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Philipp Gotico, Antonio Vecchio, Davide Audisio, Annamaria Quaranta, Zakaria Halime, et al.. Visible-Light-Driven Reduction of CO₂ to CO and Its Subsequent Valorization in Carbonylation Chemistry and ¹³C Isotope Labeling. ChemPhotoChem, 2018, 2 (8), pp.715-719. 10.1002/cptc.201800012 . cea-02503934

HAL Id: cea-02503934

<https://hal-cea.archives-ouvertes.fr/cea-02503934>

Submitted on 10 Mar 2020

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Visible Light-Driven Reduction of CO₂ to CO and Its Subsequent Valorization in Carbonylation Chemistry and ¹³C Isotope Labeling

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Abstract: A convenient and safe approach in valorizing carbon monoxide (CO) produced from the photocatalytic reduction of carbon dioxide (CO₂) has been investigated. Visible light was used to drive an optimized photocatalytic reduction using a ruthenium trisbipyridine complex as a sensitizer and a rhenium bipyridyl carbonyl complex as a catalyst to perform an efficient reduction of CO₂ to CO, which was then simultaneously utilized in a palladium-catalyzed aminocarbonylation reaction at room temperature. This approach provides a safe handling of the produced CO which also opens the way for a more efficient application of ¹³C-isotope and ¹⁴C-radioisotope labeled CO₂ in pharmaceutically-relevant drug labeling.

The constraints we are exerting on our environment due to the extensive use of fossil fuels have reached alarming levels. There is a consensus that we have to develop a circular economy scheme in order to drop to a zero-carbon emission scenario. One challenge in front of chemists is to convert the ever-increasing CO₂ level into a fuel or to use it as a source of carbon in chemical transformations. However, due to its high chemical stability, its activation or reduction is scientifically challenging, requiring appropriate catalyst and energy input.^[1–6] The energy can be ideally provided by solar energy, a strategic scheme of artificial photosynthesis.

One of the most robust and selective photocatalyst for CO₂ reduction was first reported by Lehn et. al. using fac-Re(bpy)(CO)₃Cl.^[7,8] Since then, researchers have tried to improve its efficiency by (i) modifying the nature of the ligands in the coordination sphere to improve catalysis and to shift the absorption properties in the visible range,^[9–15] and/or (ii) incorporating photosensitizers to photo-activate the catalyst in the visible spectral window.^[16–26] From turnover numbers (TON) of 5–20 when it was first published, current improvements show TONs of ca. 3000.^[27] Efforts are also guided towards designing photocatalysts employing earth-abundant metals (Cu, Ni, Co, Mn, Fe) for cost efficiency and such systems show equally promising results.^[28]

Though most studies in photocatalytic reduction of CO₂ to CO have focused on improving the efficiency, selectivity, cost, and stability of the catalyst, only little has been reported in addressing the need for capturing and storing the produced CO. The reduced product can be segregated from the headspace mixture by techniques such as swing adsorption,^[29] cryogenic distillation,^[30] and membrane gas separation,^[31] but these

usually employ specialized equipment, and high pressure and temperature, which require extra energy input. Furthermore, the inherent toxicity and flammability of CO gas impose strict handling precautions and safety procedures.

In nature, CO dehydrogenase enzymes transport the CO produced from the catalytic reduction of CO₂ in its C cluster site to the acetyl CoA synthase via direct gas channels to insert CO in a carbonylation reaction.^[32] Inspired by this enzymatic scheme, one promising strategy is to immediately use the produced CO from photocatalysis as a reagent in chemical transformations. This strategy is based on the significant difference in reactivity between the generally unreactive CO₂, and the reactive CO towards carbonylation reactions. Thus, the photocatalytic reduction and the carbonylation reaction can share the same atmosphere where CO₂ is transformed, and the produced CO is simultaneously consumed. This provides not only a clean way of capturing CO, but it might also give further drive towards the valorization of CO₂.

