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Catalytic Hydrogenation of CO₂ to Methanol Using Multinuclear Iridium Complexes in a Gas–Solid Phase Reaction

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ABSTRACT: We report a novel approach toward the catalytic hydrogenation of CO_2 to methanol performed in the gas-solid phase using multinuclear iridium complexes at low temperature (30–80 °C). Although homogeneous CO_2 hydrogenation in water catalyzed by amide-based iridium catalysts provided only a negligible amount of methanol, the combination of a multinuclear catalyst and gas-solid phase reaction conditions led to the effective production of methanol from CO_2 . The catalytic activities of the multinuclear catalyst were dependent on the relative configuration of each active species. Conveniently, methanol obtained from the gas phase could be easily isolated from the catalyst without contamination with CO, CH_4 , or formic acid (FA). The catalyst can be recycled in a batchwise manner via gas release and filling. A final turnover number of 113 was



obtained upon reusing the catalyst at 60 °C and 4 MPa of H_2/CO_2 (3:1). The high reactivity of this system has been attributed to hydride complex formation upon exposure to H_2 gas, suppression of the liberation of FA under gas–solid phase reaction conditions, and intramolecular multiple hydride transfer to CO_2 by the multinuclear catalyst.

INTRODUCTION

Methanol, which is produced industrially from syngas, is in high demand over the world as a promising alternative fuel and industrially useful bulk chemical.¹ Recently, methanol production from CO₂ is highly desirable from the viewpoint of CO₂ utilization and methanol economy.² There are numerous reports on heterogeneous catalysts (typically Cubased catalysts) used for the thermocatalytic hydrogenation of CO₂ to methanol (HCM).³ These catalysts require harsh reaction conditions due to the high thermodynamic stability and low reactivity of CO₂, although the entire HCM process is exergonic $(3H_2(g) + CO_2(g) \rightarrow CH_3OH(l) + H_2O(l): \Delta G^{\circ}_{298}$ = -8.9 kJ mol^{-1}). Significant obstacles, such as low CO₂ conversion and selectivity, still remain for heterogeneous catalysts due to the equilibrium limitations under the harsh operating temperatures (>220 °C). Lower reaction temperatures will allow a higher theoretical conversion ratio of methanol from CO₂. In the pursuit of a catalyst that can work at lower temperature, the application of homogeneous catalysts, which often operate at lower temperatures, in the HCM has received an increasing amount of attention.⁴⁻ Prakash and co-workers demonstrated efficient HCM using the Ru-pincer catalyst in triglyme/HNTf₂ at 140 $^{\circ}$ C and 7.5 MPa with a TON of 9900.¹⁹ Wass and co-worker have used the [RuCl₂(Ph₂PCH₂CH₂NHMe)₂] catalyst in ⁱPr₂NH/toluene at 100 °C and 4 MPa to obtain methanol with a TON of 8900.¹⁸ Recently, Klankermayer and co-workers reported one-pot HMC catalyzed by Ru complexes with triphos-type ligands

Scheme 1. Pathway for the Hydrogenation of CO_2 to Methanol

+H ₂	+H ₂ , –H ₂ O	нсно	+H ₂	
	<u> </u>	or -	<u> </u>	CH₃OH
-H ₂	$-H_2$, $+H_2O$	110(011)2	-H2	

in ethanol at 12 MPa and 120 °C with a TON of 1938.¹⁰ In addition, the selected reports of HMC using homogeneous catalysts are provided in Table S1.^{7–25} The homogeneous catalytic HCM generally proceeds through stepwise reactions involving single hydride transfer via formic acid (FA) and its equivalents (e.g., formate, carbamate, and urea) (Scheme 1). It is known that the hydrogenation of CO₂ to FA in the first step is an endergonic step, which is strongly limited by thermodynamic constraints (H₂(g) + CO₂(g) \rightarrow HCOOH(I): $\Delta G^{\circ}_{298} = +31.8$ kJ mol⁻¹).^{26,27} However, homogeneous catalysts generally lack the ability to promote the reduction of CO₂ to generate formaldehyde and methanol beyond the single hydride-transfer process to FA or its equivalents. In addition, the homogeneous catalytic HCM is performed in an

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We have developed several efficient iridium catalysts bearing N,N-bidentate ligands for the hydrogenation of CO₂ to formate under mild reaction conditions in an alkaline aqueous solution.^{6,28} Recently, we reported that the homogeneous HCM via FA formation at 70 °C can be achieved by the acid-promoted activation of FA in water at elevated pressure (8 MPa), albeit with limited productivity (turnover number (TON) < 8).²⁹ From these studies, we confirmed the strong limitations due to the equilibrium between FA and CO₂/H₂ in water.³⁰ On the other hand, the production of methanol from formaldehyde proceeds easily under alkaline conditions.³¹

