

Diiridium Bimetallic Complexes Function as a Redox Switch To Directly Split Carbonate into Carbon Monoxide and Oxygen

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S Supporting Information

ABSTRACT: A pair of diiridium bimetallic complexes exhibit a special type of oxidation–reduction reaction that could directly split carbonate into carbon monoxide and molecular oxygen via a low-energy pathway needing no sacrificial reagent. One of the bimetallic complexes, $\text{Ir}^{\text{III}}(\mu\text{-Cl})_2\text{Ir}^{\text{III}}$, can catch carbonate group from carbonate and reduce it to CO. The second complex, the rare bimetallic complex $\text{Ir}^{\text{IV}}(\mu\text{-oxo})_2\text{Ir}^{\text{IV}}$, can react with chlorine to release O_2 by the oxidation of oxygen ions with synergistic oxidative effect of iridium ions and chlorine atoms. The activation energy needed for the key reaction is quite low (~ 20 kJ/mol), which is far less than the dissociation energy of the C=O bond in CO_2 (~ 750 kJ/mol). These diiridium bimetallic complexes could be applied as a redox switch to split carbonate or combined with well-known processes in the chemical industry to build up a catalytic system to directly split CO_2 into CO and O_2 .

Carbon dioxide, the end product of cellular respiration in organisms and the final matter produced by combustion of organisms or fossil fuels, could have the characteristics of a greenhouse gas due to its ability to absorb and emit infrared radiation at its two IR-active vibrational frequencies.¹ This effect causes CO_2 to warm the Earth's surface and lower atmosphere and cool the upper atmosphere, which has been deemed the main reason for the rise in average global temperature.² In the time before the industrial age, the concentration of CO_2 in Earth's atmosphere was regulated by photosynthetic organisms and other processes in the ecosystem. Since the beginning of the era of industrialization, human activities, such as the consumption of fossil fuels, deforestation, and industrial development, have caused the atmospheric concentration of CO_2 to increase by about 43%, which disrupted the balance of CO_2 in Earth's atmosphere and gave rise to some problems in our ecosystem. Furthermore, the increment of global temperature also brought about an increase of the concentration of CO_2 in the atmosphere—a bad effect! Many people are devoted to confronting these challenges, and many scientists have suggested ideas and techniques to address them. Most publications have focused on three concepts: reduction of CO_2 by (i) electrocatalysis,^{3–18} (ii) photocatalysis,^{19–22} or (iii) chemical reduction.^{23–26}

There are some good reports in the field of electrocatalytic reduction, but there still remain some challenges for these methods, such as how to improve the power efficiency for the reduction of CO_2 and how to develop inexpensive and nontoxic

electrodes for mass production. In photocatalytic reduction, the recombination of photogenerated electrons and holes occurs pretty fast, which results in a poor light-harvesting capacity and a low quantum efficiency. Moreover, the adsorption ability of CO_2 is low on catalyst surfaces, which leads to a low activity of the surface for the catalysts toward the activation of CO_2 . The advantage of using chemical reaction to reduce CO_2 is that it can be applied to mass production; however, to provide the energy needed to break the C=O bond in CO_2 , high-energy reactants such as hydrogen or unsaturated compounds must be used. Additionally, stoichiometric amounts of sacrificial materials must be supplied to the systems, which may lead to some environmental problems.

In the work reported in this Communication, we discovered an approach to directly split carbonate into carbon monoxide and molecular oxygen by adopting a pair of diiridium bimetallic complexes as a redox switch set to provide a low-energy pathway to trap carbonate and release CO and O_2 . Some simple but effective processes in the chemical industry could be combined with this method to build up a self-contained system. This system could be used to absorb CO_2 and produce CO and O_2 by using the sun's power or electric power; moreover, the factors that restrict the processes of electrocatalytic and photocatalytic reduction are not problems in the approach reported here.

