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学位（専攻分野）	博士（理学）
学位記番号	総研大甲第44号
学位授与の日付	平成5年3月23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	Mechanistic Investigation of CO <sub>2</sub> Activation on Ruthenium(II)Bipyridine Complexes
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## 論文内容の要旨

Utilization of CO<sub>2</sub> under mild conditions is interesting in the viewpoints of predictable energy shortage in near future and the increase in the concentration of CO<sub>2</sub> in the atmosphere. Photo-and electrochemical CO<sub>2</sub> reductions using homogeneous catalysts have been intensively studied, and several reaction mechanisms have been proposed so far. None of them, however, is generally accepted due to the lack of the evidence concerning the structural changes in the conversion from CO<sub>2</sub> to CO on metal atoms. Such the fundamental problem, therefore, may be provided the elucidation of the bonding characters between CO<sub>2</sub> and metal complexes of the reaction intermediates, and the relative nucleophilicities of CO<sub>2</sub> and proton toward metal centers in protic media. The purpose of the present work is to give some insight into the reaction mechanism of the electro-and photochemical CO<sub>2</sub> reduction catalyzed by metal complexes.

To clarify the acidity of CO ligated on metal complexes may give fundamental information on the conversion of CO<sub>2</sub> to CO. It is reported that not only CO but also NO ligated on some metals reversibly react with OH<sup>-</sup> to form M-XO<sub>2</sub> and M-X(O)OH complexes (X=C, N) in H<sub>2</sub>O. The acidity of those ligands, however, has not been directly compared with each other under the same conditions, so far.

In the Chapter II, [Ru(NO<sub>2</sub>)(CO)(bpy)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (bpy=2,2'-bipyridine) was prepared by a reaction of [RuCl(CO)(bpy)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> with NaNO<sub>2</sub> in order to elucidate the acidic and basic characters of CO and NO<sub>2</sub><sup>-</sup> ligands on Ru. X-Ray structural analysis of [Ru(NO<sub>2</sub>)(CO)(bpy)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> reveals that CO and NO<sub>2</sub> ligands on Ru(II) are in a cis-position. The Ru-N (bpy ligands) bond distances (trans to CO and NO<sub>2</sub><sup>-</sup>) are 2.10(1) and 2.11(1) Å, respectively, and the remaining two Ru-N bond distances (trans to bpy ligands) are 2.07(1) and 2.08(1) Å. Thus, any distinct differences between CO and NO<sub>2</sub><sup>-</sup> ligands were not observed from the Ru-N bond distances. Treatment of [Ru(NO<sub>2</sub>)(CO)(bpy)<sub>2</sub>]<sup>+</sup> with HCl resulted in the formation of [RuCl(CO)(bpy)<sub>2</sub>]<sup>+</sup>, and a reaction product of [Ru(NO<sub>2</sub>)(CO)(bpy)<sub>2</sub>]<sup>+</sup> with H<sub>2</sub>SO<sub>4</sub> showed ν(C=O) and ν(N=O) at 1968 and 1911 cm<sup>-1</sup>, respectively. On the other hand, [Ru(NO<sub>2</sub>)(CO)(bpy)<sub>2</sub>]<sup>+</sup> reversibly reacts with Bu<sub>4</sub>NOH to afford [Ru(C(O)OH)(NO<sub>2</sub>)(bpy)<sub>2</sub>]<sup>+</sup> in CH<sub>3</sub>CN. These results indicate that the acidity of a carbonyl ligand is weaker than a nitrosyl one.

Among a variety of CO<sub>2</sub> metal complexes, η<sup>1</sup>(C)-CO<sub>2</sub> metal complexes are generally believed to be plausible intermediates in the electrochemical CO<sub>2</sub> reduction affording CO. In the Chapter III, the molecular structures of [Ru(CO)<sub>2</sub>(bpy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, [Ru(C(O)OCH<sub>3</sub>)(CO)(bpy)<sub>2</sub>]<sup>+</sup>BPh<sub>4</sub><sup>-</sup>·CH<sub>3</sub>CN as model of [Ru(C(O)OH)(CO)(bpy)<sub>2</sub>]<sup>+</sup>, and [Ru(η<sup>1</sup>(C)-CO<sub>2</sub>)(CO)(bpy)<sub>2</sub>]<sup>+</sup>·3H<sub>2</sub>O were described. The latter two were prepared by the reactions of [Ru(CO)<sub>2</sub>(bpy)<sub>2</sub>]<sup>2+</sup> with CH<sub>3</sub>ONa and two equiv of OH<sup>-</sup>. On the basis of the fact that the Ru-C(O)OCH<sub>3</sub> bond

distance of  $[\text{Ru}(\text{C}(\text{O})\text{OCH}_3)(\text{CO})(\text{bpy})_2]^+$  is shorter than the Ru-CO<sub>2</sub> one of  $[\text{Ru}(\eta^1(\text{C})\text{-CO}_2)(\text{CO})(\text{bpy})_2]$ , a multi-bond character of the Ru-CO<sub>2</sub> bond is not larger than that of the Ru-C(O)OCH<sub>3</sub> bond. One extra electron pair involved in  $[\text{Ru}(\eta^1(\text{C})\text{-CO}_2)(\text{CO})(\text{bpy})_2]$  resulting from dissociation of the terminal proton of  $[\text{Ru}(\text{C}(\text{O})\text{OH})(\text{CO})(\text{bpy})_2]^+$  may, therefore, localize mainly in the CO<sub>2</sub> ligand. The increase in the electron density of the CO<sub>2</sub> moiety is effectively compensated by the extended three-dimensional network of hydrogen bondings between the CO<sub>2</sub> ligand and three water molecules of  $[\text{Ru}(\eta^1(\text{C})\text{-CO}_2)(\text{CO})(\text{bpy})_2] \cdot 3\text{H}_2\text{O}$ .

