



The significance of acid-base properties in the key ligand for CO₂ hydrogenation: role of amido ligand

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Abstract. Using the density functional theoretical calculations, a series of aliphatic amido pincer based Mn-complexes are proposed for base-free CO₂ hydrogenation. We report here that the acid-base nature of the amido ligand plays a crucial role in heterolytic H₂ cleavage and proton transfer mechanism. The reaction free energy barrier values suggest that such amido ligand-assisted CO₂ hydrogenation requires a lower activation barrier compared to the previously reported noble and non-noble metal-based catalysts. Furthermore, the Mn-NNN complex is the most promising catalyst by far and this could be due to the optimum acid-base nature of the amido ligand. Such acid-base properties of the pincer ligand can be tuned by ligand substitution, which in turn controls the catalytic activity.

Keywords. Density functional calculations; hydrogenation; formic acid; heterolytic H₂ cleavage; hydride transfer.

1. Introduction

The burning of fossil fuels leads to uncontrolled emissions of CO₂, which is one of the biggest concerns of this century.¹ Considerable research works have been carried out to find an alternative source of energy, which is clean and sustainable. Researchers have been working on the conversion of CO₂ into useful products and formic acid is one of such products.²⁻⁶ In the past three decades, many noble metal-based homogenous catalysts have been reported for CO₂ hydrogenation but the cost limits their use in industries.⁷⁻¹⁴ In this respect, first-row transition metal-based complexes are cheap due to their natural abundances. Beller and co-workers reported tetraphos ligand-based iron and cobalt complexes for CO₂ hydrogenation.^{15,16} Milstein and co-workers have used aromatic pincer ligand based iron complexes for CO₂ hydrogenation.^{17,18} However, the activities of these earth-abundant transition metal-based complexes are much lower than the noble metal-based complexes. Jeletic *et al.* reported an active Co(dmpe)₂H [dmpe = 1,2-bis(dimethylphosphino)ethane] complex, which

shows excellent catalytic activity in the presence of strong Verkade's base.^{19,20} But it is a very expensive base. Bernskoetter and co-workers reported a turnover number of 60000 for CO₂ hydrogenation when catalyzed by iron (ⁱPrPN^{Me}P)Fe(H)CO(BH₄) catalyst using a Lewis acid based co-catalyst.²¹ This remains to be one of the most active first row transition metal based catalysts for CO₂ hydrogenation. Recently, Yang and co-workers computationally designed a series of iron and cobalt complexes based on the active site structure of [Fe]-hydrogenase and they predicted that such complexes are promising for CO₂ hydrogenation.²² Similarly, Co-complexes have been reported for CO₂ hydrogenation.²³ Gonsalvi and co-workers reported Mn(PNP^{NH}-ⁱPr)(H)(CO) complex for formic acid formation in the presence of an external base DBU (1,8-diazabicycloundec-7-ene).²⁴ Our group predicted Mn(bpy)(CO)₃⁺ (bpy = bipyridine) complex for CO₂ hydrogenation in the presence of an external base NH(CH₃)₂.²⁵ Dubey *et al.* experimentally reported 6, 6'-dihydroxy-2, 2'-bipyridine based Mn complex for CO₂ hydrogenation, which is very much similar to our theoretically predicted Mn(bpy)(CO)₃⁺ complex.²⁶ These experimental and computational studies suggest that

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Mn-based complexes have emerged as potential catalysts for CO₂ hydrogenation. All these studies suggest that earth abundant metal-based complexes have made a great progress towards CO₂ hydrogenation. Most of these studies reported that the heterolytic H₂ cleavage and hydride transfer are the two most important steps for CO₂ hydrogenation. However, in many cases, an external base has been used to promote heterolytic H₂ cleavage. Many times, such bases are expensive and thus a base free mechanism may be promising for CO₂ hydrogenation. Yang and co-workers reported Mn, Fe and Co pendant amine-based metal complexes for CO₂ hydrogenation where pendant amine act as a frustrated Lewis pairs and activate the H₂.^{27,28} Recently, we have demonstrated that pendant amine-based iron complexes are promising for CO₂ hydrogenation.²⁹