The experimental details for the preparation and identification of the diiridium bimetallic complexes and the other compounds are described in the Supporting Information. The molecular structures are shown in Figure 1. When the chloro-bridged bimetallic complex $[(\text{dfpbo})_2\text{Ir}^{\text{III}}(\mu\text{-Cl})_2\text{Ir}^{\text{III}}(\text{dfpbo})_2]$ (1) ($\text{dfpbo} = 2\text{-(3,5-difluorophenyl)benzoxazolato-N,C}^2$)^{27,28} was treated with silver carbonate or potassium carbonate, a carbonate-bridged bimetallic complex, $[(\text{dfpbo})_2\text{Ir}^{\text{III}}]_2(\mu\text{-CO}_3)$ (2), was the expected product. However, since the structure of 2 is too unstable for it to be isolated, it directly releases a CO and forms a stable product, the oxo-bridged diiridium bimetallic complex $[(\text{dfpbo})_2\text{Ir}^{\text{IV}}(\mu\text{-O})_2\text{Ir}^{\text{IV}}(\text{dfpbo})_2]$ (3).

A single-crystal X-ray structure determination confirmed the bimetallic nature of complex 3 (Figure 2a). Complex 3 possesses a square planar structure connecting two iridium cores, with distorted octahedral coordination geometry around iridium. In the square planar coordination geometry, the $\text{O}(2)\text{-Ir-O}(2\text{A})$ angle is $76.0(2)^\circ$, deviating from 90° by 14° , which implies that there is an angle strain in this structure. The Ir–O bond length of the core structure for complex 3 is

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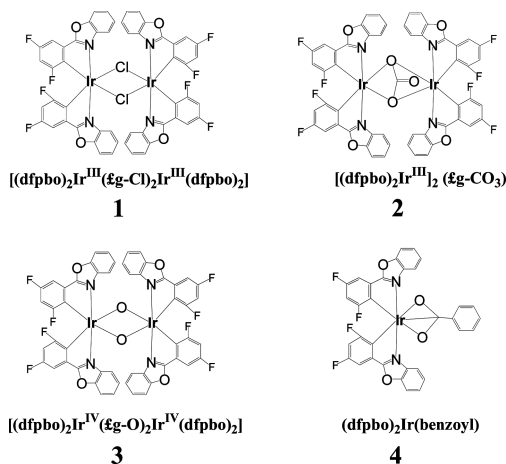


Figure 1. Molecular structures of iridium complexes 1–4.

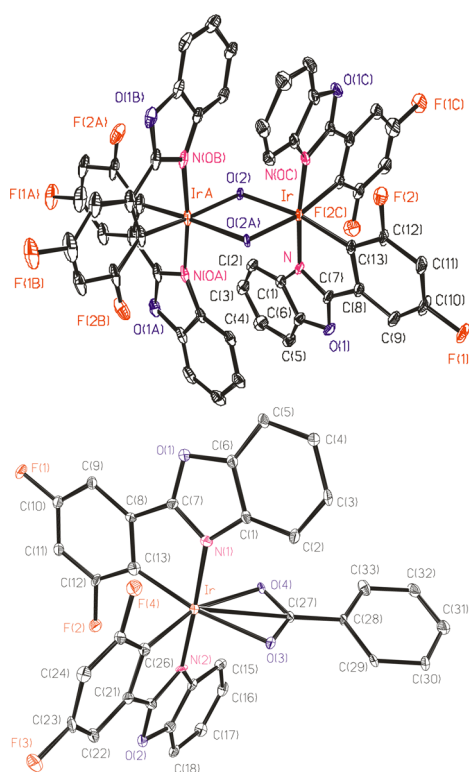


Figure 2. ORTEP diagrams of (a) $[(\text{dfpbo})_2\text{Ir}^{\text{III}}]_2(\mu\text{-CO}_3)$ and (b) $(\text{dfpbo})_2\text{Ir}(\text{benzoyl})$, with thermal ellipsoids drawn at the 20% probability level. The hydrogen atoms have been omitted for clarity.

2.163(3) Å, which is longer than that typical of singly oxo-bridged iridium bimetallic complexes.²⁹

Counting the number of valence electrons at the iridium atoms of complexes 1–3, considering the 18-electron rule for organometallic complexes,³⁰ we realized that the oxidation state of the iridium atoms in complex 3 is 4+, whereas that for complexes 1 and 2 is 3+. Furthermore, when complex 2 was transformed into 3, the carbon atom of $\mu\text{-CO}_3$ in complex 2 was reduced from 4+ to 2+ to become the carbon atom of CO, which implies that, in this reaction, the iridium atoms lost electrons and the carbon atom of $\mu\text{-CO}_3$ gained electrons.