Smooth conversion of  $[\text{Ru}(\eta^1(\text{C})\text{-CO}_2)(\text{CO})(\text{bpy})_2]$  to  $[\text{Ru}(\text{C}(\text{O})\text{OH})(\text{CO})(\text{bpy})_2]^+$  is the one of the key reactions in the catalytic cycle of the CO<sub>2</sub> reduction by  $[\text{Ru}(\text{CO})_2(\text{bpy})_2]^{2+}$ .

In the Chapter IV, the reactivity of  $[\text{Ru}(\eta^1(\text{C})\text{-CO}_2)(\text{CO})(\text{bpy})_2]$  was examined to elucidate the basicity of the CO<sub>2</sub> moiety. All the oxygen atoms of  $[\text{Ru}(\eta^1(\text{C})\text{-CO}_2)(\text{CO})(\text{bpy})_2]$  undergo an exchange reaction by H<sub>2</sub><sup>18</sup>O. The reactions of  $[\text{Ru}(\eta^1(\text{C})\text{-CO}_2)(\text{CO})(\text{bpy})_2]$  with CH<sub>3</sub>I and ICH<sub>2</sub>CH<sub>2</sub>I gave  $[\text{Ru}(\text{C}(\text{O})\text{OCH}_3)(\text{CO})(\text{bpy})_2]^+$  and  $[\text{Ru}(\text{I}(\text{CO})(\text{bpy})_2)]^+$  in quantitative yields. A C-H bond of organic molecules with active hydrogen such as malonic acid derivatives was also cleaved by the CO<sub>2</sub> moiety of  $[\text{Ru}(\eta^1(\text{C})\text{-CO}_2)(\text{CO})(\text{bpy})_2]$ .

There still remains a matter of controversy about the initial step of the CO<sub>2</sub> reduction catalyzed by metal complexes, which of proton or CO<sub>2</sub> initially attacks on low valent metal centers. In the Chapter V, interaction between CO<sub>2</sub> and reduced quinones is examined in CH<sub>3</sub>CN, CH<sub>3</sub>CN/H<sub>2</sub>O, and CH<sub>3</sub>OH to evaluate the nucleophilicity of CO<sub>2</sub> in protic media. Carboxylation predominantly took place on the oxygen atoms of 2,3,5,6-tetramethyl-1,4-benzoquinone dianion in CO<sub>2</sub>-saturated CH<sub>3</sub>OH and CH<sub>3</sub>CN/H<sub>2</sub>O (9:1 v/v).

This result implies the formation of M-CO<sub>2</sub> bond rather than that of M-H one in catalytic cycles in photo-and electrochemical CO<sub>2</sub> reduction catalyzed by transition metal complexes.

## 論文の審査結果の要旨

田中聡明君の博士論文は 1)  $\text{cis-Ru}^{\text{II}}(\text{bpy})_2$ 基に配位したCOとNOの酸性度の比較。  
2)  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CO}_2)]$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{C}(\text{O})\text{OCH}_3)]^+$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{C}(\text{O})\text{H})]^+$ ,  
 $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ の合成とそれらの分子構造に関する研究. 3)  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CO}_2)]$  錯体  
中の $\text{CO}_2$ 配位子の反応性. 4) プロトン性溶媒における $\text{CO}_2$ 配位子の求核性についての研究  
から構成され、 $\text{Ru}^{\text{II}}(\text{bpy})_2$ 基をもちいた $\text{CO}_2$ の活性化を目的としたものである。  
まず $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{NO}_2)]\text{PF}_6$ を用いてCO, NO配位子の酸性度を比較している。この錯体  
中のCO配位子が $\text{OH}^-$ と反応して $[\text{Ru}(\text{bpy})_2(\text{C}(\text{O})\text{H})(\text{NO})]$ を生成することを見だし、CO配  
位子はNO配位子より酸性度が低いことを明らかにしている。引き続き、 $\text{Ru}^{\text{II}}(\text{bpy})_2$ 基を用  
いてCO,  $\text{C}(\text{O})\text{H}$ あるいは $\text{C}(\text{O})\text{OCH}_3$ ,  $\text{CO}_2$ の配位した錯体を合成し、X線結晶解析によって  
それらの分子構造を決定した。これは錯体上でCO,  $\text{C}(\text{O})\text{OH}$ ,  $\text{O}_2$ の変換反応を確立した最  
初の例である。次いで、 $\text{CO}_2$ 還元重要なステップである $\text{Ru-CO}_2$ から $\text{Ru-C}(\text{O})\text{OH}$ への変  
換を明らかにするために、 $\text{CO}_2$ の求核反応性をTCNE, マロノニトリル、ジメチルマロネ  
ート、サクシノニトリル等との反応で調べた結果を述べ、 $\text{CO}_2$ を用いた新しい炭素-炭素  
結合生成反応を見いだしている。最後にプロトン性溶媒中での $\text{CO}_2$ と $\text{H}^+$ の還元型キノ  
ン類への競争的付加反応を調べ $\text{CO}_2$ の求核性を定量化した。

以上の研究は数物科学研究科構造分子科学専攻の博士学位論文としての内容に値するばかりでなく、金属イオンに配位したCO,  $\text{C}(\text{O})\text{OH}$ ,  $\text{C}(\text{O})\text{OMe}$ ,  $\text{CO}_2$ 等の不安定中間体の単離、結晶化に成功するなど錯体合成に関する高度な技術開発を行っている。また電気化学に関する深い知識に基づいて、専門の錯体化学のみならずその境界領域においても極めて優秀な内容を含んでいる。