

Mechanisms of Co^{\parallel} and Acid Jointly Catalyzed Domino Conversion of CO_2 , H_2 , and CH_3OH to Dialkoxymethane: A DFT Study

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ABSTRACT: The conversion mechanisms of CO₂ and H₂ in methanol to dimethoxymethane catalyzed jointly by metallic $[P^3Co-H]^+$ catalyst and acidic HNTf₂ cocatalyst in a domino sequence were investigated at the M06L-SCRF level of density functional theory. The whole conversion has the steps of the Co-catalyzed hydrogenation (CO₂ + H₂ = HCOOH; HCOOCH₃ + H₂ = CH₃OCH₂OH) and acid-catalyzed esterification (HCOOH + CH₃OH = HCOOCH₃ + H₂O; CH₃OCH₂OH + CH₃OH = CH₃OCH₂OCH₃ + H₂O) reactions. The full Gibbs free energy profiles show that the bidentate formate complex κ^2 -[P³Co-OCHO]⁺ is the resting state and methylating CH₃OCH₂OH with CH₃-NTf₂ is the rate-determining step. The whole reaction kinetics is controlled by both [P³Co-H]⁺ and HNTf₂ cocatalyst. Our study clearly shows the individual role of metal catalyst and acid cocatalyst and the need to combine both catalysts for this reaction and explains rationally why this process needs CO₂ + H₂ + CH₃OH rather than only CO₂ + H₂.



Compared to $HNTf_2$ as a cocatalyst, the lower activity of *p*-TsOH is due to the weaker interaction between acid and substrate. A mechanism for the chain growth and termination of oxymethylene ether is proposed.

KEYWORDS: DMM formation, CO₂ hydrogenation, triphos ligand, cobalt complexes, acid effect, DFT

1. INTRODUCTION

Oxymethylene ethers (OMEs, CH_3O -(CH_2O)_n- CH_3 , n = 3-5) are considered as promising clean fuels and substituents for petroleum diesel fuels due to their similar physical properties, such as boiling point, vapor pressure, and viscosity.^{1,2} The absence of C-C bonds and high oxygen content in OMEs could significantly suppress soot and NO, emission. As dimethoxymethane (DMM, CH₃OCH₂OCH₃) is the smallest building block for synthesizing industrially desired OME₃₋₅ fuels as well as environmentally friendly additive and solvent, many studies were reported on the synthesis of DMM.³⁻⁶ Industrially, DMM is synthesized via two successive reactions (Scheme 1a), where methanol is first oxidized in the gas phase to formaldehyde on a heterogeneous catalyst and then formaldehyde is further acetalized with methanol to DMM in a liquid phase.^{3,4} Alternatively, one-pot synthesis of DMM can be achieved via the oxidation of CH₃OH or CH₃OCH₃.

In 2016, Klankermayer et al.⁷ reported the first sustainable novel route for the homogeneous synthesis of DMM from CO₂ and H₂ in the presence of CH₃OH using (P³)Ru(TMM) [triphos (P³) = 1,1,1-tris(diphenylphosphinomethyl)ethane; TMM = trimethylene methane] with HNTf₂ or Al(OTf)₃ as an acidic cocatalyst (Scheme 1b). This system is proved to be efficient for the CO₂ hydrogenation to CH₃OH, and mechanistic studies revealed that the role of the acid in the (P³)Ru(TMM)/HNTf₂ system is to generate the cationic [P³Ru-H]⁺ complex as active species via reductive TMM removal.⁸ Furthermore, isotope labeling experiments were carried out for the (P³)Ru(TMM)/Al(OTf)₃-catalyzed reaction of ${}^{12}CO_2$, H_2 , and ${}^{13}CD_3OD$. The isotope distribution in the products of HCOO¹³CD₃ (methyl formate, MF), $^{13}CD_{3}OCH_{2}OH$ (methoxy methanol, MM), and ¹³CD₃OCH₂O¹³CD₃ (DMM) shows that the CD₃ groups in MF, MM, and DMM come from ${}^{13}CD_3OD$, while the C=O group in MF and the CH₂ group in MM and DMM come from CO₂. A reaction mechanism with the sequential formation of MF, MM, and DMM was proposed.⁷ Trapp et al. synthesized a series of ruthenium hetero-triphos complexes,^{9,10} such as PhSitriphos, MeSi-triphos, and N-triphos, and high activity was observed for the homogeneous catalysis of CO_2 to form-aldehyde⁹ or DMM and MF.¹⁰ Besides ruthenium triphos system, Klankermayer et al.^{11,12} showed that the cheap and abundant 3d cobalt metal in the combination of the triphos ligand with super acidic HNTf₂ as a cocatalyst could also access DMM from CO₂ and H₂ in CH₃OH. By replacing super acidic HNTf₂ with a weaker para-toluenesulfonic acid (p-TsOH) as a cocatalyst, however, did not lead to the formation

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Downloaded via SHANXI UNIV on September 29, 2021 at 14:35:02 (UTC). See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles. Scheme 1. DMM Synthesis: (a) Commercial Heterogeneous Catalysis and (b) Homogeneous Catalysis by Ru/Co-Triphos System

(a) Commercial heterogeneous catalysis for DMM synthesis



(b) Sustainable homogeneous catalysis for DMM synthesis



Scheme 2. (a) Cobalt-Catalyzed DMM Formation Using $HNTf_2$ as an Acidic Cocatalyst. (b) Proposed Mechanism of the $[P^3Co^{II}-H]^+$ -Catalyzed Hydrogenation Reactions (in Black, H1–H4) and the $HNTf_2$ -Catalyzed, Esterification, Etherification, and (De)hydration (in Blue, A1–A6)

(a) Cobalt-catalyzed transformation of CO_2 and H_2 to DMM



^aEnergies for the Respective Intermediates are Calculated Using the Mixture of [CO₂ + 2H₂ + 2CH₃OH] as the Reference State.

