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Lin Wang, Mehmed Z. Ertem, Kazuhisa Murata, James T. Muckerman, Etsuko Fujita, and Yuichiro Himeda ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.8b00321 • Publication Date (Web): 01 May 2018

Downloaded from http://pubs.acs.org on May 1, 2018

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Highly Efficient and Selective Methanol Production from Paraformaldehyde and Water at Room Temperature

Lin Wang,[†] Mehmed Z. Ertem^{*‡}, Kazuhisa Murata,[†] James T. Muckerman[‡], Etsuko Fujita[‡] and Yuichiro Himeda^{*†}

 [†]Research Institute of Energy Frontier, Department of Energy and Environment National Institute of Advanced Industrial Science and Technology Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan
 [‡]Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

ABSTRACT: An efficient catalytic system using a water-soluble iridium complex, $Cp^*IrL(OH_2)^{2^+}$ (Cp^* = pentamethylcyclopentadienyl, L = 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine), was developed for highly selective methanol production at room temperature (initial turnover frequency of 4120 h⁻¹) with a very high yield (93%). This catalytic system features paraformaldehyde as the sole carbon and hydride source, leading to a record turnover number of 18200 at 25 °C. A step–by–step mechanism has been proposed for the catalytic conversion of paraformaldehyde to methanol based on density functional theory (DFT) calculations. The proposed pathway holds the potential capacity to extend the scope of indirect routes for methanol production from CO₂.

KEYWORDS: *iridium complexes, proton-responsive ligand, methanol production, transformation of paraformaldehyde, homogeneous catalysis*

INTRODUCTION

Methanol is an extremely important building block in the chemical industry that can also serve as a sustainable and efficient energy carrier (12.6 wt% H₂) in the future based on the proposed "methanol economy" concept.^{1,2} Moreover, methanol is a sustainable source of liquid fuels and fuel additives which can be converted into high-octane gasoline (methanol-to-gasoline process), dimethyl ether, oxymethylene ethers, as well as other value-added petrochemicals.³ Currently, the industrial-scale production of methanol is by the conversion of fossil feedstock-based synthesis gas (CO, H₂, and CO₂) in the presence of heterogeneous catalysts (Cu/ZnO/Al₂O₃-type) under high pressure (50-250 bar) and elevated temperature (>200 °C).⁴

In recent years, attractive ways to produce methanol from CO_2 hydrogenation have been intensely investigated. This would slash dependence on fossil feedstocks with prospects as an effective approach for CO_2 utilization. Several research groups have investigated the conversion of CO_2 and

H₂ to produce methanol in the presence of homogeneous catalysts.⁵ However, these systems always suffer from high pressures and high operating temperatures, the use of organic solvents, and, in most cases, low turnover numbers (TONs) and frequencies (TOFs). To minimize energy consumption, improve the transformation efficiency, and provide a greener methanol economy, methanol production at a low reaction temperature and in water is highly desired.

Alternatively, significant recent research has aimed at an indirect approach for the conversion of CO_2 to methanol. For example, the use of readily available CO_2 derivatives, such as carbamates, (methyl/dimethyl/cyclic) carbonates, urea derivatives, formamides, and formic acid, as substrates to produce methanol as the product,⁶ which in certain cases also results in the formation of secondary byproducts. Very recently, we reported another promising route for efficient methanol production from the hydrogenation/disproportionation of formic acid using a Cp*Ir complex bearing 5,5'-dimethyl-2,2'-bipyridine with a TON of 1314 and selectivity up to 47.1% at low temperature (60 °C) under 5.2 MPa of H₂.⁶ In this promising pathway for methanol production, more efficient catalysts should be developed to compete against the more favorable formic acid dehydrogenation.

