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Supplementary Information

Unexpected concerted two-proton transfer for the amination of formic acid to formamide catalysed by Mn bipyridinol complexes

Xiuli Yan [‡,a,b], Hongyu Ge [‡,a,b], and Xinzheng Yang[*,a,b]

[a] *Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China. E-mail: xyang@iccas.ac.cn*

[b] *University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China.*

[‡] These authors contributed equally to this work.

1. Computational details

All DFT calculations in this study were performed by using the Gaussian 09[1] suite of programs for the M06 functional[2] with the all-electron 6-31++G(d,p) basis set[3-5] for all atoms. All structures were fully optimized by using the integral equation formalism polarizable continuum model (IEFPCM)[6] with SMD atomic radii[7] for solvent effect corrections (acetonitrile and 1,4-dioxane for the hydrogenations of carbon dioxide to formate and formamide, respectively). An ultrafine integration grid (99,590) was used for numerical integrations. The ground states of intermediates and transition states were confirmed as singlets through comparison with optimized high-spin analogues. Thermal corrections were calculated within the harmonic potential approximation on optimized structures under T = 298.15 K and 1 atm pressure. Calculating the harmonic vibrational frequencies for optimized structures and noting the number of imaginary frequency (IF) confirmed the nature of intermediate (no IF) and transition state (only one IF) structures. The latter were also confirmed to connect reactants and products by intrinsic reaction coordinate (IRC) calculations. Unless otherwise noted, the energies reported in the text are Gibbs free energies with solvent effect corrections. The 3D molecular structure figures displayed in this paper were drawn by using the JIMP2 molecular visualizing and manipulating program.[8]

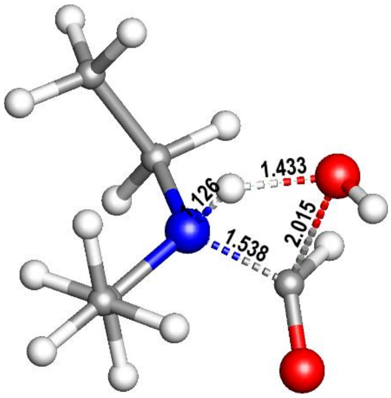
2. Evaluation of density functionals

In order to evaluate the dependency of the Mn bipyridinol complexes to density functionals, we also optimized the structures of **8a** and **$\mathbf{TS_{3,4\text{-}a}}$**, which are rate-determining states in the hydrogenation of CO_2 catalyzed by **1a**, using other six widely-used and/or recently developed density functionals, including ωB97X-D,[9] B3LYP,[10, 11] B3PW91,[12-14] TPSSh,[15] M06L,[2] and TPSS.[15] As shown in Table S1, the M06L functional has the highest relative free energy of 29.0 kcal/mol, while the B3PW91 functional has the lowest relative free energy of 23.9 kcal/mol. The difference between them is 5.1 kcal/mol, which indicates that the CO_2 hydrogenation reaction catalyzed by the manganese bipyridinol complex has a moderate dependence of density functionals. The M06 calculation result of 28.3 kcal/mol is in the middle of them, and close to the results obtained by using the ωB97X-D and M06L functionals. We use the M06 functional also because it is parametrized for the calculations of transition metals and non-covalent interactions. It can mimic some of the non-covalent interactions with the semiempirical kinetic-energy-density dependence introduced in it. M06 was also successfully used in some previously reported computational studies of similar manganese catalytic systems.[16,17] Therefore, we believe the M06 functional is suitable for the study of this Mn based catalytic system.

Table S1. Absolute and relative free energies of **8a** and **$\mathbf{TS_{3,4\text{-}a}}$** obtained by using different density functionals with the same 6-31++G(d,p) basis set.