The COware® two-chamber system consisting of a CO-producing chamber connected to a CO-consuming chamber, developed by the group of Skrydstrup et. al., seems to be fitting to our strategy.^[33] In this technique, CO precursors such as 9-methylfluorene-9-carbonyl chloride or methylphenylsilacarboxylic acid were used to produce CO, which was efficiently utilized in amino-, alkoxy-, and thio-carbonylation, carbonylative α -arylation, Suzuki–Miyaura, Heck, Sonogashira, and C–H activation.^[34] The simplicity and efficiency of the experimental set-up enables safe carbonylation chemistry without the need for direct handling of the gaseous CO reagent. To eliminate the use of expensive CO precursors, Skrydstrup has investigated the use of cesium fluoride and disilane to transform CO₂ to CO and immediately utilize it in aminocarbonylation, but this approach still requires highly sensitive, difficult-to-synthesize reagents, and the utilization of a glovebox.^[35] Recently, the same group reported the electrochemical reduction of CO₂ to CO and its application in carbonylation chemistry.^[36]

Photoredox catalysis has already been applied in various organic synthesis including carbonylation^[37] and aminocarbonylation^[38] chemistry, but usually necessitates a reactive species, such as CO at high pressures, and high energy light sources in the UV spectral range. Photoredox activation of CO₂ for direct amino acid synthesis^[39] and hydrocarboxylation of styrenes^[40] has been investigated by the group of Jamison, but requires a continuous flow of gas and UV irradiation to access the CO₂^{•–} radical. Similarly, Yu et. al. reported visible light-driven thiocarboxylation of styrenes and acrylates by accessing the reducing power of the CO₂^{•–} radical.^[41] To the best of our knowledge, we report here the first attempt to merge the field of artificial photosynthesis in reducing CO₂ to CO using visible light, and the sequential utilization of this CO in carbonylation chemistry to produce pharmaceutically-relevant products. This approach uses the new developments and advancements in both fields to achieve a simple, efficient, and cost-effective reduction and valorization of CO₂.

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Scheme 1. Reaction scheme for the photocatalyzed reduction of CO₂ to CO and its application for Pd-catalyzed aminocarbonylation. Structure of reagents and their corresponding prefixes are also shown.

In this study, the COWare® two-chamber reactor was utilized to explore the possibility of a direct use of CO₂ in carbonylation chemistry under mild conditions (1 atm, room temperature). It consists of a CO-producing chamber based on the photocatalytic reduction of CO₂ to CO using rhenium bipyridyl catalysts **[Re cat]** and ruthenium trisbipyridine photosensitizer **[Ru PS]**, and a CO-consuming chamber based on a palladium-catalyzed aminocarbonylation of aryl halides, shown in Scheme 1. This proof-of-concept short circuit the need to synthesize a CO-precursor, which usually involves high pressures of CO₂ and extremely low temperatures, thereby making it a cheaper and more accessible method. The use of visible light to drive the transformation of CO₂ to CO also allows to control the delivery of CO for the carbonylation reaction chamber, by simply controlling the intensity and duration of irradiation. Furthermore, this strategy offers a new alternative for the manipulation and use of the stable ¹³C and radioactive ¹⁴C-labeled CO₂ as labeled CO sources for its subsequent incorporation in various pharmaceutical drug preparations.

Initial physicochemical investigation on the bimolecular mixture of **[Ru PS]** and **[Re Cat]** was performed to understand the mechanistic scheme of the photocatalytic reduction of CO₂ to CO. As expected, the UV-vis spectrum of the mixture is dominated by the **[Ru PS]** features, with a maximum absorption peak at 460 nm, as shown in Figure S3. This is beneficial as it sensitizes the absorption in the visible region where solar irradiation is relatively high. Cyclic voltammetry shows catalytic current of **[Re cat]** upon purging with CO₂ (Figure S2) indicating catalytic activity towards CO₂ reduction. First reduction potential of the **[Re cat]** (-1.66 V vs. Ag/AgNO₃) is close to the first reduction of **[Ru PS]** (-1.65 V vs. Ag/AgNO₃), indicating no/little thermodynamic drive for electron transfer from **[Ru PS]** to **[Re cat]**. Emission measurements, in the absence of a sacrificial electron donor (SED), show that there is no electron nor energy transfer from the excited **[Ru PS]*** to the **[Re cat]**. In the presence of a SED, efficient quenching of the emission of the **[Ru PS]*** was observed (Table S2). The reductive quenching of **[Ru PS]*** by the SED was confirmed by the formation of **[Ru PS]⁻** which has a characteristic absorption band at 510 nm (Figure S6a). The formation of reduced **[Re cat]** from the positive absorption at 445 nm (Figure S6b-c), with similar kinetics as the decay at 510 nm, confirms that electron transfer occurs from the **[Ru PS]⁻** to the **[Re cat]**, with a diffusion-limited

Table 1. Optimizations for photocatalytic reduction of CO₂ to CO.

