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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（理学） 氏名 康 媛媛

学 位 論 文 題 名

Synthesis and Photophysical Properties of Tricarbonyl Rhenium(I) Complexes Having Arylborane Charge Transfer Units

(アリールホウ素置換基を有するトリカルボニルレニウム(I)錯体の合成および光化学物性に関する研究)

Recently, energy shortage from fossil fuels and pollution of the environments have been two largest issues to be solved in the world. Therefore, solar energy has been focused as a sustainable energy source and its utilization has been one of the important research topics. Chemical approaches toward artificial photosynthesis utilizing transition metal complexes have been studied in the past decades. In particular, a tricarbonyl rhenium(I) complex having an aromatic diimine ligand, $[\text{Re}(\text{CO})_3\text{LX}]$ (L = diimine and X = halide, phosphine or imine), has been received extensive attention due to the unique spectroscopic, photophysical, and photoredox properties, including the photocatalytic ability to CO_2 reduction.¹ Photocatalytic CO_2 reduction by $[\text{Re}(\text{CO})_3\text{LX}]$ has been known to be controllable by its electronic structures and, the ground- and excited-state properties of $[\text{Re}(\text{CO})_3\text{LX}]$ are very sensitive to a coordinating ligand(s) (L and/or X) as well as the microenvironments around the complex.² Therefore, chemical modifications and derivatizations of $[\text{Re}(\text{CO})_3\text{LX}]$ through the nature of L and/or X are extremely important for further development of an efficient photocatalytic CO_2 reduction system.

For synthetic modulation of the excited-state properties of $[\text{Re}(\text{CO})_3\text{LX}]$, the electronic structures of a triarylborane derivative are very attractive. A triarylborane derivative shows characteristic spectroscopic and photophysical properties owing to the intramolecular charge transfer interactions between the π -orbital of the aryl group ($\pi(\text{aryl})$) and the vacant p-orbital on the boron atom ($\text{p}(\text{B})$): $\pi(\text{aryl})\text{-p}(\text{B})$ CT.³ Owing to such $\pi(\text{aryl})\text{-p}(\text{B})$ CT interactions in a triarylborane derivative, an introduction of a triarylborane unit(s) to the periphery of the ligand of a metal-to-ligand CT (MLCT) type transition metal complex is expected to influence both spectroscopic and photophysical characteristics of the complex through synergistic interactions between MLCT and $\pi(\text{aryl})\text{-p}(\text{B})$ CT.

Based on these research background, two novel tricarbonyl rhenium(I) complexes having a mono-arylborane charge transfer unit at the 4-position of 1,10-phenanthroline (*fac*- $[\text{Re}(\text{CO})_3(4\text{-DBDE-phen})\text{Br}]$ = **ReBphen**) or 2,2'-bipyridine (*fac*- $[\text{Re}(\text{CO})_3(4\text{-DBDE-bpy})\text{Br}]$ = **ReBbpy**) are designed and synthesized as described in Chapter 2. It was demonstrated that **ReBphen** and **ReBbpy** showed low-energy/intense absorption and low-energy/long-lived excited states compared to the corresponding reference complexes without an arylborane unit. While the spectroscopic and photophysical properties of **ReBphen** and **ReBbpy** are explained reasonably by the synergistic interactions between MLCT and $\pi(\text{aryl})\text{-p}(\text{B})$ CT, **ReBphen** shows more efficient synergistic MLCT and $\pi(\text{aryl})\text{-p}(\text{B})$ CT interactions compared to **ReBbpy**. The differences in the properties between the bpy- and phen-type complexes were discussed in detail on the basis of the experimental and theoretical data. Theoretical calculations for the HOMO–LUMO electronic structures of the isomeric complexes of **ReBphen** and **ReBbpy**, **3-/5-ReBphen** and **3-/5-ReBbpy**, were also conducted toward future molecular design of related complexes. The results

indicated that the substituted position of a triarylborane unit in a diimine ligand played essential roles in governing the photophysical characteristics of $[\text{Re}(\text{CO})_3\text{LBr}]$.

Since the intense absorption and relatively long-lived excited states observed for **ReBphen** and **ReBbpy** are highly advantageous for an efficient photocatalytic system, further investigation and understanding of the rhenium(I)-arylborane complexes are of primary importance.

Therefore, another two novel rhenium(I) complexes having two arylborane groups to the 4- and 7-positions of 1,10-phenanthroline (*fac*- $[\text{Re}(\text{CO})_3(4,7\text{-DBDE}_2\text{-phen})\text{Br}]$: **ReB₂phen**) or 4- and 4'-positions of 2,2'-bipyridine (*fac*- $[\text{Re}(\text{CO})_3(4,4'\text{-DBDE}_2\text{-bpy})\text{Br}]$: **ReB₂bpy**) were further synthesized and studied as described in Chapter 3. **ReB₂phen** and **ReB₂bpy** showed low-energy and more intense absorption compared to **ReBphen** and **ReBbpy**, respectively, and the molar absorption coefficients of the MLCT absorption bands were largely enhanced owing to the synergistic interactions between MLCT and $\pi(\text{aryl})\text{-p(B)}$ CT caused by the presence of the two arylborane units in the periphery of the diimine ligands. Furthermore, **ReB₂bpy** displayed more effective influences on the spectroscopic and photophysical properties compared to **ReB₂phen**. Therefore, the synthetic control/tuning of the electrochemical, spectroscopic, and photophysical properties of a tricarbonyl rhenium(I) complex is achieved by a triarylborane-appended π -chromophoric ligand.

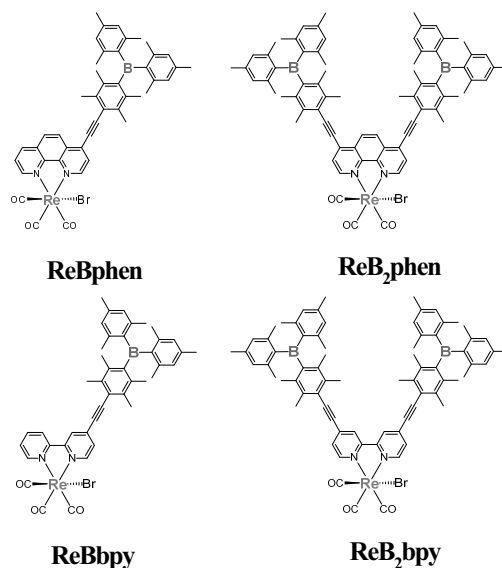
Due to the intense absorption ranging in the wide UV-visible wavelength region and the relatively long-lived excited states, the four novel tricarbonyl rhenium(I) complexes are expected to act as visible-light-driven catalysts for CO_2 photoreduction. Therefore, photocatalytic CO_2 reduction by the novel rhenium(I) complexes were studied in detail as described in Chapter 4. Emission quenching studies demonstrated that the quenching rate constants of the complex increased with an increase in the number of the arylborane charge transfer unit in the complex, indicating an efficient electron transfer reaction proceeded for the complexes having multiple borane centers. However, **ReB₂phen/ReBphen** and **ReB₂bpy/ReBbpy** showed lower turnover numbers for CO_2 formation compared to **Rephen** or **Rebpy**, probably due to the low reducing abilities and low stabilities of the complexes under the experimental conditions.

In Chapter 5, the principal findings and conclusions obtained for the spectroscopic and photophysical properties of novel rhenium(I) with an arylborane-appended diimine ligand(s) by the present study are described, together with the future perspective of the study.

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Scheme 1 Chemical structures of novel tricarbonyl rhenium(I) complexes developed in the thesis.