Density functionals	Absolute free energies (Hartree)		Relative energies (kcal/mol)
	8a	**$\mathbf{TS_{3,4\text{-}a}}$**	**8a → $\mathbf{TS_{3,4\text{-}a}}$**
M06	-2786.777255	-2325.156530	28.3
B3LYP	-2787.877911	-2325.903454	26.0
B3PW91	-2787.195116	-2325.389949	23.9
M06L	-2787.682265	-2325.778936	29.0
ωB97X-D	-2787.343979	-2325.495939	27.7
TPSS	-2788.234104	-2326.183605	25.9
TPSSh	-2787.991947	-2325.981963	26.4

3. Direct reaction between formic acid and diethylamine for the formation of formamide



$TS_{HCONEt2}$

Δ*G* = 43.0 kcal/mol

Figure S1. Optimized transition state structure of the direct formation of formamide and water from formic acid and diethylamine in 1,4-dioxane without any catalyst.

4. The IRC calculation results of $TS_{11,12\text{-}b}$,$TS_{12,1\text{-}b}$, and $TS_{13,1}$

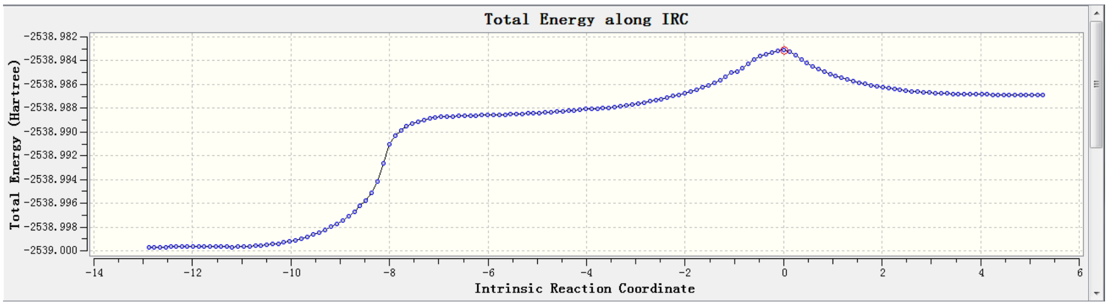


Figure S2. The IRC plots of **$TS_{11,12\text{-}b}$**.

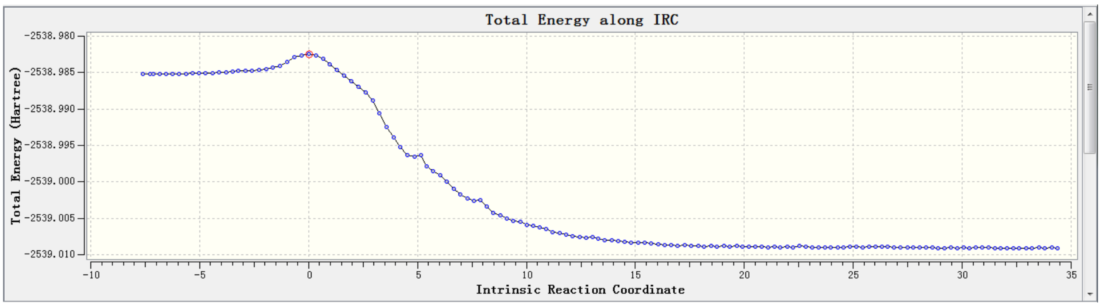


Figure S3. The IRC plots of **$TS_{12,1\text{-}b}$**.