Entry	Catalyst	Solvent ^[a]	SED ^[b]	nCO / μmol	TON ^[c]
1	Ru PS:Re cat	DMF	BNAH	-	-
2	Ru PS:Re cat	DMF:H ₂ O	BNAH	1.2	8
3	Ru PS:Re cat	DMF:H ₂ O	BIH	78.0	520
4	Ru PS:Re cat	ACN:H ₂ O	BIH	0.8	5
5	Ru PS:Re cat	DMF:TEOA	BIH	78.0	520
6	Ru PS:Re cat	DMF:PhOH	BIH	32.6	217
7	Ru PS:Re cat	DMF:TEOA:H ₂ O	BIH	117.6	784
8	Ru PS	DMF:H ₂ O	BIH	0.5	3
9	Re Cat	DMF:H ₂ O	BIH	5.6	37
10	-	DMF:H ₂ O	BIH	-	-

Reaction conditions: 0.15 μmol **[Ru PS]**, 0.15 μmol **[Re Cat]**, light source: LED lamp with λ_{em} at 485 nm (FWHM 50 nm, 180 W/m²), 20°C, 2 hr irradiation. [a] DMF: dimethylformamide, ACN: acetonitrile, TEOA: triethanolamine, PhOH: phenol [b] SED: sacrificial electron donor, BIH: 1,3-dimethyl-2-phenylbenzimidazole, BNAH: 1-benzyl-1,4-dihydronicotinamide [c] TON calculated as moles of CO divided by moles of catalyst; No H₂ was detected by GC; bicarbonate and formate were detected by ¹³C NMR but were not quantified.

rate of 4.83 × 10⁹ M⁻¹s⁻¹ (Figure S7). This result clearly indicates that even with no/little thermodynamic drive between the first reduction potentials of **[Ru PS]** and **[Re cat]**, photo-induced electron transfer is still observed. Irradiating the system with a blue LED source (emission peak at 463 nm to selectively excite **[Ru PS]**) in the presence of CO₂ substrate and SED produced CO, supporting the photocatalytic activity of the system.

As hinted by the equation of the two-electron reduction of CO₂ in equation 1,

optimizations of the photocatalytic performance were conducted by screening the sacrificial electron donor and proton sources. Conditions and results are summarized in Table 1. Higher TON were observed when 1-benzyl-1,4-dihydronicotinamide (BNAH) was replaced by 1,3-dimethyl-2-phenylbenzimidazole (BIH) as SED. This is due to the differences in the electron donation ability of these two electron and proton donors. Indeed, BNAH acts as a single electron donor with respect to the excited photosensitizer and also releases one proton upon deprotonation of the oxidized species. However, BIH differs in donating a first electron upon reaction with the excited photosensitizer, one proton upon deprotonation of the oxidized species BIH⁺, and a second electron because of the highly reducing nature of the deprotonated one-electron oxidized species BI[•] (see CO producing chamber in Scheme 1). This was confirmed by monitoring the transient absorption kinetics at 510 nm, a wavelength where selective formation of the reduced form of the **[Ru PS]** can be followed, as shown in Figure S5. When BNAH was used, **[Ru PS]⁻** was immediately formed upon laser flash excitation and decayed back due to back electron transfer, indicating reversibility of BNAH to a substantial extent. When BIH was used, however, a further increase in the concentration of the reduced photosensitizer species is observed after the end of the laser flash excitation. BI[•] is highly reducing (-2.02 vs. Fc⁺/Fc⁰)^[42] and, from a thermodynamic view point, can reduce the Ru photosensitizer, as well as the Re catalyst. However, it is important to stress, that such a reducing radical can only be accessed after an initial photo-activated electron transfer.

Dimethylformamide was a suitable solvent and water was a suitable proton source for optimal photocatalytic performance (Figure S12). The role of water as a proton source in photocatalytic systems was recently reported by the group of Kojima et. al.^[43] The synergistic effect of water and TEOA can be rationalized by the ability of TEOA in capturing and increasing the concentration of CO₂ in solution.^[44] The absence of either the photosensitizer or the catalyst, did not lead to the production of significant amounts of CO, pertaining the fact that both components are necessary to perform the photocatalytic reduction of CO₂. Henceforth, we realized the photocatalytic runs under our optimized conditions using bimolecular mixture of **[Ru PS]** and **[Re cat]** for the production of CO in the two-chamber system shown in Scheme 1. To achieve significant amounts of CO to be used in the aminocarbonylation in the second chamber, the component concentrations were increased. However, in the solvent condition DMF:H₂O:TEOA (8:1:1), a lower TON is obtained when the concentrations were increased (Figure S13). Interestingly, the use of solvents mixture of DMF and H₂O (9:1) both increased the CO production and the corresponding TON. As such, this solvent system was used hereafter.

