

Bioinorganic Chemistry Hot Paper

One Model, Two Enzymes: Activation of Hydrogen and Carbon Monoxide

Seiji Ogo,* Yuki Mori, Tatsuya Ando, Takahiro Matsumoto, Takeshi Yatabe, Ki-Seok Yoon, Hideki Hayashi, and Masashi Asano

Abstract: The ability to catalyze the oxidation of both H_2 and CO in one reaction pot would be a major boon to hydrogen technology since CO is a consistent contaminant of H_2 supplies. Here, we report just such a catalyst, with the ability to catalyze the oxidation of either or both H_2 and CO, based on the pH value. This catalyst is based on a NiIr core that mimics the chemical function of [NiFe]hydrogenase in acidic media (pH 4–7) and carbon monoxide dehydrogenase in basic media (pH 7–10). We have applied this catalyst in a demonstration fuel cell using H_2 , CO, and H_2 /CO (1/1) feeds as fuels for oxidation at the anode. The power density of the fuel cell depends on the pH value in the media of the fuel cell and shows a similar pH dependence in a flask. We have isolated and characterized all intermediates in our proposed catalytic cycles.

Hydrogen gas (H₂) is biologically and industrially important since it behaves as an electron donor and a fuel.^[1-3] However, commercially available H₂ includes a small amount of carbon monoxide (CO), which poisons the catalysts necessary to perform these functions at useful rates^[2]—the catalysts in biological H₂ oxidation is [NiFe]hydrogenase ([NiFe]H₂ase) and in fuel cell oxidation is platinum [Eq. (1)].^[3,4]

$$H_2 \rightleftharpoons 2 H^+ + 2 e^- \tag{1}$$

As part of our studies on $[NiFe]H_2$ ase mimics, we have made functional [NiRu]- and [NiFe]-based models that catalyze electron and hydride transfer from H_2 .^[5,6] As these models revealed the inner workings of H_2 ase, we became interested in CO poisoning.^[7] This focus arose from the intriguing observation that one equivalent of CO is essential as an Fe ligand (Figure 1a) but further addition deactivates the catalyst. A previous study, using the [NiRu]-based model,



Figure 1. Active-site structures of a) [NiFe]H_2ase^{[3]} and b) [NiFe]-containing CODH. $^{[10]}$

suggested that CO inhibits [NiFe]H₂ase by complexing to the Fe center rather than the Ni center.^[8]

 $\rm H_2$ oxidation has an interesting link to CO oxidation [Eq. (2)] in that a CO-oxidizing carbon monoxide dehydro-

$$CO + H_2O \rightleftharpoons CO_2 + 2H^+ + 2e^-$$
(2)

genase (CODH, Figure 1 b) can also catalyze the oxidation of H_2 .^[9,10] Significantly, CODH is also based around a [NiFe] core and this caused us to change our view of CO from as a catalyst poison to being a potential fuel. As a result, we began investigating the oxidation of CO using [NiFe]H₂ase functional models.

Following our efforts to improve the original models,^[5,6] we can now report a [NiIr]-based catalyst, which can oxidize either H_2 or CO, depending upon pH, in one flask. We have applied this reaction to a fuel cell using the [NiIr]-catalyst to promote oxidation of H_2 , CO, and H_2 /CO (1/1) fuel mixtures.

A water-soluble Ni^{II}Ir^{III} complex [Ni^{II}Cl(X)Ir^{III}Cl(η^{5} -C₅Me₅)] (**1**, X = N,N'-dimethyl-3,7-diazanonane-1,9-dithiolato) was prepared from the reaction of [Ir^{III}(η^{5} -C₅Me₅)(Cl)₂]₂ with [Ni^{II}(X)], and was characterized by X-ray analysis (see Figure S1 in the Supporting Information), electrospray ionization (ESI) mass spectrometry (ESI-MS, Figure S2), and ¹H NMR (Figure S3) and IR spectroscopies (Figure S4, Tables S1 and S2). The framework of **1** is based around Ni(μ -S)₂Ir butterfly core, where the Ni and Ir atoms are tethered by two thiolato units. The chloro ligand coordinated to the Ir^{III} center appears to be replaced by H₂O or OH⁻ when **1** is dissolved in water.