In 2016, Beller and co-workers reported a series of Mn-complexes with aliphatic PNP ligand for the hydrogenation of nitriles, ketones, and aldehydes.³⁰ Similarly, aliphatic PNN-based Ir complexes have been reported for heterolytic H₂ cleavage and ketone hydrogenation.³¹ Furthermore, arylamido PNP based Pd and Rh complexes show excellent catalytic activity for heterolytic H₂ cleavage.^{32,33} Hu and co-workers reported mono and diarylamido NNN based Ni complexes for alkylation reaction.³⁴ Interestingly, such type of ligands (PNP, PNN and NNN) facilitates heterolytic H₂ cleavage and hydride transfer simultaneously, which is very important for CO₂ hydrogenation. So, inspired by these experimental studies, we guessed that amido-based pincer ligands may be promising for heterolytic H₂ cleavage and proton transfer which are important steps in CO₂ hydrogenation. So, in this present study, we have designed aliphatic PNN and NNN based Mn(I) complexes for base free CO₂ hydrogenation. Furthermore, the aryl ligand substitution is done to tune the acid-base properties of the amido ligand, which in turn tunes the catalytic properties of the complex.

2. Computational details

All DFT calculations are performed in Gaussian 09 package³⁵ using hybrid UB3LYP exchange-correlation functional.^{36–38} The LANL2DZ basis set with an effective core potential for Mn and 6-311+G** basis sets are used for non-metals (C, H, O, N and P).^{39–42} Full geometry optimizations have been done in toluene solvent using the conductor-like polarizable continuum model (CPCM).^{43,44} Grimme's dispersion corrections (D3) have been included for all calculations.⁴⁵ Here, we have used UB3LYP functional for Mn(I) based systems as we have found that our calculated results using B3LYP functional are very much in agreement with the experimental report of CO₂ reduction over Mn(I) complexes.^{46,47}

The accuracy of this functional has been tested previously using M06 functional⁴⁸ on a similar type of Mn-PNP systems for CO₂ hydrogenation reaction. We have found that the results obtained using M06 functional are very much in agreement with our UB3LYP results. So, we have continued with UB3LYP functional for our present study. Frequency analyses have been performed to characterize the nature of stationary points and transition states (TSs) are identified with one imaginary frequency. Also, TSs are confirmed from the intrinsic reaction coordinate (IRC) calculations as they correspond to the desired reaction coordinate. Zero-point energy and thermal corrections have been included in our reaction free energy calculations under T = 298.15 K and 1 atmosphere pressure. The reaction-free energies (ΔG) are calculated from the free energy difference between the final and initial state, whereas free energy barrier (ΔG^\ddagger) are calculated from the free energy difference between the transition state and initial state structures. Natural bond orbital (NBO) analysis is done to understand the charge transfer process.⁴⁹

3. Results and Discussion

The amido ligand-based **Mn-PNP** complexes (Figure 1) are well-known for various catalytic reactions. However, **Mn-NNN** and **Mn-PNN** based complexes are yet to be popular though they are structurally very similar to **Mn-PNP** complex. In case of the **Mn-NNN** complex, P(ⁱPr)₂ ligands of **Mn-PNP** complex are substituted by N(ⁱPr)₂ ligands as shown in Figure 1 and named as **Mn-PNN**, when one of the P(ⁱPr)₂ ligands is substituted by a N(ⁱPr)₂ ligand. These complexes (**Mn-PNN** and **Mn-NNN**) are modelled keeping in mind that the N(ⁱPr)₂ group is less electron donating than the P(ⁱPr)₂ group.⁵⁰ This would decrease the electron density at the N centre of the amido group, which in turn decreases the strength of the N-H bond. Therefore, such less electron ligand facilitates the proton transfer mechanism, which is one of the most important steps for CO₂ hydrogenation. Thus, we believe that **Mn-PNN** and **Mn-NNN** pincer based complexes are more promising over **Mn-PNP** complex for CO₂ hydrogenation. In an effort to improve further, aryl ligand substitution is done in these complexes to withdraw more electron density from the N-atom. For this, mono arylamido based pincer ligand has been used to model **Mn-PNP-Ar**, **Mn-PNN-Ar**, and **Mn-NNN-Ar** complexes and diarylamido-based pincer ligand to model **Mn-PNP-Ar₂**, **Mn-PNP-Ar₂**, and **Mn-NNN-Ar₂** complexes (Figure 1 and Figure S1 in Supplementary Information).

Scheme 1 shows the proposed catalytic cycle for CO₂ hydrogenation. Our study is divided into two parts: heterolytic H₂ cleavage followed by hydride transfer mechanism.