The second chamber was screened for Pd-catalyzed aminocarbonylation reaction conditions, and an isolated yield of 41% n-hexyl-4-methoxybenzamide was achieved using Pd(dba)₂ catalyst with P(tBu)₃HBPf₄ as a ligand precursor, in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as a base, at room temperature (Table 2, entry 1). The observed low yield of the second chamber reaction is due to the formation of a double CO insertion product (n-hexyl-2-(4-methoxyphenyl)-2-oxoacetamide) during the Pd-catalyzed reaction. This type of by-product is usually observed when an equimolar amount of CO is used in room temperature Pd-catalyzed carbonylation.^[33] Increasing the concentration of reagents in Chamber 2 prevents the double insertion of CO, and greatly improved the selectivity of the reaction in favor of the mono-insertion. Under these optimized conditions, a satisfying 83% yield was reached (Table 2, Entry 2). Based on these results we turn our attention to performing such a reduction with isotopic labeled CO₂ to CO and its subsequent valorization. Carbon-14 drug radiolabeling is commonly used to study the distribution, metabolism, toxicity of a drug in vivo, in pre-clinical and early clinical studies (Phase 0/1). As part of the Food and Drug Administration safety assessment process, more than 80% of all drugs have used radioactive materials in their testing program.^[45] From a synthetic standpoint, ¹⁴CO₂ represents the primary ¹⁴C labeling source. The escalating price of ¹⁴C labeling building blocks, and the high costs for disposal of radioactive wastes represent major drawbacks in the field. For these reasons, the development of original, multi-catalytic procedures enabling the generation of highly functionalized molecules and advanced building blocks from carbon dioxide would be highly desirable.

Tritec® system is a state of the art manifold, which enables the handling of precise amounts of carbon dioxide, and is routinely used by the pharmaceutical and agrochemical industries for radiolabeling of chemicals and active pharmaceutical ingredients. This technology is particularly useful because it enables the utilization of radioactive ¹⁴CO₂ under strict and safe working practices. As a proof-of-concept application for our newly developed two chamber multi-catalytic system, we coupled it to a Tritec® system in order to synthesize ¹³C-labeled pharmaceutically-relevant drugs using ¹³CO₂. The major additional criterion to take into consideration for such an application is the elevated cost of isotope-labeled CO₂, especially ¹⁴CO₂. For this reason, we have considered the actual amount of CO₂ converted to form the desired product, rather than the production of CO normalized by the catalyst

Table 2. Optimizations for Chamber 2: Pd-catalyzed aminocarbonylation.

Ch. 1	CO ₂	Ru PS, Re Cat, BIH DMF:H ₂ O, 460nm, r.t.	CO
Ch. 2	1	Pd(dba) ₂ P(tBu) ₃ HBPf ₄ DABCO THF, r.t.	2
Entry	Limiting Reagent	Isolated yield ^[d] of 2 based on	
		CO ₂	CO
1 [a]	1	18 %	41 %
2 [b]	¹² CO	18 %	83 %
3 [c]	¹³ CO ₂	32 %	82 %

[a] Two-chamber system is utilized. Chamber 1 contains 0.19 mM **[Ru PS]**, 0.19 mM **[Re Cat]**, 0.28 M BIH, DMF + 10% H₂O producing 478 μmol CO. Chamber 2 contains 0.5 mmol of **1**, 1 mmol n-hexylamine, 0.025 mmol Pd(dba)₂, 0.05 mmol P(tBu)₃HBPf₄ (ligand), 2 mmol DABCO (base), and THF (solvent). CO₂-purged (1atm); Reaction was run for 21 hours. [b] 2.5 equivalents excess of Chamber 2 reagents in relation to CO [c] Tritec® system was used to deliver limited amount of ¹³CO₂ (501 μmol). [d] Yield of **2** isolated after column chromatography considering the amount of CO₂ used or CO produced as limiting reagent.

Table 3. Isolated yields for synthesis of labeled Moclobemide drug.

