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Cyclopropanation of alkenes catalyzed by metallophthalocyanines

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Abstract

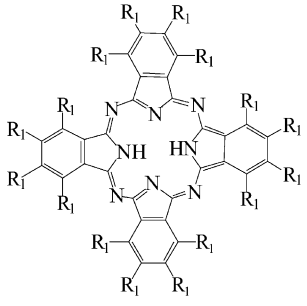
Metallophthalocyanines bearing substituents especially electron-withdrawing substituents are found to be efficient catalysts for cyclopropanation of alkenes with EDA. The influences of reaction conditions have been studied, leading to the highest yield of 91% for styrene by using fluoro-substituted ruthenium–phthalocyanine complex.

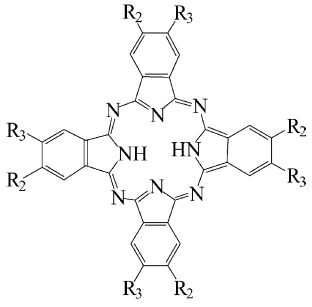
Keywords: Cyclopropanation; Metallophthalocyanine; Catalyst; Fluoro-substituted

1. Introduction

Transition metal complex-mediated cyclopropanation of alkenes with diazo compounds is one of the most attractive methods for the efficient and selective construction of synthetically and biologically important cyclopropanes [1]. Among the wide variety of catalytic systems [2], metalloporphyrin based catalysts are studied in detail owing to their excellent selectivity and highly catalytic activities, along with biological relevance [3]. Rhodium porphyrin complex was firstly introduced into this capacity by Callot et al. [4], and was later significantly explored by Kodadek [5], Woo and co-workers [6]. The central metal ions were then expanded to osmium, iron, ruthenium and others [7]. Meanwhile, asymmetric cylopropanation and mechanism were disclosed by Goss et al. [8–11].

On the other hand, metallophthalocyanines have attracted a great deal of research interests for many years because of their intense coloration and diverse redox chemistry associated with both 18π-electron system of the phthalocyanine ring and central atom [12], which are structurally similar to metalloporphyrins [13]. Moreover, Pc complexes are easier accessible, more stable to degradation than porphyrin analogues. However, low solubility of Pc complex in common organic solvents retards its application in catalysis. In continuation to our studies on transition metal catalyzed synthetic transformation and recent progress in oxidation catalyzed by metallophthalocyanines [14], herein is reported the first example of catalytic cyclopropanation of olefins by modified phthalocyanine complexes.





1: R_1 = H
2: R_1 = Cl
3: R_1 = F

4: R_2 = H or *t*-Bu, R_3 = H or *t*-Bu
5: R_2 = H or *m*-O-C_6H_4-CF_3
R_3 = *m*-O-C_6H_4-CF_3 or H

2. Experimental

2.1. Materials and instruments

All chemicals were purchased from Aldrich or Lancaster and used as received unless otherwise noted. Solvents and substrates were purified by standard procedures before use. All the phthalocyanine complexes were prepared according to the methods

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described in the literature [15–19]. Among them, **5**-FeCl and **5**-Cu have never been reported [20].

^{1}H NMR spectra were measured on a Bruker DPX300 spectrometer by using tetramethylsilane (TMS) as an internal standard, the chemical shifts are relative to TMS. Infrared spectra (KBr) were recorded on NEXUS-670 FT-IR spectrometer. Elemental analyses were performed on a Carlo Erba 1106 instrument. GC measurements were carried out on a HP model 5890 series II chromatograph equipped with a flame ionization detector. Mass spectra were recorded on a Finnigan MAT 95 Mass spectrometer.

2.2. Preparation of *5*-FeCl and *5*-Cu

4-(3-Trifluoromethylphenoxy)-phthalonitrile (0.2 g, 0.7 mmol), 1-pentanal (5 mmol) and DBU (0.3 mL) were mixed and stirred at 50 °C for 10 min in an argon atmosphere and then 0.018 g (0.015 mmol) of anhydrous iron chloride was added. The suspension was slowly brought to boiling over 2 h followed by refluxing for 40 h. The reactant was cooled down and 10 mL of methanol was added. The deep green product was filtered, washed with hydrochloric acid (5%, 30 mL) and then small amount of methanol (ca. 10 mL). The crude product was extracted with methanol in a Soxhlet extractor and purified by column chromatography (silica gel and toluene). The blue fraction was collected, evaporated under vacuum to give deep blue powder. Yield: 0.18 g (62%). IR (cm^{-1}): 1614, 1598, 1491, 1457, 1414 (C–F), 1330 (C–F), 1288, 1240 (Ar–O–Ar), 1158, 1066, 960, 895, 792, 654. MS (FAB): 1244 ($M^{+\bullet}$), 1209 (*M*–Cl). Anal calculated for $C_{60}H_{28}N_8O_4ClF_{12}Fe$: C, 50.58; H, 1.97; N, 7.87. Found: C, 50.15; H, 1.92; N, 7.48.

