Iron Phthalocyanine

Compiled by Cédric Colomban

Cédric Colomban was born in Briançon, France, in 1986. He studied bio-organic and bio-inorganic chemistry at University Joseph Fourier, Grenoble, France. He is currently pursuing a Ph.D. at University Claude Bernard (Lyon, France) under the guidance of Dr. Alexander Sorokin and Dr. Pavel Afanasiev. His research is focused on oxidative dehalogenation of polyfluorinated and polychlorinated aromatics using single-atom-bridged diiron macrocyclic complexes.

Institut de Recherches sur la Catalyse et l’Environnement de Lyon (IRCELYON), UMR 5256, CNRS – Université Lyon 1, 2 av. Albert Einstein, 69626 Villeurbanne Cedex, France
E-mail: cedric.colomban@ircelyon.univ-lyon1.fr

Introduction

Iron phthalocyanine (FePc) complexes are structurally related to porphyrin complexes; phthalocyanines have been used as alternative catalysts because they are cheaper and more stable to degradation. FePc is widely used in a variety of catalytic transformations, including N-alkylation, C–H amination, C–C bond formation, preparation of esters and oximes, reduction, oxidation, and radical reactions. Although FePc is particularly studied as a catalyst for organic reactions, this particular reagent is also described in many other applications. For example, FePc complexes are efficient catalyst for the charge/discharge process in lithium–oxygen large-capacity batteries.

The following literature data indicate that FePc displays a strong bibliographic background in a wide variety of reactions and is currently considering as an active and ‘hot’ research topic. An overview of typical iron phthalocyanine syntheses is shown in Scheme 1.

![Scheme 1](image)

Abstracts

(A) FePc has been reported as an efficient and versatile catalyst for the N-alkylation of amine-substituted heterocycles with alcohols. The one-pot syntheses of ortho-amino-substituted benzimidazoles, benzothiazoles, and benzoxazoles are achieved by using FePc in combination with a base. The best reaction conditions were found to be t-BuONa in toluene.

(B) Intramolecular C–H amination is catalyzed by FePc in the presence of AgSbF₆ under mild reaction conditions. Allylic C–H amination is preferred over aziridination. Interestingly, this very selective amination is due to the difference in reactivity, closely paralleling C–H bond dissociation energies (allylic > benzylic > ethereal > tertiary > secondary C–H bonds). C–H aminations are particularly important reactions because may biologically active molecules are amines.
(C) Lamar and Nicholas developed an efficient method for the direct synthesis of 3-arylindoles catalyzed by FePc. 3-Arylindoles are produced in moderate to excellent yields via annulation of aryl hydroxylamines with alkynes in the presence of FePc in refluxing toluene.4

(D) The preparation of various esters from a wide range of alcohols and carboxylic acids is achieved through the aerobic activation of Ph₃P catalyzed by FePc. The reaction is accelerated in the presence of pyridine N-oxide derivatives such as 4-methoxypyridine N-oxide (MPO). It is noteworthy that the only phthalocyanine derivative able to catalyze this reaction is the iron complex thanks to the ability of FePc to use O₂ for the activation of Ph₃P.5

(E) Beller and co-workers reported the first iron-catalyzed synthesis of oximes from olefins. The treatment of substituted styrenes with tert-butyl nitrite and NaBH₄ in the presence of FePc affords oximes in moderate to high yields.6

(F) Iron tetrasulfophthalocyanine (FePcS) catalyzes the reduction of nitrite (NO₂⁻) by dithionite or sulfoxylate in aqueous alkaline solution. Interestingly, different products can be obtained depending on the choice of the reductant. Using dithionite, NO₂⁻ is reduced to N₂O₃ while the use of sulfoxylate as reductant lead to ammonia as the product.7

(G) Boger and co-workers extended the initial work of Kasuga on the oxidation of styrenes8 to the first oxidation of unactivated alkenes by a FePc–NaBH₄–O₂ system. The oxidation of a range of alkenes to the corresponding alcohols is achieved by using a catalytic amount of FePc. In this system, O₂ acts as metal oxidant and as a radical trap.9

(H) The radical cyclization of 1,6-dienes to give functionalized cyclic compounds is catalyzed by FePc in the presence of NaBH₄ and O₂ in EtOH at room temperature. The reaction gives five-membered carbo- or heterocyclic compounds with a hydroxyl group.10

References