of DMM and only small amounts of MF (TON = 8) was obtained.¹² This indicates that hydrogenation can occur and the efficiency of MF formation using *p*-TsOH as a cocatalyst is lower than that using HNTf₂ (TON = 32), while the methylation step is kinetically hindered. Therefore, super acidic HNTf₂ plays a vital role in the subsequent methylation reaction. Since its first synthesis in 1984,¹³ HNTf₂ has been widely used as an acidic catalyst or additive in a wide range of organic transformations, e.g., the formation of C–C and C–X heteroatom bonds. It is generally accepted that the exceptional performance of HNTf₂ benefits from its good solubility in organic solvents as well as low nucleophilicity and non-

coordinating property of its conjugate base (Tf_2N^-) .¹³ However, the energy barrier of the acid-catalyzed organic reactions was always ignored in the literature.¹⁴

Herein, we analyzed the bonding, structure, and stability of these Co-triphos complexes and explored the full Gibbs free energy profiles of Co-triphos-catalyzed hydrogenation of CO₂, HCOOH, HCOOCH₃, and CH₂O to HCOOH, HOCH₂OH, CH₃OCH₂OH, and CH₃OH, respectively. Next, the acid-catalyzed methylation of HCOOH, CH₂O, HOCH₂OH, and CH₃OCH₂OH to HCOOCH₃, CH₃OCH₂OH, and CH₃OCH₂OH to HCOOCH₃, CH₃OCH₂OH, and CH₃OCH₂OCH₃ was investigated and compared with *p*-TsOH-catalyzed methylation from theory and experiments.



Figure 1. Optimized structures with critical bond distances (Å; white ball for H, gray ball for C, pink ball for Co, and yellow ball for P); all C–H bonds are omitted for clarity (P^3).

2. COMPUTATIONAL DETAILS

All calculations were carried out with Gaussian 16 program.¹⁵ Geometry optimization was performed in the gas phase at the $M06L^{16,17}$ level with the 6-31G(d,p)¹⁸⁻²⁰ basis set. The M06L functional has been valid in our recent work in which benchmark calculations have been performed for the thermodynamic parameters of Co^I- and Co^{III}-PNP complexes using different density functional methods in the conjugation of solvation and van der Waals dispersion correction.²¹ All optimized structures were further characterized either as energy minimums without imaginary frequencies or transition states with only one imaginary frequency by frequency analysis, which also provided zero-point vibrational energies and thermal correction to enthalpy and Gibbs free energy at 298.15 K under 1 atm. On the basis of M06L/6-31G(d,p) geometries in the gas phase, single-point energies were calculated by including the solvation effect of methanol as the solvent based on solute electron density (SMD) at M06L-SCRF level along with the def2-TZVP²² basis set. The Gibbs free energies were further corrected to the standard state in a solution with a standard concentration of 1 mol/L (p = 24.5atm) from the standard state in the gas phase (p = 1 atm). The computed energetic data and optimized Cartesian coordinates are listed in the Supporting Information. The optimized structures were displayed by the CYLview visualization program.²

3. RESULTS AND DISCUSSION

On the basis of the reactions in Scheme 2, we computed the sequential mechanisms of the DMM formation in the presence of super acidic HNTf₂, where the hydrogenation of CO₂, HCOOH, HCOOCH₃, and CH₂O to HCOOH, HOCH₂OH, CH₃OCH₂OH, and CH₃OH, respectively, is catalyzed with the Co-triphos complex and the methylation of HCOOH, CH₂O, HOCH₂OH, and CH₃OCH₂OH to HCOOCH₃, CH₃OCH₂OH, and CH₃OCH₂OH to HCOOCH₃, CH₃OCH₂OH, and CH₃OCH₂OCH₃, respectively, is catalyzed with the super acidic HNTf₂ or *p*-TsOH.

3.1. Catalyst Stability. In our previous work,²⁴ the mechanism of cobalt-triphos (triphos (P^2P) = bis(2-diphenylphosphinoethyl)phenyl phosphine)-catalyzed reductive amination was investigated experimentally and computationally. Both dicationic [P^2PCo^{II}]²⁺ and monocationic [P^2PCo^{II} -H]⁺ complexes were considered as potentially active catalysts for phenylmethanimine (Ph-CH==NH) hydrogenation. It was found that the monocationic [P^2PCo^{II} -H]⁺ complex catalyzed cycle is kinetically more favored than that catalyzed by the dicationic [P^2PCo^{II}]²⁺ complex by 46 kJ/mol. Therefore, the monocationic [P^2PCo^{II} -H]⁺ complex is proposed as the active catalyst. Using the triphos ligand of 1,1,1-tris(diphenylphosphinomethyl)ethane (P^3), the mecha-

nisms of $\mathbf{P}^{3}\mathbf{Ru}$ - and $\mathbf{P}^{3}\mathbf{Co}$ -catalyzed hydrogenation of carboxylic acids were investigated by Klankermayer et al.¹⁴ and Bruin et al.²⁵ respectively, and the monocationic $[\mathbf{P}^{3}\mathbf{Ru}^{II}$ - $\mathbf{H}]^{+}$ and $[\mathbf{P}^{3}\mathbf{Co}^{II}-(\kappa^{2}-\mathbf{OOCPh})]^{+}$ complexes were proved to be the active catalysts.²⁶