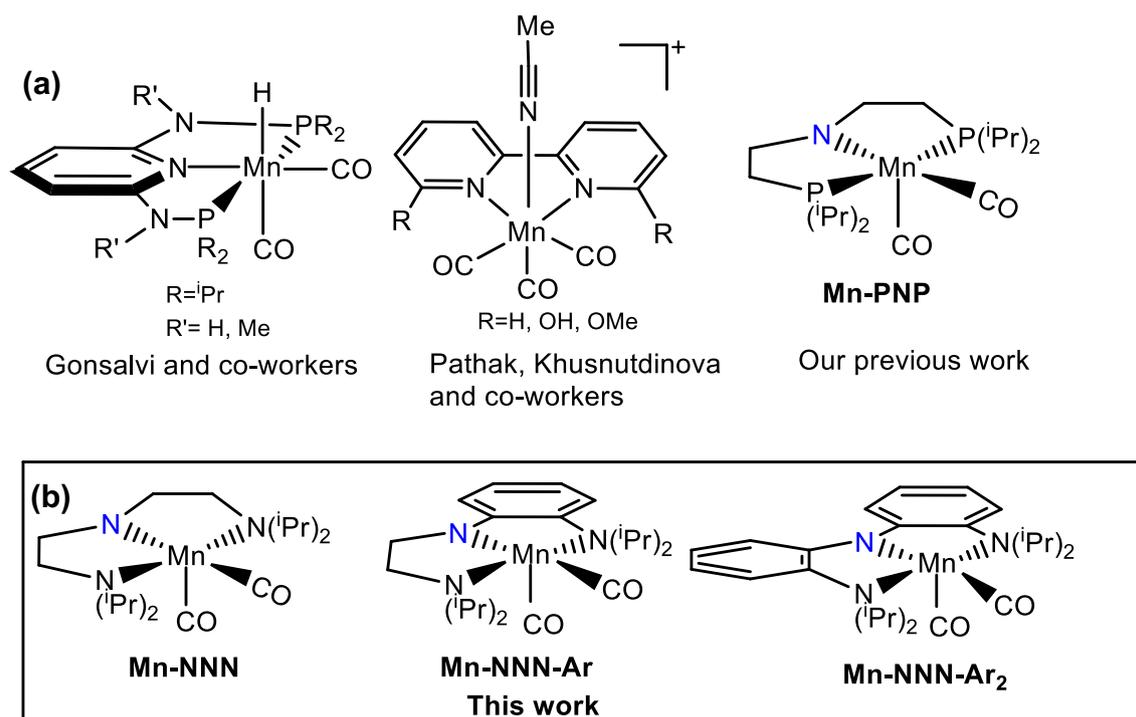


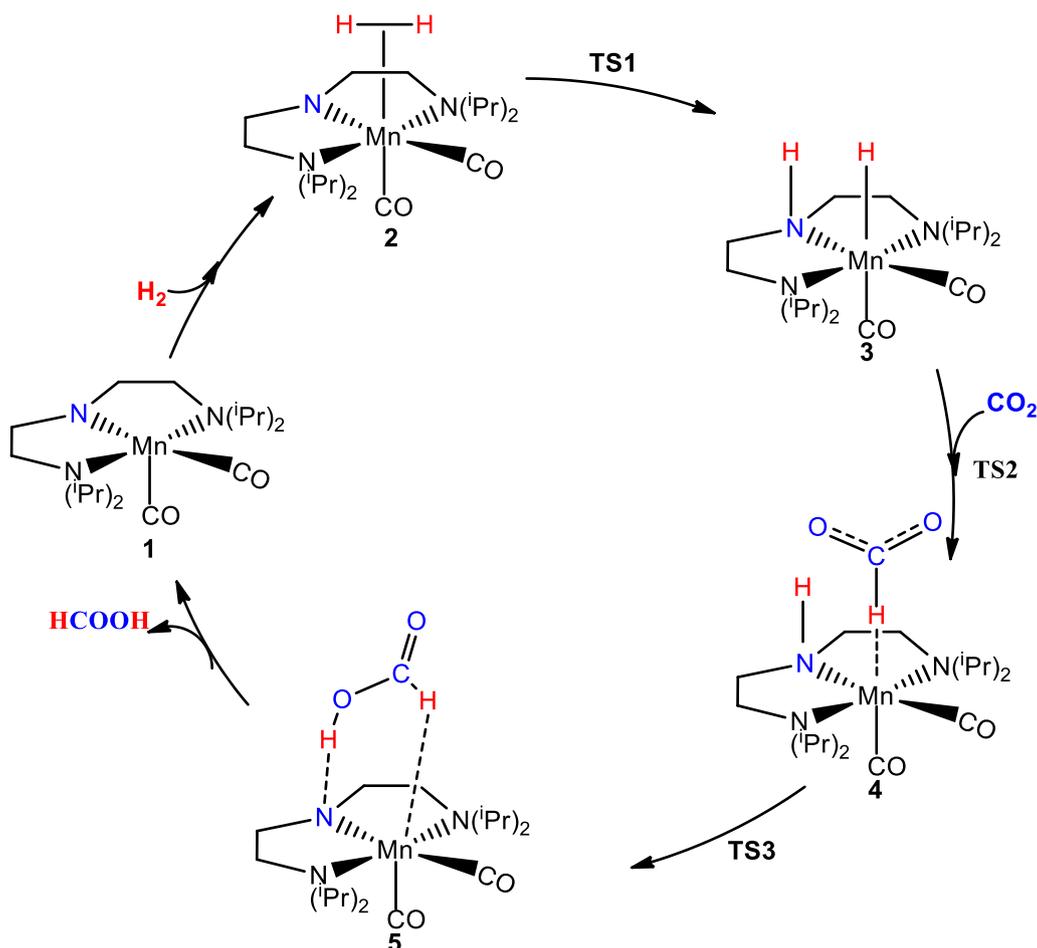
Figure 1. (a) Recently developed manganese complexes for CO₂ hydrogenation reaction; (b) our modelled aliphatic amido Mn(I) pincer complexes for CO₂ hydrogenation reaction.

