氏 名　　　　　　　　　中　島　　　洋

学位（専攻分野）　　　博士（理学）

学 位 記 番 号　　　総研大甲第１８６号

学位授与の日付　　　平成 8 年 3 月２１日

学位授与の要件　　　数物科学研究科　構造分子科学専攻

　　　　　　　　　　　学位規則第４条第１項該当

学 位 論 文 題 目　　Investigation on Molecular Catalysts for

　　　　　　　　　　　　　Activation and Effective Fixation of CO_2

論 文 審 査 委 員　　主　査　　教　授　　花　崎　一　郎

　　　　　　　　　　　　　　　　教　授　　田　中　晃　二

　　　　　　　　　　　　　　　　教　授　　渡　辺　芳　人

　　　　　　　　　　　　　　　　助教授　　鎌　田　雅　夫
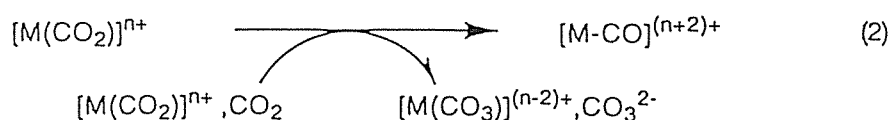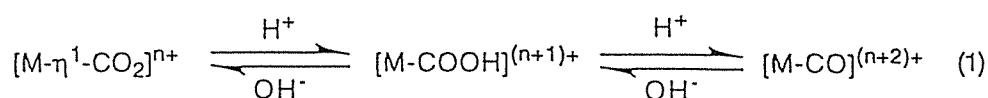
　　　　　　　　　　　　　　　　助教授　　青　野　重　利

　　　　　　　　　　　　　　　　　　　　（北陸先端科学技術大学院大学）

Utilization of CO_2 is the subject of continuing importance in the view of predictable energy shortage in near future and the increase of a green house effect. Photo- and electro-chemical CO_2 fixation catalyzed by metal complexes has a significant advantage for elucidation of the reaction mechanism because of facile physical measurements for tracing reaction intermediates. The design of the molecular catalysts based on the knowledge concening the reaction intermediates would largely contribute for improving the efficient utilization of CO_2. Recent progress in the reduction of CO_2 using metal complexes as catalyst precursors has disclosed for the formation of CO and/or $HCOO^-$ in some detail. It is generally accepted that metal-carbonyl complexes ($[M-CO]^{(n+2)+}$) formed through an acid – base equilibrium with $[M-COOH]^{(n+1)+}$ and $[M-\eta^1-CO^2]^{n+}$ in protic media play the role in CO evolution (eq 1). While the reductive disproportionation between $[M(CO_2)]^{n+}$

$$[M-\eta^1-CO_2]^{n+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [M-COOH]^{(n+1)+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [M-CO]^{(n+2)+} \quad (1)$$

$$[M(CO_2)]^{n+} \longrightarrow [M-CO]^{(n+2)+} \quad (2)$$
$$[M(CO_2)]^{n+}, CO_2 \qquad [M(CO_3)]^{(n-2)+}, CO_3^{2-}$$

and CO_2 or another $[M(CO_2)]^{n+}$ becomes predominant pathways for the $[M-CO]^{(n+2)+}$ formation in aprotic media (eq 2). The mechanism of an oxide transfer reaction of the terminal oxygen atom from η^1-coordinated CO_2 to another CO_2 (eq 3), however, has not been fully explored due to a limited

$$\left[M-C \underset{O--C}{\overset{O}{\underset{O}{\diagup}}} \right]^{n+} \longrightarrow \left[M-C\equiv O \right]^{(n+2)+} + CO_3^{2-} \quad (3)$$
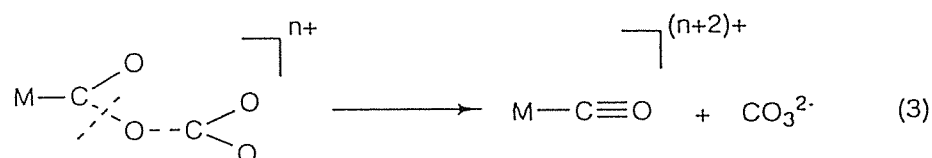
number of a well-characterized metal-η^1-CO$_2$ complexes.