Formaldehyde is also one of the important C₁ building blocks that is widely applied in the chemical industry and has been reported to be produced by catalytic hydrogenation of CO2,7 room temperature reduction of CO₂ by borane,⁸ and the electrocatalytic reduction of CO₂ and water.⁹ Moreover, an energy efficient low-temperature formaldehyde production from syngas in water (Scheme 1, left) was also reported.¹⁰ Similar to formic acid¹¹ and methanol,¹ formaldehyde could be envisioned as a new liquid organic hydrogen carrier (LOHC).¹² Lately, H₂ production from aqueous formaldehyde or paraformaldehyde has received considerable attention.^{12a,13} Miller and Goldberg et al. investigated the transfer hydrogenation of paraformaldehyde into methanol and methyl formate using a highly concentrated formic acid solution (TON = 7760; TOF = 240 h^{-1}) catalyzed by [Cp*lr(2,2'-bipyridine)(H₂O)][OTf]₂ in a supplementary study of the disproportionation of formic acid to methanol.⁶⁹ Prechtl et al. first reported selective methanol production from paraformaldehyde and water catalyzed by $[Ru(p-cymene)Cl_2]_2$ with a high yield of 93% in the absence of an external hydride source at 80 °C.¹⁴ Although attractive, this catalytic system suffers from low durability with a maximum TON of 493 after 3 cycles (i.e., all volatiles were removed in vacuo after each cycle, and the reaction was repeated). Therefore, more efficient and durable catalysts under milder conditions should be developed for this promising route for methanol production. High requirements for the equipment and energy input are needed for the direct hydrogenation of CO₂ to methanol. However, the indirect hydrogenation of CO₂ based on the use of a CO₂ derivative (formaldehyde) is beneficial because of its lower activation barrier. Furthermore, no more H₂ was required for the transformation

of formaldehyde to methanol, thus enabling milder reaction conditions and less energy input for methanol production. In this context, methanol production from paraformaldehyde would not only be of fundamental interest, but also extend the scope of indirect routes for methanol production from CO₂.

Herein we report a water-soluble Cp*Ir catalytic system for selective methanol production from paraformaldehyde and water in an open system with argon flow at room temperature, affording high TON and TOF. The overall reaction pathway does not proceed by a Cannizzaro-type reaction under the applied reaction conditions (Scheme 1). We also present a step–by–step mechanism for the conversion of paraformaldehyde to methanol, consistent with experimental observations, obtained via theoretical calculations.



Scheme 1. Highly selective methanol production from paraformal dehyde and H_2O at room temperature.

RESULTS AND DISCUSSION



Chart 1. All the catalysts screened in this study.

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In the present study, a family of Ir, Rh, and Ru complexes were evaluated for their catalytic activity towards methanol production (Chart 1). The complexes were prepared according to previously described procedures.¹⁵ In a typical reaction, the catalyst (0.083 mol%), 3 mmol paraformaldehyde, and 10 mol% K₃PO₄ were dissolved in 5 mL H₂O (pH 12) and stirred at 30 °C under argon gas. Product yields were determined by ¹H NMR spectroscopy utilizing acetonitrile as an internal standard. The catalyst screening results are summarized in Table 1. First, control reactions were carried out to test the catalytic capabilities (entries 1 and 2), indicating that K_3PO_4 alone could not catalyze the reaction, and almost no Cannizzaro reaction occurred under the applied conditions. To examine the catalytic activities systematically, multifunctional ligands (complexes 2-7) with varied σ -donor substituents¹⁶ at the 6 and 6' (or the 4 and 4') positions on the bipyridine ligand backbones were adopted. We observed remarkable enhancement in the methanol production yield with donor ligands ($\sigma_{p}^{+} < 0$), especially with -OMe and -O⁻ substituents, compared to the unsubstituted complex 1 (entry 3 vs entries 4-8), which indicates the dependence of the catalytic activity on the bipyridine ligand's σ -donor power. Interestingly, similar methanol yields were observed for the 4.4'-dihydroxy substituted complex (5, entry 7, 36%) and the corresponding 6,6' complex (6, entry 8, 34%), which illustrates that the catalytic activity is not dependent upon the position of the substituent. Notably, complex 7 bearing four hydroxyl groups displayed significantly higher activity than the other iridium complexes (entry 9, 78%). The rhodium and ruthenium analogues (8 and 9) were also tested for catalytic activity (entries 10 and 11), but lower yields were observed after 10 h (15% and 8%).