These facts imply that the formation of FA as an intermediate via single hydride transfer from the metal– hydride complex to CO_2 is unfavorable for the HCM. In other words, the liberation of FA from the intermediate formato complex via ligand exchange with water as a solvent should be avoided because the liberated FA readily dehydrogenates to H₂ and CO_2 . Therefore, we envisaged a multinuclear catalyst capable of concerted multiple hydride transfer to generate formaldehyde or methanol directly. In contrast to heterogeneous catalysts, for which the active species are nonuniformly distributed among different microenvironments, homogeneous catalysts that possess well-defined local and tunable structures may be able to act concertedly and selectively on a reactant by changing the steric and/or electronic properties of the organic ligands.³²

In addition, we have conceived a gas-solid phase reaction using complex catalysts to avoid the liberation of FA via ligand exchange with water. Conveniently, it is unnecessary to separate the product from the solvent and catalyst in the gas-solid phase reaction and can avoid the accumulation of water as a byproduct in the reaction solvent. Furthermore, water as a solvent for the hydrogenation reaction may be undesirable because of the poor solubility of H₂. However, only a limited number of examples (mainly reactions with light olefins) have been reported in regard to gas-solid phase reactions using complex catalysts.^{33–37} To date, investigations on the mechanism in these processes are less well-developed.

Herein, we propose a novel approach for the HCM using multinuclear iridium complexes in a gas-solid phase reaction to overcome its inherent obstacles. Multiple hydride transfers by multinuclear species led to the effective production of methanol from CO_2 . In addition, the gas-solid phase reaction circumvents the liberation of FA from the formato complex. Therefore, our catalytic system enables the production of methanol from CO_2 under mild reaction conditions.

RESULTS AND DISCUSSION

Homogeneous Hydrogenation of CO_2 in Water. We prepared mononuclear (1), dinuclear (2-*o*, *m*, *p*), and trinuclear (3) catalysts consisting of picolinamide-based iridium moieties, which are effective catalysts for the hydrogenation of CO_2 to formate in an aqueous basic solution and the dehydrogenation of FA in an aqueous acidic solution (Chart 1).³⁸ Catalyst 2-*p* can be obtained as a crystalline solid

Chart 1. Mononuclear (1), Dinuclear (2), and Trinuclear (3) Ir Catalysts Used for the Hydrogenation of CO_2 to Methanol

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(Figure S1a and Table S2), while the other catalysts were obtained as amorphous solids. The standard reaction was performed by using the iridium catalyst (1: 9.0 μ mol; 2: 4.5 μ mol; or 3: 3.0 μ mol) under 4 MPa of H₂/CO₂ (3:1) at 60 °C. Conventional homogeneous catalysis using mononuclear catalyst 1 (9 μ mol) in water without base generated FA, but the concentration of FA was immediately saturated (entries 1–3 in Table S4, Figure 1a). After 165 h, a small amount of methanol (0.3 μ mol) was detected, which was probably formed via the hydrogenation of FA (entry 4 in Table S4). These results were consistent with those previously reported with a mononuclear bipyridine-based catalyst.²⁹

In the case of dinuclear catalyst 2-m (4.5 μ mol), FA was immediately produced similar to that of 1, while a trace amount of methanol (0.05 μ mol) was detected after 30 min and the concentration of methanol gradually increased (entries 6–9 in Table S4, Figure 1a). The rapid generation of methanol can be attributed to concerted multiple hydride transfers by two iridium species. The ortho-substituted catalyst (2-o)showed similar activity to that of 2-m (entry 10 in Table S4), while methanol production was not detected after 15 h when using para-substituted catalyst 2-p (entry 11 in Table S4). The different activities observed among the dinuclear catalysts were likely dependent on the relative configuration of each iridium species. These results imply the viability of 2-m for the HCM via concerted multiple hydride transfer under mild reaction conditions. However, the efficiency of methanol production was unsatisfactory even when using 2-m in water because of the poor productivity of FA from H_2/CO_2 due to the equilibrium limitations.

