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Mechanism of CO₂ Reduction to Methanol with H₂ on an Iron(II)-scorpionate Catalyst

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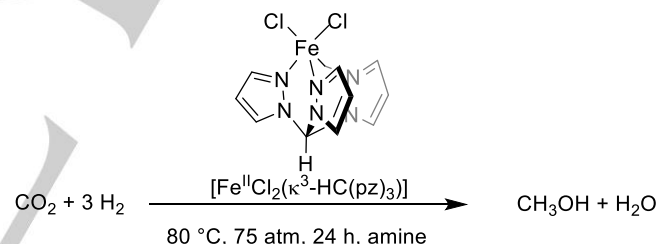
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Abstract: CO₂ utilization is an important process in the chemical industry with great environmental power. In this work we show how CO₂ and H₂ can be reacted to form methanol on an iron(II) center and highlight the bottlenecks for the reaction and what structural features of the catalyst are essential for efficient turnover. The calculations predict the reactions to proceed through three successive reaction cycles that start with heterolytic cleavage of H₂ followed by sequential hydride and proton transfer processes. The H₂ splitting process is an endergonic process and hence high pressures will be needed to overcome this step and trigger the hydrogenation reaction. Moreover, H₂ cleavage into a hydride and proton requires a metal to bind hydride and a nearby source to bind the proton, such as an amide or pyrazolyl group, which the scorpionate ligand used here facilitates. As such the computations highlight the non-innocence of the ligand scaffold through proton shuttle from H₂ to substrate as an important step in the reaction mechanism.

the proton transfer delivery.^[5] Furthermore, an iron(I)-porphyrin system with variable *meso*-substituents was shown to give competitive reduction of CO₂ to either CO or methane under a H₂ atmosphere and reaction conditions were explored to improve the selectivity.^[6]



Scheme 1. CO₂ reduction to methanol on an iron(II)-scorpionate catalyst as reported in Ref ^[10].

Introduction

Carbon dioxide is one of the main chemicals contributing to global warming and its concentration in the atmosphere has been steadily increasing since the Industrial Revolution. In recent years, therefore, research has focused on carbon dioxide utilization and its chemical conversion into valuable materials, such as hydrocarbons, esters, alcohols etc.^[1] Thus, Nature utilizes several enzymes for CO₂ reduction processes particularly in plants and bacteria.^[2] Moreover, a number of homogeneous catalysts have been designed for CO₂ reduction processes at room temperature with either porphyrinoid or nonheme ligands environments.^[3] In particular, iron-porphyrinoid complexes with groups on the second coordination sphere that can assist with proton relay mechanisms were shown to be very efficient for electrochemical CO₂ to CO reduction processes.^[4] These studies trapped and characterized short-lived intermediates and measured electrochemical reduction processes. Density functional theory studies on the CO₂ to CO reduction on iron-porphyrin systems showed the electronic features during the reaction processes and

By contrast, homogeneous iron catalysts for CO₂ reduction at room temperature are rare. Montandon-Clerc and Laurency reported an iron(II) complex with *meta*-trisulfonated-tris[2-(diphenylphosphino)ethyl]phosphine ligand that in the presence of 75 atm of H₂ and CO₂ gas reacted to form formic acid products.^[7] Using an iron(II)-pincer complex the reaction of H₂ and CO₂ gas was studied in the presence of amide.^[8] The authors established a mechanism that started with the H₂ cleavage on iron, followed by the formation of a formamide, which subsequently reacts to give methanol products in another reaction with H₂. Similar reactivity was observed on a manganese(I)-pincer complex that also produced methanol from CO₂ and H₂ gas.^[9] Pombeiro and co-workers^[10] reported a novel iron(II)-scorpionate ligand system, namely with the hydrotris(1-pyrazolyl)methane (κ³-HC(pz)₃) tripodal metal coordination (Scheme 1) that under high pressure conditions at 80 °C was shown to convert CO₂ and H₂ to methanol efficiently with 44% yield. Under relatively mild conditions and even under the absence of solvent and amine the reaction was shown to proceed. A combination of experimental

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and computational approaches investigated the $[\text{Fe}^{\text{II}}\text{Cl}_2(\kappa^3\text{-HC}(\text{pz})_3)]$ system and identified spectroscopic and electronic features of the catalyst.^[11] To understand the details of the CO_2 conversion to methanol on this iron(II)-scorpionate ligand system we decided to do a detailed density functional theory study into possible mechanisms for CO_2 reduction and obtain insight into the function and properties of the metal and ligand system.

Computational studies can give insight into fast reaction processes that are difficult to trap experimentally and consequently can establish rate-determining steps in reaction mechanisms, the nature of an active oxidant or reductant as well as electronic information on what drives the reaction processes.^[12] These insights can assist with further development and design of catalysts. Several computational studies have been reported on CO_2 reduction on iron and manganese catalysts.^[5,13] In particular, these studies show that CO_2 binding is slightly endergonic and consequently may determine the rate, while the reduction and proton abstraction steps appear to be exergonic. Here we report a computational study on $[\text{Fe}^{\text{II}}(\kappa^3\text{-HC}(\text{pz})_3)]$ and show that CO_2 reduction with H_2 gives methanol rather than CO products as the available hydride and protons enable efficient transfer to the iron-bound substrate. In particular, the reaction is initiated by heterolytic cleavage of H_2 into a hydride that binds to iron and a proton that binds to a pyrazolyl group of the ligand scaffold. These studies highlight the non-innocence and importance of the ligand in the reaction mechanism.

Results and Discussion

Binding of H_2 and CO_2 to the iron(II)-scorpionate complex.

In principle, the reaction described in Scheme 1 starts with an $[\text{Fe}(\text{Cl}_2)(\kappa^3\text{-HC}(\text{pz})_3)]$ complex and replacement of the chlorine ions with substrates. We calculated the $[\text{Fe}(\text{Cl}_2)(\kappa^3\text{-HC}(\text{pz})_3)]$, $[\text{Fe}(\text{Cl})(\kappa^3\text{-HC}(\text{pz})_3)]^+$ and $[\text{Fe}(\kappa^3\text{-HC}(\text{pz})_3)]^{2+}$ complexes in the quintet spin state as well as an isolated Cl^- ion and determined the halide binding energies to the complexes. We calculate a free energy for release of one halide ion of $\Delta G = 11.6 \text{ kcal mol}^{-1}$ and a value of $\Delta G = 25.5 \text{ kcal mol}^{-1}$ for the removal of a second halide ion. As such the halide ions are weakly bound to the complex and will split off rapidly in solution or in the presence of amine molecules in the chemical system.

Next, the possible binding of CO_2 and H_2 to the iron(II)-scorpionate complex was studied. To this end, we created models of $[\text{Fe}^{\text{II}}(\kappa^3\text{-HC}(\text{pz})_3)]^{2+}$ and added one or more H_2 and CO_2 molecules to the complex. Thus, in model **A** we included one H_2 and one CO_2 molecule bound to iron, whereas model $\mathbf{A}_{3\text{CO}_2}$ contains the iron(II)-scorpionate with one H_2 and three CO_2 molecules while in model $\mathbf{A}_{3\text{H}_2}$ the iron(II)-scorpionate is surrounded by three H_2 molecules and one CO_2 molecule. Subsequently, full geometry optimizations of these three complexes in the lowest energy singlet, triplet and quintet spin states were performed. We identify the spin state with a superscript in front of the label.