3.1 Heterolytic H₂ cleavage

We have investigated all the model complexes (Figure 1b and Figure S1) for CO₂ hydrogenation reaction. Our magnetic calculations show that singlet state is the ground state for all the intermediates and complexes. This could be due to the presence of CO ligand, which is a strong field ligand. Figure 2 shows the reaction free energy profile for heterolytic H₂ cleavage when catalyzed by the **Mn-NNN** complex. **Mn-NNN** has a vacant site, where H₂ molecule could come and bind to form **Mn-H₂** σ -complex **2**. The formation of the **Mn-H₂** complex (**1** \rightarrow **2**) is calculated to be endergonic by 13.3 kcal/mol (Figure 2).^{51,52} Further, another possibility is considered that CO ligand can dissociate simultaneously as H₂ molecule bind with **1** (Figure S2 in Supplementary Information). The calculated reaction free energies are 31.5 and 23.1 kcal/mol for the dissociation of the equatorial and axial CO ligands, respectively. This suggests the stability of the CO coordination in the Mn(I) complex, which agrees well with the previous study.³⁰ The binding of CO₂ molecule with **1** is also found to be unfavorable with the reaction free energy of 56.9 kcal/mol (Figure S2). So, these results suggest the formation **Mn-H₂** complex (**2**) is the most favorable over other intermediates. The amido group present in **Mn-NNN** complex initiates the

heterolytic H₂ cleavage (**2** \rightarrow **3**) via the transition state **TS1** (Figure 3). Figure 2 shows that **Mn-NNN** complex requires a total free energy barrier ($\Delta\Delta G^{\ddagger H_2}$) of 16.7 kcal/mol for heterolytic H₂ cleavage. Furthermore, we have calculated the reaction free energy for the N(ⁱPr)₂ group initiated heterolytic H₂ cleavage (Figure S3 in Supplementary Information). The calculated reaction free energy is -2.9 kcal/mol, which is less favorable by 9.7 kcal/mol compared to the amido group initiated H₂ cleavage. This suggests that the amido group-initiated heterolytic H₂ cleavage is more favorable over N(ⁱPr)₂ group-initiated heterolytic H₂ cleavage.

The respective values for other model complexes are given in Table 1 and Table S1 (Supporting Information). Therefore, the **Mn-NNN** complex is the most promising catalyst among all the modelled complexes for heterolytic H₂ cleavage. Beller and co-workers reported (using a different level of calculations) $\Delta\Delta G^{\ddagger H_2}$ of 17.1 kcal/mol when catalysed by an aliphatic amido PNP ligand-based iron complex.⁵³ Yang and co-workers reported (using different level of calculations) that $\Delta\Delta G^{\ddagger H_2}$ is 26.9 kcal/mol when catalyzed by the aromatic PNP-based ruthenium complex.⁵⁴ Pidko and co-workers reported a barrier of 22.7 kcal/mol (using a different level of theory) using pyridine-based Ru-PNP catalyst, where metal–ligand cooperative mechanism



Scheme 1. Proposed catalytic cycle for CO₂ hydrogenation catalysed by **Mn1-NNN** complex.