Complex **1** reacts with H_2 in water at 20 °C within 30 min (Figure S5) to afford a hydride-coordinated Ni^{II}Ir^{III} complex [Ni^{II}Cl(X)(μ -H)Ir^{III}(η^5 -C₅Me₅)] (**2**) (Figures 2 and 3) via heterolytic cleavage of H_2 , which we characterized by X-ray analysis (Figure 2), ESI-MS (Figure S6), and IR spectroscopy (Figure S7). The X-ray structure of **2** reveals that the Ni-S-Ir angles are significantly smaller than those for **1**, which is similar to the structural change seen in the [NiFe] and [NiRu] systems.^[5,6] To establish the origin of the hydrido ligand of **2**,

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Wiley Online Library

These are not the final page numbers!

^[*] Prof. S. Ogo, Y. Mori, Dr. T. Ando, Dr. T. Matsumoto, Dr. T. Yatabe, Dr. K.-S. Yoon
Center for Small Molecule Energy
Department of Chemistry and Biochemistry
Graduate School of Engineering, Kyushu University
744 Moto-oka, Nishi-ku, Fukuoka 819-0395 (Japan)
and
International Institute for Carbon-Neutral Energy Research
(WPI-I2CNER), Kyushu University
744 Moto-oka, Nishi-ku, Fukuoka 819-0395 (Japan)
E-mail: ogo.seiji.872@m.kyushu-u.ac.jp

Homepage: http://www.cstm.kyushu-u.ac.jp/ogo/ Dr. T. Ando, Dr. H. Hayashi, Dr. M. Asano

JNC Corporation, 2-1, Otemachi 2-chome, Chiyoda-ku Tokyo 100-8105 (Japan)

Supporting information for this article can be found under: https://doi.org/10.1002/anie.201704864.

Angew. Chem. Int. Ed. 2017, 56, 1-5



Figure 2. ORTEP drawing of the solid-state structure of 2 with ellipsoids at the 50% probability level. The hydrogen atoms of the ligand X (N,N'-dimethyl-3,7-diazanonane-1,9-dithiolato) and C₅Me₅ are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ni1--Ir1 2.7796(6), Ir1–H1 1.62(5), Ni1–H1 2.03(5), Ir1–S1 2.3689(9), Ir1–S2 2.3810(9), Ni1–S1 2.3802(10), Ni1–S2 2.3874(10), Ni1–N1 2.181(3), Ni1–N2 2.151(3), Ni1–Cl1 2.3357(10); Ni1-S1-Ir1 71.64(3), Ni1-S2-Ir1 71.31(3).

 $[Ni^{II}Cl(X)(\mu-D)Ir^{III}(\eta^5-C_5Me_5)]$ (D-labeled 2), was synthesized from the reaction of 1 with D₂. The ESI-MS signal and IR band shifted upon isotopic substitution of D for H (Figures S6 and S7), which demonstrates that the hydrido ligand is derived from hydrogen gas.

Complex 2 is capable of performing both hydride and electron transfers (Figure 3, Figures S8–S13, Table S3), with



Figure 3. Proposed H_2 oxidation cycle with NiIr complexes in H_2O . DCIP: 2,6-dichlorobenzeneindophenol. DCIPH₂: reduced form of DCIP that obtains two electrons and two protons.