The optimized geometries of the complexes **A**, $\mathbf{A}_{3\text{CO}_2}$ and $\mathbf{A}_{3\text{H}_2}$ are shown in Figure 1. The quintet spin state is **A** the ground state for all complexes by more than $\Delta G = 20 \text{ kcal mol}^{-1}$. In particular, ${}^3\mathbf{A}$ and ${}^1\mathbf{A}$ are higher in free energy than the quintet spin state by $\Delta G = 20.7$ and $23.1 \text{ kcal mol}^{-1}$, respectively. As can be seen in all complexes CO_2 binds to iron with an Fe–O bond of 2.252 – 2.266 Å in the quintet spin state structures. This is a typical distance for

the interaction of a neutral ligand to iron and, for instance, seen for the interaction of a histidine to iron in protein structures,^[14] but also in previous studies on CO_2 binding to homogeneous iron catalysts as well as biomimetic model complexes.^[5,15] The H_2 molecule binds side-on with the Fe–H bonds of similar length. In the triplet spin state it is stronger bound with much shorter Fe–H distances that in the quintet spin state, where they are 2.124/2.182 Å in ${}^5\mathbf{A}$ and 2.247/2.249 Å in ${}^5\mathbf{A}_{3\text{H}_2}$. Interestingly, when multiple CO_2 molecules are in the model as in ${}^5\mathbf{A}_{3\text{CO}_2}$, then H_2 binding is weakened and the nearest Fe–H distance is 3.124 Å. A structure with excess CO_2 , therefore, may not give hydrogenation of CO_2 and more efficient catalysis will be obtained with access H_2 . Indeed the experimental work of Pombeiro et al^[10] used a 3:1 ratio of the pressures of H_2 and CO_2 in support of the models described in Figure 1.

To find possible reaction mechanisms of CO_2 reduction to methanol we continued with the model with one CO_2 and H_2 molecule bound to iron and after the hydrogenation added the second H_2 molecule, while the third H_2 molecule was added after the second hydrogenation step was completed.

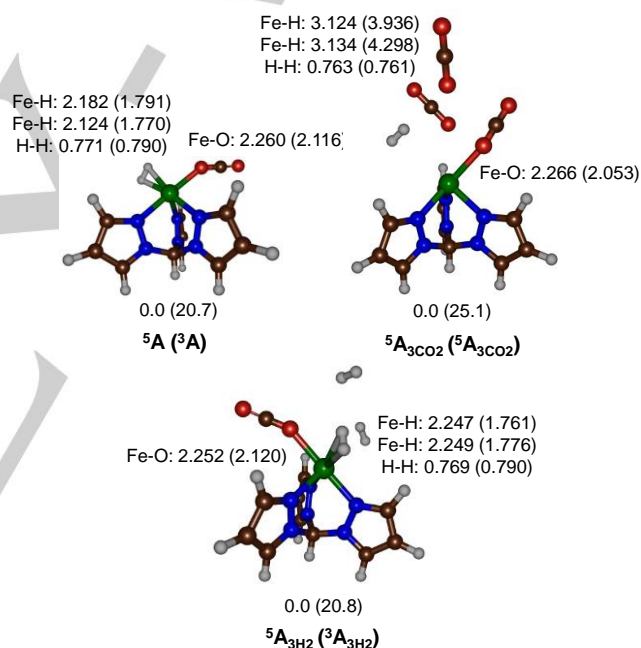
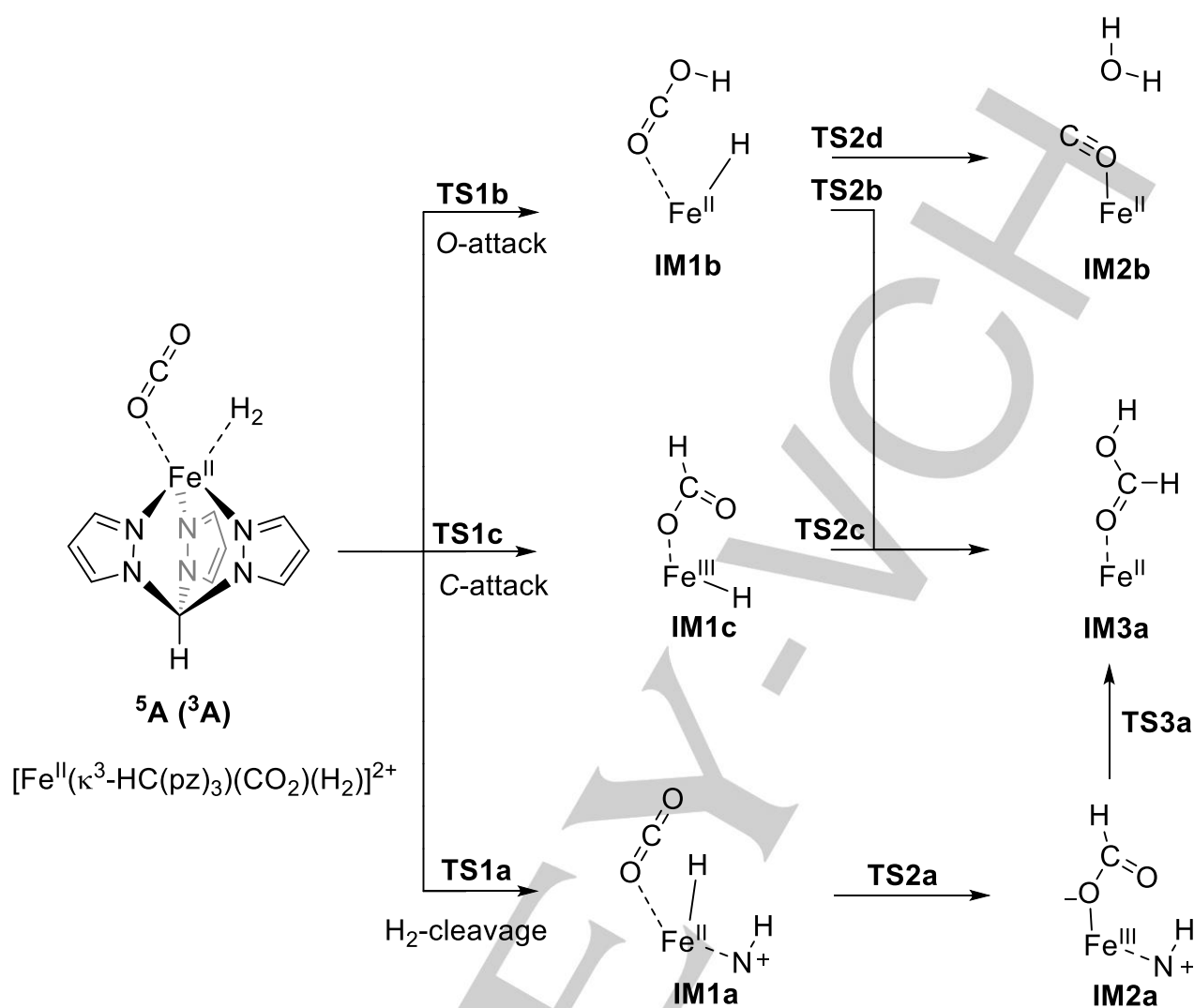


Figure 1. UB3LYP-GD3/BS1 optimized geometries of CO_2 and H_2 bound iron(II)-scorpionate complexes. Bond lengths are in angstroms.

First hydrogenation step of CO_2 by H_2 .

Subsequently, three consecutive reaction cycles were explored for the H_2 addition to CO_2 on the iron(II)-scorpionate center to form methanol products. The work started from the iron(II)-scorpionate complex containing one H_2 and one CO_2 molecule (Model **A**) and in reaction cycle 1 (Scheme 2) focused on the hydrogenation of CO_2 to form formic acid products. For reaction cycle 1, we considered the initial H_2 cleavage to form **IM1a** via transition state **TS1a** and the subsequent hydride transfer to the carbon atom of CO_2 to form formate (via transition state **TS2a** to give **IM2a**). Structure **IM2a** would be an iron(III)-formate bound complex that can pick up a proton to form formic acid products **IM3a** via transition state **TS3a**. In addition, we considered direct attack of



Scheme 2. Catalytic mechanism with definitions of transition states and local minima as calculated for the first reduction of CO₂ on [Fe^{II}(κ³-HC(pz)₃)]²⁺ upon addition of one molecule of H₂.

bound and free H₂ to the oxygen atom of CO₂ in the reactant-bound structure ^{5,3}**A** to form **IM1b** via **TS1b** and attack of H₂ on the carbon atom of CO₂ to give **IM1c** via **TS1c**, while in all these cases the hydride remains attached to iron. For the protonated CO₂-bound structure **IM1b** we also considered a mechanism for formic acid bound iron(II) products formation **IM3a** via transition state **TS2b** or alternatively a pathway for addition of another proton to the protonated carbon dioxide species through the formation of CO and water (**IM2b** via **TS2d**). The internal proton transfer from the Fe–H group in **IM1c** to formate will give **IM3a** via **TS2c**. All mechanisms and pathways were calculated with DFT on the lowest energy quintet and triplet spin state surfaces, see Supporting Information for details.