In Klankermayer's work, 11,12 Co(BF₄)₂6H₂O as a catalyst precursor and triphos (P3) as a ligand were mixed and the dimeric $[Co_2(P^3)_2(\mu-OH)_2](BF_4)_2$ complex was proved to form spontaneously.²⁶ Herein, the formation of the dimeric $[Co_2(P^3)_2(\mu-OH)_2]^{2+}$ complex from $[P^3Co(OH_2)]^{2+}$ and H_2O was calculated in methanol. The reaction of the dimeric complex formation, $[2[P^3Co^{II}(OH_2)]^{2+} + 2H_2O =$ $[Co_2(P^3)_2(\mu-OH)_2]^{2+} + 2H_3O^+]$, is endergonic by 183 kJ/ mol (107 kJ/mol in the gas phase). Furthermore, the formation of $[P^3Co^{II}-H]^+$ from the reaction, $[[Co_2(P^3)_2(\mu OH_{2}^{2+} + 2H_{2} = 2[P^{3}Co-H]^{+} + 2H_{2}O]$, is slightly endergonic by 17 kJ/mol (137 kJ/mol in the gas phase). The total reaction, $[2[P^{3}Co^{II}(H_{2}O)]^{2+} + 2H_{2} = 2[P^{3}Co-H]^{+} + 2H_{3}O^{+}],$ is endergonic by 200 kJ/mol (244 kJ/mol in the gas phase). The high endergonic reaction energy cannot explain the formation of the [P³Co-H]⁺ species. To find the driving force for $[Co_2(P^3)_2(\mu-OH)_2]^{2+}$ formation, the triphos (P^3) ligand was considered as the base as proposed by Sacconi.²⁶ The reaction of $[2[P^{3}Co^{II}(OH_{2})]^{2+} + 2P^{3} = [Co_{2}(P^{3})_{2}(\mu - OH)_{2}]^{2+}$ + $2HP_3^+$ is exergonic by 34 kJ/mol (-534 kJ/mol in the gas phase). The total reaction, $[2[P^3Co^{II}(H_2O)]^{2+} + 2H_2 + 2P^3 =$ $2[\mathbf{P}^{3}\mathbf{Co}\cdot\mathbf{H}]^{+} + 2\mathbf{H}\mathbf{P}_{3}^{+} + 2\mathbf{H}_{2}\mathbf{O}]$, is exergonic by 17 kJ/mol (-397 kJ/mol in the gas phase), and the high H₂ pressure can enhance the equilibrium to $[P^3Co-H]^+$. Therefore, the triphos (\mathbf{P}^3) ligand is found as a base for $[\mathbf{P}^3\mathbf{Co}(\mathbf{OH}_2)]^{2+}$ deprotonation to dimeric $[Co_2(P^3)_2(\mu-OH)_2]^{2+}$. This finding can reasonably explain recent experimental results reported by Schaub et al.²⁷ that the catalytic performance is enhanced by adding monodentate ligands such as PPh₃, which is converted into phosphonium salt within the system. Besides, the stabilities of [P³Co-H]⁺ and its phosphorus-protonated isomer $[HP^{3}Co]^{+}$ were compared (Figure 1). The phosphorusprotonated isomer [HP³Co]⁺ in which one of the phenyl groups on the protonated phosphorus in $[HP^{3}Co]^{+}$ is coordinated to the Co center in the η^4 form is much less stable than $[{\bf P^3Co{-}H}]^+$ by 119 kJ/mol. Therefore, the monocation $[P^3Co-H]^+$ complex was used as the active catalyst for the hydrogenation of CO₂, HCOOH, HCOOCH₃, and CH₂O.

3.2. Hydrogenation Thermodynamics. The direct reductive synthesis of DMM from the mixture of $CO_2/H_2/CH_3OH$ [$CO_2 + 2H_2 + 2CH_3OH = CH_3OCH_2OCH_3 + 2H_2O$] is calculated as a four-step process (Scheme 2). In the first step, formic acid formation from CO_2 and H_2 [$CO_2 + H_2 = HCOOH$, H1] is endergonic by 34 kJ/mol. In the second step, the esterification of formic acid with methanol to produce



Figure 2. Gibbs free energy profile of the $[P^3Co-H]^+$ -catalyzed CO₂ hydrogenation (reactions H1 and H2).

MF [HCOOH + CH_3OH = HCOOCH₃ + H_2O_1 A1] is exergonic by 15 kJ/mol. In the third step, MF hydrogenation to MM [HCOOCH₃ + H₂ = CH₃OCH₂OH, H3] is endergonic by 34 kJ/mol. Alternatively, MM can be formed via stepwise hydrogenation of HCOOH [HCOOH + H_2 = HOCH₂OH, H2] to HOCH₂OH (methanediol, MD) and the etherification of MD to MM [HOCH₂OH + CH₃OH = $CH_3OCH_2OH + H_2O, A3$]. The final step is the etherification of MM to DMM $[CH_3OCH_2OH + CH_3OH =$ CH₃OCH₂OCH₃+ H₂O, A5], and this step is exergonic by 12 kJ/mol. Alternatively, CH₂O can be formed via the stepwise hydrogenation of HCOOH via HOCH₂OH [HCOOH + H₂ = $HOCH_2OH = CH_2O + H_2O$, H2 and A2], and this process is endergonic by 12 kJ/mol. The formation of CH₂O from CO₂ and $H_2 [CO_2 + 2H_2 = HCOOH + H_2 = HOCH_2OH = CH_2O$ + H₂O, H1, H2, and A2] is endergonic by 46 kJ/mol. Further hydrogenation of CH_2O to CH_3OH [$CH_2O + H_2 = CH_3OH$, H4] is exergonic by 73 kJ/mol.

Next, the dehydration of CH₃OH to CH₃OCH₃ [2CH₃OH = CH₃OCH₃ + H₂O, **A6**] as a side reaction is calculated. It is found that the generation of CH₃OCH₃ (dimethyl ether, DME) from CO₂ and H₂ [2CO₂ + 6H₂ = CH₃OCH₃ + 3H₂O] is exergonic by 66 kJ/mol. Therefore, the formation of CH₃OCH₃ is much more favorable than the DMM formation. On the other hand, the formation of DMM by CH₃OH as a feedstock [3CH₃OH = CH₃OCH₂OCH₃ + H₂O + H₂] is endergonic by 68 kJ/mol in methanol (57 kJ/mol in the gas phase) and hard to be balanced by CH₃OCH₃ formation [2CH₃OH = CH₃OCH₃ + H₂O], which is only exergonic by 12 kJ/mol.

The total reaction of the DMM formation from $[CO_2 + 2H_2 + 2CH_3OH = 2H_2O + DMM]/[3CO_2 + 8H_2 = 4H_2O + DMM]$ in CH₃OH has an enthalpy change (ΔH) of -14/-143 kJ/ mol (-37/-135 kJ/mol deduced from the standard enthalpy of formation in the gas phase²⁸), and the corresponding Gibbs free energy change (ΔG) is 41/-12 kJ/mol. This indicates that this process is accessible thermodynamically and the formation of DMM can be promoted by adjusting the ratios of the components in the reaction mixture, i.e., adding either adducts or removing products as well as changing the reaction condition from the gas phase to liquid phase. This is why the reaction-distillation process is always applied for heterogeneous catalysis when using CH_3OH as a feedstock.

