

CARBENE INSERTION INTO X-H BONDS PROMOTED BY PHTHALOCYANINE COMPLEXES

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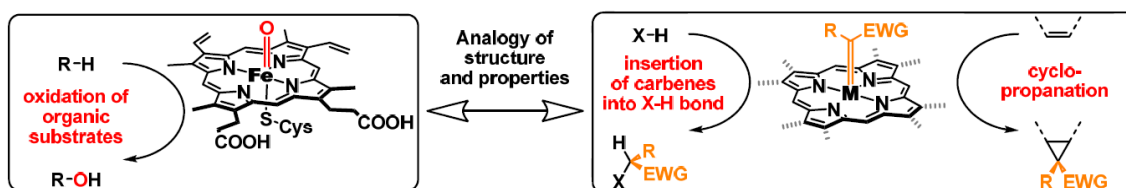
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The carbene insertion to X-H bonds ($X = N, S, C, Si \dots$) is a powerful synthetic strategy to access elaborated organic compounds. These versatile reactions rely on the use of porphyrin-based catalysts and involve carbene-metal active species [1]. Metallophthalocyanines (MPc) have been often considered as porphyrin analogues but their catalytic properties are often different from those of the porphyrin counterparts. While MPc are efficient catalysts for oxidation [2], they have been rarely explored for catalytic carbene transfer reactions. Given the similarity of oxidizing oxo species with isoelectronic carbene intermediates and the high efficiency of phthalocyanine complexes in oxidation, MPc deserve a more careful evaluation in the carbene transfer reactions.



Herein, we show a particular efficiency of Fe and Ru mono- and binuclear phthalocyanine complexes in the carbene transfer to N-H bonds of amines and cyclopropanation of olefins [3]. These catalysts demonstrate a large substrate scope, in particular, in the carbene N-H insertion with 80-100 % yields under practical reaction conditions (0.05 mol% catalyst loading, high amine concentration, 1.1 eq. of carbene precursor). The mechanistic background of particular reactivity of MPc as well as the relationship between the MPc structure and the catalytic activity in carbene transfer reactions will be discussed in details.

[1] (a) Damiano, C.; Sonzini, P.; Gallo, E. *Chem. Soc. Rev.* **2020**, *49*, 4867-4905; (b) Yang, Y.; Arnold, F. *H. Acc. Chem. Res.* **2021**, *54*, 1209-1225.

[2] (a) Sorokin, A.B. *Chem. Rev.* **2013**, *113*, 8152-8191; (b) Afanasiev, P.; Sorokin, A.B. *Acc. Chem. Res.* **2016**, *49*, 583-593.

[3] (a) Kroitor, A.P.; Dmitrienko, A.A.; Martynov, A.G.; Gorbunova, Yu.G.; Sorokin, A.B. *Org. Biomol. Chem.* **2023**, *21*, 69-74; (b) Cailler, L.P.; Kroitor, A.P.; Martynov, A.G.; Gorbunova, Yu.G.; Sorokin, A.B. *Dalton Trans.* **2021**, *50*, 2033-2031; (c) Cailler, L.P.; Clémancey, M.; Barilone, J.; Maldivi, P.; Latour, J.-M.; Sorokin, A.B. *Inorg. Chem.* **2020**, *59*, 1104-1116; (d) Cailler, L.P.; Martynov, A.G.; Gorbunova, Yu.G.; Tsivadze, A.Yu.; Sorokin, A.B. *J. Porphyrins Phthalocyanines* **2019**, *23*, 497-506; (e) Cailler, L.P.; Martynov, A.G.; Gorbunova, Yu.G.; Tsivadze, A.Yu.; Sorokin, A.B. *Dalton Trans.* **2017**, *46*, 15651-1565