In chapter 2, to obtain a definitive evidence for the reductive disproportionation the author discusses the oxide transfer reaction from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$ to afford $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ which is well-known as a stable η^1-CO$_2$ complex. The reaction proceeds through two steps: a nucleophilic attack of CO_3^{2-} to the carbonyl ligand of $[Ru(bpy)_2(CO)_2]^{2+}$, and the subsequent dissociation of CO_2 to afford $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ (Scheme 1).

Scheme 1
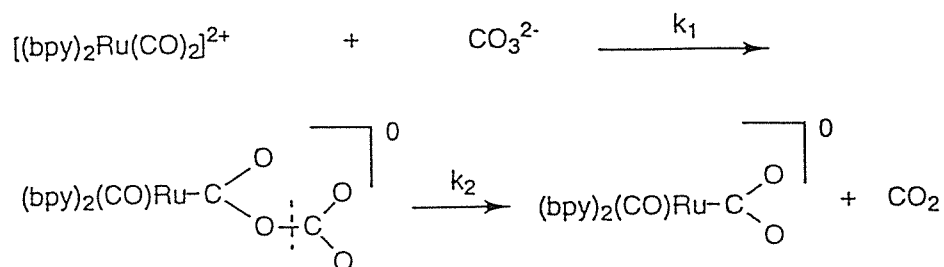
The observed rate constant of the first step (k1obs) is followed by the first-order with respect to the concentrations of both the complex and CO_3^{2-}, and that of the second one (k2obs) was essentially independent on the concentration of CO_3^{2-} under the pseudo-first order reaction conditions. The similarities of ^{13}C-NMR spectrum and the MLCT band of the intermediate ($\delta =$ 201.7 and 205.2 ppm , and λmax = 390 nm) to those of $[Ru(bpy)_2(CO)(COOH)]^+$ ($\delta =$ 201.5 and 204.3, and λmax = 390 nm) also support the adduct formation between $[Ru(bpy)_2(CO)_2]^{2+}$ with CO_3^{2-} prior to the oxide transfer from CO_3^{2-} to $[Ru(bpy)_2(CO)_2]^{2+}$. The finding of the reverse reaction of eq 3 via the proposed intermediate in eq 3 demonstrates the validity of eq 3 for the reductive disproportionation of CO_2 under aprotic conditions.

The smooth conversion from $[Ru(bpy)(trpy)(\eta^1\text{-}CO_2)]$ to $[Ru(bpy)(trpy)(CO)]^{2+}$ (trpy = 2.2':6', 2"-terpyridine) in EtOH/H$_2$O (eq 1), and the subsequent reduction to $[Ru(bpy)(trpy)(CHO)]^+$ and $[Ru(bpy)(trpy)(CH_2OH)]^+$ in the same solvent has been applied to the first catalytic generation of HCHO, CH$_3$OH, HOOCCHO, and HOOCCH$_2$OH in electrochemical reduction of CO_2. Multi-electron reduction of CO_2 using organic electrophiles instead of protons would provide more versatile routes for the catalytic carbon-carbon bond formation in the viewpoint of CO_2 as potential C1 sources for organic compounds. The

smooth conversion from CO_2 to CO under aprotic conditions, therefore, may be a promising gateway to the multi-electron reduction of CO_2 in the presence of organic electrophiles. In contrast to the conversion from $[M-\eta^1-CO_2]^{n+}$ to $[M-CO_2]^{(n+2)+}$ assisted by proton (eq 1), strong basicity of $[M-\eta^1-CO_2]^{n+}$ would be required for the facile reductive disproportionation of CO_2 under mild conditions (eq 2). The basicity of η^1-CO_2, species is estimated from the pKa values of the hydroxycarbonyl complexes ($[M-COOH]^{(n+1)+}$) in eq. 1. On the basis of the pKa Of $[Ru(bpy)_2(CO)(COOH)]^+$ (9.6), and the wide range of pKa values from over 14 to 2.5 of hydroxycarbonyl complexes reported so far, the replacement of the carbonyl ligand in $[Ru(bpy)_2(CO)(\eta^1-CO_2)]$ with an electron donating group would greatly enhance the basicity of the η^1-CO_2 moiety to enable the smooth oxide transfer from η^1-CO_2 to CO_2. In chapter 3, the author discusses the first catalytic formation of acetone and acetoacetic acid in electrochemical CO_2 reduction by $[Ru(bpy)_2(qu)(CO)]^{2+}$ (qu = quinoline) under aprotic conditions, which is composed of two key reactions. The first is the double methylation of the two electron form of $[Ru-CO]^{2+}$ to afford $CH_3C(O)CH_3$ where $[Ru-CO]^{2+}$ is regenerated through the oxide transfer from $[Ru-\eta^1-CO_2]^0$ to CO_2 (eq 3). The second is the subtraction of the proton from resulting $CH_3C(O)CH_3$ by $[Ru-\eta^1-CO_2]$ to give $[Ru-COOH]^+$ and $CH_3C(O)CH_2-$, the latter of which further undergoes carboxylation to produce $CH_3C(O)CH_2COO^-$. Tetramethyl ammonium as an electrolyte was proved to function as the methyl source for the methylation of $[Ru-CO]^0$. Current efficiencies of CO, $HCOO^-$, $CH_3C(O)CH_3$, and $CH_3C(O)CH_2COO^-$ were 42,7,16 and 6% respectively, after 60 passed. The first catalytic formation of ketones and ketoacids by double alkylation of metal-carbonyl species resulting from reductive disproportion-ation of CO_2 demonstrates the feasibility of CO_2 as a building block in organic synthesis, although the main products of the CO_2 reduction is still CO.

As mentioned above, one of the advantage of homogeneous reactions using molecular catalysts is facile physical measurements for tracing reaction intermediates. Another advantage is the capability of the modification of the reaction sites to suit to the reaction by choosing appropriate ligands. In homogeneous catalytic reactions, site opening of catalysts only when reactions take place would be preferable for stabilization of the catalysts, inhibition

of side reactions, and promotion of eliminating the products from a reaction center. Metal complexes with the ligands which can vary their coordination modes reversibly with a little configurational barrier would serve to construct such a reaction system. Taking into account that some metal-1, 8-naphthyridine (napy) complexes undergo fast isomerization reactions between η^1- and η^2-modes in solutions, napy is expected to be a suitable ligand for the design of homogeneous catalysts provided with the function of site-opening and -closing in catalytic cycles. In chapter 4, dynamic behavior of $[Ru(bpy)_2(\eta^1\text{-napy})(solvent)]^{n+}$ and $[Ru(bpy)_2(\eta^2\text{-napy})]^{n+}$ (n = I and 2) is discussed in connection with the efficient catalytic activity of the analogous $[Ru(bpy)_2(qu)(CO)]^{2+}$ for electro-chemical reduction of CO_2 as described in chapter 3. The detailed study revealed that relative stability between Ru-η^1- and η^2- napy complexes is largely dependent on the charges of the complexes and temperatures, which gives fundamental knowledge of controlling η^1- and η^2- modes of napy directed toward effective site-opening and -closing system in homogeneous electrochemical catalysis.

Based on the achievements of the smooth oxide transfer from $[Ru(bpy)_2(qu)(\eta^1\text{-}CO_2)]$ to CO_2 (chapter 3) and the control of the coordination modes of the napy ligand in $[Ru(bpy)_2(\eta^1\text{-napy})(solvent)]^{n+}$ and $[Ru(bpy)_2(\eta^2\text{-napy})]^{n+}$ (n = 1, 2) (chapter 4), activation of the carbonyl moiety of $[Ru(bpy)_2(\eta^1\text{-napy})(CO)]^{2+}$ resulting from the reductive disproportionation of the CO_2 ligand of $[Ru(bpy)_2(\eta^1\text{-napy})(\eta^1\text{-}CO_2)]$ was conducted by taking advantage of the smooth inter conversion of the coordination modes of the napy ligand. In chapter 5, the author discussed the Reversible conversion from the carbonyl moiety to the metallacyclo ring driven by the $[Ru(bpy)_2(\eta^1\text{-napy})(CO)]^{2+/+}$ redox reaction. One-electron reduction of $[Ru(bpy)_2(\eta^1\text{-napy})(CO)]^{2+}$ takes place on a molecular orbital localized in the napy ligand. The increase in the electron density in the napy ligand results in intra-molecular nucleophilic attack of the free nitrogen atom of the ligand against the carbonyl group to afford a five-membered carbamoyl ring (Ru-C(O)-N-C-N), which can be opened to regenerate $[Ru(bpy)_2(\eta^1\text{-napy})(CO)]^{2+}$ quantitatively upon the reoxidation. Thus, the participation of a well designed ligand in the activation of the carbonyl group is expected to afford new methodology for