By comparing the normalized X-ray absorption near edge structure (XANES) spectrum at the Ir L₃ edge of complex 1 (Figure 3a) with that of complex 3 (Figure 3b), we can see that

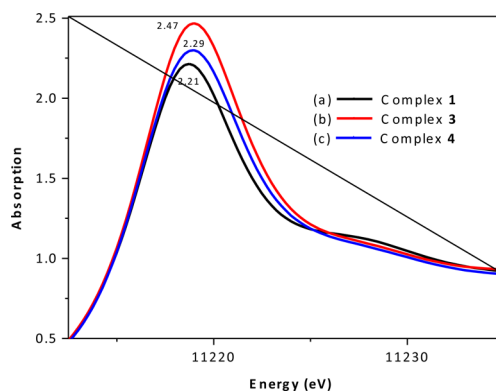


Figure 3. Ir L₃ edge XANES of crystalline (a) $[(\text{dfpbo})_2\text{Ir}^{\text{IV}}(\mu\text{-Cl})_2\text{Ir}^{\text{IV}}(\text{dfpbo})_2]$ (1), (b) $[(\text{dfpbo})_2\text{Ir}^{\text{IV}}(\mu\text{-O})_2\text{Ir}^{\text{IV}}(\text{dfpbo})_2]$ (3), and (c) $[(\text{dfpbo})_2\text{Ir}(\text{benzoyl})]$ (4). A Si (111) double-crystal monochromator was employed for energy scanning. Fluorescence data were obtained at room temperature using an Ar-filled ionization chamber detector; each sample was scanned three times for averaging.

the iridium atoms of complex 3 have a higher positive charge than those of complex 1,³¹ which reveals that the iridium atoms were oxidized when complex 1 reacted with carbonate. It is an unusual phenomenon for the carbonate group act as an oxidizer at a low reaction temperature (~ 25 °C). It is also worth noting that, when complex 1 was transformed into complex 3, the central metal was subject to a reaction like an oxidation addition, but the bond number of the iridium did not change, which indicates a special oxidation reaction with a long-distance electron transfer from the iridium atom to the β -atom, i.e., the carbon atom of $\mu\text{-CO}_3$.

By counting the d^n configuration of complex 3, we can deduce that complex 3 has a 17e configuration, which, in general, is reactive and tends to react with several kinds of reagents to form stable structures with an 18e configuration. For example, complex 3 is apt to react with aldehydes and halogen. When benzaldehyde was added to the solution of complex 3 in *o*-dichlorobenzene, the color of complex 3 immediately disappeared. In this reaction, the benzaldehyde caught an oxygen atom from complex 3; the benzaldehyde was oxidized to become a benzoyl, and the benzoyl bonded directly to iridium to form the complex $[(\text{dfpbo})_2\text{Ir}(\text{benzoyl})]$ (4) (Figure 1). By comparing the normalized XANES spectra at the Ir L₃ edge of complexes 3 (Figure 3b) and 4 (Figure 3c), we can see that the iridium atoms of complex 4 have a lower positive charge than those of complex 3, which shows that iridium atoms were reduced when complex 3 reacted with benzaldehyde.

When chlorine gas was introduced into the solution of complex 3 in *o*-dichlorobenzene, the color of complex 3 again immediately disappeared. The product of this reaction has been identified by NMR (Figure S1, lower), IR (Figure S2, lower), and MS spectra (Figure S3, lower), which are identical to those of the initial material, complex 1 (Figures S1–S3, upper). Therefore, we know that when complex 3 reacted with chlorine, the initial material, $[(\text{dfpbo})_2\text{Ir}^{\text{IV}}(\mu\text{-Cl})_2\text{Ir}^{\text{IV}}(\text{dfpbo})_2]$, was formed, and the bridged oxygen was excluded from complex 3. Furthermore, we can also see that both of the iridium atoms of complex 3 and the chlorine atoms were reduced and the oxygen ions of $\mu\text{-O}$ were oxidized, which implies that when the iridium atoms got electrons from oxygen ions, chlorine atoms were also acquiring electrons from oxygen

ions; that is, there is a synergistic oxidative effect of iridium ions and chlorine atoms on the oxidation of oxygen ions.

