Study on Visible-light-driven Photocatalytic Carbon-Carbon Cross-couplings by Vitamin B12 Derivative for Green Organic Synthesis

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論文の要約

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論 文 名: Study on Visible-light-driven Photocatalytic Carbon-Carbon Cross-couplings by Vitamin B₁₂ Derivative for Green Organic Synthesis (グリーン有機合成を志向 したビタミンB₁₂誘導体による可視光駆動型の炭素-炭素カップリング反応 に関する研究)

Organometallic B₁₂ compounds are unique metal complexes having a cobalt-carbon σ -bond present in biological systems, playing various important roles in the metabolism of microorganisms, animals and humans. Cleavage of the cobalt-carbon σ -bond could initiate many B₁₂-dependent enzymatic reactions. The alkylated Co(III)-complex, which is the key factor in such reactions, is generally formed by the reaction of the Co(I) species of the B_{12} complex with electrophiles, such as organic halides, in vivo. Therefore, the reductive formation of the Co(I) species and the followed oxidative addition of the organic halide to form the alkylated Co(III)-complex are the key steps for the development of the B₁₂-mediated enzymatic reactions. The visible light-driven formation of the Co(I) species of the B₁₂ derivative, heptamethyl cobyrinate perchlorate, in the presence of photosensitizer (such as [Ru(bpy)₃)Cl₂, cyclometalated Ir(III)-complexes, etc.), catalyzed various B₁₂ model reactions (1,2-migration of the functional group, methyl-transfer reaction, dichlorination reaction, etc.). These B₁₂-based visible light-driven photocatalytic systems have promising significance in organic synthesis, from the viewpoint of green and sustainable chemistry, because of their advantages of being clean, low-cost, sustainable, and environmentally benign. As expanding application of such B₁₂-based photocatalytic system, in this work, the visible light-driven photocatalytic Mizoroki-Heck-type reaction and Sonogashira-type reaction catalyzed by vitamin B₁₂ derivative (Scheme 1) was investigated for the C-C bond elaboration in green organic synthesis. The details of this work were described as below.

Chapter 1 A brief overview of the vitamin B_{12} -based chemistry and C-C bond cross-couplings was outlined. In the part of vitamin B_{12} -based chemistry, the general function and corresponding catalytic systems of vitamin B_{12} and its derivatives were introduced. The part of C-C bond cross-couplings mainly focused on the significance and development of Mizoroki-Heck-reaction and Sonogashira-reaction.

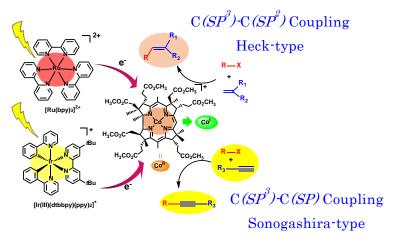
Chapter 2 The photo-driven Mizoroki-Heck-type reaction catalyzed by vitamin B_{12} derivative in the presence of $[Ru(bpy)_3]Cl_2$ as photosensitizer was described. In this work, the reaction proceeded through a radical intermediate to react with an alkene, and the β -elimination problem encountered in conventional Pd-catalysis could be well avoided. The catalytic efficiencies of the B_{12} catalyst were compared to that of other cobalt complexes (cobaloxime, *etc.*). A variety of control experiments supported a radical-based mechanism similar with those for typical B_{12} model reactions. A unique coupling reaction combined with 1,2-migration of the functional group was also conducted. The most probable mechanism was proposed. With the vitamin B_{12} derivative as one efficient catalyst in this study, the B_{12} -based

enzyme reaction was advanced to develop C-C bond formation between organic halide and alkene in synthetic organic chemistry.

Chapter 3 The vitamin B_{12} derivative-mediated photo-driven catalytic Sonogashira-type reaction in the presence of $[Ir(dtbbpy)(ppy)_2][PF_6]$ as photosensitizer at room temperature was investigated. In this study, with the vitamin B_{12} derivative as catalyst and $[Ir(dtbbpy)(ppy)_2][PF_6]$ as photosensitizer, such B_{12} -based visible light-driven photocatalytic system showed excellent efficiency with remarkable high turnover in the $C_{Sp}^{3-}C_{Sp}$ bond formation between organic halides and alkynes. The most preferable mechanism was proposed. Compared with the conventional Pd- and Cu- mediated heating method, this B_{12} -catalyzed visible-light-driven system showed the clear advantage of being clean, low-cost, sustainable, and environmentally benign, furthermore, this straightforward protocol avoided the homocoupling reaction of alkynes.

Chapter 4 Redox active ionic liquid as efficient media and solvent for vitamin B₁₂ derivative-catalyzed photo-driven Mizoroki-Heck-type reaction and Sonogashira-type reaction discovered. In this chapter, redox active ionic was the liquid, 1-ethyl-4-(methoxycarbonyl)pyridinum bis(trifluoromethanesulfonyl)amide $(\mathbf{RIL}),$ was synthesized from its iodide form by an anion exchange reaction of Li(NTf₂) as one viscos liquid $(\eta = 122 \text{ cp at } 25 \text{ °C})$, and characterized by NMR, and elemental analysis. The **RIL** showed reversible redox couples at -0.65 V and -1.48 V vs. Ag/AgCl, worked as an electron mediator in the B₁₂ derivative catalyzed Mizoroki-Heck-type reaction and Sonogahsira-reaction under visible-light irradiation. The catalytic efficiency in the **RIL** was higher than those in MeOH and the redox inactive ionic liquid, 1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)amide. To the best of our knowledge, this is the first example of the Mizoroki-Heck-type reaction/Sonogashira-type reaction combined with the cobalt-mediated IL-system.

Chapter 5 The summary of this work and perspective of the future work were depicted. Such environmentally benign vitamin B₁₂ derivative, which derived from the natural B₁₂, catalyzed visible-light-driven C-C bond cross-couplings provided one promising and practical pathway for the green organic synthesis.



Scheme 1