a reactivity similar to that of [NiFe]H₂ase. The reaction of **2** with H⁺ in acetonitrile resulted in the evolution of H₂ (Figure S8). 2,6-Dichlorobenzeneindophenol (DCIP) was reduced by **2** in water to the corresponding 2-electron-reduced form (DCIPH₂) under stoichiometric conditions (**2**:DCIP = 1:1) in the absence of H₂ (Figures S9–S12) and under catalytic conditions (**1**:DCIP = 1:85) in the presence of H₂ (Figure S13). The pH-dependent turnover numbers (TONs, mol of DCIPH₂/mol of catalyst) at 60 °C for 2 h were determined, at a maximum value of 84 at pH 4.0 (Figure S13). Acidic conditions are favorable for H₂ oxidation because coordination of OH⁻ seems to block the metal center

from activating H_2 , as seen in the previously reported [NiRu] system.^[11]

Complex **1** also uptakes CO in water at 20 °C within 1 s (Figure S14) to form a CO-coordinated Ni^{II}Ir^{III} complex $[Ni^{II}(X)Ir^{III}(CO)(\eta^5-C_5Me_5)]^{2+}$ (**3**, Figure 4), as characterized



Figure 4. Proposed CO oxidation cycle with NiIr complexes. DCIP: 2,6dichlorobenzeneindophenol. DCIPH₂: reduced form of DCIP that is obtained by addition of two electrons and two protons.

by X-ray analysis (Figure S15), ESI-MS (Figure S16), and IR (Figure S17) and ¹H NMR spectroscopies (Figure S18). The CO coordination is much faster than H₂ activation. Analysis by X-ray crystallography of **3** reveals that CO is coordinated to the Ir center. This is contrary to the situation in CODH where CO is bound to the Ni center.^[10] The Ir1-C1 length is 1.875(4) Å and the Ir1-C1-O1 angle is 171.9(3)°. The C=O bond length {1.135(5) Å} is slightly longer than that of a free CO (1.128 Å).^[12]

Isotope-labeling experiments using ¹³CO in place of CO were carried out to confirm that the CO ligand originates from CO gas. The ESI-MS results show that the signal m/z 317.1 shifts to 317.6 assigned to ¹³CO-coordinated complex [Ni^{II}(X)Ir^{III}(¹³CO)(η^5 -C₅Me₅)]²⁺ (¹³CO-labeled **3**) (Figure S16). The IR spectra reveal that the stretching vibration at 2037 cm⁻¹ derived from ν (C=O) of **3** shifts to 1987 cm⁻¹ upon replacing CO with ¹³CO (Figure S17).

Under basic conditions, OH⁻ attacks CO nucleophilically to afford the μ -COOH complex [Ni^{II}(OH)(X)(μ -COOH)Ir^{III}-(η^{5} -C₅Me₅)] (**4**, Figure 4, Figure S19) as characterized by Xray analysis (Figure S20), ESI-MS (Figure S21), and IR spectroscopy (Figure S22). Although the protonated COOH species (**C**, Figure S23) has been proposed in the catalytic cycle of CODH before,^[10] this is the first time it has been isolated and characterized in a model system.^[13,14] In the CODH cycle, subsequent deprotonation of the COOH species affords a CO₂ species (**D**, Figure S23), but such an intermediate was not observed in our [NiIr] system.

Complex **4** was converted to the hydrido complex **2** with evolution of CO₂ (Figure 4) by heating at 90 °C for 30 min (Figure S24), as confirmed by ESI-MS (Figure S25) and IR spectroscopy (Figure S26). It is meaningful that the reducing ability of the COOH⁻ moiety remains in the form of a hydride ion. This is the first example of the conversion of the COOH species to the hydride species with decarboxylation in a CODH model systems.^[13,14] In the CODH catalysis, the



2

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

decarboxylation of the CO_2 species yields a postulated hydride species (**F**, Figure S23) or a low-valent species (**E**, Figure S23), which releases two electrons to return to the starting species (**A**, Figure S23) via an unidentified intermediate (**G**, Figure S23). Such low-valent species and unidentified intermediates were not detected in our catalytic cycle.