Hydrogenation of CO₂ in the Gas-Solid Phase Reaction. To improve the efficiency of the HCM, we envisioned an alternate route to circumvent the liberation of FA into the reaction medium because FA in water is hardly hydrogenated but easily forms H₂ and CO₂ by dehydrogenation.^{30,38} We speculated that the liberation of FA occurs via ligand exchange with water as a solvent. Thus, we tested an unconventional gas-solid phase reaction conducted in the absence of a solvent. Specifically, the complex catalyst was exposed to 4 MPa of H_2/CO_2 (3:1) at 60 °C (Figure S2). After the reaction, the pressurized gases were immediately released into an aluminum bag containing 2-10 mL of water, which absorbed the produced methanol, to quantify the amount of methanol in the gas phase. The residual catalyst dissolved in an aqueous NaCl solution to suppress the competing dehydrogenation of FA. Both aqueous samples were analyzed by using high-performance liquid chromatography (HPLC) and gas chromatography (GC) equipped with a flame ionization detector (FID). Interestingly, methanol was detected from both samples obtained from the gas phase as well as the residual catalyst in this system.



Figure 1. Time course of the production of methanol (red) and FA (blue) with 1 (9 μ mol) and 2-*m* (4.5 μ mol) under 4 MPa of H₂/CO₂ (3:1) at 60 °C in (a) water (1: squares and dotted line; 2-*m*: circles and solid line) and (b) the gas–solid phase (1: squares and dotted line; 2-*m*: circles and solid line (stationary conditions), rhombus and solid line (stirring gases at 500 rpm)).

To our delight, when the reaction was performed with 2-*m* as an amorphous powdery solid, the yield of methanol increased with the reaction time (entries 3–5 in Table 1, Figure 1b). Furthermore, methanol was exclusively detected without contamination with CO and CH₄ in the gas phase (Figures S9 and S10). On the other hand, a negligible amount of FA was observed in the residual catalyst, and formaldehyde (methanediol) was not detected (Figure S11). It was confirmed that the reproducibility of this reaction system was sufficient (Table S6). The methanol produced during the reaction was confirmed by using ¹H NMR spectroscopy in DMSO-*d*₆ (Figure S3) and the detection of ¹³CH₃OH (*m*/*z* 33) generated from ¹³CO₂ in GC–MS (Figure S4). No methanol was detected in the control experiments lacking either the catalyst, H₂, or CO₂ (entries 10–12 in Table S5). On the other hand, using mononuclear catalyst 1 in the gas–

Table 1. Hydrogenation of CO_2 to Methanol Using Ir Catalysts in the Gas–Solid Phase Reaction under Stationary Conditions^{*a*}

			methanol		
entry	$\operatorname{complex}/[\mu \operatorname{mol}]$	<i>t</i> [h]	$[\mu mol]^{b}$	TON ^c	
1	1/9	188	0.4 (0.1)	<0.1	
2	1/9	360	1.0 (0.2)	0.1	
3	2 - <i>m</i> /4.5	1	0.3 (0.1)	< 0.1	
4	2 - <i>m</i> /4.5	15	$4.6 (2.6)^d$	1.0	
5	2 - <i>m</i> /4.5	165	39.1 (37.0)	8.7	
6	2 -0/4.5	15	0.2 (0)	<0.1	
7^e	$2 - p_c/4.5$	15	0.1 (0)	< 0.1	
8	$2 - p_a/4.5$	15	2.6 (2.4)	0.65	
9 ^f	$2 - p_{ac}/4.5$	15	1.9 (1.8)	0.4	
10	3/3	15	4.7 (3.1)	1.6	
11	3/3	165	32.1 (29.1)	10.7	

^{*a*}The reaction was performed under 4 MPa H₂/CO₂ (3:1) at 60 °C. The loaded catalyst was an amorphous and powdery solid, except for 2- p_c . ^{*b*}The total amount of methanol produced from the residual catalyst and gas phase. The parentheses indicate the amount of methanol obtained from the gas phase. All values were determined from the average of at least two different runs. ^{*c*}TON = mol of produced methanol/mol of catalyst. ^{*d*}Average of five different runs (see Table S6). ^{*c*}A powder was obtained from crushing the crystalline solid in a mortar. ^{*f*}An amorphous solid was obtained from an aqueous solution of the crystalline solid (2- p_c) used in entry 7.

solid phase reaction produced a very small amount of methanol upon prolonging the reaction time (entries 1 and 2 in Table 1). This implies that intermolecular multiple hydride transfer from the mononuclear catalysts to CO_2 hardly occurs.