	3(CH ₂ O) _n + nH	20 Catalyst	$2n CH_3OH + n CO_2$	
		Temperature	Z	
entry	catalyst	K ₃ PO ₄ /mol%	HCOOH yield ^b /%	MeOH yield ^b /%
1	-	-	0	0
2	-	10	0	0
3	1	10	0	1
4	2	10	0	3
5	3	10	<1	3
6	4	10	1	16
7	5	10	<1	36
8	6	10	7	34
9	7	10	2	78

Table 1. Catalyst screening results for methanol production from paraformaldehyde and	water ^a
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10	8	10	3	15
11	9	10	1	8

^a Reaction conditions: paraformaldehyde (3 mmol, 90 mg), catalyst (2.5 μmol), H₂O (5 mL), time (10 h), 30 °C, under Ar atmosphere. ^{b 1}H NMR yield, average of at least two runs, CH₃CN as the internal standard. All values are normalized to the reaction stoichiometry, only allowing a maximum of 67% methanol.

Catalyst **7** was selected for further studies as a model catalytic system. Various additives were tested to determine the optimal conditions and to gain a better understanding of the factors influencing the catalytic reaction (Table 2). It is clearly observed that the base additives could promote high conversion of paraformaldehyde into methanol (entries 1-6), and the additive K_2CO_3 exhibited the highest methanol yield (pH 11) (entry 2, 80%). However, only a trace amount of methanol (<1%) was observed in the presence of the 10 mol% weak base NaOAc (pH 7.4) (entry 7) and no activity for the formation of methanol was detected in the presence of H₂SO₄ (pH 1.2) (entry 8) indicating the requirement for highly basic conditions.

Table 2. Additive screening for methanol production from paraformaldehyde and w	atera
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entry	additive/mol%	yield ^b /%
1	K ₃ PO ₄ /10%	78
2	K ₂ CO ₃ /10%	80
3	Na ₂ CO ₃ /10%	76
4	KHCO ₃ /10%	72
5	NaHCO ₃ /10%	70
6	NaOH/10%	78
7	NaOAc/10%	<1
8	H ₂ SO ₄ /10%	0
9	K ₂ CO ₃ /5%	59
10 ^c	K ₂ CO ₃ /10%	93
11 ^c	K ₂ CO ₃ /20%	89

^a Reaction conditions: paraformaldehyde (3 mmol, 90 mg), catalyst **7** (2.5 μmol), 30 °C, 10 h, all the reactions were carried out under Ar atmosphere. ^b HPLC yield. ^c Run for 22 h.

Next, we examined the effect of the amount of K_2CO_3 on the formation of methanol. Decreasing the amount of K_2CO_3 to 5% led to a much lower yield (59%, entry 9). Most notably, with the extension

of the reaction time to 22 h for the full conversion of paraformaldehyde, a 93% yield of methanol was obtained with 10% K_2CO_3 (entry 10). On the other hand, a lower methanol yield of 89% was observed in the presence of 20 mol% K_2CO_3 compared to the use of 10 mol% K_2CO_3 (entries 10 and 11) and under this condition, the Carnnizzaro reaction occurred (producing a 5% final formate yield), thus decreasing the methanol selectivity. Therefore, 10 mol% of K_2CO_3 was chosen as the optimal amount. The results of further experiments on the optimization of other reaction conditions such as paraformaldehyde concentration and temperature are presented in Tables S1 and S2.



Figure 1. Reaction progress of methanol production in the presence of catalyst **7**. Conditions: paraformaldehyde (3 mmol, 90 mg, 94% purity), catalyst **7** (2.5 μ mol), H₂O (5 mL), K₂CO₃ (10 mol%), 30 °C. All the data were determined by HPLC.

It is known that formaldehyde can be released from paraformaldehyde, which is subsequently hydrated to produce methanediol in basic aqueous solutions.^{12a,13a,13c,17} In order to gain mechanistic insights into the transformation to methanol, we monitored the reaction progress in the presence of complex **7** via the high-performance liquid chromatography (HPLC) technique (Figure S1). The simultaneous conversion of formaldehyde and the yield of methanol are clearly displayed in Figure 1. Interestingly, a clear change in the trend of formate concentration can be observed during the catalytic process. After 15 min the yield of formate achieved the highest level (9% yield). However, the formed formate finally was almost completely consumed (0.19% yield) after 22 h. *In situ* analysis of the pH of the reaction process under the optimal conditions indicated a clear change (gradually decreasing from pH 11 to 7) as seen in Figure S2, which arises from consumption of the base K₂CO₃