The pH-dependent catalytic reduction of DCIP shows a maximum TON value of 212 at pH 10.0 under catalytic conditions (1:DCIP = 1:213) in the presence of CO (Figure 5, Figure S27). This profile indicates that key step in the catalytic cycle is the nucleophilic attack of OH⁻ on the CO ligand. CODH also catalyzes CO oxidation under basic conditions.^[15]



Figure 5. pH-Dependent TON for oxidation of H₂ (solid red line) and CO (solid green line) in flask catalyzed by the NiIr complex **1**. pH-Dependent maximum power density of H₂ (anode gas)/O₂ (cathode gas) fuel cell (dotted red line) and CO (anode gas)/O₂ (cathode gas) fuel cell (dotted green line) with **1** (anode catalyst) and Pt/C (cathode catalyst).

Perhaps most significantly, **1** is able to catalytically reduce DCIP using $H_2/CO(1/1)$ gas mixture, in water under catalytic conditions (**1**:DCIP = 1:170) (Figure 6). The pH-dependent



Figure 6. pH-Dependent activation of H_2 and CO with NiIr complexes. DCIP: 2,6-dichlorobenzeneindophenol. DCIPH₂: reduced form of DCIP that obtains two electrons and two protons. Structures of **1**, **2**, **3**, and **4** were determined by X-ray analysis (Figure S1, Figure 2, Figure S15, and Figure S20, respectively).

TONs are shown in Figure S28, and have a profile more similar to the CO reduction profile since the reaction of $\mathbf{1}$ with CO is much faster than the reaction of $\mathbf{1}$ with H₂.

To investigate resistance to fuel cell poisoning, we followed the pH-dependent performance of our NiIr catalyst in a polymer electrolyte fuel cell (PEFC) using H_2 , CO, or $H_2/$ CO (1/1 mixture) feeds (Figure 5, Figures S29–S34). The PEFC was constructed with 1 as the anode catalyst and Pt/C as the cathode catalyst, separated by a Nafion membrane 212 as a proton-conducting polymer electrolyte. The [NiIr] anode was prepared by loading a mixture of 1 and carbon black on a waterproof carbon cloth to make a gas diffusion electrode, in which the loading amount of 1 is 1.0 mg cm⁻². A piece of Nafion membrane was sandwiched between two gas diffusion electrodes to form a membrane electrode assembly (MEA) and the MEA was assembled in fuel cell hardware. The pH in the media of anode can be changed from 4.0 to 10.0 by flowing a pH-controlled aqueous solution into the anode conduit together with the feed of water-saturated H_2 , CO, or H_2 /CO (1/1 mixture).

The H₂-O₂ PEFCs at pH 4.0–10.0 in the anode produce almost the same open circuit voltage (OCV) of around 0.60 V, but different maximum power densities of 155 μ W cm⁻² at pH 4.0 (Figure S29) and 30 μ W cm⁻² at pH 10.0. The pH dependent maximum power densities of the H₂-O₂ PEFCs indicate that acidic conditions are more favorable than basic conditions for the [NiIr] complex to oxidize H₂ in anode, and its pH profile is similar to the TON profile in the flask experiments (Figure 5, Figure S30).

The CO-O₂ PEFCs also show a pH-dependent profile of maximum power densities, but in this case the maximum density is in the basic region around pH 10.0 (Figure 5, Figures S31 and S32). A similar profile was observed for the mixed-feed H₂/CO-O₂ PEFCs, suggesting that CO oxidation dominates H₂/CO oxidation due to the faster coordination of CO on the Ir center (Figures S33 and S34). The fuel cell performances of H₂, CO, and H₂/CO (1/1) gas mixture at pH 7.0 are comparable, which corresponds to the TON profile for oxidation of H₂, CO, and H₂/CO (1/1) gas mixture at pH 7.0 (Figure 5, Figures S28 and S34).