Dinuclear catalyst 2-o provided a small amount of methanol $(0.2 \ \mu mol)$ over 15 h, probably due to the relative configuration of each iridium species being too close (entry 6). Interestingly, in the case of para-substituted catalyst 2-p, the production of methanol was dependent on the solid state of the catalyst. Specifically, crushed crystalline $2-p_c$ gave a negligible amount of methanol after 15 h (entry 7), whereas amorphous $2-p_a$ provided 2.6 μ mol of methanol (entry 8). Interestingly, amorphous $2 - p_{ac}$ obtained from the dissolution of the less active crystalline catalyst $(2-p_c)$ in an aqueous solution showed reactivated catalytic activity (entry 9). These results imply that crystalline $2-p_c$ cannot perform efficient intramolecular multiple hydride transfer because the iridium species in $2-p_c$ are too far away from each other (Figure S1b and Table S3). At this stage, we believe that a suitable configuration of amorphous $2 - p_a$ (or $2 - p_{ac}$) due to $\pi - \pi$ stacking led to favorable intermolecular multiple hydride transfer to produce methanol. As expected, trinuclear catalyst 3 afforded a similar amount of methanol to that of 2-m (entries 10 and 11). These results suggest that the relative configuration of each active species plays an important role in the production of methanol during the HCM in the gas-solid phase reaction.

Furthermore, it was observed that the yield of methanol was significantly improved upon stirring the catalyst by using a magnetic bar in the reaction vessel, probably due to gas agitation and catalyst grinding, which exposes the active surface sites (entries 1-4 in Table 2, Figure 1b). Under these conditions, the influence of the reaction conditions with 2-m was examined in detail. Methanol production was proportional to the amount of catalyst (Figure S5a and Table S8). Increasing the temperature and pressure led to an exponential

Table 2. Hydrogenation of CO_2 to Methanol Using 2-*m* in the Gas–Solid Phase Reaction under Magnetic Stirring^{*a*}

				methanol	
entry	$T [^{\circ}C]$	P [MPa]	<i>t</i> [h]	$[\mu \text{mol}]^{b}$	TON ^c
1	60	4	15	8.9 (8.6)	2.0
2	60	4	47	18.1 (17.9)	4.0
3	60	4	90	30.0 (28.9)	6.7
4	60	4	336	104 (103)	23
5	60	5	24	14.1 (14.0)	3.1
6	80	4	24	16.1 (16.0)	3.6
7	60	0.9	768	20.2 (20.0)	4.5
8	70	0.5	480	13.4 (13.2)	3.0
9	30	5	168	9.2 (8.2)	2.0
10	60	4	336×5^d	(507)	113
11	70	5	24×7^{e}	(122)	27.1

^{*a*}The reaction was performed under the desired pressure of H_2/CO_2 (3:1) by using 4.5 μ mol of 2-*m* as an amorphous powdery solid. All numbers are the average of two runs. ^{*b*}The total amount of methanol produced from the solid and gas phases. The parentheses indicate the amount of methanol obtained from the gas phase. All values were determined from the average of at least two different runs. ^{*c*}TON = mol of produced methanol/mol of catalyst. ^{*d*}Recycling experiment: 5 cycles, 336 h for each run (see Figure 2). ^{*e*}Recycling experiment: 7 cycles, 24 h for each run (see Figure S6).

increase in methanol production (Figure S5b-e). In particular, the pressure of H_2 seems to strongly affect the production of methanol. It is worth noting that methanol was generated catalytically, even at low pressure (<1.0 MPa, entries 7 and 8 in Table 2) and low temperature (30 °C, entry 9 in Table 2). These results indicate that the catalytic system (i.e., multi-nuclear catalysts in the gas-solid phase reaction) performs the HCM under mild reaction conditions.

Conveniently, the methanol produced in the reaction mainly exists in the gas phase, and its separation from the catalyst is much easier than that of homogeneous catalysis (i.e., an aqueous phase reaction). Therefore, the catalyst can be repeatedly used in a batchwise manner via gas release and filling with the catalyst exhibiting excellent reusability without any obvious loss in its activity due to its tolerance to water as a byproduct (Figure 2 and Figure S6). A recycling experiment using five cycles afforded 0.507 mmol of methanol with a TON of 113 under 4 MPa of H_2/CO_2 (3:1) at 60 °C and 336 h for each run (entry 10 in Table 2). From the NMR spectra obtained for catalyst 2-*m* in D_2SO_4/D_2O before and after the reaction, apparent degradation was not observed (Figure S12).

Mechanistic Investigation. Our proposed mechanism for the HCM with dinuclear catalyst 2-m under gas-solid phase reaction conditions is shown in cycle 1 of Scheme 2. The following experiments were performed to support the proposed mechanism.

First, exposing 2-*m* to H₂ led to a rapid color change from yellow to orange, which is similar to that of the corresponding hydride complex generated in an aqueous solution of 2-*m* under pressurized H₂ (Figure S7). The ¹H MAS NMR spectrum shows new peaks at -11.8 and -15.6 ppm, which may be assigned to its mono- and dihydride complexes, respectively (Figure S8). The addition of water to the hydride complex converted to precatalyst 2-*m* along with the evolution of H₂ in ~35% yield per iridium species (Figure S13 and Table S10). The hydride complex seems to be generated at the interior site as well as the surface, although the species on the



Figure 2. Catalyst recycling experiments using **2**-*m* (4.5 μ mol) under 4 MPa of H₂/CO₂ (3:1) at 60 °C for 336 h in each run. The red bars indicate the amount of methanol obtained from the gas phase for each run.

Scheme 2. Proposed HCM Mechanism for 2-*m* in the Gas-Solid Phase Reaction (Heterogeneous Catalysis: Cycle 1) and Liquid Phase Reaction (Homogeneous Catalysis: Cycle 2) (X = H or H₂O, n = 1 or 2)



surface undoubtedly act as the most active sites for catalysis rather than the interior site.³⁷ However, strict identification of the actual catalytic regime seems to be difficult from these observations.

Second, the hydride complex generated from 2-*m* (4.5 μ mol) was exposed to 4 MPa of CO₂ at 60 °C (Table S11). As a result, FA (0.4–0.5 μ mol) was generated without detection of methanol and formaldehyde. Furthermore, re-exposure of the resulting complex to 4 MPa of H₂ produced methanol (0.5 μ mol) without FA. The slight discrepancy between the amount of FA and methanol may be due to the decomposition of FA during the measurement. These results strongly support that the catalysis is a stepwise reaction, which occurs via a formato complex.

Third, the effect of the counteranion was examined by using BF₄⁻ and PF₆⁻ analogues of 2-*m* (Table S7). The BF₄⁻ and PF₆⁻ analogues provided methanol of 1.6 and 0.9 μ mol, respectively. The activities seem to be correlated to the acidity of the conjugated acid.³⁹ This result indicates that the counterion may serve as a proton acceptor.

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Finally, the HMC reaction was performed in suspension of anhydrous toluene and hexane under standard conditions (Table S9). When the reaction was performed by using mononuclear catalyst 1, a negligible amount of methanol was detected, similar to that under liquid phase and gas-solid phase conditions. In the case of the dinuclear catalyst (2-*m*), the amount of methanol produced in the suspension of toluene and hexane was higher than that in H₂O. The results strongly support the role of the multinuclear catalysts and the unsuitability of water as a solvent in this system.

In step i, mono- or dihydride complex A may be formed upon exposure of 2-m to H_2 . It is known that exposure of the active metal species to H_2 in gas-solid phase reactions generally leads to its homolytic cleavage.^{36,40} According to the results, it was assumed that the heterolytic cleavage of H_2 likely proceeds due to the presence of proton acceptors, such as the counterion (HSO₄⁻) or coordinated nitrogen atoms, near the active species.⁴¹ In step ii, one of the hydride species in A reacts with CO_2 to generate the formato-hydride complex B. In step iii, intramolecular hydride transfer from the hydride species to the formato complex occurs to generate complex C.⁸ The hydrogenation of FA can be ruled out because FA cannot be liberated from B for the lack of water. In step iv, further intra- or intermolecular hydrogenation of the formaldehyde equivalent in C gives methoxide complex D. Solid-state ¹H-¹³C HETCOR NMR spectroscopy revealed the formation of a methoxy moiety (Figure 3).⁴² Finally, liberation of methanol into the gas phase led to the regeneration of A in step v.



Figure 3. Solid-state ${}^{1}H-{}^{13}C$ HETCOR spectrum of 2-*m* after exposure to 4 MPa of $H_2/{}^{13}CO_2$ (3:1).

On the other hand, in the homogeneous catalysis of 2-m performed in water, which is a liquid-phase reaction, it was presumed that the liberation of FA from the formato complex **B** via ligand exchange with water preferentially occurs (step vi). Thus, the liberated FA in water may not be hydrogenated because of the high catalytic activity of the picolinamide-based iridium moieties toward the dehydrogenation of FA under acidic aqueous conditions.⁴³ Consequently, a small amount of methanol was detected via intramolecular hydride transfer of **B** as a minor reaction (step iii).

Apparent differences were observed in mononuclear catalyst 1 under the gas—solid phase reaction conditions, in which a negligible amount of methanol and FA were produced (entries 1–3, Table S5). Almost all of the generated formato complexes (b) remain unchanged, except for intermolecular hydride transfer with the hydride complexes that exist in a suitable configuration (step iii*, Scheme S1a). At the end of the reaction, a negligible amount of FA was detected because the generated FA will be dehydrogenated to CO_2 and H_2 during sampling. The compatibility with efficient catalysts used for CO_2 hydrogenation was investigated (Scheme S2). Several catalysts provided a small amount of methanol. Similar to that previously reported,²⁹ homogeneous catalysis (i.e., in water) using mononuclear catalyst 1 immediately generates FA, whose concentration was saturated by the equilibrium limitation between CO_2/H_2 and FA (Scheme S1b).

