

論文内容の要旨

論文題目 Iron-Catalyzed Synthesis of Fused Aromatic Compounds
via C–H Bond Activation

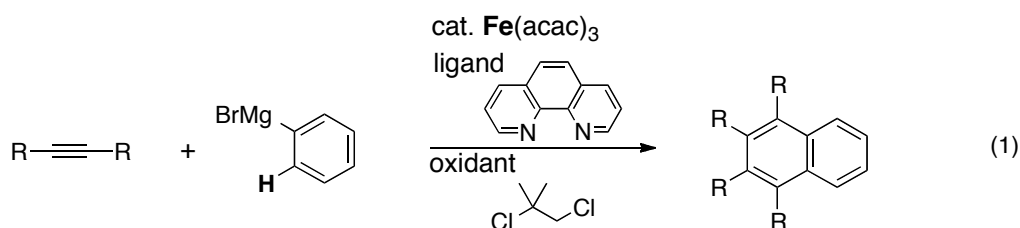
〔鉄触媒を用いた炭素-水素結合活性化による縮合多環芳香族化合物の合成〕

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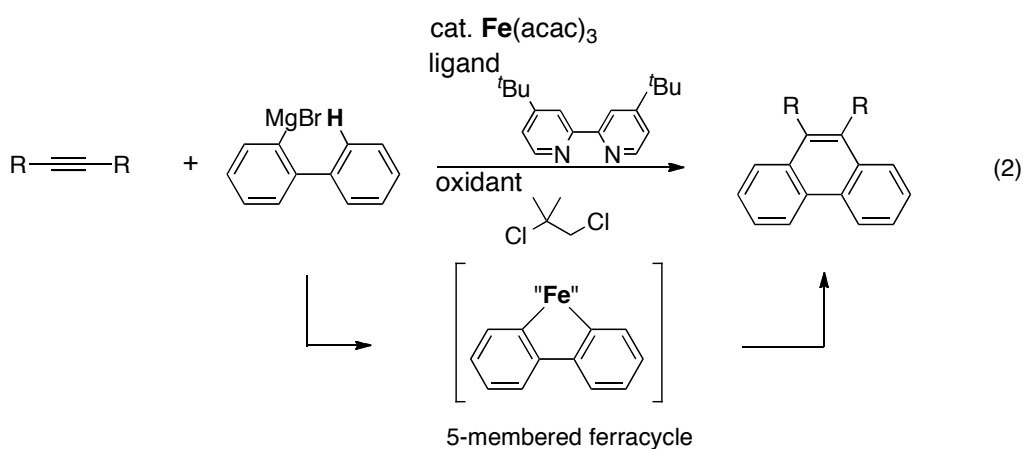
The present thesis describes the investigation of a new reaction of organoiron species and the development of iron-catalyzed synthesis of fused aromatic compounds via C–H bond activation.

Chapter 1 describes the importance of ubiquitous metals such as iron for sustainable catalysis, iron-catalyzed C–H bond activation reactions, and synthesis of fused aromatic compounds via C–H bond activation. Development of iron-catalyzed reactions for the synthesis of fused aromatic compounds is the main topic of the present thesis.

In Chapter 2, the initial finding of iron-catalyzed synthesis of fused aromatics via [2 + 2 + 2] annulation reaction of two alkynes and a Grignard reagent was described (eq 1). The reaction with internal alkynes and phenylmagnesium bromide took place in the presence of a catalytic amount of iron salt and bipyridine-type ligand and dichloroalkane as an oxidant to give 1,2,3,4-tetrasubstituted naphthalene derivatives. The key of this reaction is the use of a bulky dichloride, 1,2-dichloro-2-methylpropane, as an oxidant.



In Chapter 3, a [4 + 2] benzannulation reaction of an alkyne with a biaryl Grignard reagent was described (eq 2). The reaction of internal or terminal alkynes and phenyl Grignard reagent took place in the presence of a catalytic amount of iron salt and bipyridine-type ligand, and a dichloroalkane as an oxidant to give 9,10-disubstituted or 9-substituted phenanthrenes and congeners. The reaction took place under mild conditions and bromide, chloride, trimethylsilyl, trifluoromethyl, and olefinic groups were tolerated. Mechanistic investigations suggest that this reaction involves a 5-membered ferracycle formation via C–H bond activation.



In Chapter 4, a more practical method for iron-catalyzed C–H bond activation reaction was described. The iron-catalyzed [4 + 2] benzannulation reaction of alkyne also took place with aryl bromide and metallic magnesium instead of Grignard reagent (eq 3). The use of convenient aryl bromides instead of the Grignard reagent is a significant practical advantage from the viewpoint of synthetic chemistry.