5-Cu was prepared according to the method described as **5**-FeCl except that $CuCl_2$ was used instead of $FeCl_3$ to give deep green solid. Yield: 0.15 g (57%). IR (cm^{-1}): 1620, 1594, 1491, 1457, 1414 (C–F), 1320 (C–F), 1288, 1228 (Ar–O–Ar), 1162, 1064, 960, 888, 750, 652. MS (FAB): 1217($M^{+\bullet}$). Anal calculated for $C_{60}H_{28}N_8O_4F_{12}Cu$: C, 59.21; H, 2.30; N, 9.21. Found: C, 58.82; H, 2.43; N, 8.89.

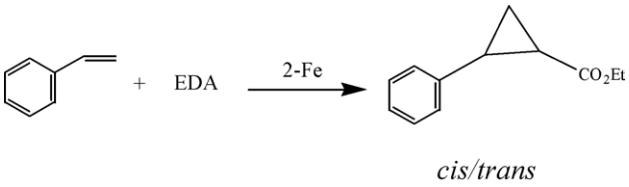
2.3. General procedure for catalytic cyclopropanation of alkenes

In a typical procedure of catalytic cyclopropanation: a solution of EDA (1.5 mmol) in dichloromethane (5 mL) was added slowly to a solution of olefine (1 mmol) and metallophthalocyanine (2 μmol) in dichloromethane (5 mL) over 2 h at room temperature under argon. The mixture was then stirred for an additional 2 h. After removal of the catalysts by flash chromatography on a short column of silica gel, the results were determined by GC.

3. Results and discussion

3.1. Optimization of reaction conditions

The influences of reaction conditions such as temperature, solvents and amount of catalyst used were optimized by using



Scheme 1.

2-Fe as catalyst shown in Scheme 1, and the results were listed in Table 1.

As shown in Table 1, running the reactions in various solvents, disclosed of either yield or *trans*:*cis* selectivity a dependence on the nature of them. In normal organic solvents, *trans* configuration products predominated over *cis* with the highest ratio of 6:1 in methanol and the lowest yield as 23% (entry 3). In ion liquid, on the contrary, the main product was in *cis* configuration (entry 5). Among the solvents examined, aprotic solvent dichloromethane is superior to others with 78% yield.

For the reaction temperature, lower temperature than 25 °C decreased reaction rate, while yields remained almost the same (entries 1, 6 and 7). When the temperature increased from 25 to 40 °C, yield decreased significantly from 78 to 39%, which is different from recently reported results of Cu-Pc catalysis in xylene [21].

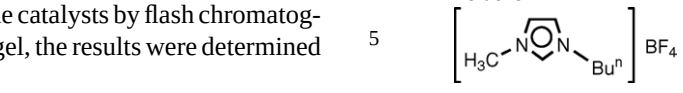
The effect of the amount of catalyst used was also studied, when 0.1, 0.2, 1 or 2% catalyst was used, cyclopropane could be obtained in the yields of 56, 78, 80 or 80%, respectively. The *trans*:*cis* selectivity varied slightly from 2.2 to 2.5. The results suggested that more catalyst used than 0.2% was not necessary.

From the results obtained, the reaction conditions were optimized to be dichloromethane as solvent, 25 °C as reaction temperature and 0.2% catalyst was used for further studies.

3.2. Cyclopropanation of styrene catalyzed by different metallophthalocyanines

As usual, the catalytic activity of Pc complexes is strongly dependent upon both central metal and ligands. In our research,

Table 1
Influences of reaction conditions[a]

Entry	Condition	Yield (%)[b]	Conversion (%)	*Trans*:*cis*[b]
1	25 °C, CH_2Cl_2	78	51	2.4
2	CH_3CN	40	69	1.9
3	CH_3OH	23	63	6.0
4	Toluene	63	72	3.0
5		52	95	0.67
6	CH_2Cl_2, −25 °C[c]	80	46	2.0
7	0 °C[d]	76	58	2.1
8	40 °C	39	39	2.6

[a] Reactions were performed with a cat.:styrene:EDA molar ratio of 1:500:750, for 4 h at room temperature.
[b] Determined by GC (column: SE-30).
[c] 10 h was needed for the completion of reaction.
[d] 6 h was needed for the completion of reaction.

15 different phthalocyanine complexes including five different Pc ligands were applied for the catalytic cyclopropanation of styrene, and the results were listed in Table 2.

In general, time course experiments for reaction catalyzed by metallophthalocyanines revealed that the reaction proceeded smoothly without an induction period. As shown in Table 2, Fe, Cu and Ru complexes exhibited high catalytic abilities with moderate yields from 59 to 75% when the same ligand of non-substituted phthalocyanine was used, while only small amount of product was obtained by using Ni or Mn complexes (entries 1–5). Aroused from the literature that solubility of metallophthalocyanine was an important factor during catalysis, we modified metallophthalocyanines with substituents. Indeed, substituted ligand especially with electron-withdrawing groups benefited to the reactions and the highest yields as 91 and 90% could be obtained with **3**-Ru and **5**-FeCl as homogeneous catalysts, respectively (entries 12 and 14), which were much higher than the yields of 71 or 77% by Rh or Ru porphyrinato analogues.

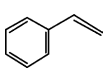
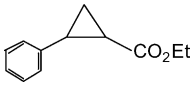
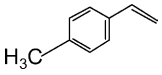
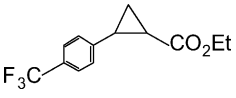
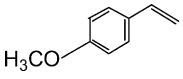
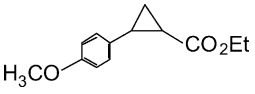
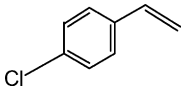
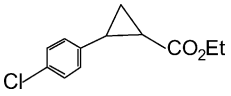
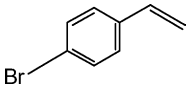
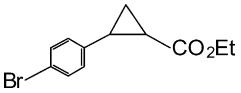
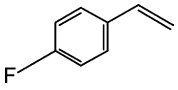
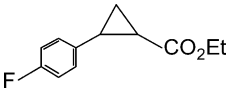
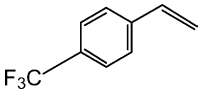
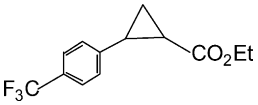
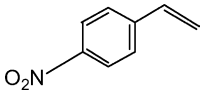
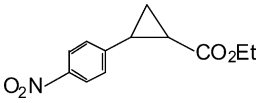
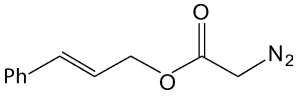
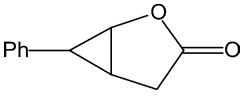
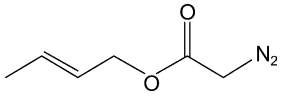
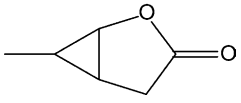
Thus, the excellent yields indicated **3**-Ru and **5**-FeCl to be highly robust toward catalytic cyclopropanation reactions.

Table 2
Cyclopropanation of olefins with EDA using different metallophthalocyanine as catalysts

Entry	Cat.	Yield (%)	Conversion (%)	*Trans*:*cis*
1	**1**-Fe(III)Cl	62	51	2.4
2	**1**-Mn(II)	4	90	1.6
3	**1**-Ni(II)	8	88	1.5
4	**1**-Cu(II)	59	68	1.2
5	**1**-Ru(III)Cl	75	79	1.9
6	**2**-Fe(II)	78	75	2.1
7	**2**-Mn(II)	13	95	1.5
8	**2**-Ni(II)	12	64	1.8
9	**2**-Cu(II)	55	70	1.5
10	**3**-Fe(III)Cl	89	76	5.0
11	**3**-Cu(II)	86	68	2.8
12	**3**-Ru(II)	91	88	3.2
13	**4**-Fe(II)	80	73	2.8
14	**5**-Fe(III)Cl	90	99	2.0
15	**5**-Cu(II)	65	89	4.5

Reactions were performed in CH_2Cl_2 at room temperature for 4 h with a cat.:styrene:EDA molar ratio of 1:500:750.

Table 3
Catalytic cyclopropanation by **3**-Ru

Entry	Substrate	Product	Yield (%)	*Trans*:*cis*
1			91	3.2
2			90	5.2
3			88	4.8
4			88	5.3
5			82	5.8
6			86	4.5
7			81	4.0
8			83	5.0
9			67	–
10			62	–

Because of the simpler procedure of preparation, **3**-Ru was selected for other substrates.

3.3. Catalytic cyclopropanation of other substrates

Catalytic cyclopropanation of other substrates was investigated under the optimized reaction conditions by using **3**-Ru as catalyst. The predominant products detected were exclusively the respective cyclopropanes as depicted in Table 3. Differently from the reported ruthenium poprhyrin complex, which benefited to the electron rich styrene with 98% yield while only 65% for 4-Cl-styrene, **3**-Ru catalyzed styrenes without obvious changes in yields changing from 81 to 91%. And the highest yield of 91% was obtained for styrene.

Intramolecular cyclopropanation has also been examined by using allylic diazoacetates in moderate yields (entries 8 and 9).

4. Conclusion

Metallophthalocyanines were found to be efficient catalysts for the cyclopropanation of a variety of alkenes. Substituted especially electron-withdrawing substituted phthalocyanine complexes exhibited excellent catalytic abilities. The highest yield of 91% for styrene was obtained by using fluoro-substituted ruthenium–phthalocyanine complex.

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