The differences observed between the mono- and dinuclear catalysts were attributed to the intramolecular hydrogenation of formato moiety **B** in step iii, which leads to the rapid generation of methanol upon further hydride transfer. As a result, only the combination of a multinuclear catalyst and gas-solid phase reaction conditions exhibits remarkable performance for the HCM.

CONCLUSIONS

We have reported the production of methanol via the hydrogenation of CO₂ under mild reaction conditions (30 °C, 5 MPa (TON 2.0) and 0.5 MPa, 70 °C (TON 3.0)) using multinuclear complexes under gas-solid phase reaction conditions. The reactivity under mild conditions is due to (i) facile formation of a hydride complex upon exposure to H_{2} , (ii) circumvention of the liberation of FA from the formato complex using unconventional gas-solid phase reaction conditions, and (iii) multiple intramolecular hydride transfer to CO_2 by the multinuclear catalysts. Apparent differences were observed with the mononuclear catalyst and homogeneous catalysis (liquid phase reaction), in which both provided a negligible amount of methanol. The combination of multinuclear catalysts and gas-solid phase reaction conditions overcame the inherent barriers of the HCM, that is, the equilibrium limitation between FA and CO₂/H₂. These studies provide novel insights into gas-solid phase hydrogenation and the effect of multinuclear active sites by using a complex catalyst toward the hydrogenation of CO2. In addition, the catalytic system can be easily recycled, since the produced methanol is exclusively released into the gas phase. After five cycles, 0.507 mmol of methanol with a TON of 113 was produced under 4 MPa of H_2/CO_2 (3:1) at 60 °C without any clear degradation. This catalytic system opens the door to new possibilities for the practical production of methanol from CO₂ at lower reaction temperatures. For advancement of this system, the surface chemistry of the complex may need to be established besides development of an efficient catalyst and detailed analysis of the mechanism.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c11927.

Figures S1–S27, Tables S1–S11, and Schemes S1 and S2 (PDF)

Crystallographic data of 2-m (CIF)

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Notes

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REFERENCES

(1) Olah, G. A. Beyond oil and gas: the methanol economy. Angew. Chem., Int. Ed. 2005, 44, 2636–2639.

(2) Olah, G. A. Towards oil independence through renewable methanol chemistry. *Angew. Chem., Int. Ed.* **2013**, *52*, 104–107.

(3) Porosoff, M. D.; Yan, B. H.; Chen, J. G. G. Catalytic reduction of CO_2 by H_2 for synthesis of CO, methanol and hydrocarbons: challenges and opportunities. *Energy Environ. Sci.* **2016**, *9*, 62–73.

(4) Kar, S.; Kothandaraman, J.; Goeppert, A.; Prakash, G. K. S. Advances in catalytic homogeneous hydrogenation of carbon dioxide to methanol. J. CO₂ Util. **2018**, 23, 212–218.

(5) Alberico, E.; Nielsen, M. Towards a methanol economy based on homogeneous catalysis: methanol to H_2 and CO_2 to methanol. *Chem. Commun.* **2015**, *51*, 6714–6725.

(6) Onishi, N.; Laurenczy, G.; Beller, M.; Himeda, Y. Recent progress for reversible homogeneous catalytic hydrogen storage in formic acid and in methanol. *Coord. Chem. Rev.* **2018**, *373*, 317–332.

(7) Scharnagl, F. K.; Hertrich, M. F.; Neitzel, G.; Jackstell, R.; Beller, M. Homogeneous catalytic hydrogenation of CO_2 to methanolimprovements with tailored ligands. *Adv. Synth. Catal.* **2018**, *361*, 374–379. (8) Wesselbaum, S.; Moha, V.; Meuresch, M.; Brosinski, S.; Thenert, K. M.; Kothe, J.; Stein, T. V.; Englert, U.; Holscher, M.; Klankermayer, J.; Leitner, W. Hydrogenation of carbon dioxide to methanol using a homogeneous ruthenium-triphos catalyst: from mechanistic investigations to multiphase catalysis. *Chem. Sci.* **2015**, *6*, 693–704.

(9) Wesselbaum, S.; vom Stein, T.; Klankermayer, J.; Leitner, W. Hydrogenation of carbon dioxide to methanol by using a homogeneous ruthenium-phosphine catalyst. *Angew. Chem., Int. Ed.* **2012**, *51*, 7499–7502.