On the basis of the computed stability of the active catalyst and the reaction thermodynamics, we explored the reaction kinetics of the hydrogenation reaction of CO_2 (H1), HCOOH (H2), HCOOCH₃ (H3), and CH₂O (H4). The full Gibbs free energy profiles are shown in the Supporting Information (Figures S1–S4), and the simplified Gibbs free energy profiles are used for comparison and discussion.

3.2.1. CO₂ Hydrogenation. The simplified Gibbs free energy profiles of CO₂ hydrogenation (H1; Scheme 2b) to HOCH₂OH are shown in Figure 2. There are many computational studies on the CO₂ hydrogenation to formic acid, and the mechanism is well accepted. As shown in Figure 2, the first transition state (TS1-H) is the transfer of the Co-H hydride to the carbon center of CO2, and this can be considered as a nucleophilic attack of the hydride on the lowest unoccupied molecular orbital (LUMO) of CO_{2} , and the Gibbs free energy barrier is 26 kJ/mol. In TS1-H, the forming C-H and the breaking Co-H distances are 1.156 and 1.985 Å, respectively. This step results in the formation of the intermediate with the agostic Co-H interaction [P³Co-OCHO_{ago}]⁺, which can arrange to form the intermediate with bidentate formate coordination κ^2 -[P³Co-OCHO]⁺. This is totally exergonic by 45 kJ/mol. The second transition state (TS2-H) is the heterolytic H₂ metathesis leading to the formation of HCOOH and the regeneration of the active catalyst [P³Co-H]⁺. In TS2-H, the forming Co-H and O-H distances are 1.608 and 1.264 Å, respectively, and the breaking H–H distance is 0.972 Å. The Gibbs free energy barrier for H_2 metathesis is 75 kJ/mol and the formation of $[P^3Co-$ $H(HCOOH)_{\sigma}]^+$ is endergonic by 71 kJ/mol. The release of HCOOH from $[P^3Co-H(HCOOH)_{\sigma}]^+$ with the regeneration of $[P^3Co-H]^+$ is endergonic by 8 kJ/mol.

Next, we computed the subsequent hydrogenation of HCOOH to HOCH₂OH (H2; Scheme 2b). Since the reaction was carried out under acidic conditions and formic acid is a weak acid, we computed its neutral form hydrogenation, which also has two steps. The first step is the hydrogenation of HCOOH to $[P^3Co-OCH_2OH]^+$, which is similar to the hydrogenation of aldehydes or ketones. In the transition state, TS3-H, the forming C-H and breaking Co-H distances are 1.523 and 1.779 Å, respectively. This step has a Gibbs free energy barrier of 23 kJ/mol and is endergonic by 10 kJ/mol. The second step is the heterolytic H_2 metathesis [P³Co-OCH₂OH]⁺ via the transition state TS4-H, where the forming Co-H and O-H distances are 1.644 and 1.386 Å, respectively, and the breaking H-H distance is 0.924 Å. This step has a Gibbs free energy barrier of 87 kJ/mol and is endergonic by 21 kJ/mol.

On the Gibbs free energy profiles, HOCH₂COH formation has an apparent Gibbs free energy barrier of 131 kJ/mol and is endergonic by 65 kJ/mol. Considering the intermediate with the bidentate formate coordination κ^2 -[**P**³**Co-OCHO**]⁺ as the resting state, the effective barrier is as high as 176 kJ/mol. All these show that this transformation is very unfavored both kinetically and thermodynamically, despite the fact that HOCH₂OH and H₂CO can have equilibrium in the aqueous solution (H₂CO + H₂O = HOCH₂OH). To escape this energetic disadvantage, we computed the alternative routes leading to the DMM formation.

3.2.2. Hydrogenation of HCOOCH₃. Having the kinetic and thermodynamic disadvantage of CO₂ hydrogenation to HOCH₂OH, we computed the hydrogenation of MF to MM (H3; Scheme 2b), which can be formed from the condensation of formic acid and methanol [HCOOH + CH₃OH = HCOOCH₃ + H₂O], which is exergonic by 15 kJ/mol. Starting from [CO₂ + 2H₂ + 2CH₃OH], the formation of HCOOCH₃ is endergonic by 19 kJ/mol (Scheme 2b). The simplified Gibbs free energy profiles of HCOOCH₃ hydrogenation to CH₃OCH₂OH are shown in Figure 3. There are many computational studies on the hydrogenation of carboxylic ester, and the mechanism is well accepted.

Starting from HCOOCH₃ formed from $[CO_2 + 2H_2 +$ $2CH_3OH$ (Figure 3), the hydride transfer from Co-H to the carbon of HCOOCH₃ via the transition state TS5-H has a Gibbs free barrier of 11 kJ/mol. In TS5-H, the forming C-H and breaking Co-H distances are 1.508 and 1.800 Å, respectively. This step leads to the formation of an intermediate $[P^{3}Co-OCH_{2}OCH_{3}]^{+}$, which is slightly endergonic by 3 kJ/mol. The second step is the heterolytic H_2 metathesis [P³Co-OCH₂OCH₃]⁺ via the transition state TS6-H, where the forming Co-H and O-H distances are 1.644 and 1.299 Å, respectively, and the breaking H-H distance is 0.978 Å. This step has a Gibbs free energy barrier of 98 kJ/mol and is endergonic by 34 kJ/mol for the formation of CH₃OCH₂OH and the regeneration of the active catalyst. Compared with Figure 2, TS6-H is lower in energy than TS4-H by 14 kJ/mol.

3.2.3. CH_2O Hydrogenation. Although HOCH₂OH formation from CO₂ and H₂ needs a very high apparent barrier (131 kJ/mol) and is endergonic (65 kJ/mol), we computed the hydrogenation of CH₂O (H4; Scheme 2b), which can be formed from the HOCH₂OH dehydration [HOCH₂OH =



Figure 3. Gibbs free energy profile of the $[P^3Co-H]^+$ -catalyzed HCOOCH₃ hydrogenation (reaction H3).