The lowest energy pathway for the first hydrogenation step of CO₂ by H₂ on the iron(II)-scorpionate complex is shown in Figure 2. Although we tested direct attack of H₂ on CO₂ either on the iron center or as unbound molecules via **TS1b** or **TS1c**, this did not give any low energy pathways, see Supporting Information for details. Consequently, direct attack is unfeasible and a metal catalyst is needed to guide the CO₂ hydrogenation reaction. Indeed, an initial step for dihydrogen bond cleavage via ⁵**TS1a** is

found to trigger the hydrogenation reaction, whereby the hydride remains bound to iron and the proton is transferred to one of the pyrazolyl nitrogen atoms, which then loses its bond to iron. A free energy of activation of ΔG[‡] = 19.6 kcal mol⁻¹ is calculated for dihydrogen bond cleavage. However, the local minimum with the proton attached to nitrogen and the hydride bound to iron is endergonic with respect to reacts by ΔG = 17.5 kcal mol⁻¹. Therefore, it is likely that the reverse reaction from the transition state will dominate and make the reaction inefficient. Not surprisingly, experimental work showed the reaction only to proceed under high pressure conditions of 75 atm,^[10] which is consistent with an endergonic initial reaction step for dihydrogen cleavage. These high pressures, therefore, will push the reaction process further and enable the next reaction step for heterolytic cleavage of the H₂ bond to proceed. The dihydrogen bond cleavage transition state ⁵**TS1a** is shown in Figure 2. It has a large imaginary frequency of i1071 cm⁻¹ for the H–H stretch vibration. This large value implicates the reaction is likely to proceed with a considerable amount of quantum chemical tunneling and particularly will be affected by hydrogen by deuterium substitution leading to a kinetic isotope effect.^[16] The dihydrogen bond has

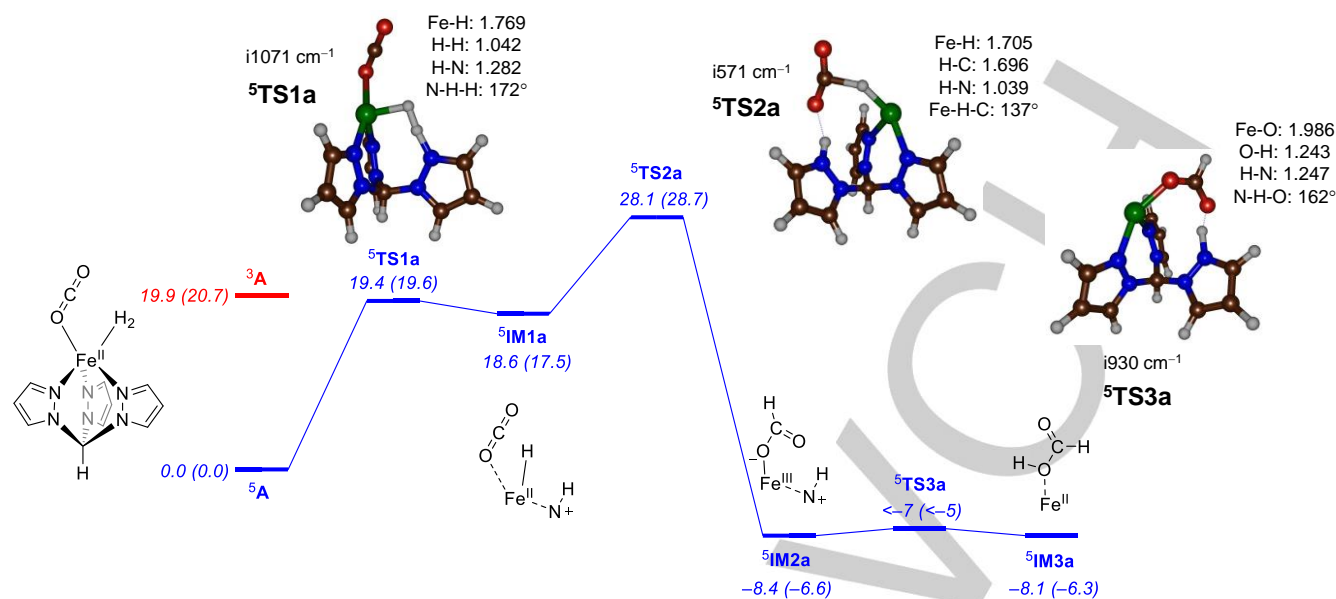


Figure 2. UB3LYP-GD3/BS2//UB3LYP-GD3/BS1 calculated potential energy profile for the first hydrogenation step of CO₂ by an iron(II)-scorpionate complex. Outside parenthesis are $\Delta E+ZPE$ energies (in kcal mol⁻¹) with free energy differences calculated at 298 K are in parenthesis. Transition state structures are shown with bond lengths in Å, bond angles in degrees and the imaginary frequency in cm⁻¹.

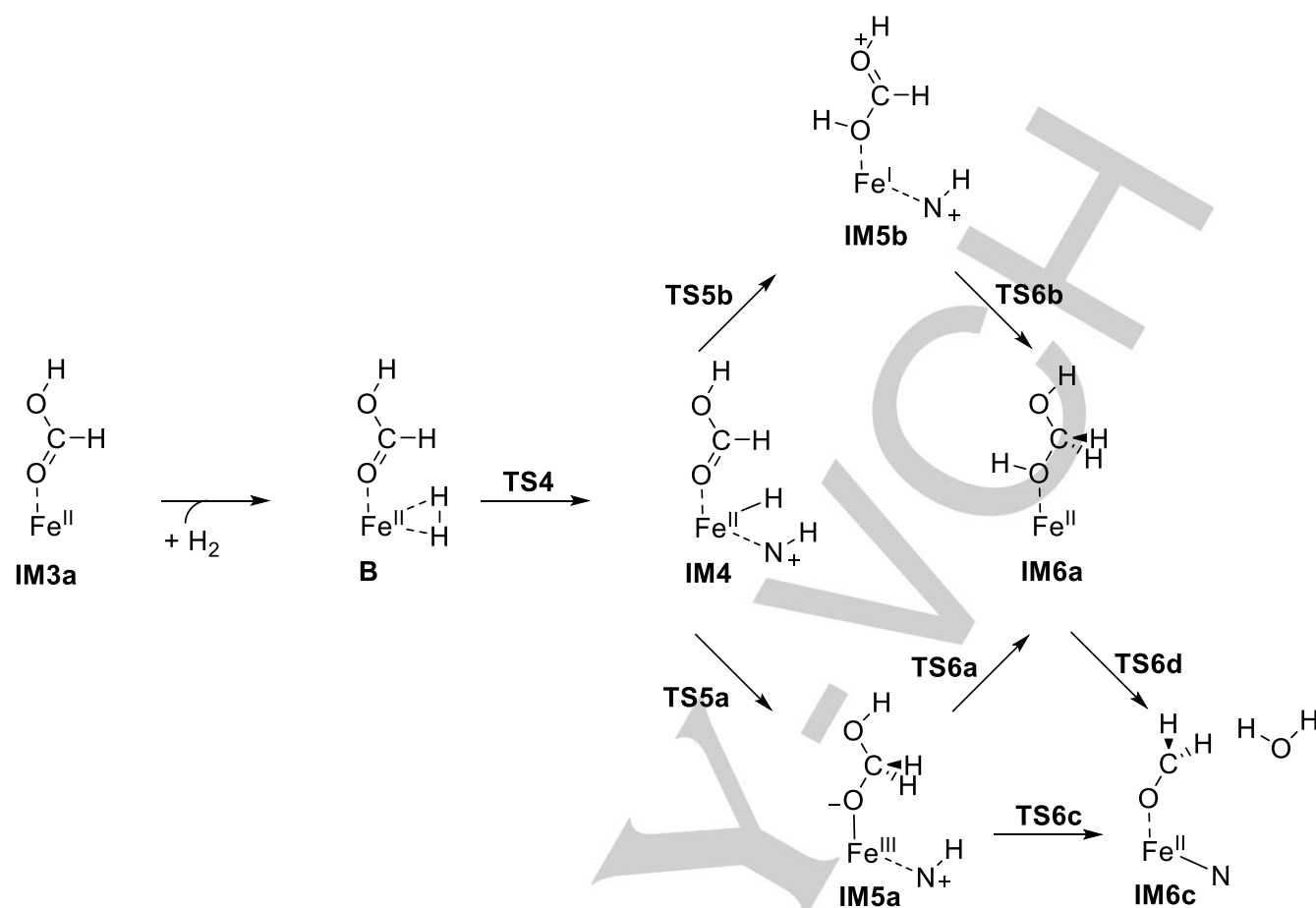
weakened in the transition state to 1.042 Å, while the N–H distance is shortened to 1.282 Å. Also the Fe–H bond has considerably shortened from 2.124 Å in **5A** to 1.769 Å in **5TS1a**. The N–H–H angle is almost linear in the transition state at 172°. After dihydrogen cleavage, a hydride transfer from the iron atom to the carbon atom of CO₂ takes place via transition state **5TS2a**. Its barrier is significant and located at $\Delta G^\ddagger = 28.7$ kcal mol⁻¹, which makes it the rate determining step in the first hydrogenation cycle of CO₂. The transition state has an imaginary frequency of i571 cm⁻¹, which is a low value for a hydride transfer step, but its animation gives a clear C–H–Fe stretch vibration. Most likely the low value is due to the significant bending of the Fe–H–C interaction (137°), probably due to the hydrogen bonding interaction of one of the oxygen atoms of CO₂ with the proton on the pyrazolyl group. Interestingly, the Fe–H distance has not changed significantly from **5IM1a** to **5TS2a** (1.703 vs 1.705 Å, respectively); consequently, the transition state is early on the potential energy surface and is closer in resemblance to reactants than products. The formate-bound iron(III) complex **5IM2a** is lower in free energy than the reactants complex by $\Delta G = -6.6$ kcal mol⁻¹. It forms a strong hydrogen bonding interaction through one of its oxygen atoms with the proton on the pyrazolyl group. A negligible barrier of less than 1 kcal mol⁻¹ above **5IM2a** leads to the formic acid bound product structure **5IM3a**, which is of similar energy as **5IM2a** hence the two structures will be in equilibrium. We managed to characterize **5TS3a** and it has a large imaginary frequency of i930 cm⁻¹ for proton transfer. Structurally, in **5TS3a** the transferring proton is midway between the donor nitrogen atom and accepting oxygen atom: H–O and H–N distances of 1.243 and 1.247 Å are found.

We also attempted mechanisms for direct H₂ attack on CO₂ in the reactant complexes, see Supporting Information. On the triplet

spin state both of these transition states (**3TS1b** and **3TS1c**) were characterized and found to be >40 kcal mol⁻¹ higher in energy than **3TS1a**. Geometry scans on the quintet spin state for the direct attack pathway of H₂ on either the carbon atom or the oxygen atom of CO₂ gave a similar result with high energy barriers. Therefore, a direct H₂ pathway for CO₂ hydrogenation is not a feasible mechanism. Instead the reaction will take place through binding of H₂ to the iron center and an initial H₂ heterolytic cleavage mechanism that gives a hydride bound to iron and a protonated pyrazolyl group. Consequently, the CO₂ hydrogenation to form formic acid products happens through consecutive hydride followed by proton transfer steps.

Second hydrogenation step by H₂.

After the initial hydrogenation cycle of CO₂, we took the formic acid-bound iron(II) structure (**IM3a**) and added another H₂ molecule to form structure **B** and proceeded the reaction mechanism for the next hydrogenation step as described in Scheme 3. In particular, we studied the reaction cycle to form either formaldehyde and water or methanediol. For reaction cycle 2 we considered dihydrogen bond cleavage via transition state **TS4** to form **IM4**. Thereafter, either a hydride is transferred to the carbon atom of formic acid (via **TS5a** to form **IM5a**) or to the carbonyl group of formic acid (via **TS5b** to form **IM5b**). Both intermediates can react with the remaining proton to form the methanediol intermediate **IM6a**. An alternative pathway considered was proton transfer to the alcohol group in **IM5a** to form water and formaldehyde products **IM6c** via transition state **TS6c**. This intermediate can also be reached from proton shuttle between the two OH groups in the diol structure **IM6a** via transition state **TS6d**.



Scheme 3. Catalytic mechanism with definitions of transition states and local minima as calculated for the second reduction of CO₂ on [Fe^{II}(κ³-HC(cz)₃)₂]²⁺ upon addition of a second molecule of H₂.

Thus, to calculate cycle 2 of the process, we took the optimized geometry of ⁵IM3a and added another H₂ molecule to the complex to form ^{5,3}B and did a full geometry optimization on the mechanism for hydrogenation of formic acid and the results are shown in Figure 3. Dihydrogen cleavage in ⁵B requires a free energy of activation of $\Delta G^\ddagger = 22.2 \text{ kcal mol}^{-1}$, which is slightly higher in energy as the H–H cleavage barrier in cycle 1. At ΔE level of theory the barrier ⁵TS4 is higher in energy than the subsequent intermediate ⁵IM4 by 1.6 kcal mol⁻¹; however, addition of zero-point corrections reverses the energy gap and brings it slightly below the energy of the intermediate, which is caused by the removal of a high-energy C–H vibration in the transition state frequency. Nevertheless, the calculations imply a shallow saddle point for ⁵IM4 that is set-up for subsequent hydride transfer. The optimized geometry of transition state ⁵TS4a is very similar to ⁵TS1a with an imaginary frequency of $i1035 \text{ cm}^{-1}$ and an H–H distance of 1.057 Å. The H₂ molecule is at a distance of 1.767 Å from the iron atom and 1.265 Å from the proton acceptor from the pyrazolyl group. From ⁵IM4a a hydride transfer takes place to give ⁵IM5a. The barrier for this step is considerably higher in free energy than the hydride transfer in cycle 1 (at $\Delta G^\ddagger = 46.3 \text{ kcal mol}^{-1}$) and consequently requires high pressure and high concentration and elevated temperatures to proceed. Structure ⁵TS5a has a large imaginary frequency typical for H-transfer processes with a magnitude of $i756 \text{ cm}^{-1}$. The hydride is located midway in between the donor and acceptor atoms, i.e. the Fe–H distance is 1.755 Å and the C–H distance is 1.725 Å, while the

angle for the Fe–H–C interaction is strongly bent at 91°. The small angle may be the origin for the large energetic barrier for this step. Typical hydrogen transfer barriers have a linear orientation between the donor and acceptor groups with a typical angle close to 180°. [17]

Next, two pathways for proton transfer were tested, namely proton transfer to the hydroxo group to form water or proton transfer to the oxo group to form methanediol. The latter barrier was low in energy and a geometry scan located it at $<1.3 \text{ kcal mol}^{-1}$ above ⁵IM5a, Supporting Information Figure S6. Unfortunately, we failed to characterize a transition state for this step, but it is clear the proton transfer to form methanediol is low in energy. The alternative pathway via ⁵TS6c was also explored; however, during the geometry scan from ⁵IM5a for proton transfer to the hydroxo group, the proton moved to the oxo group and ⁵IM6a was formed instead. Consequently, the pathway via ⁵TS6c is unfeasible. We did, however, characterize ⁵TS6d for the intramolecular proton transfer in methanediol to form water and formaldehyde, see Figure 3. This transition state is $\Delta G^\ddagger = 23.8 \text{ kcal mol}^{-1}$ higher in energy than ⁵B and leads to ⁵IM6c. Structurally, ⁵TS6d has a large imaginary frequency of $i1519 \text{ cm}^{-1}$ characteristic for proton transfer. The transferring proton is closer to the donor oxygen atom than the acceptor group: 1.171 versus 1.325 Å.