In conclusion, we have been able to choose between H_2 and CO oxidation by adjusting the pH value in a flask and fuel cell and using a [NiIr]-based complex as catalyst. We have fully characterized all intermediates in our proposed catalytic cycles. H_2 oxidation is accelerated in acidic media while CO oxidation is accelerated in basic media. Such trends are significantly related to enzymatic catalysis. In the case of [NiFe]H₂ase-type catalysis, the heterolytic cleavage of H_2 to form $H^+ + H^-$ is essential to start H_2 activation. In CODH-type catalysis, nucleophilic attack of OH⁻ on CO is principal. Furthermore, both H_2 and CO oxidation pass through hydride species.

Experimental Section

 $[Ni^{II}Cl(X)Ir^{III}Cl(\eta^5-C_5Me_5)]$ (1): A methanol solution (10 mL) of $[Ni^{II}(X)]$ (55.8 mg, 0.20 mmol) was added to an acetonitrile solution (5.0 mL) of $[Ir^{III}(\eta^5-C_5Me_5)Cl_2]_2$ (79.7 mg, 0.10 mmol). The resulting solution was stirred for 3 h at room temperature, and then it was

Angew. Chem. Int. Ed. 2017, 56, 1-5

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

einheim www.angewandte.org These are not the final page numbers! filtrated and the solvent was removed under reduced pressure. Water (4.0 mL) was added to the brown residue and the insoluble material was removed by filtration. The solvent was removed under reduced pressure to generate a brown powder of **1**, which was dried in vacuo (yield: 74% based on [Ir^{III}(η^5 -C₅Me₅)Cl₂]₂). Complex **1** was recrystallized by diffusion of diethyl ether into its acetone solution, suitable for X-ray analysis. ESI-MS (in methanol): m/z 641.1 {[**1**-Cl]⁺, relative intensity (I) = 100% in the range m/z 200–2000}. FT-IR (cm⁻¹, solid state): 2986 (aliphatic C–H), 2960 (aliphatic C–H), 2924 (aliphatic C–H), 2852 (aliphatic C–H), 1459 (aromatic C=C), 1439 (aromatic C=C), 1374 (aromatic C=C). ¹H NMR (300 MHz, in D₂O, referenced to TSP, 25°C): δ 1.75 {s, 15H, C₅(CH₃)₅}, 2.17–3.66 (m, 14H, -CH₂-), 2.70 (s, 6H, *N*-CH₃). Anal. Cald for **1** (C₁₉H₃₅N₂Cl₂S₂NiIr): C, 33.69; H, 5.21; N, 4.14%. Found: C, 33.64; H, 5.26; N, 4.09%.

 $[Ni^{II}Cl(X)Ir^{III}(\mu-H)(\eta^{5}-C_{5}Me_{5})]$ (2): $[Ni^{II}Cl(X)Ir^{III}Cl(\eta^{5}-C_{5}Me_{5})]$ (1) (50.8 mg, 0.075 mmol) was dissolved in water (8.0 mL) and it was stirred for 5 h under an H₂ atmosphere (0.8 MPa) at room temperature. The solvent of the resulting solution was evaporated, and acetone (4.0 mL) was added to the residue. The insoluble material was removed by filtration and the solvent was removed by evaporation to yield a yellow power of 2, which was dried in vacuo (yield: 72% based on 1). Complex 2 was recrystallized by diffusion of diethyl ether into its acetone solution under an N2 atmosphere, suitable for Xray analysis. ESI-MS (in methanol): m/z 607.1 ([2-Cl]⁺, I = 100% in the range m/z 200–2000). FT-IR (cm⁻¹, KBr disk): 2956 (aliphatic C-H), 2917 (aliphatic C-H), 2851 (aliphatic C-H), 1954 (Ni-H-Ir) 1641 (aromatic C=C), 1470 (aromatic C=C), 1460 (aromatic C=C), 1451 (aromatic C=C) 1427 (aromatic C=C). Anal. Cald for 2·CH₃COCH₃ (C₂₂H₄₂N₂OClS₂NiIr): C, 37.69; H, 6.04; N, 4.00%. Found: C, 37.70; H, 5.89; N, 4.27%.