 $CH_2O + H_2O$], and it is noted that CH_2O and $HOCH_2OH$ form an equilibrium in the aqueous solution. The simplified Gibbs free energy profile of the CH_2O hydrogenation to CH_3OH is shown in Figure 4.



Figure 4. Gibbs free energy profile of the $[P^3Co-H]^+$ -catalyzed CH₂O hydrogenation (reaction H4).

As shown in Figure 4, the first step of CH₂O insertion into Co–H is barrierless and the formation of agostic species $[P^3Co-OCH_3]^+$ is exergonic by 81 kJ/mol. The next step is the heterolytic H₂ metathesis of $[P^3Co-OCH_3]^+$ to methanol. In the transition state (TS7–H), the breaking H–H distance is 0.952 Å, and forming Co–H and O–H distances are 1.663 and 1.339 Å, respectively. This step has a Gibbs free energy barrier of 83 kJ/mol and is endergonic by 8 kJ/mol. Totally, the CH₂O hydrogenation to methanol has an apparent barrier of 2 kJ/mol and is exergonic by 73 kJ/mol.

3.2.4. Correlation between Descriptor and Gibbs Free Energy Barrier. Based on the Gibbs free energy profiles, it is found that the rate-determining step for the hydrogenation of CO_2 , HCOOH, HCOOCH₃, and CH₂O is H₂ metathesis.



Figure 5. Correlation between (a) deprotonation Gibbs free energy of the hydrogenated product ΔG_{DH^+} and reverse barrier $\Delta G^{\neq,-}(\text{H}^+)$ and (b) formation Gibbs free energy of $[\mathbf{P}^3\mathbf{Co}\cdot\mathbf{OR}]^+\Delta G_{\text{M-OR}}$ and apparent Gibbs free energy of proton transfer $\Delta G^{\neq,-}_{\text{app}}(\text{H}^+)$ (unit: kJ/mol).



Figure 6. Gibbs free energy profile of HNX_2 (X = SO_2CF_3)-catalyzed esterification of HCOOH to HCOOCH₃ by CH₃OH (reaction A1).

Since an excellent relationship between the deprotonation energy of the hydrogenated product ($\Delta G_{DH^+} = G[R_1R_2CHO^-]$ - $G[R_1R_2CHOH])$ and the reverse barrier of H⁺ transfer $(\Delta G^{\neq,-}(\mathbf{H}^+))$ was found in our recent work,²¹ the relationship between the deprotonation energy of the hydrogenated product $\Delta G_{\mathrm{DH}^{*}}$ was explored. As shown in Figure 5a, a correlation ($R^2 = 0.92$) between the deprotonation Gibbs free energy of the hydrogenated product ΔG_{DH^+} and the reverse Gibbs free energy barrier of H₂ metathesis $\Delta G^{\neq,-}(H^+)$ was found. Furthermore, a correlation ($R^2 = 0.98$; Figure 5b) is found between the formation Gibbs free energy of [P³Co-OR]⁺ ΔG_{M-OR} and the apparent Gibbs free energy of the H₂ metathesis $\Delta G_{app}^{\neq}(\mathrm{H}^{+})$. Therefore, both the deprotonation energy of the hydrogenated product ΔG_{DH^+} and the formation Gibbs free energy of $[\mathbf{P}^{3}\mathbf{Co}\mathbf{-OR}]^{+} \Delta G_{M-OR}$ can be used as potential descriptors for estimating the Gibbs free energy of the rate-determining step of proton transfer.

3.3 Acid-Catalyzed Esterification, Etherification, and (De)hydration. Since acid was used as a cocatalyst and different acids have different catalytic activities, we investigated the acid-catalyzed HCOOCH₃ (A1), HOCH₂OH (A2), CH₃OCH₂OH (A3 and A4), and CH₃OCH₂OH (A5)

formation using HN(SO₂CF₃)₂ as a catalyst (abbreviated as X_2 NH, $X = SO_2$ CF₃). For comparison, we computed the energies of the corresponding rate-determining step by replacing X_2 NH with *p*-TsOH as an acidic cocatalyst. It is reported that in the water solution, *p*-TsOH has a pK_a of -1.6, while HN(SO₂CF₃)₂ has a pK_a of 1.7,¹³ and this shows that both acids have different strengths in the water solution, and therefore their different activity in DMM formation should not come from their different acid strengths. On the basis of these facts, we computed the acid-catalyzed kinetics first and then the kinetics from methylation agents. The full Gibbs free energy profiles are shown in the Supporting Information (Figures S5 and S6), and the simplified Gibbs free energy profiles are used for comparison and discussion.

3.3.1. Esterification of HCOOH with CH_3OH . As shown in Figure 6, the esterification of HCOOH (A1 in Scheme 2b) can occur through either the nucleophilic attack of H-bonded CH_3OH ... HNX_2 by HCOOH via the carbonyl group or H-bonded HCOOH... HNX_2 by CH₃OH. First, the formation of H-bond between CH_3OH or HCOOH with HNX_2 is endergonic by 14 and 19 kJ/mol (Figure S5). The nucleophilic attack of CH_3^+ by carbonyl via TS8-CH₃OH-HCOOH has a



Figure 7. Gibbs free energy profile of X_2NH (X = SO₂CF₃)-catalyzed formation of MM and DMM starting from [CH₂O + 2CH₃OH + H₂O] (reactions A2–A5).

free energy barrier of 162 kJ/mol. Alternatively, the methoxymethanediol $CH_3OCH(OH)_2$ can be generated through the C–O coupling by the nucleophilic attack of carbonyl by CH_3OH via **TS9-HCOOH-CH_3OH**, which has a Gibbs free energy barrier of 59 kJ/mol. Therefore, the dehydration of HCOOH with CH_3OH via $CH_3OCH(OH)_2$ intermediate is kinetically more favorable. Subsequently, the dehydration of $CH_3OCH(OH)_2$ resulting in the formation of HCOOCH₃ via **TS10-H₂O** has a Gibbs free energy barrier of 50 kJ/mol.