by the formed formic acid and CO_2 . In our investigations herein, a basic condition is very important for this reaction. In combination with the pH changes during the reaction process, after the fast initial reaction stage, one major reason for the decreasing rate of methanol production is due to the decreasing pH. Indeed, the paraformaldehyde was almost fully converted after 20 h with a yield of >92.5%. Furthermore, the released gases during the reaction were analyzed by gas chromatography (GC). Only a trace amount of H₂ (~55 ppm) was detected; and no other gases were observed except the major product CO_2 . In 2015, Fukuzumi *et al.* reported catalytic H₂ and CO_2 production from paraformaldehyde using $Cp^*IrL'(OH_2)]^+$ (L' = 4-(1H-pyrazol-1-yl- κN^2)benzoic acid- κC^3) in basic solution.^{13a} In contrast, our catalytic system produces methanol with very good selectivity.

In order to investigate the catalytic activity of catalyst **7** in more detail, the time course of the TON for methanol production at room temperature (25 °C) was carried out (Figure 2). A very high TOF of 4120 h⁻¹ (average TOF for initial 30 min) was achieved. Remarkably, catalyst **7** is highly robust under the applied conditions. A maximum TON of 18200 was obtained after 380 h, affording a very good yield of >91%. These results, to our knowledge, represent the highest TON and TOF yet reported at room temperature. We also examined the catalytic activities for **5**, **6** and **7** under the optimal conditions obtained for catalyst **7** and observed significantly less catalytic activity for **5** and **6** compared to **7** (Figure S3), which is attributed to less electron donating ability of ligands in **5** and **6**.



Figure 2. Highly robust methanol production from a paraformaldehyde–water solution. Reaction conditions: paraformaldehyde (15 mmol), 0.5 μ mol catalyst **7**, K₂CO₃ (10 mol%), 25 mL H₂O, 25 °C.

Mechanistic Studies

Based on the results obtained above and previous investigations on the transformation of paraformaldehyde^{12a,13a,13c,14,18,19} as well as our computational mechanistic investigation (see below), a plausible mechanism for methanol production from paraformaldehyde and water is proposed in Scheme 2. We performed density functional theory (DFT) calculations at the M06 level of theory²⁰ in conjunction with the SMD aqueous continuum solvation model²¹ (see computational methods in the SI for details) and propose a step-by-step mechanism for the conversion of paraformaldehyde to methanol by catalysts 1, 6 and 7 in basic aqueous solutions. Catalysts 6 and 7 involve proton-responsive OH groups that can exist in protonated and deprotonated forms with distinct hydrogen bonding modes and electron donating ability. Therefore, in order to examine the methanol formation mechanisms, we applied a speciation approach²² in which the relative free energies of the intermediates and transition-state structures of relevant protonation states of the complexes are computed, and the changes in relative free energies with changes in pH are tracked. The results are summarized in Scheme 2 and Table 3 for only the most stable protonation states of complexes 1, 6 and 7 at pH 12.0 (i.e., all OH groups are deprotonated), and detailed information on the energetics of the other protonation states of the complexes is provided in the SI. Total charges of various Cp*Ir complexes are omitted in the following discussions for clarity.



Scheme 2. Proposed mechanism for methanol production from a paraformaldehyde-water solution. Total charges of various Ir complexes in the scheme are omitted.

Here we describe the proposed mechanism for MeOH generation by complex **7** at pH 12 (Scheme 2), but energetics associated with complex **1** and **6** along with complex **7** are presented in Table 3. In basic solution, the Cp*Ir complexes bearing an aqua ligand are predicted to be in equilibrium with