Since the above-discovered diiridium bimetallic complexes exhibited remarkable characteristics, we built a catalytic system as shown in Figure 4 to treat CO₂ to give CO and O₂. The

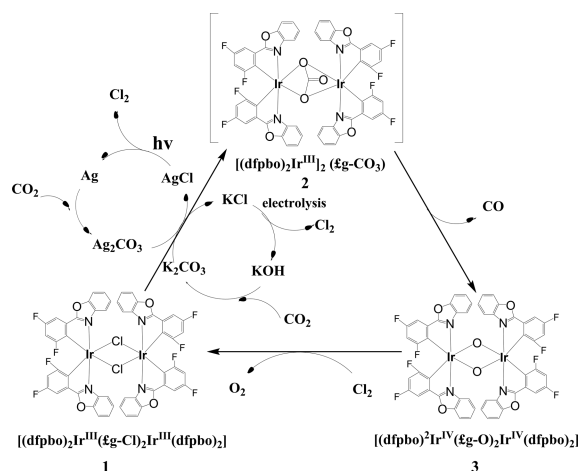


Figure 4. Catalytic system for splitting carbon dioxide into carbon monoxide and oxygen.

system has at its core a cycle involving the above-mentioned reactions of diiridium bimetallic complexes, which functions as a redox switch to catch a carbonate group from a carbonate and release CO and O₂. Two materials, carbonate and chlorine, must be supplied for the core cycle; therefore, two sub-cycles were added to the system. One is called the CO₂ cycle, where the CO₂ is absorbed by hydroxide to form a carbonate. The chloride formed in the CO₂ cycle can be transformed into hydroxide and chlorine. The hydroxide is used to absorb CO₂, and the chlorine is applied to the second sub-cycle, the chlorine cycle. In the chlorine cycle, the chlorine is reacted with complex 3 to form 1 and release O₂; the chlorine atoms become components of iridium complex. When complex 1 reacts with a carbonate group, the chlorine atoms are released out of the core cycle. The two sub-cycles can be pushed forward by some well-known techniques in chemical industry with high efficiency, for example, the photolysis or electrolysis of chloride; therefore, we will focus on the core cycle.

To investigate the energy needed for the catalytic system, we performed computational studies on the materials used for the system. The calculation results, including electronic and zero-point energies, thermal energies, enthalpies, and free energies for all the materials, are summarized in Table S3. The thermal properties (ΔE , ΔH , ΔG , and ΔS) for the reaction of complex 1 with silver carbonate or potassium carbonate are summarized in Table S4. Other calculation data are also summarized in the Supporting Information (Tables S5, S8–S13). According to these data, we can see that the standard free energy of complex 3 ($\Delta G_f^\circ = -115.6$ kcal/mol) is higher than that of complex 1 ($\Delta G_f^\circ = -118.7$ kcal/mol) by ~ 3 kcal/mol, which implies that a free energy higher than 3 kcal/mol should be supplied for the transformation of complex 1 into complex 3.

In detail, we can see that when complex 1 reacted with silver carbonate ($\Delta G_f^\circ = -43.5$ kcal/mol), 2 mol of silver chloride ($\Delta G_f^\circ = -30.5$ kcal/mol), 1 mol of carbon monoxide ($\Delta G_f^\circ = -24.1$ kcal/mol), and 1 mol of complex 3 were formed. Therefore, the standard free energy change for the reaction of

complex 1 with silver carbonate is -38.5 kcal/mol, which shows that the free energy released from the reaction of complex 1 with silver carbonate can provide the energy needed for the transformation of complex 1 into complex 3, and the reaction is exergonic and spontaneous at room temperature. When reactant potassium carbonate ($\Delta G_f^\circ = -41.5$ kcal/mol) was used instead of silver carbonate, the standard free energy change for the reaction was -38.3 kcal/mol. If calcium carbonate ($\Delta G_f^\circ = -36.3$ kcal/mol) was used instead of potassium carbonate, the standard free energy change for the reaction was -18.7 kcal/mol. That is, no matter what kind of carbonate is used, the transformation of complex 1 into complex 3 is an exergonic and spontaneous reaction at room temperature.