3.3.2. CH_3OCH_2OH and $CH_3OCH_2OCH_3$ Formation. Starting from CH_2O , CH_3OCH_2OH can be formed directly with methanol [$CH_2O + CH_3OH = CH_3OCH_2OH$, **A4**] or stepwise via HOCH₂OH intermediate [$CH_2O + H_2O + CH_3OH = HOCH_2OH + CH_3OH = CH_3OCH_2OH + H_2O$, **A2** and **A3**]. The simplified Gibbs free energy profiles are shown in Figure 7. For the direct formation of CH_3OCH_2OH , the reaction via the concerted transition state (**TSB11-CH₂O-CH₃OH**) has a Gibbs free energy barrier of 54 kJ/mol and is endergonic by 7 kJ/mol.

For the stepwise formation of CH_3OCH_2OH , the first step is the formation of $HOCH_2OH$ between CH_2O and H_2O , and this step via the corresponding transition state (**TSB12-CH_2O-H_2O**) has a Gibbs free energy barrier of 68 kJ/mol and is endergonic by 19 kJ/mol. The next methylation of HOCH_2OH with CH_3OH to CH_3OCH_2OH via **TS13-CH_3OH-MD** has a Gibbs free energy barrier of 156 kJ/mol and is exergonic by 12 kJ/mol. As shown on the Gibbs free energy profiles, the direct formation of CH_3OCH_2OH is much favored kinetically by 121 kJ/mol. The following methylation of CH_3OCH_2OH with CH_3OH to CH_3OCH_2OCH_3 via **TS14-CH_3OH-MM** has a Gibbs free energy barrier of 154 kJ/mol and is exergonic by 12 kJ/mol.

Taking the complex of formate-coordinated κ^2 -[P³Co-OCHO]⁺ as the resting state (-45 kJ/mol; Figure 2) and

the transition state (**TS14-CH₃OH-MM**) of CH₃OCH₂OCH₃ formation as the rate-determining state, the effective barrier is as high as 252 kJ/mol, and such a high barrier is incompatible with the high TON (92) obtained at 100 °C. Therefore, one should think about the ultimate role of acid in this reaction.

3.3.3. Alternative Mechanism for Etherification. Having the problem of the rather high apparent (207 kJ/mol) and effective (252 kJ/mol) barriers for the last step of DMM formation, we reconsidered the ultimate role of the super acidic HNX₂ for the high activity in the reaction. As shown in Scheme 3a, we computed the reaction of HNX₂ with CH₃OH resulting in the formation of CH₃-NX₂, DME as well as the ion pair of oxonium ion $[(CH_3)_3O]^+$ and $^-NX_2$, $[(CH_3)_3O]^+/$ $[NX_2]^-$. Then, we computed their etherification activity for CH₃OCH₂OH and CH₃OCH₂OCH₃ formation (A3 and A5; Scheme 2b) and compared with that of CH₃OH as the methyl group donor (Scheme 3b). The full Gibbs free energy profiles

Scheme 3. (a) Interconversion of Methyl Donors. (b) Etherification of HOCH₂OH and CH₃OCH₂OH by CH₃OH, DME, CH₃-NX₂, and $[(CH_3)_3O]^+/[NX_2]^-$





(b) Etherification of HOCH₂OH and CH₃OCH₂OH



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Figure 8. Gibbs free energy profile for the formation of CH_3OCH_3 , CH_3-NX_2 , and $[(CH_3)_3O]^+/[NX_2]^-$ (X = SO₂CF₃, reactions M1–M3).

are shown in the Supporting Information (Figures S7-S11), and simplified Gibbs free energy profiles are used for comparison and discussion.

First, CH₃OCH₃ can be formed via a concerted mechanism from two CH₃OH (M1; Scheme 3a) via TS15-DME (Figure 8; black line), and this step has a Gibbs free energy of 130 kJ/ mol and is exergonic by 13 kJ/mol. In addition, the formation of CH₃-NX₂ and $[(CH_3)_3O]^+/[NX_2]^-$ (M2 and M3; Scheme 3a) are computed. Interestingly, the formation of CH₃-NX₂ via TS16-CH₃ (red line) is highly exergonic by 25 kJ/mol and has a Gibbs free energy barrier of 124 kJ/mol, indicating that the CH₃-NX₂ formation is more favored kinetically and thermodynamically. Next, the reaction of DME and CH₃-NX₂ with the formation of $[(CH_3)_3O]^+/[NX_2]^-$ via TS17- $O(CH_3)_3^+$ (blue line) has a Gibbs free energy barrier of 110 kJ/mol and is highly endergonic by 76 kJ/mol. The formation Gibbs free energies of CH_3 -NX₂ and $[(CH_3)_3O]^+/[NX_2]^$ indicate that CH₃-NX₂ might be the key methyl donor in this process, while the formation of $[(CH_3)_3O]^+/[NX_2]^-$ is thermodynamically unfavorable. Nevertheless, we computed the etherification of HOCH2OH and CH3OCH2OH with DME, CH₃-NX₂, and $[(CH_3)_3O]^+/[NX_2]^-$ as methylation agents for comparison.

For the etherification of HOCH₂OH and CH₃OCH₂OH by DME, CH₃-NX₂, and $[(CH_3)_3O]^+/[NX_2]^-$, we used the same reference line $[X_2NH + 4CH_3OH + CO_2 + 2H_2]$ for general comparison. As shown in Figure 9, the etherification of HOCH₂OH by DME, CH₃-NX₂, and $[(CH_3)_3O]^+/[NX_2]^-$ to CH₃OCH₂OH via X₂NH-TS-DME-MD, X₂N-TS-CH₃-MD, and X₂NH-TS-(CH₃)₃O-MD have apparent Gibbs free energy barriers of 211, 170, and 167 kJ/mol, which is lower or much lower than that by CH₃OH (221 kJ/mol). The barrier of the CH₃OCH₂OH etherification by DME, X₂N-CH₃, and