 $[Ni^{II}(X)Ir^{III}(CO)(\eta^{5}-C_{5}Me_{5})](PF_{6})_{2} {[3](PF_{6})_{2}}: [Ni^{II}Cl(X)Ir^{III}Cl (\eta^5-C_5Me_5)$] (1) (41.0 mg, 0.060 mmol) was dissolved in water (5.0 mL) and it was stirred for 1 h under a CO atmosphere at room temperature. The resulting solution was filtered and the filtrate was evaporated to yield a red powder of [3](Cl)₂ (yield: 97% based on 1), which is used for the reactions in water as a water-soluble complex. An aqueous solution (2.0 mL) of KPF₆ (71 mg, 0.39 mmol) was added to the aqueous solution of $[3](Cl)_2$ to generate a red solid, which was collected by filtration. Acetone (2.0 mL) was added to the solid and the insoluble material was removed by filtration. The solvent was removed under reduced pressure to yield a red powder of $[3](PF_6)_2$ (yield: 43% based on 1). Complex 3 was recrystallized by diffusion of diethyl ether into its acetone solution under an N2 atmosphere, suitable for X-ray analysis. ESI-MS (in acetonitrile): m/z 317.1 ([3]²⁺, I = 100% in the range m/z 200–2000). FT-IR (cm⁻¹, KBr disk): 3009 (aliphatic C-H), 2919 (aliphatic C-H), 2867 (aliphatic C-H), 2037 (C=O), 1629 (aromatic C=C), 1479 (aromatic C=C), 1464 (aromatic C=C), 1436 (aromatic C=C), 838 (PF₆). ¹H NMR (300 MHz, in $[D_6]$ acetone, referenced to TMS, 25 °C): δ 2.20 {s, 15H, C₅(CH₃)₅}, 2.42-3.68 (m, 14H, -CH2-), 2.87 (s, 6H, N-CH3). Anal. Cald for 3·(PF₆)₂·CH₃COCH₃ (C₂₃H₄₁N₂O₂F₁₂P₂S₂NiIr): C, 28.12; H, 4.21; N, 2.85%. Found: C, 28.00; H, 4.19; N, 2.92%.

[Ni^{II}(OH)(X)Ir^{III}(COOH)(η⁵-C₅Me₅)] (4): [Ni^{II}Cl(X)Ir^{III}Cl(η⁵-C₅Me₅)] (1) (138 mg, 0.20 mmol) was dissolved in water (8.0 mL) and it was stirred for 1 h under a CO atmosphere at room temperature. To the resulting solution was added 1.0M NaOH/H₂O (0.50 mL) to yield a light-green powder of **4**, which was collected by filtration and dried in vacuo (yield: 87% based on **1**). ESI-MS (in acetonitrile): m/z 651.1 ([**4**-OH]⁺, I = 100% in the range m/z 200–2000). FT-IR (cm⁻¹, solid state): 2954 (aliphatic C–H), 2907 (aliphatic C–H), 2845 (aliphatic C–H), 1610 (C=O), 1464 (aromatic C=C), 1435 (aromatic C=C), 1423 (aromatic C=C). Anal. Cald for **4** (C₂₀H₃₇O₃N₂S₂NiIr): C, 35.93; H, 5.58; N, 4.19%. Found: C, 36.10; H, 5.48; N, 4.16%.

Acknowledgements

This work was supported by Grants-in-Aid: 26000008 (Specially Promoted Research), 16K05727, and 15K05566 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan and the World Premier International Research Center Initiative (WPI), Japan.

Conflict of interest

The authors declare no conflict of interest.