In summary, the second reaction cycle has a rate-determining hydride transfer reaction of high energy that will require high pressures and temperatures. Thereafter, proton transfer can happen to give either the diol or formaldehyde intermediates. As

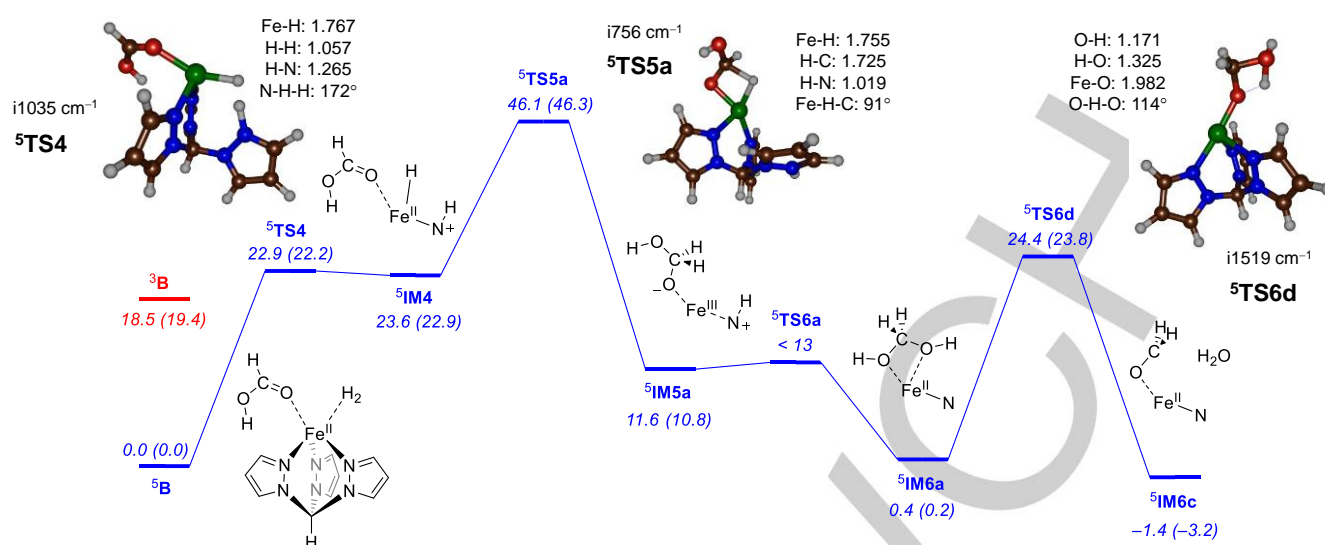


Figure 3. UB3LYP-GD3/BS2/UB3LYP-GD3/BS1 calculated potential energy profile for the second hydrogenation step of CO₂ by an iron(II)-scorpionate complex. Outside parenthesis are $\Delta E + \text{ZPE}$ energies (in kcal mol⁻¹) with free energy differences calculated at 298 K are in parenthesis. Transition state structures are shown with bond lengths in Å, bond angles in degrees and the imaginary frequency in cm⁻¹.

these two intermediates may both be stable, we continued the final reaction cycle from both intermediates by adding another hydrogen molecule to the structure to get structures **C** and **D**.

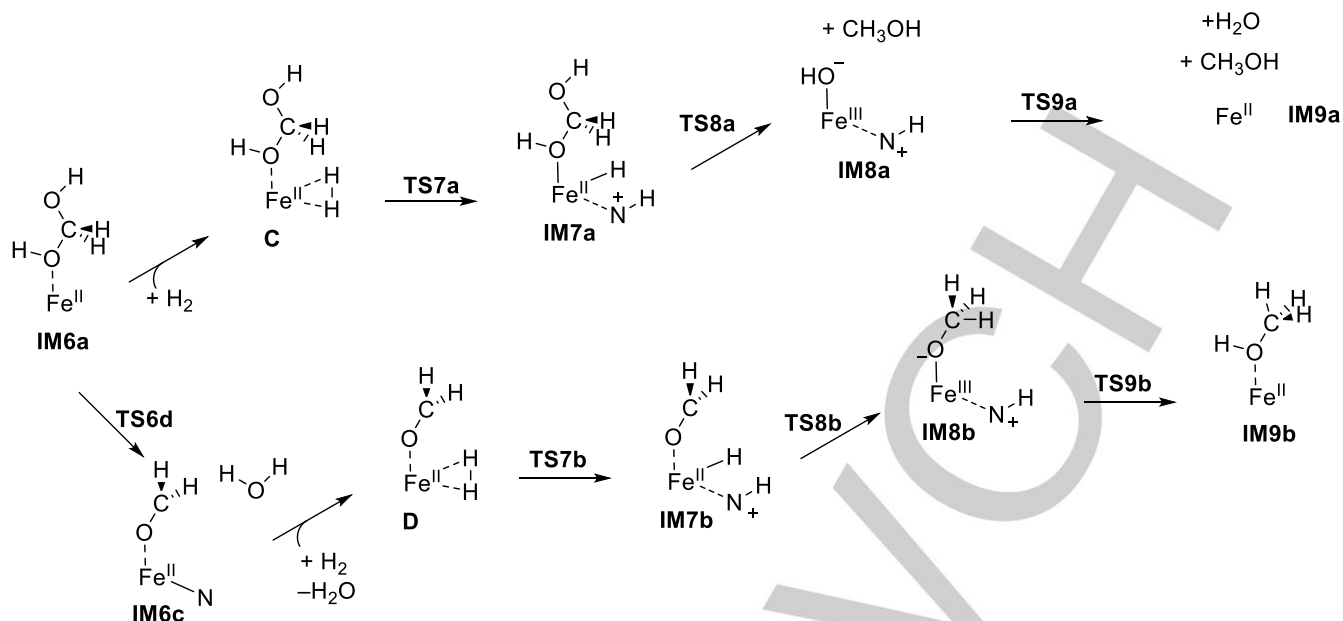
Third hydrogenation step by H₂.

For the final reaction cycle for the third hydrogenation step of CO₂, we took the methanediol-bound iron(II) structure **IM6a** and the formaldehyde-bound iron(II) structure **IM6c** and added another H₂ molecule to give the structures **C** and **D**, respectively. A final reaction cycle with another H₂ molecule added then focused on the generation of methanol final products, see Scheme 4. Similarly to the second cycle, we calculated H₂ cleavage via **TS7a/TS7b** to form structures **IM7a/IM7b**. Both of these intermediates can react through hydride transfer to the carbon atom to form **IM8a** and **IM8b**, although the former may release the methanol group. In the final step either the OH⁻ in **IM8a** is protonated to form water and methanol products **IM9a** via **TS9a** or from **IM8b** the protonation of the methoxy group takes place via **TS9b** gives **IM9b**.

Subsequently, the final hydrogenation cycle was calculated starting from structures **C** and **D** and the potential energy landscape is shown in Figure 4. Structure **C** binds H₂ in a side-on fashion and leads to heterolytic cleavage of H₂ through a barrier **TS7a** to form **IM7a**. The transition states (**TS7a** and **TS7b**) are both on a cusp close in free energy to their subsequent intermediates (**IM7a** and **IM7b**) and even though they are higher in energy than **IM7a/IM7b** at ΔE level of theory, they become degenerate after zero-point and thermal corrections are included,

hence are labelled as < 28 and < 23 kcal mol⁻¹ in Figure 4. Geometrically, the structure of **TS7a** resembles **TS1a** and **TS4** with the H₂ bond elongated to 1.067 Å and Fe-H and N-H distances of 1.763 and 1.259 Å, respectively. The N-H-H angle is close to linearity at 172° and a large imaginary frequency for the H-H stretch vibration of i1051 cm⁻¹ is obtained. This structure is similar to **TS7b** that has Fe-H and N-H distances of 1.767 and 1.265 Å, respectively, while an imaginary frequency of i1019 cm⁻¹ is obtained. The pathway starting from **5C** is then followed by a hydride transfer step via **TS8a**, which was located at a free energy of $\Delta G^\ddagger = 70.5$ kcal mol⁻¹. This is an exceptionally high free energy, which at room temperature will unlikely make the process possible. Consequently, the pathway via **5C** is a dead-end reaction channel and will not lead to methanol products and stop at the methanediol products.