To find the minimum energy needed for disrupting the carbonate group, we investigated the characteristic kinetics of the reaction of complex 1 with carbonate. When complex 1 reacted with silver carbonate in an inert solvent, complex 3 was the only product in solution; complex 3 is very stable and has typical absorption peaks at 415, 437, and 486 nm, distinct from those of complex 1. Therefore, UV–visible spectrometry was used to monitor the progress of the reaction. The experimental details are described in the Supporting Information, and the experimental data are also summarized therein (Figures S6–S9 and Tables S6 and S7). According to those data, we can see that the activation energy for the reaction of complex 1 with a carbonate group is 20.11 kJ/mol (4.81 kcal/mol), which is much lower than the free energy released from the reaction ($\Delta G = -38.5$ kcal/mol). In other words, only an initial energy should be supplied to the reaction, and then it will go forward automatically.

We know that the dissociation energy of the C=O bond in CO₂ is quite high (~ 750 kJ/mol); this is a robust chemical bond that is hard to cleave. In general, a high processing temperature is needed to release a carbonyl group from CO₂ or a carbonate group. In most cases, high-energy reactants such as hydrogen or unsaturated compounds should be used to supply chemical energy, and stoichiometric amounts of sacrificial materials should be supplied to the systems. It is a marvel that, by using diiridium bimetallic complexes as a redox switch, the activation energy needed is quite low, the reaction is exergonic, and no sacrificial material is needed. The activation energy needed is so low that the reaction can take place at room temperature (Supporting Information).

An apparatus was set up to evaluate the performance of this redox switch for splitting carbonate (Supporting Information), where complex 1 reacted with silver carbonate or potassium carbonate, and the CO evolved was collected and identified by the reaction of the gas collected with cuprous chloride solution or with Tollens's reagent. The progress for the reaction of complex 1 with silver carbonate is shown in Figure 5a, and that for complex 1 with potassium carbonate in Figure 5b. According to the reaction progresses, we can see that no matter what kind of carbonate was used, 99% of carbonate could be split to CO in a 60 min reaction time. That is a quite good outcome.

In summary, a simple but important reaction system has been discovered, in which a pair of diiridium bimetallic complexes can act as a redox switch to split carbonate into carbon monoxide and oxygen by a pathway with a low energy barrier. The activation energy needed for the reaction system is quite low, and the performance of the redox switch is quite good. The reaction system is quite stable in inert solvents, in

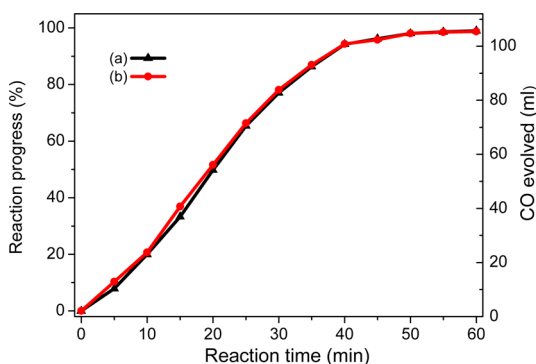


Figure 5. Reaction progress (a) for the reaction of complex **1** with silver carbonate (black symbols and line) and (b) for the reaction of complex **1** with potassium carbonate (red symbols and line), where the reaction progress in percentage was calculated on the basis of the ratio of the volume of carbon monoxide collected to the maximum volume (theoretically).

which no degradation has been observed. This redox switch could be combined with traditional technology to build up a self-contained system for absorbing carbon dioxide and releasing carbon monoxide and oxygen, which could be a promising strategy for the development of sustainable energy and treatment of the troublesome problems resulting from the greenhouse effect on the Earth.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.6b00715](https://doi.org/10.1021/jacs.6b00715).

Synthesis, characterization data, calculation details, and crystal refinements (PDF)

Crystallographic data for **3** (CIF)

Crystallographic data for **4** (CIF)

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Notes

The authors declare no competing financial interest.

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