 $[(CH_3)_3O]^+/[NX_2]^-$ to CH_3OCH_2OCH_3 via X_2NH-TS-DME-MM, X2N-TS-CH3-MM, and X2N-TS-(CH3)3O-MM have apparent Gibbs free energy barriers of 173, 134, and 156 kJ/mol, respectively, which are lower or much lower than that by CH₃OH (207 kJ/mol). The comparison shows that X_2N_2 CH₃ and $[(CH_3)_3O]^+/[NX_2]^-$ significantly decrease the free energy barrier of CH₃OCH₂OH etherification by 52 and 30 kJ/mol, respectively. Considering the whole process, the Gibbs free energy barrier via HCOOH and HCOOCH₃ intermediates $[CO_2 + H_2 = HCOOH (H1); HCOOH + CH_3OH =$ $HCOOCH_3$ (A1); $HCOOCH_3 + H_2 = CH_3OCH_2OH$ (H3); $CH_3OCH_2OH + CH_3OH = CH_3OCH_2OCH_3$ (A5)] is lower than that via HOCH₂OH and CH₂O $[CO_2 + H_2 = HCOOH]$ (H1); HCOOH + H_2 = HOCH₂OH (H2); HOCH₂OH = $CH_2O + H_2O (A2); CH_2O + CH_3OH = CH_3OCH_2OH (A4);$ $CH_3OCH_2OH + CH_3OH = CH_3OCH_2OCH_3$ (A5)] by 14 kJ/mol for DMM formation (117 for TS6-H vs 131 kJ/mol for TS4-H). This is in good agreement with the experimental result that HCOOCH₃ is formed in the catalytic system. The rate-determining step is the etherification of CH₃OCH₂OH to CH₃OCH₂OCH₃ by CH₃-NX₂ as a methylation agent. The calculated effective Gibbs free energy barrier (179 kJ/mol) by taking κ^2 -[P³Co-OCHO]⁺ (-45 kJ/mol) as the resting state agrees with the experimental results that acid is vital for the selective transformation of CO₂ and H₂ to DMM.

Inspired by the mechanism of acidic zeolite catalyzed DMM formation from CH₂O and CH₃OH, the stepwise mechanism through X_2N -CH₂OCH₃ is also considered (Figure 10). In our previous investigation, the CH₂OCH₃⁺ cation stabilized by the deprotonated anion ZO⁻ was found to be a crucial intermediate for C–O and C–C bond formation.²⁹ Herein, the generation of X_2N -CH₂OCH₃ from CH₂O and X_2N -CH₃ via **TS-CH₃-CH₂O** has a Gibbs free energy barrier of 136 kJ/



Figure 9. Gibbs free energy profile for HOCH₂OH/CH₃OCH₂OH to CH₃OCH₂OH/CH₃OCH₂OCH₃ methylation by CH₃OH, CH₃OCH₃, X_2N -CH₃, and $[(CH_3)_3O]^+/[NX_2]^-$ as a methyl donor for DMM generation (X = SO₂CF₃, reactions A3 and A5).

mol. The reaction between X_2N -CH₂OCH₃ and CH₃OH with DMM formation has a Gibbs free energy barrier of 87 kJ/mol. The effective Gibbs free energy barrier for DMM formation via the X_2N -CH₂OCH₃ route (202 kJ/mol) is 23 kJ/mol higher than via the etherification of CH₃OCH₂OH by X_2N -CH₃. Therefore, X_2N -CH₃ should be the key methylation agent.

3.3.4. *p*-TsOH-Catalyzed Etherification. To get a deep understanding of the effect of acid on the DMM formation, the rate-determining step of the etherification catalyzed by *p*-TsOH was computed and compared with that catalyzed by HNTf₂. As shown in Figure 11, the Gibbs free energy barrier of the rate-determining step of the CH₃OCH₂OH etherification by CH₃OH, DME, *p*-TsO-CH₃, and *p*-TsO⁻...(CH₃)₃O⁺ to CH₃OCH₂OCH₃ via *p*-TsOH-TS-CH₃OH-MM, *p*-TsOH-TS-DME-MM, *p*-TsO-TS-CH₃-MM, and *p*-TsO-TS-(CH₃)₃O-MM have apparent Gibbs free energy barriers of 205, 198, 171, and 186 kJ/mol, respectively. Therefore, the most favorable route via *p*-TsO-CH₃ as a methyl donor has an effective Gibbs free energy barrier of 216 kJ/mol, which is 37 kJ/mol higher than that via X₂N-CH₃.

To understand the acidic effect, we further analyze the structures of the corresponding transition states by the ASM (activation strain model; Figure S12 and Table S1) analysis.³⁰

Compared with *p*-TsO-CH₃, CH₃-NTf₂ provides stronger interaction energy by 21 kJ/mol (164 vs 143 kJ/mol), while the distortion energies of them are very similar (231 vs 237 kJ/mol). Therefore, the lower free energy barrier for X_2 N-CH₃ can be attributed to the higher interaction energy than that of *p*-TsO-CH₃.

Since the Gibbs free energy profiles have the same reference line $[X_2NH + 4CH_3OH + CO_2 + 2H_2]$, one can compare the kinetics between the $[P^3Co-H]^+$ complex and $HNTf_2$ catalyzed reactions. We can conclude that the most favored reaction route involves the following elementary reaction steps: (a) CO_2 hydrogenation to formic acid catalyzed by Co complex; (b) acid-catalyzed esterification between formic acid and methanol to methyl formate; (c) hydrogenation of methyl formate to methoxy methanol catalyzed by the Co complex; and (d) acid-catalyzed condensation between methoxy methanol and methanol to dimethoxymethane.

The Gibbs free energy profiles show methyl formate and dimethoxymethane as detectable intermediates, in agreement with the experiment. The bidentate formate coordination κ^2 -[**P**³**Co-OCHO**]⁺ is the resting state and the H₂ metathesis step in HCOOCH₃ hydrogenation is the rate-determining step, and the apparent barrier is 117 kJ/mol. For the HNTf₂-catalyzed

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Figure 10. Gibbs free energy profile for DMM formation via the $X_2N-CH_2OCH_3$ route (X = SO₂CF₃).

etherification reaction from CH_3OCH_2OH and CH_3OH to $CH_3OCH_2OCH_3$, the apparent barrier is 134 kJ/mol. For DMM formation, the HNTf₂-catalyzed etherification of CH_3OCH_2OH is the rate-determining transition state, and

the catalytic activity is controlled by both $[P^3Co-H]^+$ complex and acidic cocatalyst. This indicates that it is necessary to consider both metal- and acid-based catalysis, i.e., the stability of metal-formate intermediate (ligand effect) and the interaction between methylation agent and substrate (acid effect), they are decisive for the formation of the desired products.

