

SYNLETT Spotlight

Iron Phthalocyanine

Compiled by Cédric Colomban



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

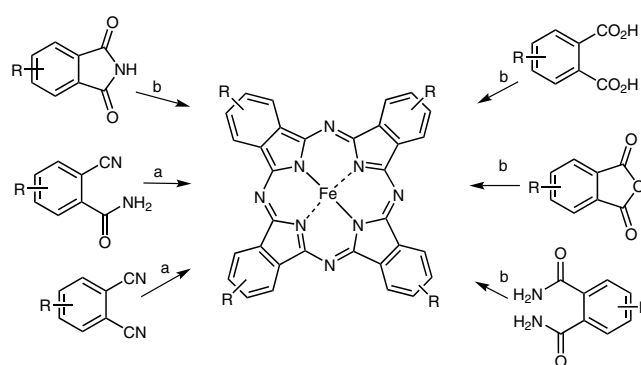
Cédric Colomban was born in Briançon, France, in 1986. He studied bio-organic and bio-inorganic chemistry at University Joseph Fourier, Grenoble, France. He is currently pursuing a Ph.D. at University Claude Bernard (Lyon, France) under the guidance of Dr. Alexander Sorokin and Dr. Pavel Afanasiev. His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

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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,¹ including N-alkylation,² C–H amination,³ C–C bond formation,⁴ preparation of esters⁵ and oximes,⁶ reduction,⁷ oxidation,^{8,9} and radical reactions.¹⁰ 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.¹¹ 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

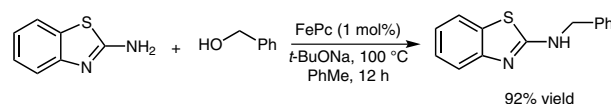
and ‘hot’ research topic. An overview of typical iron phthalocyanine syntheses is shown in Scheme 1.



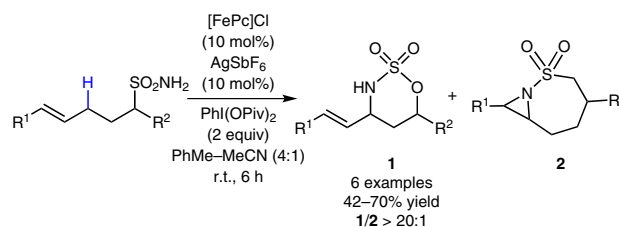
Scheme 1 Preparation of FePc complexes from cyclotetramerization of common precursors. *Reagents and conditions:* (a) iron salt, Δ ; (b) iron salt, urea, catalyst, Δ .

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.²



(B) Intramolecular C–H amination is catalyzed by FePc in the presence of AgSbF_6 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 > etheral > tertiary > secondary C–H bonds). C–H aminations are particularly important reactions because many biologically active molecules are amines.³



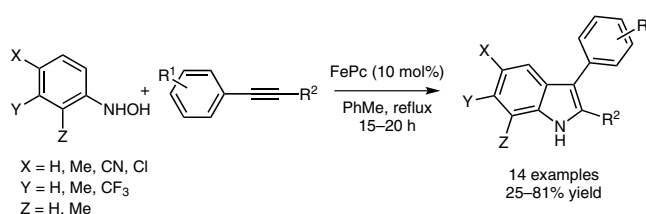
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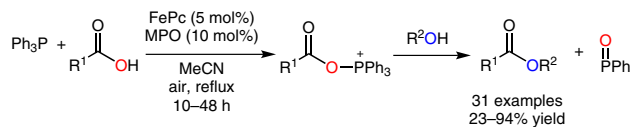
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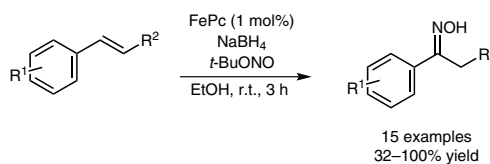
(C) Lamar and Nicholas developed an efficient method for the direct synthesis of 3-aryloxyindoles catalyzed by FePc. 3-Aryloxyindoles are produced in moderate to excellent yields via annulation of aryl hydroxylamines with alkynes in the presence of FePc in refluxing toluene.⁴



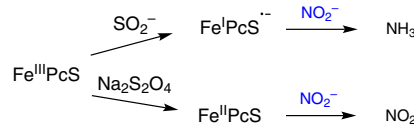
(D) The preparation of various esters from a wide range of alcohols and carboxylic acids is achieved through the aerobic activation of Ph₃P catalyzed by FePc. The reaction is accelerated in the presence of pyridine *N*-oxide derivatives such as 4-methoxypyridine *N*-oxide (MPO). It is noteworthy that 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



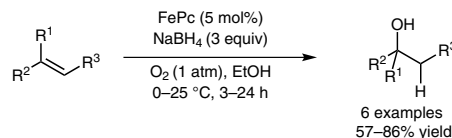
(E) Beller and co-workers reported the first iron-catalyzed synthesis of oximes from olefins. The treatment of substituted styrenes with *tert*-butyl nitrite and NaBH₄ in the presence of FePc affords oximes in moderate to high yields.⁶



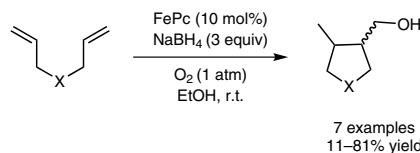
(F) Iron tetrasulfophthalocyanine (FePcS) catalyzes the reduction of nitrite (NO₂⁻) by dithionite or sulfoxylate in aqueous alkaline solution. Interestingly, different products can be obtained depending on the choice of the reductant. Using dithionite, NO₂⁻ is reduced to N₂O, while the use of sulfoxylate as reductant leads 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

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