As discussed above in Figure 3 the methanediol complex **5C** through internal proton transfer can split off water and form formaldehyde complex **IM6c** that after binding H₂ gives complex **5D**. We then followed the hydrogenation of formaldehyde from **5D**. This system has a much lower free energy for hydride transfer via **TS8b** of $\Delta G^\ddagger = 32.6$ kcal mol⁻¹ above **5D**. The transition state structure is shown in Figure 4 and has an imaginary frequency of i270 cm⁻¹ for the C-H-Fe stretch vibration. The distances in the transition state are 1.652 Å for the Fe-H bond and 2.075 Å for the C-H bond. After the hydride transfer the system relaxes to methanolate-bound iron(III) with large exothermicity. A final barrierless proton transfer then gives final methanol products.



Scheme 4. Catalytic mechanism with definitions of transition states and local minima as calculated for the third reduction of CO₂ on [Fe^{II}(κ³-HC(cz)₃)₂]²⁺ upon addition of a third molecule of H₂.

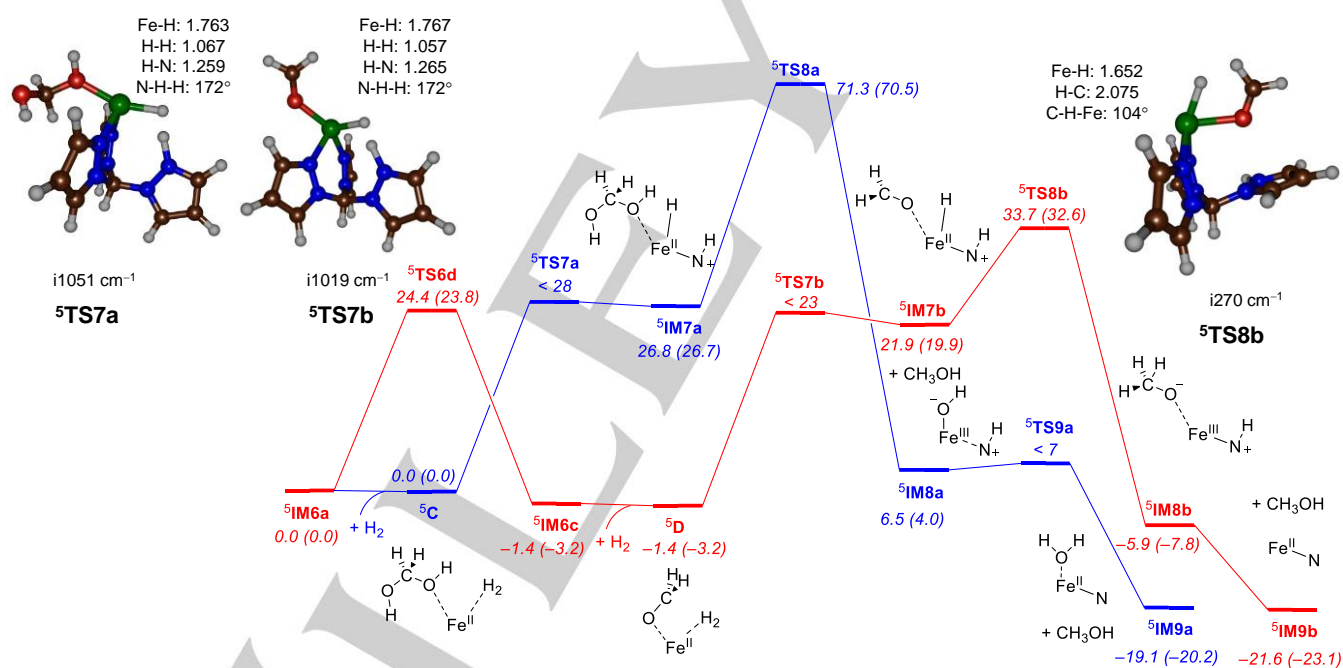
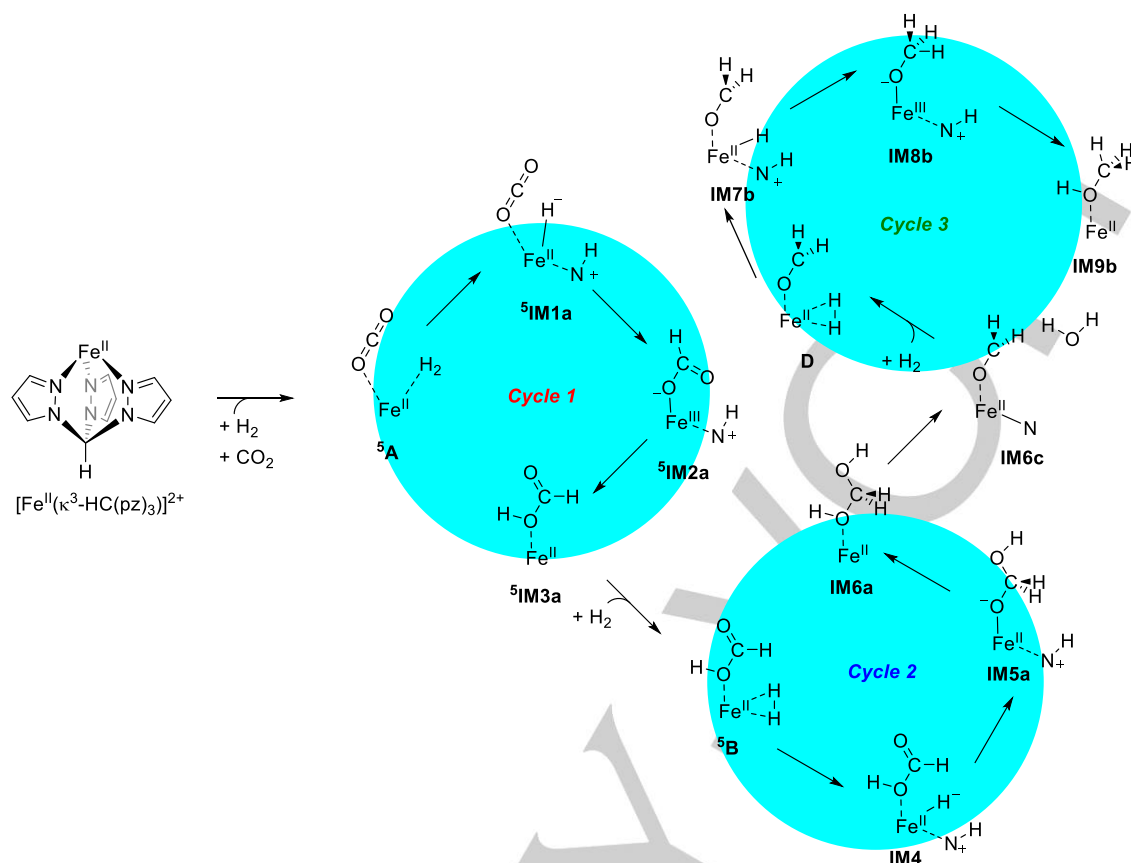


Figure 4. UB3LYP-GD3/BS2//UB3LYP-GD3/BS1 calculated potential energy profile for the third hydrogenation step of CO₂ by an iron(II)-scorpionate complex. Outside parenthesis are $\Delta E + \text{ZPE}$ energies (in kcal mol⁻¹) with free energy differences calculated at 298 K are in parenthesis. Key transition state structures are shown with bond lengths in Å, bond angles in degrees and the imaginary frequency in cm⁻¹.



Scheme 5. Reaction mechanism of CO₂ reduction by H₂ on an iron(II)-scorpionate system as established from this work.

Overall reaction pathway established from DFT calculations.

