Carbon Dioxide Utilization by the Five-Membered Ring Products of Cyclometalation Reactions

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Abstract:

In carbon dioxide utilization by cyclometalated five-membered ring products, the following compounds are used in four types of applications:

1. 2-Phenylpyrazole iridium compounds, pincer phosphine iridium compounds and 2-phenylimidazoline iridium compounds are used as catalysts for both formic acid production from CO₂ and H₂, and hydrogen production from the formic acid. This formic acid can be a useful agent for H₂ production and storage for fuel cell electric vehicles.
2. Other chemicals, *e.g.*, dimethyl carbonate, methane, methanol and CO, are produced with dimethylaminomethylphenyltin compounds, pincer phosphine iridium compounds, pincer phosphine nickel compound and ruthenium carbene compound or 2-phenylpyridine iridium compounds, and phenylbenzothiazole iridium compounds as the catalysts for the reactions with CO₂.
3. The five-membered ring intermediates of cyclometalation reactions with the conventional substrates react with carbon dioxide to afford their many types of carboxylic acid derivatives.
4. Carbon dioxide is easily immobilized at room temperature with immobilizing agents such as pincer phosphine nickel compounds, pincer phosphine palladium compounds, pincer *N,N*-dimethylaminomethyltin compounds and tris(2-pyridylthio)methane zinc compounds.

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1. INTRODUCTION

The world population in 1000 AD was 300 million, and the concentration of carbon dioxide in the atmosphere on the surface of the earth was approximately 270 ppm in equilibrium with sea water and the ground surface through absorption and desorption. Since that time, the concentration of carbon dioxide has increased due to the burning of fossil fuels such as coal and petroleum [1-4]. Recently, the concentration has increased rapidly, as shown in Table 1 [3-8].

In 2014, the world population and the concentration of carbon dioxide compared with those in 1000 AD are 7 billion (23 times) and 400 ppm (1.5 times), respectively [8].

In 1997, the Kyoto Protocol in Japan provided targets for the reduction of CO₂ production for only advanced countries such as Japan -6 %, the United States -7 % and the EU -8 % for 2008 – 2012, based on the concentration of carbon dioxide in 1990. However, recently, because the growth of population in developing countries continues to steadily increase, the amount of carbon dioxide in atmosphere is steadily rising, as shown in Table 1. Both advanced countries and developing countries have to pursue a drastic reduction in the exhaust of carbon dioxide to moderate recent frequent abnormal climate change. The utilization of atomic energy and natural energies is considered as the best countermeasure for this purpose. However, in the current circumstances, abnormal climate changes occur frequently because of global warming, and in the Marshall Islands and the Southern India Islands, the ring roads in their islands have already been partly submerged by the rising

sea level. On these islands, inhabitants are now being reviewed for migration to other islands. For the sake of these peoples, we should deal seriously with issues caused by global warming [9].

Unfortunately, in March 11, 2011, the Fukushima earthquake and tsunami forced the decommissioning of four nuclear power plants and the suspension of operation of almost all of the other 50 plants in Japan in the middle of 2012 because of safety issues in the nuclear power plants and anti-nuclear demonstrations around the world.

Therefore, we have to depend more on thermal power generation through coal burning, which emits the most carbon dioxide exhaust of all methods of electric power productions. The production of carbon dioxide is expected to increase in the future. Therefore, we increasingly rely on natural energy sources such as water-power, wind-power, solar power, tidal power and geothermal power. As to other countermeasure, these include CCS (carbon dioxide capture and storage) and carbon dioxide utilization [1-4].

In the previous review [4], four types of compounds are cited as reactive chemical compounds towards stable carbon dioxide: 1. oxygen-containing compounds such as epoxide and alcohols; 2. nitrogen-containing compounds such as ammonia, amides and aziridines; 3. carbon-carbon unsaturated compounds such as alkynes, alkenes, dienes; and 4. others, such as hydrogen.

The products of the reaction of the above compounds with carbon dioxide are carbonates, urea, carbamic acid esters, polyurethanes, oxazolidinones, carbamic acids, carboxylic acid lactones, formic acid and methanol. In particular, 157 million tons of urea was produced from carbon dioxide in 2010.

This review reports on carbon dioxide utilization using the five-membered products of cyclometalation reactions. There are four types of utilizations with these products, as follows:

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Table 1. Variations in carbon dioxide concentration over approximately 1,000 years [3-8].

Year	Period	Concentration	Increase	Increase Rate
	(year)	(ppm)	(ppm)	(ppm/year)
1000-1800	800	270-280	10	0.01
1800-1950	150	280-310	30	0.2
1958-1975	17	315-330	15	0.9
1975-2002	27	330-370	40	1.5 (8 billion tons ^a)
2002-2014	12	370-400 ^b	30	2.5(13 billion tons ^a)

a. The increased amount in the atmosphere.

b. An estimated amount for 2010-2014 based on the trends in atmospheric carbon dioxide at Maura Loa in Hawaii.

1. The simple derivative of carbon dioxide with hydrogen is formic acid. This product may be useful for both of the production and storage of hydrogen for fuel cell electric vehicles.

2. Other chemicals, *e.g.*, dimethyl carbonate, methane, methanol and carbon monoxide are produced by the reaction of carbon dioxide in the presence of cyclometalated five-membered ring compounds.

3. As the metal atoms of the five-membered ring intermediates in some cyclometalation reactions are very reactive sites, the metal atoms easily react with carbon dioxide to afford their carboxylic acid derivatives.

4. Carbon dioxide immobilizing agents, *e.g.*, pincer phosphine nickel compounds and pincer *N,N*-dimethylaminomethyl tin compounds are easily used at room temperature.

2. HYDROGEN PRODUCTION AND STORAGE WITH FORMIC ACID USING CYCLOMETALATED FIVE-MEMBERED RING PRODUCTS

Recently, one of the countermeasures considered for use against global warming gas emission is the use of hydrogen gas for fuel cell electric vehicles. The ultrahigh pressure container in Honda vehicles is light weighted, but, has a big shape, then, energy density per unit capacity per unit density is low. On the other hand, the volume of hydrogen absorbent with a metal substrate in a hydrogen rotary engine vehicle produced by Matsuda is compact, but, the metal adsorbent is heavy.

Recently, formic acid has been considered to be very useful both for production and storage of hydrogen for fuel cell electric vehicles.

In 2013, Fukuzumi and Suenobu [10] reported that the hydrogenation of carbon dioxide with hydrogen is catalyzed by 1-phenylpyrasole iridium compound ((Ir-OH)₂SO₄, (**2.1** (Ir -OH₂))) under atmospheric pressure of H₂ and CO₂ in weakly basic water (pH 7.5) at room temperature as shown in Eq. (2.1). The turnover number (TON) increases linearly with time to exceed 100, which is

significantly larger than the maximum TON for the catalytic formation of formates in the case of a similar bipyridine chelate type iridium compound (**64**).

The reverse reaction, *i.e.*, hydrogen evolution from formates, is also catalyzed by the iridium compound [Ir -OH₂]⁺ in acidic water (pH 2.8) at room temperature as shown in Eq. (2.2). The TOF value of 1880 h⁻¹ is obtained at pH 2.8 at 298 K. The catalytic systems reported in this perspective for H₂ storage and evolution are expected to supply pristine H₂ free from the by-product CO, which is a poison for the electrode catalyst of fuel cells [10].

Pincer phosphine iridium compounds **2.2** and **2.3** rapidly insert CO₂ into an Ir-H bond to yield formate monohydrides (**2.4** and **2.5**) in THF as shown in Eq. (2.3).

In acetonitrile/H₂O mixtures, these compounds become efficient selective catalysts for the electrocatalytic reduction of CO₂ to formate. Controlled-potential electrolysis at -1.45 V in 5 % H₂O/MeCN for 25 h yielded formic acid as a predominant product upon acidic workup, with a turnover of ca. 40 and a Faradaic effi-

	Cat. 2.10	Cat. 2.11
Initial TOF h ⁻¹	1090	1960
Vol H ₂	49 ml (2 h)	120 ml (2 h)
TON	200 (2 h)	490 (2 h)

ciency of 85 %. H₂ was found as a side product (15%). It was formed *via* a nonspecific background reduction of water at an electrode. The catalysts are selective for the reduction of CO₂ to formates. No CO is formed and the small amount of hydrogen that is formed comes from the background reaction of water [11].

Cyclometalated 2-phenylimidazoline iridium compounds are also very useful catalyst for producing hydrogen from formic acid. For example, 2-phenylimidazoline iridium compounds **2.10**, **2.11** are found to be excellent catalysts for the decomposition of azeotropic HCOOH-NEt₃ mixtures to give H₂ and CO₂ under mild conditions with high turnover frequencies (up to 147000 h⁻¹ at 40 °C) and essentially no CO formation as shown in Eq. (2.5) [12].

The proposed catalytic cycle for the dehydrogenation of HCOOH is shown in Scheme 1.

3. CHEMICALS OTHER THAN FORMIC ACID DERIVED FROM CARBON DIOXIDE WITH CYCLOMETALATED FIVE-MEMBERED RING PRODUCTS

Apart from formic acid, the other chemicals that can be produced from CO₂ using cyclometalated five-membered ring products the catalysts, as in the second chapter, are carbonates, methane, methanol, and carbon monoxide.

The synthesis of dimethylcarbonate (DMC) by the reaction of carbon dioxide with methanol generally has a low yield because many catalysts are deactivated by the formation of water. However, Sakakura, Choi and Sako [13, 14] reported an excellent process which uses an acetal and a 3 Å molecular sieve as dehydrating agents in the presence of a Bu₂Sn(OMe)₂ catalyst, as described in the previous review [3c,3d].

Using cyclometalated organotin five-membered products, in 2011, Růžička, Švec, Padělková, Weidlich, Dušek and Plasseraud. [15] reported on the synthesis of the DMC with carbon dioxide and methanol in the presence of organotin cyclometalated *N,N*-dimethylbenzylamine compounds **3.1** and **3.2**. The reaction of **3.1** (0.884 g, 0.91 mmol) with 20 ml of methanol at 200 bar of CO₂ and 150 °C for 20 h led to the formation of only 0.3 mmol of DMC. The catalyst was not recycled due to its poor catalytic activity and no additional runs were carried out. When the same reaction was catalyzed by **3.2** (0.922 g, 1.05 mmol) under the same conditions, somewhat higher yield of DMS was obtained.

However, in 2012, a reaction with similar organotin cyclometalated *N,N*-dimethylbenzylamine trifluoromethanesulfonates **3.3** showed a promising yield of dimethyl carbonate under the same pressure of 200 bar at 150 °C, as shown in Eq. (3.2) [16].

Scheme 1. Proposed catalytic cycle for the dehydrogenation of HCOOH.

The third catalytic utilization of cyclometalated five-membered ring products, such as pincer iridium compound **3.4**, is their use as a catalyst for the conversion of carbon dioxide to methane with trialkylsilanes, as shown in Eq. (3.3) [17]. The use of less bulky silanes such as Me₂EtSiH or Me₂PhSiH, results in the rapid formation of CH₄ and siloxane with no detection of bis(silyl)acetal and methyl silyl ether intermediates. The catalyst system is long-lived, and

8300 turnover can be achieved using Me₂PhSiH with a 0.0077 mol % loading of iridium [17].

The pincer nickel phosphinite **3.5**, similar to the above iridium catalyst **3.4**, caused the catalytic hydroboration of carbon dioxide with the highest TOF (495 h⁻¹ based on B-H) reported to date for the reduction of carbon dioxide to the methoxide level as shown in Eq. (3.4) [18, 19].

In CO₂ saturated solution, using 1 mM of compound **3.6** in 0.1 M ⁿBu₄NPF₆/CH₃CN, controlled potential electrolysis at potentials from -1.125 to -1.55 V at a glassy carbon electrode (0.071 cm²), gave carbon monoxide as the only gaseous product above background as shown in Eq. (3.5). The coulombic efficiency of the formation of ~7 μM of CO (1.8 C, ~5 turnover/catalyst) over a 5 h electrolysis period at -1.52 V was ~85 % for **3.6** at -1.46 V [20].

A mononuclear Ir compound photocatalyst ([Ir(tpy)(R-ppy)Cl]) **3.7** was developed for efficient and selective CO₂ reduction, driven by visible light in a homogeneous solution, even in solutions containing H₂O as shown in Eq. (3.6). The most efficient photocatalyst was [Ir-Me-ppy], which had the best turn over number (up to 50) and a quantum yield (Φ_{CO}) of [Ir-Me-ppy] of 0.21, which is the best reported quantum yield in homogeneous photocatalytic systems using low-energy visible light at wavelength such as 480 nm [21].

Bis(2-(4-trifluoromethyl)phenylbenzothiazole)-2,2'-bipyridine-4,4'-dicarboxylate **3.8** is a photosensitizer (PS), which displays distinct visible-light photo catalytic properties for the generation of hydrogen from water and selective CO₂ conversion [22a]. The photoinduced reaction activities of compound (PS) **3.8** were initially evaluated by a typical three-component, hydrogen-evolving system

that contained PS **3.8** and a colloidal Pt catalyst (K₂PtCl₄) together with triethanolamine (TEOA) as a sacrificial electron donor in water at a neutral pH. Hydrogen production increased stepwise with time during the first few hours and then gradually reached a maximum over the next few hours. It is clear that the hydrogen production increased with increasing concentration of PS **3.8**. Hydrogen is indeed produced efficiently and the turnover numbers of approximately 1600 mol hydrogen per mole PS **3.8** can be achieved at a concentration of 1 mM of PS **3.8** (216 mM of H₂ produced). When the concentration of PS **3.8** was increased to 50 mM, a total of 3420 mM of hydrogen was produced representing a TON of 507 for the catalytic system.

On the other hand, visible-light-assisted CO₂ reduction in the presence of water was established in a gas-solid system over a solid sample of PS **3.8** (radiation λ > 420 nm). CO₂ was effectively and selectively reduced to CO by PS **3.8**, as suggested by the electrochemical properties, and the amount of CO increased stepwise with increasing time up to 84 ppm, without reaching saturation after 6 h of irradiation [22a].

However, the higher photocatalytic activity could be associated with the photoexcited state of PS **3.8** absorbed on TiO₂(P-25),

which promotes rapid electron injection into the conduction band of the Pt-loaded TiO₂. Subsequently, electrons are transferred to the reduction site (Pt) over the titania to initiate water reduction. A limited number of metal compounds showed a photocatalytic activity for CO₂ reduction to CO, whereas the creation of molecular systems that produce CH₄ from CO₂ is seldom observed in solar-energy conversion. It is proposed that TiO₂ plays an important role by increasing the probability of a multi-electron reaction through carrier-bound intermediates for the formation of CH₄. More inter-

estingly, the photocatalytic reaction with PS **3.8** sensitized by TiO₂ could be significantly improved by the loading of Pt (ca. 3 wt %) as a catalytic active gate; this yielded 3.6 ppm CO and 70.5 ppm CH₄ with a ratio of approximately 1 : 20, implying that the product selectivity shifts from CO to CH₄ as shown in Eq. (3.7) [22a].

Further, in 2012, they reported on derivatives of electron-withdrawing CF₃ and of electron-donating NMe₂. The electron-withdrawing CF₃ 5-derivative **3.9** exhibits a maximum hydrogen production with the total TON of 1501 from an aqueous solution at pH 7.0 (λ > 420 nm). The photo induced hydrogen evolution is approximately 2000 μM at 20 h with *in situ* generated colloidal Pt (0.02 mM) [22b].

4. PRODUCTION OF CARBOXYLIC ACID ESTERS FROM CARBON DIOXIDE WITH CYCLOMETALATED FIVE-MEMBERED RING INTERMEDIATES

Carbon dioxide is easily inserted into a bond between a metal and an aryl or alkyl carbon atom in an organic metal compounds. For example, in the reaction of lithiophenyl isocyanide with carbon dioxide, the carbon dioxide molecule is inserted in between the lithium and phenyl carbon atom, followed by cyclization together with the isocyano group, finally yielding isatoic anhydride, as shown in Eq. (4.1) [23].

The other reaction involving the insertion of carbon dioxide into a Ni-C bond is the carboxylation of enyne compounds in the presence of atmospheric carbon dioxide, in which the cyclization proceeds in the presence of a nickel catalyst and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The hydrolysis of the resulting mixture is followed by a treatment with diazomethane to give a carboxylate cyclization product, as shown in Eq. (4.2) [24].

Cyclometalation reactions with conventional substrates mostly proceed easily and form very stable five-membered ring products

because the five-membered products are the most stable compounds compared to other ring products such as four- and six-membered rings. However, some cyclometalation reactions form highly labile five-membered ring products. The metal atoms in these products create active centers in the molecules.

For example, the cyclometalation of 2-phenylpyridine in the presence of a rhodium compound easily proceeds to give the five-membered ring rhodium intermediate. The carbon dioxide can be inserted into the rhodium-phenyl carbon bond, and a methyl ester is formed with TMSCH₂N₂ from a rhodium carboxylate as shown in Eq. (4.3) [25].

The similar carboxylic acid esters may be synthesized by the reactions of an active metal atom by donated the heteroatoms such as N, P and S in the cyclometalated five-membered ring products with conventional substrates and carbon dioxide, as shown in Table 2.

These compounds may also be useful for the intermediates of pharmaceuticals and the other fine chemicals such as agrochemicals and additives.

Table 2. Representative carboxylic acids derivatives from cyclometalation reaction five-membered ring intermediates with carbon dioxide.

R, R¹, R², R³ = aryl, heteroaryl groups

5. CARBON DIOXIDE IMMOBILIZATION USING CYCLOMETALATED FIVE-MEMBERED PRODUCTS

Carbon dioxide can be immobilized by pouring it into a solution of cyclometalation reaction five-membered ring products at room temperature, or while heating the solution, and the immobilized solution is able to desorb the carbon dioxide.

Pincer PCP nickel compounds **5.1** and **5.2** also easily react with carbon dioxide at room temperature to form the carboxylate product **5.3** and **5.4** for 10 min in quantitative yields as shown in Eq. (5.1) [26].

The pincer PCP crotyl palladium compound **5.5** also reacts with carbon dioxide at room temperature with full conversion within a few minutes to afford the carboxylate **5.6** as shown in Eq. (5.2) [27].

Another application for cyclometalation reaction five-membered ring products is their utilization as compounds for carbon dioxide fixation. For example, pincer *N,N*-dimethylbenzylamine type tin compounds **5.7** and **5.8** readily absorb carbon dioxide at room temperature to yield organotin carbonates **5.9** and **5.10** as shown in Eq. (5.3) [28]. Easy desorption and reversible carbon dioxide fixation were achieved.

This desorption process was achieved at rather low temperatures, followed by the successful reabsorption of CO₂. For example, the heating of 200 mg of organotin oxides **5.7**, **5.8** at 150 °C for 2 h under argon atmosphere resulted in the released of CO₂ and the residual material was identified by the ¹H and ¹¹⁹Sn NMR spectroscopy as the starting organotin oxides **5.7**, **5.8**, respectively.

Tris(2-pyridylthio)methane zinc cyclometalation product reacts rapidly with carbon dioxide to give the carboxylate product as shown in Eq. (5.4) [29, 30].

The zinc hydride tris(2-pyridylthio)methane is an effective catalyst for the rapid generation of hydrogen demand and for the functionalization of CO₂, thereby producing a useful formylating agent.

These results provide further evidence that, in suitable ligand environments, inexpensive and abundant non-transition metals can perform reactions that are typically catalyzed by compounds that contain precious metals.

6. CONCLUDING REMARKS

1. As the number of fuel cell electric environmentally friendly cars has begun to increase, H₂ storage and production with formic acid system by the catalysts of cyclometalated five-membered products will be expected to reduce CO₂ increase rate by replacing a large amount of conventional gasoline engines in the near future.

2. Other chemicals produced by the catalysts of cyclometalated five-membered products, are dimethyl carbonate, methane, methanol and CO. In particular, 2-phenylbenzothiazole photosensitizer **3.8** is expected to become a good production system of fuel gas.

3. Cyclometalated five-membered ring intermediates with conventional substrates may react with carbon dioxide to afford their many types of carboxylic acid derivatives. These products may be useful intermediates for pharmaceuticals and other fine chemicals such as agrochemicals and additives.

4. Cyclometalated five-membered ring products are easily used as immobilizing agents for carbon dioxide under mild reaction conditions. This immobilization technology is very useful for both CO₂ storage and usage under mild conditions.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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