the hydroxo complexes ($\Delta G_1 = -6.3$ kcal/mol), either of which could react with methanediol $(H_2C(OH)_2)$ produced from paraformaldehyde and H_2O . The displacement of the aqua ligand by methanediol (H₂C(OH)₂) is uphill by only ΔG_2 = 3.4 kcal/mol. Then β -hydride elimination from [Ir-HOCH₂OH] (ΔG_{1}^{\dagger} = 15.0 kcal/mol) (Figure 3a) affords an iridium hydride complex, [Ir-H] (ΔG_{3} = -15.6 kcal/mol), with simultaneous production of formate (HCOO⁻) (Scheme 2). The [Ir-H] complex could react with $H_2C(OH)_2$, $H_2C(OH)O^-$ or alternatively with formaldehyde (H_2CO) to produce the methoxide intermediate [Ir–OCH₃]. The optimized transition state structure for the reaction of the [Ir-H] complex with H₂C(OH)₂ involves three additional water molecules to stabilize the newly forming OH⁻ anion (Figure 3b) and is associated with an inhibitively high activation free energy ($\Delta G_{\pm 2}^{\pm}$ = 45.2 kcal/mol) (see SI for details on optimized TSs with different numbers of explicit H₂O molecules and details on the effects of inclusion of explicit solvent molecules on solvation of reacting species and computed $\Delta G^{\dagger}s$). Another possibility is the reaction of [Ir–H] with H₂C(OH)O⁻, which could exist in equilibrium with $H_2C(OH)_2 (pK_a = 13.3)^{23}$ under high pH conditions. The optimized TS structure with $H_2C(OH)O^-$ (Figure 3c) features a significantly lower activation free energy of ΔG^{\ddagger} = 21.3 kcal/mol. We also considered the reaction of H₂CO with [Ir-H] (Figure 3d) which proceeds with a very low free energy of activation (ΔG_{3}^{\ddagger} = 7.8 kcal/mol). Although H₂CO is predicted to react with H₂O to generate H₂C(OH)₂ ($\Delta G = -4.2$ kcal/mol) in aqueous solutions, the formation of H₂CO inside the solvent cage of [Ir-H] reacting with $H_2C(OH)_2$ cannot be ruled out. The common product of all three possible pathways investigated is the methoxide intermediate [Ir–OCH₃], which could further react with a H₂O molecule to generate methanol (CH₃OH) and [Ir–OH] (ΔG_6 = -4.2 kcal/mol) followed by protonation to regenerate the initial agua complex [Ir–OH₂] ($\Delta G_1 = -6.3$ kcal/mol).

In addition, the aqua complex can also react with the formed HCOO⁻ to generate a formato complex [Ir–OCHO] ($\Delta G_7 = 5.0$ kcal/mol), which then could evolve CO₂ by β -hydride elimination ($\Delta G^{\ddagger}_4 = 11.5$ kcal/mol) (Figure 3e) to produce the [Ir–H] complex ($\Delta G_8 = -2.5$ kcal/mol). Similarly, methanol could be produced from the reaction of the [Ir–H] complex with H₂C(OH)O⁻ or H₂CO (Scheme 2). Furthermore, the formation of the hydride complex [Ir–H] in the proposed catalytic cycle has been supported by ¹H-NMR analyses as shown in Figure S4 (see SI for general procedure for the formation of Ir-H species).

Table 3. Computed free-energy changes (ΔG s) and activation free energies (ΔG^{\ddagger} s) at pH 12 for the chemical steps in the proposed mechanism for the methanol production in Scheme 2 for the most stable protonation states of complexes **1**, **6** and **7**

	1	6	7
∆ G 1	3.5	-4.8	-6.3
∆G₂	1.0	1.8	3.4
ΔG^{\ddagger}_{1}	27.0	18.4	15.0
∆G₃	-28.4	-18.3	-15.6
$\Delta G^{\ddagger}{}_{2}$	45.1 ^a	46.3 ^a (22.2) ^b	45.2 ^a (<i>21.3</i>) ^b
∆G₄	-2.5	-2.7	-3.7
ΔG^{\ddagger}_{3}	-	8.5	7.8
∆G₅	-6.7	-7.0	-7.9
∆G ₆	-0.1	-2.4	-4.2
∆G ₇	-5.6	2.2	5.0
ΔG^{\ddagger}_{4}	11.3	11.7	11.5
∆G ₈	-7.0	-3.9	-2.5

^a The computed activation free energies are with respect to [Ir-H] and $[H_2C(OH)_2(H_2O)_3]$ complexes as reactants. ^b The computed activation free energies are with respect to [Ir-H] and $[(H_2C(OH)O^-)(H_2O)_3]$ complexes as reactants.



Figure 3. Optimized transition state structures of **7** for **(a)** β -hydride elimination from [Ir–HOCH₂OH]²⁻, [Ir–H]³⁻ reaction with **(b)** H₂C(OH)₂, **(c)** H₂C(OH)O⁻ **(d)** H₂CO and **(e)** β -hydride elimination from [Ir–OCHO]³⁻.