Ch. 1 CO_2 $\xrightarrow[\text{DMF:H}_2\text{O, 460nm, r.t.}]{\text{Ru PS, Re Cat, BIH}}$ CO

Ch. 2

Entry	Method	Isolated yield
1	$^{12}\text{CO}_2$ purging	91 % ^[a]
2	$^{13}\text{CO}_2$ Tritec®	30 % ^[b]

[a] Isolated yield of Moclobemide using the amount of CO produced as limiting reagent. [b] Isolated yield of ¹³C-labeled Moclobemide calculated using ¹³CO₂ as limiting reagent.

concentration in presence of a large excess of CO₂. However, when the optimized conditions for the two-chamber system were applied to a limited amount of ¹³CO₂ from Tritec® system, only around 30% conversion of the ¹³CO₂ was achieved (Table 2, entry 3). Control experiments from each separate chamber in the presence of controlled amounts of CO₂ or CO revealed that the reaction in chamber 1 was the limiting step in this tandem photocatalytic-catalytic process (see Table S3). Monitoring the course of the reaction in chamber 1 by ¹³C NMR (Figure S16), evidenced the formation of significant amounts of formate and bicarbonate. The detection of formate under these reaction conditions was unprecedented inasmuch as the **[Re cat]** is a well-known selective catalyst towards the production of CO. Since one of the major differences in our study resides in the use of water as a proton source for CO₂ reduction, it is very likely that water could affect the selectivity pattern. As such, formate can either stem from the activity of the **[Re cat]** in presence of water,^[24] and/or the activity of the degraded form of

the [Ru PS] (Figure S14–15). As previously reported, the Ru(bpy)₂(solvent)₂ complex, resulting from the loss of a bipyridine, has been shown to catalytically reduce CO₂ to formate.^[8,24,46,47] On the other hand, in the absence of water as proton source (DMF:TEOA), a large amount of bicarbonate is formed as a result of CO₂ acting as an oxygen atom acceptor ($2\text{CO}_2 + 2\text{e}^- + \text{H}^+ \rightarrow \text{CO} + \text{HCO}_3^-$).^[48] Ongoing efforts in our group aim to further optimize the two-chamber system. In the meantime, as a proof-of-concept, we expanded the scope of this multi-catalytic system to the preparation of the Moclobemide drug, a reversible inhibitor of monoamine oxidase A^[49] (Table 3).

In conclusion, we have shown, for the first time, the direct and easy valorization of CO produced from the visible light-driven catalytic reduction of CO₂ at the scale of molecular photocatalysis. Such a strategy can be considered as a stepping stone on the way towards artificial photosynthesis where the challenging task is to use water as an electron and proton donor to perform chemical transformations of CO₂. Further work is in progress in the development of efficient and selective photocatalysis of CO₂ and its use as a C1 unit in chemical transformations.

Experimental Section

All reagents including the [Ru PS] and COWare® were purchased from Sigma Aldrich. [Re cat]^[50] and sacrificial electron donors^[42,51,52] were prepared by literature method. The COWare® two-chamber system was prepared by filling Chamber 1 with the photocatalytic system and Chamber 2 with the Pd-catalyzed aminocarbonylation system. CO₂ was introduced either by purging the system for 15 minutes (at 1 atm) or by utilizing the Tritec® system to deliver accurate quantities of ¹³CO₂. Chamber 1 was exposed to blue LED light (emission peak at 463 nm with FWHM of 50 nm; 180 mW/cm²) to selectively excite the [Ru PS] and both chambers are stirred at room temperature for 21 hours. After the reaction, the system was opened, and the solution from Chamber 2 was filtered, solvent evaporated and the residual oil purified by column chromatography in silica gel (cyclohexane:AcOEt = 3:1) to give the appropriate amide compound. Optimizations of the photocatalytic system in Chamber 1 was done by quantifying the amount of CO in the headspace using Trace GC Ultra, Thermo Scientific gas chromatography equipped with a 30 m molecular sieve porous layer open tubular (PLOT) column having an internal diameter of 0.53 mm, helium carrier gas, and a thermal conductivity detector (TCD).

Acknowledgements

This work was supported by CEA IRTTELIS PhD fellowship program, LabEx CHARMMAT, and by the French Infrastructure for Integrated Structural Biology (FRISBI) ANR-10-INSB-05-01.

Keywords: artificial photosynthesis • photocatalysis • carbon dioxide • carbon monoxide • amino carbonylation • isotopic labeling

- [1] M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709–1742.
- [2] Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933.
- [3] M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley, **2010**.
- [4] A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, et al., *Chem. Rev.* **2013**, *113*, 6621–6658.
- [5] M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8510–8537.
- [6] S. C. Roy, O. K. Varghese, M. Paulose, C. A. Grimes, *ACS Nano* **2010**, *4*, 1259–1278.
- [7] J. Hawecker, J.-M. Lehn, R. Ziessel, *J. Chem. Soc. Chem. Commun.* **1983**, 536–538.
- [8] J. Hawecker, J.-M. Lehn, R. Ziessel, *Helv. Chim. Acta* **1986**, *69*, 1990–2012.
- [9] H. Hori, K. Koike, M. Ishizuka, K. Takeuchi, T. Ibusuki, O. Ishitani, *J. Organomet. Chem.* **1997**, *530*, 169–176.
- [10] H. Tsubaki, A. Sekine, Y. Ohashi, K. Koike, H. Takeda, O. Ishitani, *J. Am. Chem. Soc.* **2005**, *127*, 15544–15555.
- [11] H. Tsubaki, S. Tohyama, K. Koike, H. Saitoh, O. Ishitani, *Dalton Trans.* **2005**, *0*, 385–395.
- [12] P. Kurz, B. Probst, B. Spingler, R. Alberto, *Eur. J. Inorg. Chem.* **2006**, *2006*, 2966–2974.
- [13] H. Takeda, K. Koike, H. Inoue, O. Ishitani, *J. Am. Chem. Soc.* **2008**, *130*, 2023–2031.
- [14] J. M. Smieja, C. P. Kubiak, *Inorg. Chem.* **2010**, *49*, 9283–9289.
- [15] A. J. Huckaba, E. A. Sharpe, J. H. Delcamp, *Inorg. Chem.* **2016**, *55*, 682–690.
- [16] B. Gholamkhass, H. Mametsuka, K. Koike, T. Tanabe, M. Furue, O. Ishitani, *Inorg. Chem.* **2005**, *44*, 2326–2336.
- [17] S. Sato, K. Koike, H. Inoue, O. Ishitani, *Photochem. Photobiol. Sci.* **2007**, *6*, 454–461.
- [18] T. L. Easun, W. Z. Alsindi, M. Towrie, K. L. Ronayne, X.-Z. Sun, M. D. Ward, M. W. George, *Inorg. Chem.* **2008**, *47*, 5071–5078.
- [19] Z.-Y. Bian, K. Sumi, M. Furue, S. Sato, K. Koike, O. Ishitani, *Dalton Trans.* **2009**, 983–993.
- [20] K. Koike, S. Naito, S. Sato, Y. Tamaki, O. Ishitani, *J. Photochem. Photobiol. Chem.* **2009**, *207*, 109–114.
- [21] Z.-Y. Bian, S.-M. Chi, L. Li, W. Fu, *Dalton Trans.* **2010**, *39*, 7884.
- [22] Y. Tamaki, K. Watanabe, K. Koike, H. Inoue, T. Morimoto, O. Ishitani, *Faraday Discuss.* **2012**, *155*, 115–127.
- [23] S. Meister, R. O. Reithmeier, A. Ogródnik, B. Rieger, *ChemCatChem* **2015**, *7*, 3562–3569.
- [24] A. Nakada, K. Koike, T. Nakashima, T. Morimoto, O. Ishitani, *Inorg. Chem.* **2015**, *54*, 1800–1807.
- [25] Y. Yamazaki, H. Takeda, O. Ishitani, *J. Photochem. Photobiol. C Photochem. Rev.* **2015**, *25*, 106–137.
- [26] L. Frayne, N. Das, A. Paul, S. Amirjalayer, W. J. Buma, S. Woutersen, C. Long, J. G. Vos, M. T. Pryce, *ChemPhotoChem* **2018**, *2*, 323–331.
- [27] Y. Tamaki, K. Koike, T. Morimoto, O. Ishitani, *J. Catal.* **2013**, *304*, 22–28.
- [28] H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal.* **2017**, *7*, 70–88.
- [29] R. Yang, in *Gas Sep. Adsorpt. Process.*, Elsevier Ltd, Butterworth-Heinemann, **1987**, pp. 237–274.