(10) Schieweck, B. G.; Jürling-Will, P.; Klankermayer, J. Structurally versatile ligand system for the ruthenium catalyzed one-pot hydrogenation of CO_2 to methanol. *ACS Catal.* **2020**, *10*, 3890–3894.

(11) Huff, C. A.; Sanford, M. S. Cascade catalysis for the homogeneous hydrogenation of CO_2 to methanol. J. Am. Chem. Soc. **2011**, 133, 18122–18125.

(12) Kothandaraman, J.; Goeppert, A.; Czaun, M.; Olah, G. A.; Prakash, G. S. Conversion of CO_2 from air into methanol using a polyamine and a homogeneous ruthenium catalyst. *J. Am. Chem. Soc.* **2016**, 138, 778–781.

(13) Schneidewind, J.; Adam, R.; Baumann, W.; Jackstell, R.; Beller, M. Low-temperature hydrogenation of carbon dioxide to methanol with a homogeneous cobalt catalyst. *Angew. Chem., Int. Ed.* **2017**, *56*, 1890–1893.

(14) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J.; Milstein, D. Efficient hydrogenation of organic carbonates, carbamates and formates indicates alternative routes to methanol based on CO_2 and CO. *Nat. Chem.* **2011**, *3*, 609–614.

(15) Chu, W. Y.; Culakova, Z.; Wang, B. T.; Goldberg, K. I. Acidassisted hydrogenation of CO_2 to methanol in a homogeneous catalytic cascade system. *ACS Catal.* **2019**, *9*, 9317–9326.

(16) Ribeiro, A. P. C.; Martins, L.; Pombeiro, A. J. L. Carbon dioxide-to-methanol single-pot conversion using a C-scorpionate iron(II) catalyst. *Green Chem.* **2017**, *19*, 4811–4815.

(17) Rezayee, N. M.; Huff, C. A.; Sanford, M. S. Tandem amine and ruthenium-catalyzed hydrogenation of CO_2 to methanol. *J. Am. Chem. Soc.* **2015**, *137*, 1028–1031.

(18) Everett, M.; Wass, D. F. Highly productive CO_2 hydrogenation to methanol - a tandem catalytic approach via amide intermediates. *Chem. Commun.* **2017**, *53*, 9502–9504.

(19) Kar, S.; Sen, R.; Kothandaraman, J.; Goeppert, A.; Chowdhury, R.; Munoz, S. B.; Haiges, R.; Prakash, G. K. S. Mechanistic insights into ruthenium-pincer-catalyzed amine-assisted homogeneous hydrogenation of CO_2 to methanol. *J. Am. Chem. Soc.* **2019**, *141*, 3160–3170.

(20) Kar, S.; Goeppert, A.; Prakash, G. K. S. Combined CO_2 capture and hydrogenation to methanol: amine immobilization enables easy recycling of active elements. *ChemSusChem* **2019**, *12*, 3172–3177.

(21) Kar, S.; Sen, R.; Goeppert, A.; Prakash, G. K. S. Integrative CO_2 capture and hydrogenation to methanol with reusable catalyst and amine: toward a carbon neutral methanol economy. *J. Am. Chem. Soc.* **2018**, *140*, 1580–1583.

(22) Kar, S.; Goeppert, A.; Kothandaraman, J.; Prakash, G. K. S. Manganese-catalyzed sequential hydrogenation of CO_2 to methanol via formamide. *ACS Catal.* **2017**, *7*, 6347–6351.

(23) Khusnutdinova, J. R.; Garg, J. A.; Milstein, D. Combining lowpressure CO₂ capture and hydrogenation to form methanol. *ACS Catal.* **2015**, *5*, 2416–2422.

(24) Lane, E. M.; Zhang, Y. Y.; Hazari, N.; Bernskoetter, W. H. Sequential hydrogenation of CO_2 to methanol using a pincer iron catalyst. *Organometallics* **2019**, *38*, 3084–3091.

(25) Sen, R.; Goeppert, A.; Kar, S.; Prakash, G. K. S. Hydroxide based integrated CO_2 capture from air and conversion to methanol. *J. Am. Chem. Soc.* **2020**, *142*, 4544–4549.

(26) Jessop, P. G.; Ikariya, T.; Noyori, R. Homogeneous hydrogenation of carbon dioxide. *Chem. Rev.* **1995**, 95, 259–272.

(27) Alvarez, A.; Bansode, A.; Urakawa, A.; Bavykina, A. V.; Wezendonk, T. A.; Makkee, M.; Gascon, J.; Kapteijn, F. Challenges in the greener production of formates/formic acid, methanol, and DME

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by heterogeneously catalyzed CO₂ hydrogenation processes. *Chem. Rev.* **2017**, *117*, 9804–9838.

