

論文の内容の要旨

論文題目

Light-Induced Acceleration of Anionic Ligand Substitutions on Transition-Metal Complexes

(遷移金属錯体におけるアニオン性配位子置換反応の光誘起加速)

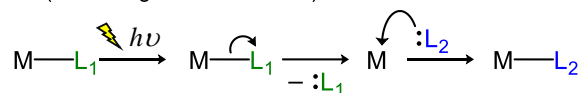
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Introduction (chapter 1)

Ligand substitution reactions of transition metals are key elementary processes in various biological systems and organometallic catalysis.^{1,2} Therefore, it is important to develop the methodology for controlling the reactivity of ligand substitution. The deciding factor of the reaction depends on the environment, such as electronic state of the ligand and metal, leaving ability of the ligand, steric hindrance, solvent coordination, and temperature. In contrast, in some cases, photo-excitation can accelerate ligand substitution. For example, light irradiation on M-L type metal complexes (M: transition metal, L: coordinative ligand) induces the dissociation of the ligands, such as pyridine or CO, resulting in their substitutions by other ligands (Figure 1a).³ However, light-induced ligand substitution of M-X type metal complexes (X: covalent ligand) have been limited to reactions involving radical intermediates generated by homolytic M-X bond cleavage, especially M-C(sp³) bonds (Figure 1b).⁴ Nevertheless, M-X type ligand substitution processes without radical species (anionic ligand substitution) are common in many organometallic reactions and involve heterolytic cleavage of M-C(sp) and M-C(sp²) bonds. Accordingly, the development of methodology for the dramatic light-induced acceleration of such anionic ligand substitutions would enable previously unavailable

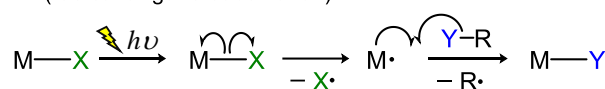
catalytic reaction systems in organometallic chemistry. In this thesis, a new type of light-induced ligand substitution which utilizes the transient reactive frontier orbital in the excited state is mainly described (Figure 1c).

(a) Heterolytic cleavage on M-L type transition-metal complexes (neutral ligand substitution)



$\text{:L}_1 = \text{:N}(\text{C}_6\text{H}_5)_3, \text{:CO}, \text{:N}_2, \text{etc.}$

(b) Homolytic cleavage on M-X type transition-metal complexes (radicalic ligand substitution)



$\text{X} = \text{C}(\text{sp}^3), \text{C}(\text{sp}^2), \text{OH}, \text{etc.}$

(c) This work
Heterolytic cleavage on M-X type transition-metal complexes (anionic ligand substitution)

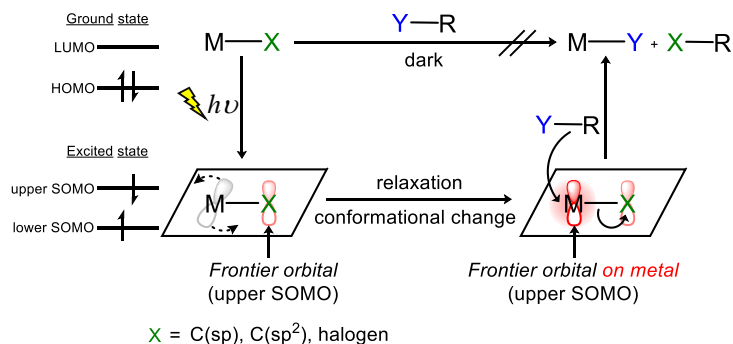


Figure 1. Light-induced ligand substitution of (a) M-L type transition-metal complexes through heterolytic cleavage, (b) M-X type transition-metal complexes through homolytic cleavage, and (c) M-X type transition-metal complexes through heterolytic cleavage.

Complementary Color Tuning by HCl via Phosphorescence-to-Fluorescence Conversion on Insulated Metallopolymer Film and Its Light-Induced Acceleration (Chapter 2)

The author first investigated the anionic ligand substitution of insulated platinum acetylide polymer as a color tuning material. This platinum acetylide polymer showed high visibility by a phosphorescence-to-fluorescence conversion (Figure 2a). In addition, the platinum acetylide polymer showed high selectivity toward HCl gas (Figure 2b). In this research, the anionic ligand substitution (polymer decomposition) was accelerated by UV irradiation, resulting in rapid and sensitive detection of HCl gas (Figure 2c).

Considering that this phenomenon leads to the development of light-induced anionic ligand substitution reaction, the author worked on the elucidation of the accelerated reaction.