- [30] W. F. Castle, *Int. J. Refrig.* **2002**, *25*, 158–172.
- [31] R. W. Baker, *Ind. Eng. Chem. Res.* **2002**, *41*, 1393–1411.
- [32] T. I. Doukov, L. C. Blasiak, J. Seravalli, S. W. Ragsdale, C. L. Drennan, *Biochemistry (Mosc.)* **2008**, *47*, 3474–3483.
- [33] P. Hermange, A. T. Lindhardt, R. H. Taaning, K. Bjerglund, D. Lupp, T. Skrydstrup, *J. Am. Chem. Soc.* **2011**, *133*, 6061–6071.
- [34] S. D. Friis, A. T. Lindhardt, T. Skrydstrup, *Acc. Chem. Res.* **2016**, *49*, 594–605.
- [35] C. Lescot, D. U. Nielsen, I. S. Makarov, A. T. Lindhardt, K. Daasbjerg, T. Skrydstrup, *J. Am. Chem. Soc.* **2014**, *136*, 6142–6147.
- [36] M. T. Jensen, M. H. Rønne, A. K. Ravn, R. W. Juhl, D. U. Nielsen, X.-M. Hu, S. U. Pedersen, K. Daasbjerg, T. Skrydstrup, *Nat. Commun.* **2017**, *8*, 489.
- [37] M. Majek, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2015**, *54*, 2270–2274.
- [38] T. Kawamoto, A. Sato, I. Ryu, *Chem. – Eur. J.* **2015**, *21*, 14764–14767.
- [39] H. Seo, M. H. Katcher, T. F. Jamison, *Nat. Chem.* **2017**, *9*, 453.
- [40] H. Seo, A. Liu, T. F. Jamison, *J. Am. Chem. Soc.* **2017**, *139*, 13969–13972.
- [41] J.-H. Ye, M. Miao, H. Huang, S.-S. Yan, Z.-B. Yin, W.-J. Zhou, D.-G. Yu, *Angew. Chem. Int. Ed.* **2017**, *56*, 15416–15420.
- [42] X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, J.-P. Cheng, *J. Am. Chem. Soc.* **2008**, *130*, 2501–2516.
- [43] D. Hong, Y. Tsukakoshi, H. Kotani, T. Ishizuka, T. Kojima, *J. Am. Chem. Soc.* **2017**, *139*, 6538–6541.
- [44] T. Morimoto, T. Nakajima, S. Sawa, R. Nakanishi, D. Imori, O. Ishitani, *J. Am. Chem. Soc.* **2013**, *135*, 16825–16828.
- [45] N. Penner, L. Xu, C. Prakash, *Chem. Res. Toxicol.* **2012**, *25*, 513–531.
- [46] J.-M. Lehn, R. Ziessel, *J. Organomet. Chem.* **1990**, *382*, 157–173.
- [47] J. Van Houten, R. J. Watts, *Inorg. Chem.* **1978**, *17*, 3381–3385.
- [48] Y. Tamaki, K. Koike, O. Ishitani, *Chem. Sci.* **2015**, *6*, 7213–7221.
- [49] I. Berlin, R. Zimmer, H. Thiede, C. Payan, T. Hergueta, L. Robin, A. Puech, *Br. J. Clin. Pharmacol.* **1990**, *30*, 805–816.
- [50] E. Portenkirchner, K. Oppelt, C. Ulbricht, D. A. M. Egbe, H. Neugebauer, G. Knör, N. S. Sariciftci, *J. Organomet. Chem.* **2012**, *716*, 19–25.
- [51] D. Mauzerall, F. H. Westheimer, *J. Am. Chem. Soc.* **1955**, *77*, 2261–2264.
- [52] E. Hasegawa, T. Seida, N. Chiba, T. Takahashi, H. Ikeda, *J. Org. Chem.* **2005**, *70*, 9632–9635.

Entry for the Table of Contents

Layout 1:

COMMUNICATION

A CO₂ valorization strategy based on its photocatalytic reduction to CO and the direct use of the latter in carbonylation chemistry has been established which opens far greater opportunities in merging the fields of artificial photosynthesis and transformative chemistry.

Philipp Gotico, Antonio Del Vecchio, Davide Audisio, Annamaria Quaranta, Zakaria Halime, * Winfried Leibl, and Ally Aukauloo*

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Visible Light-Driven Reduction of CO₂ to CO and Its Subsequent Valorization in Carbonylation Chemistry and ¹³C Isotope Labeling