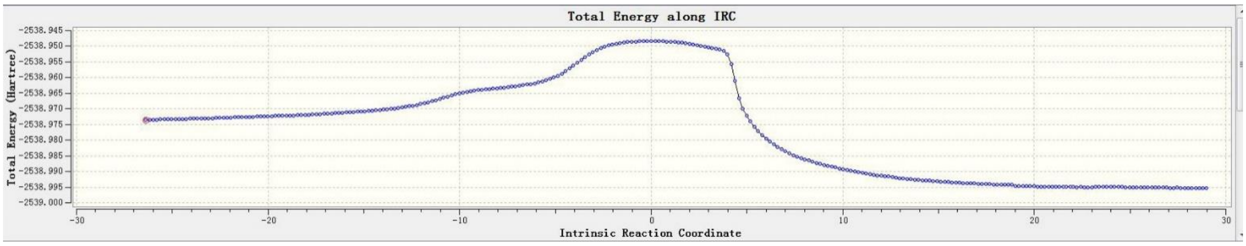
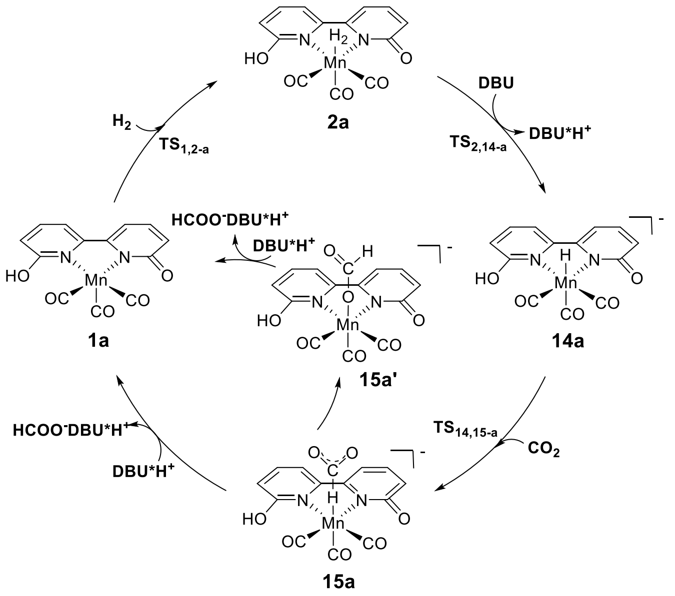


Figure S4. The IRC plots of **$TS_{13,1}$**.

5. An alternative base-assisted mechanism of H_2 activation for hydrogenation of CO_2 to formate catalysed by the Mn bipyridinol complex

In order to find out all possible reaction pathways for the hydrogenation of CO_2 to formate, we also evaluated the base-assisted mechanism for H_2 activation proposed by Das and Pati (Scheme S1).[17] Our calculation results indicate that the total barrier of this reaction pathway is 29.5 kcal/mol (**$TS_{2,14\text{-}a}$** – **15a’** – 2.4 kcal/mol) for the formation of $HCOO^{-}DBUH^{+}$ even without the consideration of the interaction between DBU and the formate anion in **15a’**. Although Pati and co-workers also calculated a structure similar to **15a’** (complex **7** in Ref. 17) with a Mn–O bond, but that structure is not the most stable isomer because a strong O···H interaction between the formate anion and the hydroxyl in the bipyridinol lignad is missing. The optimized structures of **15a’** in our study and the complex **7** in Pati and co-worker’s study (atomic coordinates obtained from the supporting information in Ref. 17) clearly show their difference (Figure S7).



$CO_2 + H_2 + DBU \xrightarrow{Cat.} HCOO^{-}DBU{*}H^{+}$

Scheme S1. The hydrogenation of CO_2 to formate catalysed by the Mn bipyridinol complex with DBU assisted H_2 cleavage.