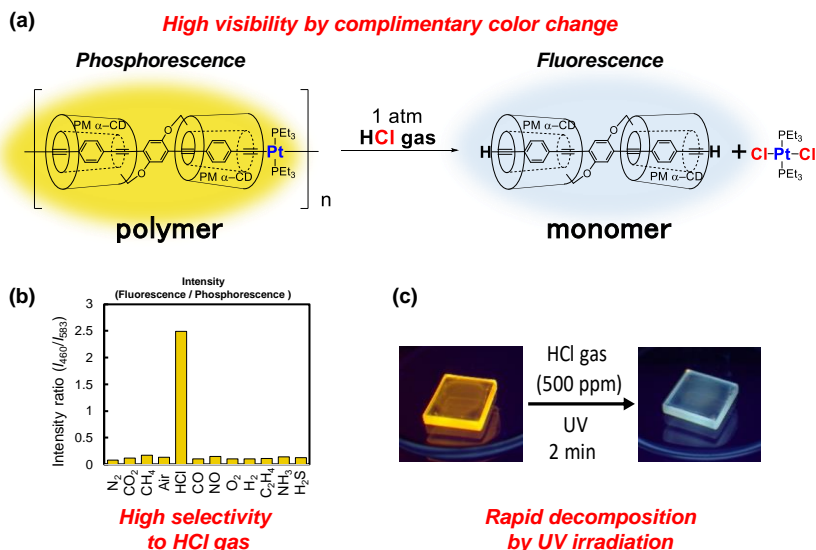


Figure 2. Optochemical HCl gas detection on insulated metallopolymer using anionic ligand substitution reaction.

Elucidation of the Excited Structure, Electronic State, and Reactivity of Platinum Acetylide (Chapter 3)

The reactivity of the monomer platinum acetylide in the excited state was examined. As a result, even in the monomer form, the anionic ligand substitution of platinum acetylide was accelerated by light irradiation. Several experiments supported that the accelerated anionic ligand substitution differed from photo-dissociation reaction or photo-induced homolytic cleavage reaction. TD-DFT study of the excited platinum acetylide showed that the excitation causes the rotation of the P-Pt-P axis, resulting in the transient frontier orbital on the metal which enhances its reactivity toward a reagent (Figure 3).

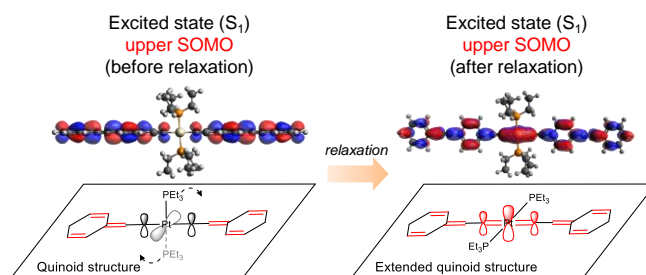
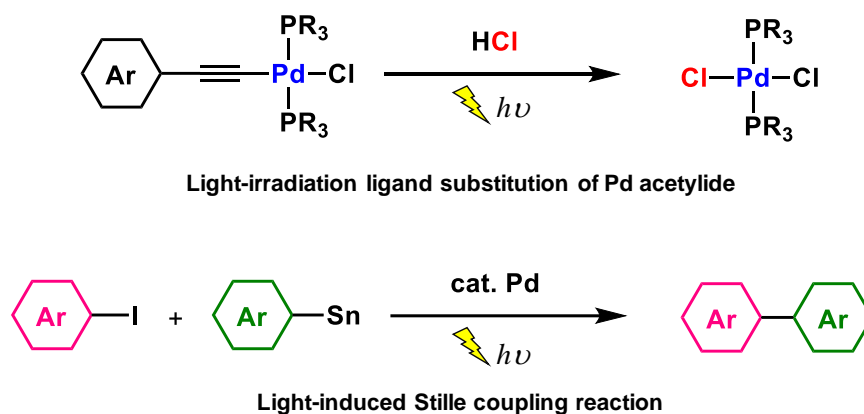


Figure 3. Structures and electronic states of the monomer platinum acetylide in the excited state calculated by DFT and TD-DFT (B3LYP/LanL2DZ).

Light-Induced Ligand Substitution of Palladium Acetylide and Light-Induced Stille Coupling Reaction (Chapter 4)

The accelerated anionic ligand substitution reactions of palladium complexes were investigated. As expected from TD-DFT calculation, the ligand substitution of palladium acetylide was accelerated by light-irradiation (Scheme 1 above). In addition, this concept involving the light-promoted formation of a new frontier orbital (upper SOMO) was applied to the light-accelerated Stille coupling reaction through the heterolytic cleavage of M-C(sp²) bonds. As a result, the coupling reaction was progressed at lower temperature than normal condition by light-irradiation (Scheme 1 below).

Scheme 1. Light-induced ligand substitution of a Pd acetylide (above) and Stille coupling reaction (below).



Conclusion (Chapter 5)

The large conformational changes of metal acetylide complexes in the excited state enhanced the reactivity toward ligand substitution. The concept involving the light-induced formation of a new frontier orbital on a metal center was applied to catalytic reaction. As a result, the Stille coupling was accelerated by light-irradiation, indicating versatility and practicality of the concept.

Reference

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