(28) Wang, W.-H.; Himeda, Y.; Muckerman, J. T.; Manbeck, G. F.; Fujita, E. CO_2 hydrogenation to formate and methanol as an alternative to photo- and electrochemical CO_2 reduction. *Chem. Rev.* **2015**, 115, 12936–12973.

(29) Sordakis, K.; Tsurusaki, A.; Iguchi, M.; Kawanami, H.; Himeda, Y.; Laurenczy, G. Carbon dioxide to methanol: the aqueous catalytic way at room temperature. *Chem. - Eur. J.* **2016**, *22*, 15605–15608.

(30) Tsurusaki, A.; Murata, K.; Onishi, N.; Sordakis, K.; Laurenczy, G. b.; Himeda, Y. Investigation of hydrogenation of formic acid to methanol using H_2 or formic acid as a hydrogen source. *ACS Catal.* **2017**, *7*, 1123–1131.

(31) Wang, L.; Ertem, M. Z.; Murata, K.; Muckerman, J. T.; Fujita, E.; Himeda, Y. Highly efficient and selective methanol production from paraformaldehyde and water at room temperature. *ACS Catal.* **2018**, *8*, 5233–5239.

(32) Okamura, M.; Kondo, M.; Kuga, R.; Kurashige, Y.; Yanai, T.; Hayami, S.; Praneeth, V. K. K.; Yoshida, M.; Yoneda, K.; Kawata, S.; Masaoka, S. A pentanuclear iron catalyst designed for water oxidation. *Nature* **2016**, *530*, 465–468.

(33) Pike, S. D.; Weller, A. S. Organometallic synthesis, reactivity and catalysis in the solid state using well-defined single-site species. *Philos. Trans. R. Soc., A* **2015**, 373, 20140187.

(34) Martinez-Martinez, A. J.; Royle, C. G.; Furfari, S. K.; Suriye, K.; Weller, A. S. Solid-state molecular organometallic catalysis in gas/ solid flow (Flow-SMOM) as demonstrated by efficient room temperature and pressure 1-butene isomerization. *ACS Catal.* 2020, *10*, 1984–1992.

(35) Kumar, A.; Zhou, T.; Emge, T. J.; Mironov, O.; Saxton, R. J.; Krogh-Jespersen, K.; Goldman, A. S. Dehydrogenation of n-alkanes by solid-phase molecular pincer-iridium catalysts. high yields of alphaolefin product. J. Am. Chem. Soc. **2015**, 137, 9894–9911.

(36) Wang, C.; An, B.; Lin, W. B. Metal-organic frameworks in solidgas phase catalysis. *ACS Catal.* **2019**, *9*, 130–146.

(37) Pike, S. D.; Kramer, T.; Rees, N. H.; Macgregor, S. A.; Weller, A. S. Stoichiometric and catalytic solid-gas reactivity of rhodium bisphosphine complexes. *Organometallics* **2015**, *34*, 1487–1497.

(38) Kanega, R.; Ertem, M. Z.; Onishi, N.; Szalda, D. J.; Fujita, E.; Himeda, Y. CO₂ hydrogenation and formic acid dehydrogenation using Ir catalysts with amide-based ligands. *Organometallics* **2020**, *39*, 1519–1531.

(39) Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I.; Sonoda, T.; Mishima, M. Gas-phase acidities of some neutral Brønsted superacids: a DFT and ab Initio study. *J. Am. Chem. Soc.* **2000**, *122*, 5114–5124.

(40) Huang, Z.; White, P. S.; Brookhart, M. Ligand exchanges and selective catalytic hydrogenation in molecular single crystals. *Nature* **2010**, *465*, 598–601.

(41) Kanega, R.; Onishi, N.; Szalda, D. J.; Ertem, M. Z.; Muckerman, J. T.; Fujita, E.; Himeda, Y. CO₂ hydrogenation catalysts with deprotonated picolinamide ligands. *ACS Catal.* **2017**, *7*, 6426–6429.

(42) Lam, E.; Larmier, K.; Wolf, P.; Tada, S.; Safonova, O. V.; Coperet, C. Isolated Zr surface sites on silica promote hydrogenation of CO_2 to CH_3OH in supported Cu catalysts. *J. Am. Chem. Soc.* **2018**, 140, 10530–10535.

(43) Kanega, R.; Onishi, N.; Wang, L.; Murata, K.; Muckerman, J. T.; Fujita, E.; Himeda, Y. Picolinamide-based iridium catalysts for dehydrogenation of formic acid in water: effect of amide N substituent on activity and stability. *Chem. - Eur. J.* **2018**, *24*, 18389–18392.