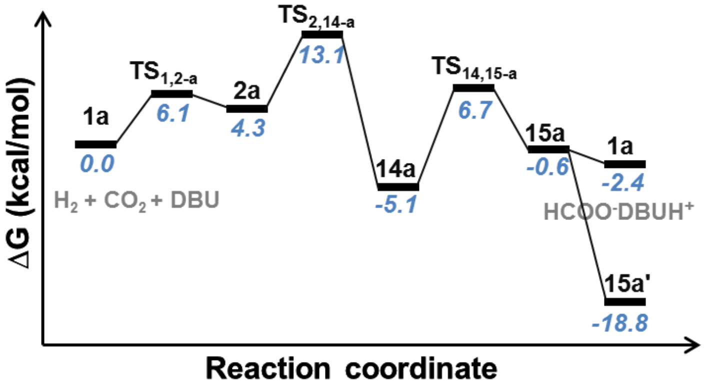
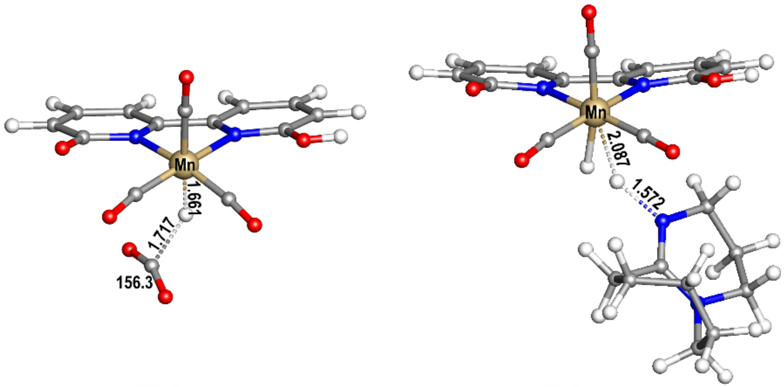
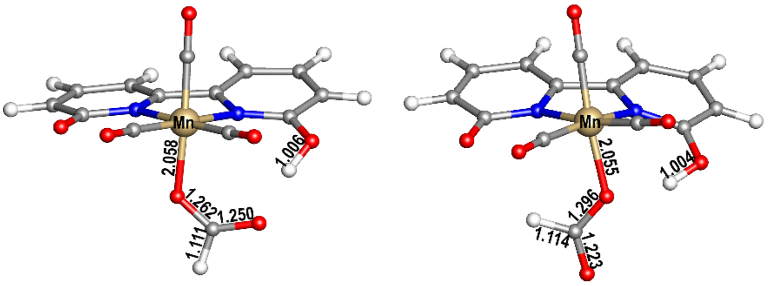


Figure S5. Free energy profile for the hydrogenation of CO_2 to formate catalysed by the Mn bipyridinol complex with DBU assisted H_2 cleavage.



TS$_{2,14\text{-}a}$ **TS$_{14,15\text{-}a}$**

Figure S6. Optimized structures of **TS$_{2,14\text{-}a}$** (564*i* cm^{-1}), and **TS$_{14,15\text{-}a}$** (618*i* cm^{-1}) in acetonitrile with DBU assisted H_2 cleavage. Bond lengths are in angstrom.



15a’ **Pati-7**

Figure S7. Optimized structures of **15a’** in acetonitrile in this study and complex **7** in Das and Pati’s study (atomic coordinates obtained from the supporting information in Ref. 17). Bond lengths are in angstrom.

6. Hydricity of intermediate 3a

The hydricity of **3a** was computed by using the equation S1-S3 listed below. A value of 44.0 kcal/mol for the hydricity free energy of $HCOO^-$ in CH_3CN was used to calculate the hydricity of **3a**.[18] The calculated hydricity free energy of **3a** is 55.2 kcal/mol (ΔG^{o} = 11.2 kcal/mol). Such a high hydricity energy indicates a strong metal-hydride interaction in **3a**. Therefore, hydride transfer from Mn to CO_2 (**$TS_{3,4\text{-}a}$**) has a higher relative energy than the transition state for H_2 cleavage (**$TS_{2,3\text{-}a}$**).

$$[HML] \rightleftharpoons [ML]^{+} + H^{-} \qquad \Delta G^{o}_{H^-} \tag{S1}$$

$$H^{-} + CO_2 \rightleftharpoons HCO_2^{-} \qquad -\Delta G^{o}_{H^-}(HCO_2^{-}) \tag{S2}$$

$$[HML] + CO_2 \rightleftharpoons [ML]^{+} + HCO_2^{-} \qquad \Delta G^{o} = (\Delta G^{o}_{H^-}) - \Delta G^{o}_{H^-}(HCO_2^{-}) \tag{S3}$$

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