The calculations described in this work focus on CO₂ reduction to methanol with three molecules of H₂ on a nonheme iron(II)-scorpionate complex. The work has established a mechanism with three successive reaction cycles for H₂ binding and addition to substrate as described and summarized in Scheme 5. Calculations with multiple CO₂ and H₂ molecules nearby iron(II) show that excess H₂ is needed to enable direct binding of H₂ to the metal center as it binds weaker than CO₂ and will not be able to compete with it. Upon H₂ binding each reaction cycle starts with heterolytic cleavage of H₂ into a hydride and a proton, whereby the metal binds the hydride and one of the pyrazolyl rings binds the proton. The H₂-cleavage barriers in cycle 1, 2 and 3 have similar free energies of activation and lead to an endergonic reaction step for the formation of the cleaved H₂-molecule complex. Therefore, high pressures will be needed to overcome this initial endergonic step in the reaction mechanism and enable the CO₂ hydrogenation reactions. The H₂-cleavage barrier is not rate-determining but the subsequent hydride transfer from iron to substrate, which has barriers of $\Delta G^\ddagger = 28.7$, 46.3 and 32.6 kcal mol⁻¹ for cycles 1, 2, and 3, respectively. The free energy of activation of the second cycle is relatively high and therefore will require considerably high pressures and temperatures to proceed. Moreover, significant amount of acetic acid should be observed after completion of the first cycle. After the hydride is transferred a facile proton transfer completes each cycle. In all three cycles the proton transfer step is fast and rapidly takes place to form the products of each reaction cycle. In summary, in cycle 1 the CO₂ is reduced to formic acid, in cycle 2 the formic acid is reduced to formaldehyde and water via a methanediol intermediate, while in

the final cycle formaldehyde is reduced to methanol. As some barriers, particularly those for hydride transfer are relatively high in free energy, it may be possible to trap formic acid and formaldehyde intermediates experimentally.

The mechanisms for CO₂ reduction to methanol shown in Scheme 5 highlight some important features for catalyst development and design. Firstly, an environmentally benign CO₂ reduction process that utilizes H₂ is energetically demanding as H₂ will need to be cleaved heterolytically and bind to the catalyst center as individual hydride and proton. Therefore, a transition metal is needed to bind the hydride. Generally, heavy metals ions bind a hydride relatively easily and hence are commonly employed for CO₂ reduction processes. However, as shown here, a hydride can bind to iron as well, but in our system it requires a lot of energy to form the hydride-bound complex from H₂ and iron(II) and consequently is energetically demanding. Secondly, the work described here highlights that CO₂ reduction by H₂ will need a proton donor in the vicinity of the catalyst complex and ideally the proton acceptor is bound to the metal center. The scorpionate ligand has several pyrrole groups that can bind and hold a proton for proton shuttle processes. Upon heterolytic cleavage of H₂ one of the iron-pyrazolyl bonds breaks and it picks up the proton instead and thereby facilitates proton transfer within the reaction complex efficiently. The pyrazolyl ligand that picks up the proton of H₂ loses its bond with iron and twists away from the metal center. However, it is close enough to the substrate so that an internal proton transfer is facilitated in the later stage of the reaction. As such, the iron(II)-scorpionate complex provides an ideal scaffold for hydrogenation of CO₂ by H₂ by enabling H₂ cleavage, proton and

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hydride storage and thereafter bringing all components together for efficient hydrogenation.

Orbital analysis of the reaction mechanism.

To understand the origin of the catalytic mechanism and the features that drive the reaction, we analyzed the unpaired spin densities and orbital occupations of key local minima along the reaction mechanism. Figure 5 shows a valence bond description of the bond-forming and bond-breaking processes that happen in the initial cycle for first hydrogenation of CO₂ by a molecule of H₂ on the iron(II)-scorpionate complex. These schemes were used previously to rationalize regio- and chemoselectivities in reaction processes.^[18] Thus, complex **5A** has four unpaired electrons located on the metal (spin of 3.84) in 3d-type molecular orbitals and electronic configuration $\pi^*_{xy}{}^2 \pi^*_{xz}{}^1 \pi^*_{yz}{}^1 \sigma^*_{z2}{}^1 \sigma^*_{x2-y2}{}^1$. These molecular orbitals represent metal 3d atomic orbitals and their interactions with first-coordination sphere ligands. Thus, the π_{xy} , π_{xz} and π_{yz} orbitals form bonding interactions of the iron 3d_{xy}, 3d_{xz} and 3d_{yz} orbitals with 2p orbitals on the nitrogen atoms of the pyrazolyl groups and are all doubly occupied. On the other hand, the antibonding combination of these orbitals, i.e. π^*_{xy} , π^*_{xz} and π^*_{yz} are singly occupied. In addition, there are two s-type molecular orbitals of relevance, namely σ^*_{z2} and σ^*_{x2-y2} . The latter is located in the plane that goes through two pyrazolyl nitrogen atoms, the bound oxygen atom of CO₂ and the H₂ molecule. The orbital is shown on the left-hand-side of Figure 5. As can be seen the H₂ molecular orbital interacts with one of the lobes of the metal 3d_{x2-y2} orbital and provides a stable side-on interaction for H₂ binding.

As all first-coordination sphere ligands are weakly bound and neutral, most of the unpaired spin density is on the metal and the valence molecular orbitals are metal-based. In addition, **5A** binds a H₂ and CO₂ molecule with a H–H of 0.771 Å and C–O distances of 1.171 (inner) and 1.152 (outer) Å. These distances are not

significantly longer than those found for isolated H₂ and CO₂ molecules; consequently, they are weakly bound to the iron(II) complex without formation of a covalent bond. Alternative triplet and singlet spin states were also tested but found to be well higher in energy. This is not surprising as trigonal bipyramidal iron(II) complexes generally are in a high-spin state.^[19] The iron(II) complex is in a high-spin state with four metal-based unpaired electrons and hence give a large spin density of 3.84 on the iron atom.

The CO₂ hydrogenation reaction starts with heterolytic cleavage of the H–H bond, whereby the two electrons from the H–H bond form the new iron-hydride covalent bond σ_{Fe-H} that is occupied by two electrons. The proton originating from H₂ is transferred to a nitrogen atom of the pyrazole group, which loses its bond to iron and twists away, thereby making space for an Fe–H bond. The hydride electron-pair interacts with the iron 3d_{z2} atomic orbital to form a new σ -type bonding orbital, σ_{Fe-H} , shown in Figure 5. Despite the changes in bond topology on iron, the unpaired spin density does not change much and is $\rho = 3.86$ in **5IM1a**. Therefore, the four unpaired electrons are assigned to metal-type orbitals in π^*_{xz} , π^*_{yz} , σ^*_{z2} and σ^*_{x2-y2} . Consequently, the electronic configuration and oxidation state on iron have not changed during the H₂ cleavage process. The iron-hydride bond in **5IM1a** is long, namely 1.703 Å but little spin density is accumulated on the hydride ($\rho = 0.06$ in **5IM1a**). Moreover, the charge on the hydride ion is $Q = -0.31$, which implies a charge-transfer from hydride to iron has taken place through the formation of the covalent Fe–H bond. Therefore, the Fe–H interaction is drawn as a covalent bond (σ_{Fe-H}) with two electrons. The CO₂ group has no unpaired spin density ($\rho = 0.0$) and consequently no charge-transfer to the CO₂ group has taken place in the process from **5A** to **5IM1a**.