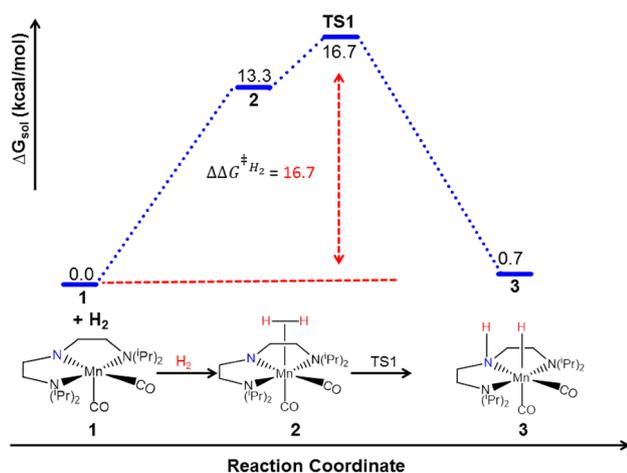


Figure 2. Reaction free energy profile for heterolytic H₂ cleavage catalyzed by **Mn-NNN** complex.

plays an important role.¹⁴ Therefore, **Mn-NNN** complex requires a lower free energy barrier for heterolytic H₂ cleavage compared to the previously theoretically studied noble/non-noble metal-based catalysts.

Table S1 shows that **Mn-PNN-Ar₂** requires a total free energy barrier of 26.3 kcal/mol for heterolytic H₂ cleavage, which is the highest among all the modelled Mn-complexes. Further to this, we find that the heterolytic cleavage barrier increases in the presence of Ar. This indicates that such aromatic substitution withdraws electron density from the metal centre, which in turn increases the activation barrier for heterolytic H₂ cleavage. So, the optimum electronic nature of the ligand is very important for H₂ cleavage. Interestingly, aliphatic NNN pincer ligand is a promising ligand, for which the free energy barrier is 3.4 kcal/mol for H₂ cleavage. This suggests that such aliphatic NNN pincer ligand provides an optimum electronic requirement for H₂ cleavage and can be a promising ligand for CO₂ hydrogenation reaction. On the other hand, aryl substitution on PNN and NNN based aliphatic pincer ligands does not favour the heterolytic H₂ cleavage and thus not promising for CO₂ hydrogenation reaction. On the other hand, aryl substitution on PNP ligand shows promising results on heterolytic H₂ cleavage and thus carried out further for CO₂ hydrogenation reaction.

