

Electrochemical Fluoroalkylation of Arenes and Heteroarenes Catalyzed by a Hydrophobic Vitamin B12

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論 文 名 : Electrochemical Fluoroalkylation of Arenes and Heteroarenes
Catalyzed by a Hydrophobic Vitamin B₁₂
ビタミン B₁₂ 誘導体を触媒とするアレーンとヘテロアレーンに対する
電解フルオロアルキル化反応

区 分 : 甲

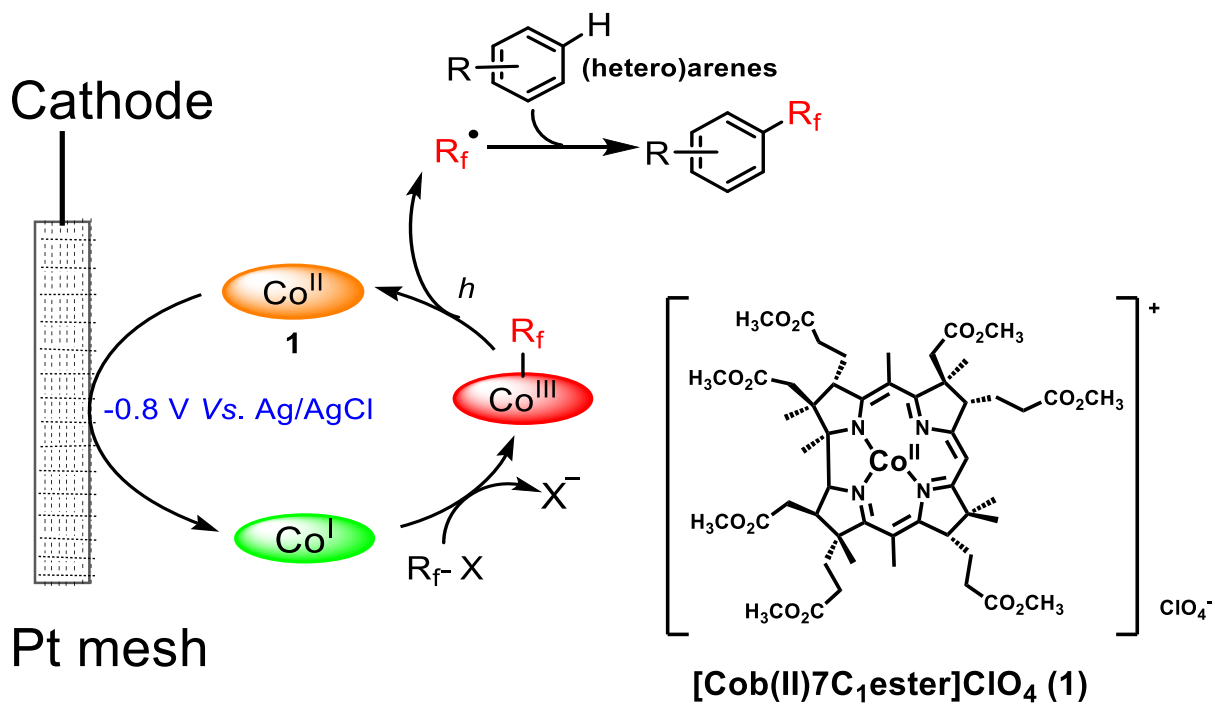
論 文 内 容 の 要 旨

This thesis describes a straightforward methodology to demonstrate the radical difluoroalkylation, trifluoromethylation and perfluoroalkylation of aromatic compounds catalyzed by a Hydrophobic Vitamin B₁₂ [Co(II)7C₁ester]ClO₄ (1) via an electrochemical technique.

Chapter one introduces the history and significance of fluorine in organic chemistry, and details the effect that substitution of a CF₃ group can have on the properties of organic molecules and its many applications in fields ranging from pharmaceuticals to materials sciences. The exploration of a versatile fluoroalkylation reagents and methods to incorporate various fluoroalkyl groups are also described for the syntheses of bioactive fluoroalkylated compound. Brief history, general functions and synthesis of various model complexes of Vitamin B₁₂ has also been discussed here.

Chapter two demonstrates the electrochemical trifluoromethylation and perfluoroalkylation of aromatic compounds mediated by a Vitamin B₁₂ derivative as a cobalt-based catalyst. The Co(I) species of a Vitamin B₁₂ derivative, prepared by controlled-potential electrolysis at -0.8 V vs. Ag/AgCl in methanol, reacted with R_f (R_f = CF₃, *n*-C₃F₇, *n*-C₄F₉, *n*-C₈F₁₇ and *n*-C₁₀F₂₁) to form a Co-R_f complex. This complex released an R_f radical under visible light irradiation, which then reacted directly with non-activated (hetero)arenes to form the desired fluoroalkylated molecules through direct C-H functionalization.

Chapter three describes the synthesis of atom economical difluoro-alkylated arene and (hetero)arene catalyzed by a Vitamin B₁₂ derivative employing readily available reagent bromodifluoroacetate (Br-CF₂COOEt) as a CF₂⁻ source through direct C-H functionalization. Different aspects of these reaction such as radical trapping experiment, catalyst concentration, reaction potential, substrate scope and solvent effects are discussed. The new protocol provides a much cheaper, mild and efficient way to difluoro, trifluoro and perfluoroalkylated organic compounds with the strategy outlined in **Scheme 1**.



[$\text{R}_f\text{X} = \text{C}_3\text{F}_7\text{I}, \text{C}_4\text{F}_9\text{I}, \text{C}_8\text{F}_{11}\text{I}, \text{C}_{10}\text{F}_{21}\text{I}$ and $\text{Br}-\text{CF}_2\text{COOEt}$]

Scheme 1 Proposed electro-catalytic cycles of radical fluoroalkylation of aromatic compounds mediated by $[\text{Co(II)7C}_1\text{ester}]\text{ClO}_4(1)$

Chapter four reports the synthesis of Cobalt- CF_3 complex and describes the investigation of photolytic cleavage of Co-C bond in trifluoromethylated Vitamin B_{12} complex. Furthermore, a preliminary mechanistic study of fluoroalkylated complex mediated by a Vitamin B_{12} derivative in organic media is also reported.