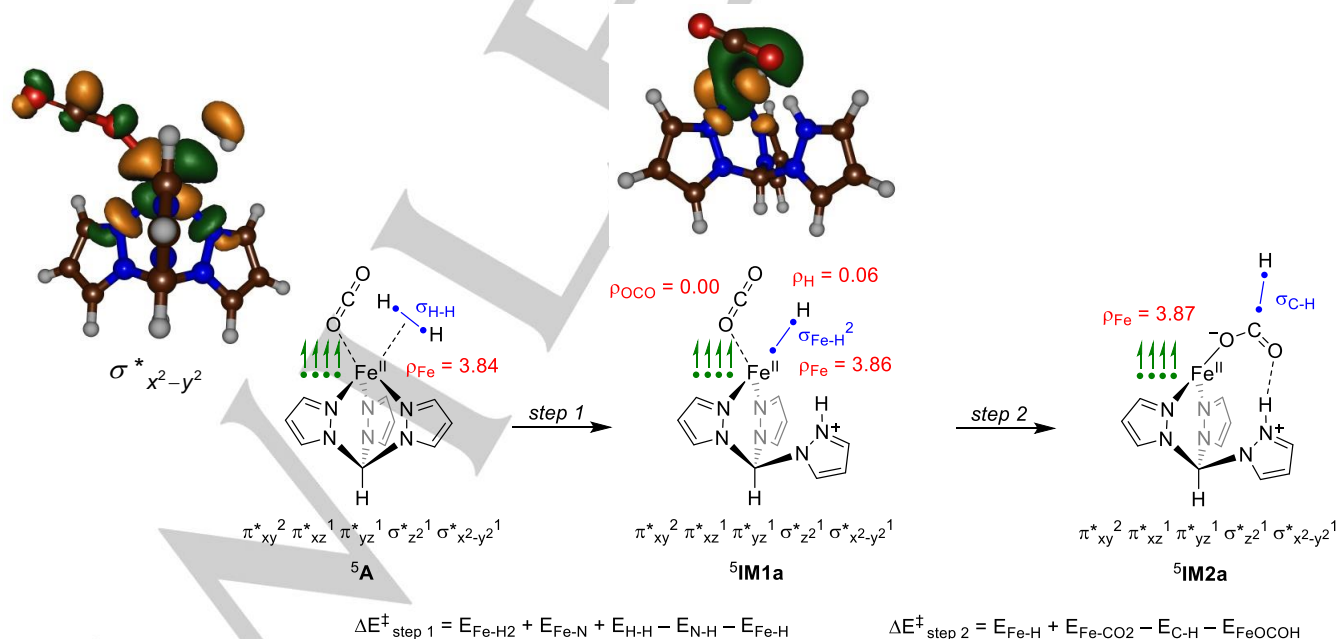


Figure 5. Valence bond description of the first two steps in the reaction mechanism. Unpaired electrons are shown with a dot and arrow (in green), while bonding orbitals are shown as a line between elements with two dots. Group spin densities (ρ) are given in red with values in atomic units. Key valence orbitals are shown.

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We estimated the energy to cleave the H₂ bond in structure ⁵A from the bonds that are broken and formed in the process. Thus, the iron(II)-H₂ bond is broken as well as the heterolytic cleavage of H₂ and both of these interactions are replaced by an iron(II)-hydride interaction. In addition, one of the iron-pyrazolyl bonds breaks and an N–H bond is formed. To estimate the iron(II)-H₂ bond energy (E_{Fe-H₂}), we did a single point calculation on the structure of ⁵A with H₂ removed and find a value of E_{Fe-H₂} = 2.4 kcal mol⁻¹ with respect to ⁵A and H₂. In addition, we did a single point calculation of ⁵IM1a with H₂ removed and its difference in energy with the structure of ⁵A with H₂ removed gives us the strength of the Fe–N bond that is broken (E_{Fe-N}), for which we predict a bond energy of 16.3 kcal mol⁻¹. To estimate the heterolytic cleavage energy of H₂ and the N–H bond that are formed we calculated the reaction of H₂ with water to form hydride and H₃O⁺ as a sum of the two values from full geometry optimizations at B3LYP/BS2 level of theory and find E_{H-H} – E_{N-H} = 87.2 kcal mol⁻¹. Finally, a single point calculation on ⁵IM1a with the hydride removed was done to estimate the iron(II)-hydride bond energy: E_{Fe-H} = 75.6 kcal mol⁻¹. Based on these estimated bond energies, we predict the heterolytic cleavage of H₂ on the iron(II)-scorpionate complex to be strongly endergonic by 30.4 kcal mol⁻¹. Indeed this step is calculated to be endergonic by close to 20 kcal mol⁻¹, see Figure 2. Therefore, high pressures will be needed to overcome this thermodynamically unfavorable step and push the reaction further into the formate-bound intermediate.

In the next step for cycle 1 the hydride transfer takes place and converts CO₂ into formate into ⁵IM2a. As such the two electrons from the σ_{Fe-H} bond form the new C–H bond orbital σ_{C-H} in formate. At the same time the two π-electrons of one of the C–O bonds in ⁵IM1a become a lone-pair and the formate anion in ⁵IM2a. Energetically, reaction step 2 also includes the replacement of the weakly bound iron(II)-CO₂ interaction into the ionic interaction of iron(II) with formate ion. As such, reaction step 2 will be exergonic and irreversible from ⁵IM1a. This reaction step does not change the spin density on iron and the metal retains four unpaired electrons with a spin density of ρ = 3.87 in ⁵IM2a and therefore also the oxidation state of iron does not change. Consequently, the CO₂ hydrogenation is a nucleophilic reaction mechanism rather than a radical reaction type. This is in contrast to aliphatic dehydrogenation reactions by an iron(IV)-oxo complex that proceeds via two successive hydrogen atom abstraction reactions via a radical mechanism.^[20]

In summary, the valence bond scheme in Figure 5 shows that the metal acts as a spectator element in the reaction cycle and stays in the iron(II) oxidation state throughout the reaction. However, the metal assists with the H₂ cleavage process and binds donor and acceptor groups and assists with the hydride and proton transfer processes by bringing the donor and acceptor groups close together. In addition, the pyrazolyl groups enable storage of a proton for the final reaction stage leading to products.

Conclusion

In this work a computational study is presented on CO₂ reduction to methanol on an iron(II)-scorpionate catalyst in a reaction with H₂. The calculations show that H₂ and CO₂ bind to the iron(II) center where the reaction takes place in three successive reaction cycles that use one molecule of H₂ each. Each cycle starts with

heterolytic cleavage of H₂ into a hydride and a proton, whereby the hydride binds iron(II) and the proton binds to one of the pyrazolyl groups that loses its bond with iron. Thereafter each cycle continues with successive hydride followed by proton transfer to substrate. In cycle one, therefore, CO₂ is converted into formic acid, while in cycle 2 the formic acid is reduced to formaldehyde and water and in the final reaction cycle gives methanol as final product. The calculations give valuable insights into the nature of the catalyst and what drives the reaction. In particular, heterolytic cleavage of H₂ needs to take place, which is an endergonic reaction on the iron(II)-scorpionate system. From a design perspective, the catalysts, therefore, should contain a group that can bind a hydride and a group that can hold a proton prior to reshuttle to substrate. The pyrrole groups of the ligand are excellent sources for the proton relay and even though iron(II) can bind hydride the step is generally endergonic. Moreover, the rate-determining step is hydride transfer to substrate, which particularly is slow for the second cycle and consequently the reaction may stop after formation of formic acid products. The work gives detailed insight on the thermodynamic challenges of using H₂ for CO₂ utilization. In particular, H₂ needs to be cleaved heterolytically and on an iron center that reaction is endergonic. Furthermore, a basic group on the ligand scaffold of the iron is needed to store the proton until it is needed later in the reaction mechanism.

Experimental Section

Density functional theory approaches were used as implemented in the Gaussian-09 software package.^[21] The [Fe^{II}(κ³-HC(pz)₃)] structure was manually created and one CO₂ and H₂ molecule added to obtain the initial reactant complex. Geometry optimizations, analytical frequencies and constraint geometry scans were performed with the unrestricted B3LYP density functional method in combination with the GD3 dispersion correction with Becke-Johnson damping.^[22,23] In addition, all calculations included the self-consistent reaction field approach with a dielectric constant for methanol and an all-electron def2-SVP basis set on all atoms.^[24,25] Energies were improved by running a single point calculation with the def2-TZVP basis set on all atoms. Intrinsic reaction coordinate scans were performed from the transition state structures, which confirmed their assignment and what local minima they connect to, see Supporting Information for details. These methods and approaches were validated against experimental rate constants previously and shown to predict free energies of activation by iron complexes to within 3 kcal mol⁻¹ and confirm product distributions.^[26]

Acknowledgements

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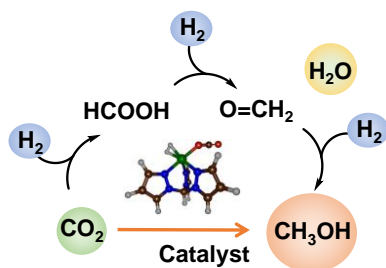
Keywords: Density functional theory • Inorganic Reaction Mechanisms • CO₂ reduction • Iron • Homogeneous catalysis

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Entry for the Table of Contents

Graphic for Table of Contents:



Text for Table of Contents: Density functional theory calculations on the mechanism of the reduction of CO₂ by H₂ on an iron(II) center show the reaction to proceed through heterolytic cleavage of H₂, whereby the ligand holds the proton during the reaction.

Institute and/or researcher Twitter usernames: The University of Manchester (@OfficialUoM); Department of Chemical Engineering (@UoMSciEng); Manchester Institute of Biotechnology (@UoMMIB).