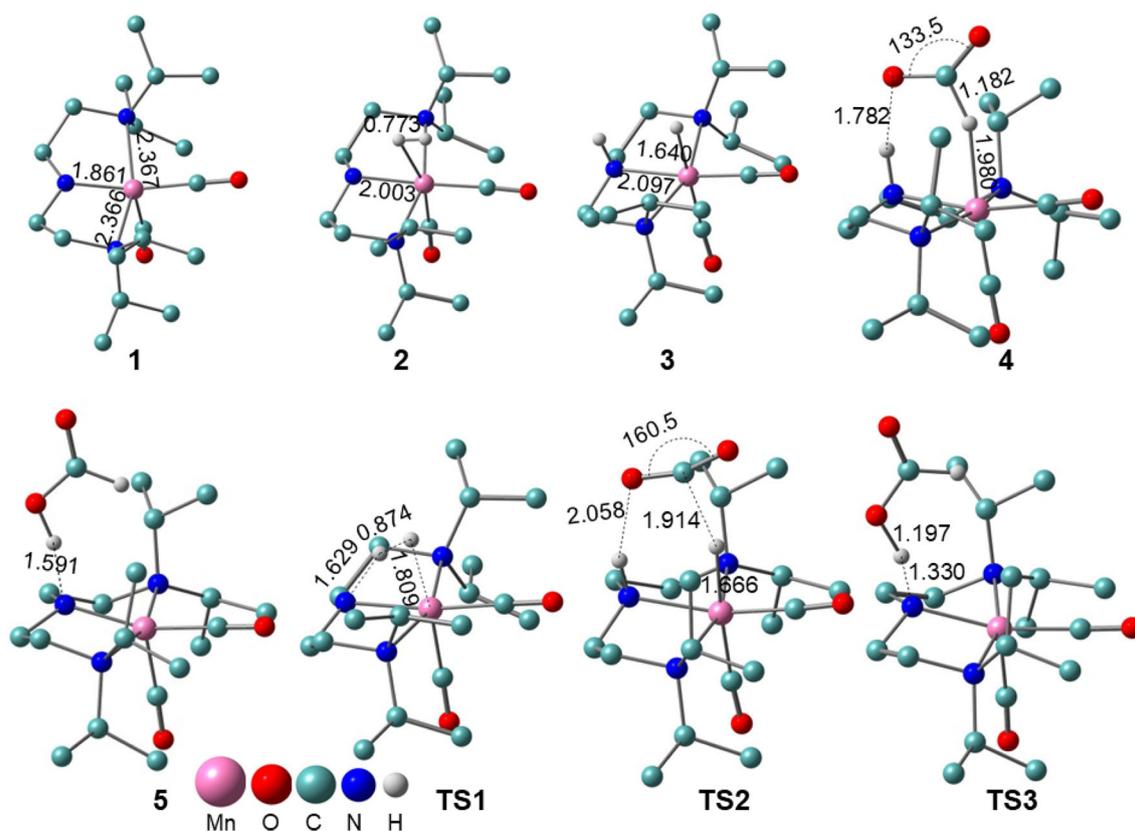


Figure 3. Optimized geometries of all the intermediates and transition states for **Mn-NNN**. Hydrogen atoms are omitted for clarity. Bond lengths and bond angle are in Å and °, respectively.

Table 1. Reaction free energy (ΔG), free energy barrier (ΔG^\ddagger), total reaction free energy ($\Delta\Delta G$) and total free energy barrier ($\Delta\Delta G^\ddagger$) for CO_2 hydrogenation catalysed by amido ligand-based Mn-complexes.

	H ₂ cleavage				H-transfer		$\Delta\Delta G$			$\Delta\Delta G^\ddagger$	
	ΔG	ΔG^\ddagger	ΔG	$\Delta\Delta G^\ddagger$	ΔG^\ddagger	ΔG	TS1	3	4	$\Delta\Delta G^\ddagger_{\text{CO}_2}$	$\Delta\Delta G^\ddagger_{\text{R}}$
	1 → 2	2 → TS1	2 → 3	$\Delta\Delta G^\ddagger_{\text{H}_2}$	3 → TS2	3 → 4					
Mn-NNN	13.3	3.4	-12.6	16.7	10.9	1.6	16.7	0.7	2.3	10.9	16.7
Mn-PNN	13.4	6.3	-16.2	19.7	8.2	0.3	19.7	-2.8	-2.5	10.7	22.5
Mn-PNP^a	12.2	5.1	-16.8	17.3	8.9	-1.4	17.3	-4.6	-6.0	13.9	23.3
Mn-PNP-Ar	8.9	9.4	0.6	18.3	5.9	-3.0	18.3	9.5	6.5	5.9	18.3
Mn-PNP-Ar₂	6.5	14.6	9.6	21.1	5.6	-3.3	21.1	16.1	12.8	5.6	21.7

Here, $\Delta\Delta G^\ddagger_{\text{H}_2}$, $\Delta\Delta G^\ddagger_{\text{CO}_2}$ and $\Delta\Delta G^\ddagger_{\text{R}}$ represent the total free energy barriers for heterolytic H₂ cleavage, CO₂ hydrogenation and reaction (heterolytic cleavage+CO₂ hydrogenation reaction), respectively. Here, all energies are in kcal/mol. ^aOur calculated values are compared with the previous report of CO₂ hydrogenation catalyzed by the **Mn-PNP** complex.⁵⁵

3.2 Hydride transfer

Hydride transfer (**3** → **4**) is another important step for CO₂ hydrogenation reaction. In the case of hydride transfer, it is important for Mn-H σ -bond to interact with CO₂. This leads to the formation of intermediate **4**, which releases formic acid to complete the catalytic cycle. For **Mn-NNN** complex, the calculated free energy barrier and reaction free energy (Figure 4) for

the hydride transfer (**3** → **4**) are 10.9 and 1.6 kcal/mol, respectively. Soon after the hydride transfer, N-H proton is transferred to CO₂ for the formation (**4** → **5**) of formic acid. The free energy barrier and reaction free energy for the proton transfer is calculated to be 3.4 and 1.5 kcal/mol respectively for **Mn-NNN**. Thus, for **Mn-NNN** complex, the total free energy barrier for CO₂ hydrogenation ($\Delta\Delta G^\ddagger_{\text{CO}_2}$) is 10.9 kcal/mol with an overall reaction free ($\Delta\Delta G^\ddagger_{\text{R}}$) energy barrier