Keywords: bioinorganic chemistry · carbon monoxide · dehydrogenase · hydrogenase · hydrogen

- Special issue on "Toward a Hydrogen Economy", Science 2004, 305, 957-976.
- [2] X. Cheng, Z. Shi, N. Glass, L. Zhang, J. Zhang, D. Song, Z. S. Liu, H. Wang, J. Shen, J. Power Sources 2007, 165, 739–756.
- [3] a) Special issue on "Hydrogenases", Eur. J. Inorg. Chem. 2011, 915–1171; b) Special issue on "Renewable Energy", Chem. Soc. Rev. 2009, 38, 1–300; c) C. Tard, C. J. Pickett, Chem. Rev. 2009, 109, 2245–2274; d) Special issue on "Hydrogen", Chem. Rev. 2007, 107, 3900–4435; e) J. A. Denny, M. Y. Darensbourg, Chem. Rev. 2015, 115, 5248–5273.
- [4] a) M. L. Perry, T. F. Fuller, J. Electrochem. Soc. 2002, 149, S59–S67; b) J. Z. Zhang, Z. Liu, J. G. Goodwin, Jr., J. Power Sources 2010, 195, 3060–3068.
- [5] S. Ogo, K. Ichikawa, T. Kishima, T. Matsumoto, H. Nakai, K. Kusaka, T. Ohhara, *Science* 2013, 339, 682–684.
- [6] S. Ogo et al., Science 2007, 316, 585-587.
- [7] W. Lubitz, H. Ogata, O. Rüdiger, E. Reijerse, Chem. Rev. 2014, 114, 4081–4148.
- [8] T. Matsumoto, R. Kabe, K. Nonaka, T. Ando, K.-S. Yoon, H. Nakai, S. Ogo, *Inorg. Chem.* 2011, *50*, 8902–8906.
- [9] a) S. Menon, S. W. Ragsdale, *Biochemistry* 1996, 35, 15814–15821; b) J. Heo, M. T. Wolfe, C. R. Staples, P. W. Ludden, J. Bacteriol. 2002, 184, 5894–5897.
- [10] a) M. Can, F. A. Armstrong, S. W. Ragsdale, *Chem. Rev.* 2014, *114*, 4149–4174; b) V. C.-C. Wang, S. T. A. Islam, M. Can, S. W. Ragsdale, F. A. Armstrong, *J. Phys. Chem. B* 2015, *119*, 13690–13697; c) J. C. Fontecilla-Camps, P. Amara, C. Cavazza, Y. Nicolet, A. Volbeda, *Nature* 2009, *460*, 814–822.
- [11] T. Matsumoto, T. Ando, Y. Mori, T. Yatabe, H. Nakai, S. Ogo, J. Organomet. Chem. 2015, 796, 73–76.
- [12] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, 1999, pp. 636–639.
- [13] a) Z. Lu, C. White, A. L. Rheingold, R. H. Crabtree, Angew. Chem. Int. Ed. Engl. 1993, 32, 92–94; Angew. Chem. 1993, 105, 121–123; b) Z. Lu, R. H. Crabtree, J. Am. Chem. Soc. 1995, 117, 3994–3998.
- [14] C. Yoo, Y. Lee, Chem. Sci. 2017, 8, 600-605.
- [15] J. Seravalli, M. Kumar, W.-P. Lu, S. W. Ragsdale, *Biochemistry* 1995, 34, 7879–7888.

Manuscript received: May 11, 2017 Accepted manuscript online: June 6, 2017

Version of record online:

www.angewandte.org

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers!



Communications

Bioinorganic Chemistry

S. Ogo,* Y. Mori, T. Ando, T. Matsumoto, T. Yatabe, K.-S. Yoon, H. Hayashi, M. Asano _____ IIII

One Model, Two Enzymes: Activation of Hydrogen and Carbon Monoxide



Enzymatic catalysis: If the oxidation of both H_2 and CO could be catalyzed in one reaction pot, this would be a major boon to hydrogen technology since CO is a consistent contaminant of H_2 supplies. A catalyst is reported with the ability to catalyze the oxidation of either or both H_2 and CO (see picture), based on the chosen pH value.

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers!