable intermediate **4′** (Figure 4), which is 13.5 and 7.1 kcal/mol more stable than **4** and **5**, respectively. The Fe−O bond length in **4** is only 2.121 Å. Therefore, **4′** could be considered as the resting state of the catalytic reaction. According to the energy span model, **4′** and **TS$_{3,4}$** are the rate-determining states in the catalytic cycle with an free energy difference of 25.2 kcal/mol (**4′** → **TS$_{3,4}$**), which indicates that the reaction could happen under a mild condition. The stability of the structure with the vacant position in **1** filled by a water molecule (**2$_{H2O}$**) was also examined. Calculation results indicate that **2$_{H2O}$** is 2.9 kcal/mol more stable than **1**, but 4.2 kcal/mol less stable than **4**. We can see that although water is more competitive than $H_2$ in filling the vacant spot in **1**, the total catalytic barrier will not be affected.

**Table 1** The influence of substituents to the free energy barrier

| | Catalyst | | $\Delta G$ (kcal/mol) | | $\Delta\Delta G^{\ddagger}$ (kcal/mol)[a] |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | **4′** | **TS$_{3,4}$** | **4′ → TS$_{3,4}$** |
| **1** | H | H | −7.1 | 18.1 | 25.2 |
| **1b** | H | Me | −7.2 | 17.7 | 24.9 |
| **1c** | H | OH | −5.5 | 19.5 | 25.0 |
| **1d** | H | OMe | −5.7 | 19.0 | 24.7 |
| **1e** | Me | H | −6.4 | 17.7 | 24.1 |
| **1f** | Me | Me | −7.4 | 16.5 | 23.9 |
| **1g** | Me | OH | −6.0 | 18.6 | 24.6 |
| **1h** | Me | OMe | −6.5 | 19.1 | 24.6 |

[a] Total free energy barriers calculated as the relative free energies between **TS$_{3,4}$** and the most stable intermediate **4′**.

In order to find out the iron complexes with higher catalytic activities, we also examined the influence of various functional groups to the energy barrier of the reaction. As shown in Figure 1, seven analogues of **1** are constructed by replacing the hydrogen atoms at the para and meta positions of the acylmethylpyridinol ligand with methyl, hydroxyl and/or methoxyl groups. Table 1 shows the free energies of the analogues of **4′** and **TS$_{3,4}$** relative to the corresponding analogues of **1**, and the relative free energies between **4′** and **TS$_{3,4}$**. In general, the influence of different functional groups for the free energy barrier is less than 1.5 kcal/mol. The iron complexes with a hydrogen at the meta positions of the acylmethylpyridinol ligand ($R_1$ = H, R2 = H, Me, OH, OMe) have free energy barriers near 25 kcal/mol, slightly higher than the iron complexes with a methyl group at the meta positions of the acylmethylpyridinol ligand ($R_1$ = Me, R2 = H, Me, OH, OMe). The complex with three methyl groups at the para and meta positions of the acylmethylpyridinol ligand ($R_1$ = $R_2$ = Me, **1f**) has the lowest free energy barrier of 23.9 kcal/mol, which is 1.3 kcal/mol lower than the barrier of **1**. Such a low barrier indicates that **1f** is a highly active catalyst for potential base free hydrogenation of carbon dioxide under a mild condition.

In conclusion, we have computationally designed and examined a series of iron complexes built from experimentally ready-made acylmethylpyridinol and aliphatic PNP ligands. DFT calculations indicate that the newly designed iron complexes are very promising to catalyse the hydrogenation of $CO_2$ in aqueous solution, and the dehydrogenation of formic acid in organic solvents. Among the proposed iron complexes, **1f** is the most active catalyst with a total free energy barrier of 23.9 kcal/mol. The key role of the acylmethylpyridinol ligand in the catalytic reaction is assisting the cleavage $H_2$ by forming an iron, $Fe{-}H^{\delta-}\cdots H^{\delta+}{-}O$, dihydrogen bond in a fashion of frustrated Lewis pairs. Our findings not only provide a series of promising catalysts for low-cost and high efficiency hydrogenation of carbon dioxide, but also reveal the importance of metal dihydrogen bond in hydrogen activation, and enlighten ideas for novel catalyst design based on the active site structures of metalloenzyme. Further design and evaluation of iron complexes with various tridentate pincer ligands for more hydrogenation and dehydrogenation reactions are underway.

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