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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（薬科学）　氏　名　　水上　雄貴

学 位 論 文 題 名

Transformation of Organic Molecules Featuring “Cleavage of Strong Chemical Bonds”: Development and Mechanistic Studies

（「安定な結合の切断」を伴う分子変換法の開発とその機構解明）

The author focuses on the design and mechanistic studies of new transformation of organic molecules featuring the cleavage of carbon–carbon bond or carbon–fluorine bond, which are regarded as “strong chemical bonds”, with “titanium” as the key transition metal. The thesis is composed of three chapters.

Chapter 1 and chapter 2 describe the synthesis of aromatic compounds via titanium-mediated carbon–carbon bond cleavage and formation. Takahashi and co-workers reported sequential transformation of titanacyclopentadienes by C–C bond cleavage and formation. The treatment of titanacyclopentadiene with several kinds of reactants or additives induced the coupling of Cp ligand with diene moiety of the titanacycle, affording a dihydroindenyl titanium complex. Next, the dihydroindene moiety of the complex was transformed via metathesis to give the corresponding organic compounds such as tetrasubstituted indene or dihydroindene derivatives. The author investigated the detailed effects of reactants and additives in the transformation of these dihydroindenyl titanium complexes and found two kinds of transformation. Chapter 1 deals with the trisubstituted indene derivatives formation by the use of PMe_3 and azobenzene. C–C bond cleavage led to the elimination of one alkyl substituent on the diene moiety of the titanacyclopentadiene. Chapter 2 refers to the synthesis of benzene derivatives using 2-aminothiazole. Two-carbon unit separated from Cp ligand of titanacyclopentadiene by C–C bond cleavage was introduced into the product.

Chapter 3 describes the halogen exchange reaction of aliphatic fluorine compounds with organic halides as halogen source. The use of organic halide as halogen source in halogen exchange reaction is challenging mainly because the halogen exchange of two kinds of alkyl halides results in their equilibrium. In addition, to the best of our knowledge, there has been no report on halogen exchange of alkyl “fluorides” with an “organic” halogen source. The author found that the fluorine/halogen exchange with organic halogen source was achieved by the use of trialkyl aluminum and a catalytic amount of titanocene dihalide. The F/Cl and F/Br exchange proceeded under the above-mentioned conditions. Surprisingly, no titanocene catalyst is needed for the F/I exchange.