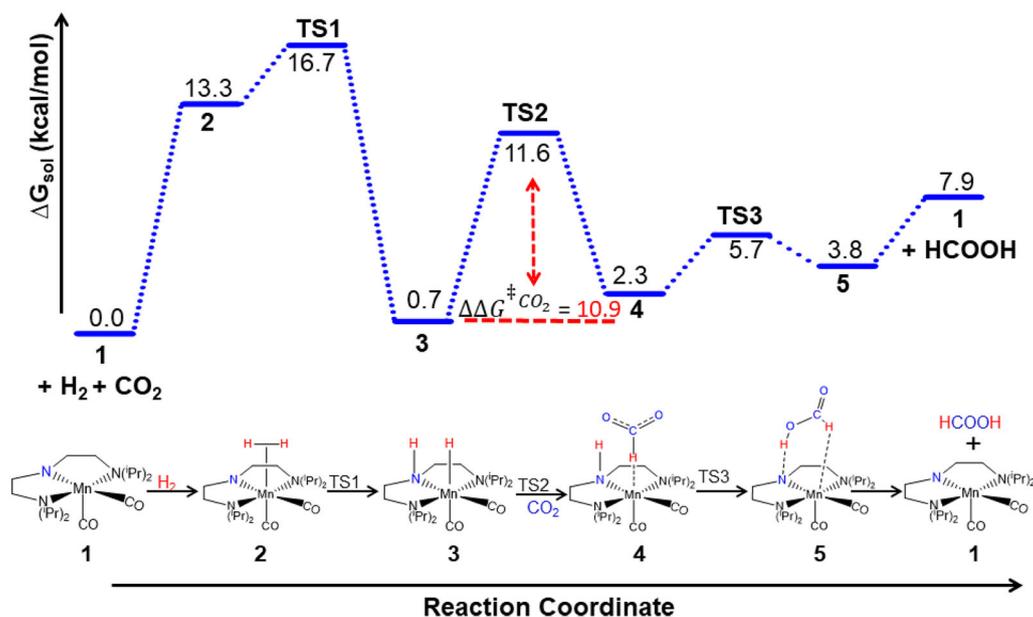


Figure 4. Reaction free energy profile of CO₂ hydrogenation catalysed by Mn-NNN complex. Here, $\Delta\Delta G^{\ddagger CO_2}$ is the total free energy barrier for CO₂ hydrogenation.

of 16.7 kcal/mol. Furthermore, Table 1 shows that the overall reaction free energy barrier ($\Delta\Delta G^{\ddagger R}$) are much higher for Mn-PNP based complexes than the Mn-NNN complex. So, the modelled Mn-NNN complex is predicted as the most promising catalyst for CO₂ hydrogenation reaction compared to the studied aliphatic pincer based Mn complexes, and heterolytic H₂ cleavage ($\Delta\Delta G^{\ddagger H_2} = 16.7$ kcal/mol) is the rate-determining step. Previously, we have reported (using the same level of calculations) an overall reaction free energy barrier of 21.7 kcal/mol when catalyzed by Mn(bpy)(CO)₃⁺.²⁵ Pidko and co-workers reported a total barrier of 22.7 kcal/mol (using a different level of calculations) using a pyridine-based Ru-PNP catalyst.¹⁴ Recently, Gonsalvi and co-workers reported (using a different level of calculations) an overall reaction free energy barrier of 27.6 kcal/mol using Mn(PNP^{NH-iPr})(H)(CO)₂.²⁴ Therefore, our results suggest that Mn-NNN is a very promising catalyst compared to the previously studied (theoretical) noble and non-noble metal-based catalysts. We are not able to compare our results with the excellent work of Beller and co-workers as they have reported activation barrier for heterolytic cleavage only. On the other hand, the calculated energetic span⁵⁶ (δE) is 24.6 kcal/mol if we include the reaction free energy (7.9 kcal/mol) to the overall reaction free energy (16.7 kcal/mol). However, the calculated total energy span for complex Mn-NNN is far less compared to the previously studied (theoretical) noble and non-noble metal based catalysts.

Furthermore, we have analysed the frontier molecular orbitals (Figure S4 in Supporting Information) of **3** to understand their role towards heterolytic H₂ cleavage and proton transfer mechanism. Based on the HOMO-LUMO gap, we find that **3** is most stable in Mn-PNP. Thus, the Mn-PNP complex is good for heterolytic H₂ cleavage but not for proton transfer mechanism. This is very much in agreement with our reaction free energy data (Table 1). However, the Mn-NNN complex has an optimum HOMO-LUMO gap, which in turn promotes both the heterolytic H₂ cleavage and proton transfer mechanism.