On the basis of these results, we propose the mechanism of the chain growth via the repeating cycle of esterification between formic acid and alcohol to formate catalyzed by acid and the subsequent hydrogenation of formate to the next higher alcohol (Scheme 4); and this is the chain growth





sequence, and the etherification of the formed alcohol to the corresponding ether is the chain termination step. Therefore, it should be possible to control the chain length by changing the metal complex and acid.

4. CONCLUSIONS

The goal of this study is the elucidation of the mechanisms of the transformation of CO_2 , H_2 , and CH_3OH to $CH_3OCH_2OCH_3$ catalyzed jointly by the $[\mathbf{P}^3\mathbf{Co-H}]^+$ complex and $HNTf_2$ as an acidic cocatalyst in a domino sequence. This



Figure 11. Gibbs free energy profile for the CH₃OCH₂OH etherification by CH₃OH, CH₃OCH₃, *p*-TsO-CH₃, and $[(CH_3)_3O]^+/[p-TsO]^-$ as the methyl donor for DMM generation (reaction A5).

transformation has four sequential steps, $CO_2 + H_2 =$ HCOOH and HCOOCH₃ + H₂ = CH₃OCH₂OH catalyzed by the [**P³Co-H**]⁺ complex, and HCOOH + CH₃OH = HCOOCH₃ + H₂O and CH₃OCH₂OH + CH₃OH = CH₃OCH₂OCH₃ + H₂O. All energetic data are discussed on the same reference line and can be used for general comparison.

With respect to the experimentally observed dimeric $[P^3Co-OH]_2^{2+}$ complex, the triphos ligand plays a role of the base to deprotonate $[P^3Co(OH_2)]^{2+}$ to dimeric $[Co_2(P^3)_2(\mu-OH)_2]^{2+}$. The monocationic $[P^3Co-H]^+$ complex has been found to have high thermal stability under H_2 atmosphere and is also the active catalyst for the hydrogenation steps.

In the $[\mathbf{P}^{3}\mathbf{Co}-\mathbf{H}]^{+}$ -catalyzed hydrogenation reaction, \mathbf{H}_{2} metathesis is the rate-determining step, and the apparent barriers for CO_{2} , HCOOCH_{3} , and $\mathrm{CH}_{2}\mathrm{O}$ are 34, 117, and 48 kJ/mol, respectively. The correlation between the deprotonation Gibbs free energy of the hydrogenated product $\Delta G_{\mathrm{DH}^{+}}$ and the reverse barrier $\Delta G^{\neq,-}(\mathbf{H}^{+})$ as well as that between the formation Gibbs free energy of $[\mathbf{P}^{3}\mathbf{Co}-\mathbf{OR}]^{+} \Delta G_{\mathrm{M}-\mathrm{OR}}$ and the apparent Gibbs free energy of proton transfer $\Delta G_{\mathrm{app}}^{\neq}(\mathbf{H}^{+})$ indicates that the deprotonation energy of the hydrogenated product $\Delta G_{\mathrm{DH}^{+}}$ and the formation Gibbs free energy of $[\mathbf{P}^{3}\mathbf{Co}-\mathbf{OR}]^{+} \Delta G_{\mathrm{M}-\mathrm{OR}}$ can be used as potential descriptors for estimating the Gibbs free energy of the rate-determining step of the hydrogenation reactions. The descriptors found in this work can be used for related catalyst screening and prediction.

For the methylation reactions using HNT f_2 as a cocatalyst, different methylation steps have been considered. Taking the acid catalyst interconversion into account, methylating CH₃OCH₂OH using CH₃OCH₃, CH₃-Tf₂N, and $[(CH_3)_3O]^+/[NX_2]^-$ is more favorable than that using CH₃OH by 51, 73, and 51 kJ/mol, respectively. In addition, the formation of CH₃-Tf₂N is favored kinetically and thermodynamically. Consequently, the methylation of CH₃OCH₂OH by CH₃-Tf₂N is the most favorable route. Compared to HNTf₂ as a cocatalyst, the lower activity of *p*-TsOH as an acidic cocatalyst is due to the weaker interaction between the methylation agent and the substrate.

Taking the whole Gibbs energy profile into consideration, the route of the CH₃OCH₂OCH₃ formation via HCOOH and HCOOCH₃ intermediates is more favored than that via HOCH₂OH and CH₂O. This can reasonably explain the formation of HCOOCH₃ as a detectable product in the catalytic system. The whole Gibbs energy profile also shows that the bidentate formate coordination κ^2 -[P³Co-OCHO]⁺ is the resting state and the HNTf2-catalyzed etherification of CH₃OCH₂OH is the rate-determining transition state. Therefore, the catalytic activity is controlled by both $[P^3Co-H]^+$ and acidic cocatalyst and reducing the stability of the metal-formate intermediate (ligand effect), and the Gibbs free energy barrier of the etherification of CH3OCH2OH by enhancing the interaction between the methylation agent and the substrate (acid effect) can improve the activity and selectivity for the formation of the desired products. Finally, our study shows the individual role of the metal catalyst and acid cocatalyst and the need to combine both catalysts for this reaction and also explains why this process requires $CO_2 + H_2 + CH_3OH$ rather than only $CO_2 + H_2$ for this dual system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c01795.

Full Gibbs free energy profiles for the $[P^3Co-H]^+$ catalyzed CO₂, HCOOH, HCOOCH₃, and CH₂O hydrogenation (S1) and HNX₂ and *p*-TsOH-catalyzed, esterification, etherification, and (de)hydration (S2); ASM (activation strain model) analysis for CH₃OCH₂OH etherification by CH₃-NTf₂ and *p*-TsO-CH₃ (S3); and energies and Cartesian coordinates for all optimized structures (S4) (PDF)

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Notes

The authors declare no competing financial interest.

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