the smooth conversion from CO_2 to organic carbonyl groups without accompanying an unfavorable CO dissociation due to an M–CO bond cleavage in the reduction of CO_2.

<div align="center">審査結果の要旨</div>

　本論文の主題は金属錯体触媒を用いた炭酸ガス固定の研究である。とくにこの研究では、炭酸ガスから炭素原子を複数個ふくむ有機化合物を得ることを目指した触媒、反応の開発に重点がおかれている。本研究でとりあげられたのは、非プロトン性の溶媒を用い、CO_2を配位した金属錯体$[M(CO_2)]$とCO_2から $[M-CO]$をつくり、さらにこれを還元して有機化合物を得ようとするものである。非プロトン性溶液中でのCO_2からCOへの還元反応は中間体として$[M(CO_2)]$の酸素にもう一つのCO_2の炭素原子が結合したadductを経由すると考えられていたが、その機構は明確でなかった。本論文では$[M-CO]$とCO_3^{2-}からadductをつくり、吸収スペクトルと^{13}C-NMRによって推定された構造を確認し、反応経路を明らかにした。ついで、キノリンを含むルテニウム錯体を用いてアセトニトリル中でこの反応を行い、生成した$[Ru-CO]^{2+}$をと$(CO_3)_4N^+$とともに電解還元するとアセトン、アセト酢酸のようなC_3, C_4化合物が得られることを見いだした。

　このような反応は必要なときに金属触媒が配位座を解放し、不要なときには閉じるようにできると、反応の選択性と触媒の安定性が向上すると期待される。著書は1.8-naphthyridine(napy)がルテニウムに配位する際、1座配位と2座配位の異性体をつくることをX線構造解析、ESR、分子軌道法計算などによって確認し、その応用の可能性を示唆した。また、napyを配位子として含むルテニウム錯体$[Ru(napy)(Co)]^{2+}$が電解還元によって金属をふくむ5員環-Ru-N-C-N-C(O)-を可逆的に生成することを見いだし、この構造をX線解析、^{13}C-NMRなどの手法で決定するとともに、この機構を利用して$[M(CO_2)]$からできた$[M-CO]$中のCOを活性化する新しい方法の可能性を示唆した。

　このように、本博士論文は高度な物質合成技術を駆使し、また、さまざまな測定手段を用いて、中間体などの構造を決定することによって複雑な反応経路をあきらかにしたものである。また、$Cn(n>1)$化合物の形での二酸化炭素固定に新たな発展をもたらし、さらに、配位子の配位状態の変化によるより選択性の高い反応の可能性を指摘するなど、十分な成果を挙げている。

　本論文は英語で書かれており、その文章・表現等についても問題はない。よって、本論文は博士の学位を与えるにふさわしい内容をそなえていると判定した。

　また、平成7年12月25日、13：30より、2時間あまりにわたって面接試験を実施した。形式は出願者が論文に書かれた研究の主要な内容を発表し、審査委員が質問するという形で行われた。発表の仕方は明確で、出願者が研究内容を十分把握し、主体的な研究を行ったことが明らかである。また、審査委員の質問に対しても、明快、かつ柔軟な応答をし、本研究テーマと関連する周辺の問題に関する広いバックグラウンドを

持っていることを示した。平成8年1月31日に実施された公開発表会においても、同様になんら問題のない発表、討論をおこなった。よって、試験結果は合格であった。