3.3 Acid-base properties (protonation/de-protonation)

The aliphatic amido pincer ligand plays an interesting role for CO₂ hydrogenation reaction, where it not only behaves as a base but also as an acid too. The amido ligand acts as a base during the heterolytic H₂ cleavage (**2** → **3**) process on the other hand, the protonated amido ligand acts as an acid (**4** → **5**). Therefore, the strength of the N-H bond is very important as it forms (basic nature of N-atom) during the heterolytic H₂ cleavage, whereas the N-H bond dissociates (acidic nature of N-H bond) during the proton transfer mechanism. Therefore, we can say that acid-base properties in the amido ligand are very important for such reaction. To understand this, we have calculated N-H bond dissociation energy (BDE) in **3**. Our results (Table 2) suggest that the strength of

Table 2. Reaction free energies (ΔG) for heterolytic H₂ cleavage (**2** \rightarrow **3**) and proton transfer (**4** \rightarrow **1**) steps.

Complexes	ΔG		BDE 3	NBO Mn (1)	pKa 1
	2 \rightarrow 3	4 \rightarrow 1			
Mn-NNN	-12.6	5.7	81.5	-0.494	37.7
Mn-PNN	-16.2	10.4	84.1	-0.922	38.2
Mn-PNP	-16.8	13.9	87.1	-1.307	38.5
Mn-PNP-Ar	0.6	1.4	72.8	-1.254	30.5
Mn-PNP-Ar₂	9.6	-4.9	65.5	-1.137	24.5

Here, NBO charges and pK_a values are calculated for complex **1** and N-H bond dissociation energy (BDE) values for **3**. All the energies are in kcal/mol.

N-H bond is strongest in the **Mn-PNP** complex (87.1 kcal/mol) and weakest in **Mn-PNP-Ar₂** (65.5 kcal/mol). So, the amido ligand of the **Mn-PNP** complex is more basic than in other complexes. This further indicates that such groups [(N^tPr)₂ and Ar] withdraw electron density from the amido group, which is responsible for weakening the N-H bond (weakening the basic nature). Our calculated NBO charges for these complexes show that Mn is most electronegative in **Mn-PNP** complex and least in **Mn-NNN** for intermediate **1**. Further to this, we have calculated pK_a values (Figure S5 in Supporting Information) in complex **1** (Table 2) to understand the proton affinity of the amido group. Our results show that **Mn-PNP** has a maximum affinity for proton, whereas **Mn-PNP-Ar₂** has least affinity for proton. Therefore, we can say that the formation of a strong N-H bond is good for heterolytic H₂ cleavage but not for proton transfer mechanism. Therefore, it is important to have a combination of both properties. Interestingly, **Mn-NNN** has an optimum pK_a value and this could be due to the more electron withdrawing nature of the **NNN** ligand over **PNP** ligand. Thus, it pulls out the electron density from the Mn centre, which in turn affects the back donation from Mn to C-O π^* orbital. We have further confirmed this from the calculated C-O frequencies. We find that the C-O frequencies rise (symmetric, 1944.7 \rightarrow 1964.6 cm⁻¹) in the Mn-NNN complex. Therefore, such optimum acid-base nature of the amido ligand in **Mn-NNN** complex is the main reason for lowering the free energy barrier for heterolytic H₂ cleavage and hydride transfer mechanism.

4. Conclusions

In summary, we have designed a series of aliphatic amido pincer-based Mn complexes for CO₂ hydrogenation. We find that the amido ligand behaves as a base and the protonated form of the amido ligand behaves as an acid. Such acid-base nature of the amido ligand is very crucial for heterolytic H₂ cleavage and proton

transfer during CO₂ hydrogenation. In the **Mn-NNN** complex, the amido ligand shows an optimum nature of the acid-base properties, which in turn shows excellent activity towards heterolytic H₂ cleavage and hydride transfer steps compared to the previously studied (theoretically) noble and non-noble metal-based catalysts. Furthermore, we show that such acid-base properties can be tuned by ligand substitution. This suggests that ligand substitution is very crucial for designing catalysts for hydrogenation reactions. Our results show that **Mn-NNN** is the most promising catalyst for formic acid formation with an overall free energy barrier of 16.7 kcal/mol and heterolytic H₂ cleavage is the rate-determining step. Though the low barrier suggests that it may no longer be a rate-determining step. Therefore, we believe that **Mn-NNN** based catalysts are promising for non-noble metal-based catalysts for CO₂ hydrogenation reactions.

Supplementary Information (SI)

Modelled aliphatic amido Mn(I) complexes (Figure S1); reaction free energies (Figures S2–S3); reaction free energies for other Mn(I) complexes (Table S1); molecular orbitals (Figure S4) calculations for pK_a values (Figure S5); references and optimized coordinates of all intermediates and transition states are given in Supplementary Information related to this article which is available at www.ias.ac.in/chemsci.

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