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The proposed mechanism based on the computations agrees favorably with several experimental observations. Firstly, isotope and proton NMR studies of complex 7 show that during the conversion of (HCHO)₀ in D₂O only CH₃OD was observed, but no CH₂DOD, CHD₂OD, or CD₃OD (determined by ¹H NMR spectroscopy, see Figure S5). In contrast, when $(DCDO)_{n}$ was used in H₂O, only CD₃OH (no CH₃OH) formed. These results demonstrate that the existing C–H (or C–D) bond of methanediol is preserved through the reduction; moreover, indicating that paraformaldehyde acts as the sole carbon and hydride source in line with the computed mechanism as shown in Scheme 2 (note that the hydrogen atoms originating from the C-H group of methanediol are colored red). Secondly, we carried out a deuterium kinetic isotope effect (KIE) study with catalyst 7. The reaction rates over the initial 15 min were investigated using deuterated substrates and solvents as shown in Figure S6. Moreover, the relative KIE results based on the reaction rates obtained from Figure S6 are shown in Table S3. The KIE experiments suggest that the deuterated formaldehyde substrate (KIE: 1.6, entry 3) is more influential than deuterated water (KIE: 1.1, entry 2) on the reaction rate. This is in line with the proposed catalytic cycles in Scheme 2 and the computed data in Table S4, which show the important role of [Ir–H], with the possible rate determining step of [Ir–H] to [Ir–OCH₃] in both cycles A and B for methanol production. Thirdly, 1 shows only a negligibly small methanol yield and our computations show that the β -hydride elimination from the [Ir-HOCH₂OH] intermediate involves guite a high ΔG^{\dagger}_{1} of 27.0 kcal/mol compared to those of **6** (ΔG^{\dagger}_{1} = 18.4 kcal/mol) and **7** (ΔG^{\dagger}_{1} = 15.0 kcal/mol), which is predicted to be the limiting factor for methanol production for complex 1 as other reaction steps display energetics similar to 6 and 7 (Table 3). On the other hand, for complexes 6 and 7 the methoxide intermediate ([Ir-OCH₃]) production is predicted to be rate limiting and for all three possible pathways investigated for the reaction of $H_2C(OH)_2$, $H_2C(OH)O^-$ or H_2CO with the [Ir–H] intermediate, complex 7 exhibits more favorable kinetics and thermodynamics compared to those of **6**, in line with the observed improved activity of **7**. Finally, the computed $\Delta G^{\dagger}s$ indicate that β-hydride elimination from [Ir–OCHO] (ΔG_{4}^{\dagger} = 11.5 kcal/mol for 7) to be much faster compared to β-hydride elimination from [Ir–HOCH₂OH] (ΔG_1^{\dagger} = 15.0 kcal/mol for **7**) so that the formate product which builds up from the latter reaction is predicted to be consumed at a fast rate in line with experimentally observed formate concentration profiles during the course of methanol production (Figure 1).

CONCLUSIONS

The first example of the robust and selective catalytic production of methanol from paraformaldehyde and water at room temperature has been developed. For the case of complex **7**, a

very high yield of methanol with a high TOF and TON was achieved. Furthermore, a step-by-step mechanism for the production of methanol from paraformaldehyde and water is provided based on density functional theory calculations. On the basis of current rapid development of CO_2 transformations and establishment of a methanol economy, we herein add a promising pathway to the important field of C_1 chemistry, which may eventually open up the possibility of the renewable production of methanol from CO_2 at room temperature and low pressures (ideally atmospheric pressure).

ASSOCIATED CONTENT

Supporting Information.

Experimental section including general methods, NMR studies and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* Yuichiro Himeda, E-mail: <u>himeda.y@aist.go.jp</u>

* Mehmed Z. Ertem, E-mail: mzertem@bnl.gov

ORCID

Lin Wang: 0000-0001-5644-8865

Mehmed Z. Ertem: 0000-0003-1994-9024

Kazuhisa Murata: 0000-0002-5857-7668

James T. Muckerman: 0000-0001-5169-8929

Etsuko Fujita: 0000-0002-0407-6307

Yuichiro Himeda: 0000-0002-9869-5554

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was supported by ENEOS Hydrogen Trust Fund. The work at BNL was carried out with support from the U.S. Department of Energy, Office of Science, Division of Chemical Sciences, Geosciences & Biosciences, Office of Basic Energy Sciences under contract DE-SC0012704.

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