JOC*Note*

Asymmetric Cyclopropanation of Styrenes Catalyzed by Metal Complexes of D_2-Symmetrical Chiral Porphyrin: Superiority of Cobalt over Iron

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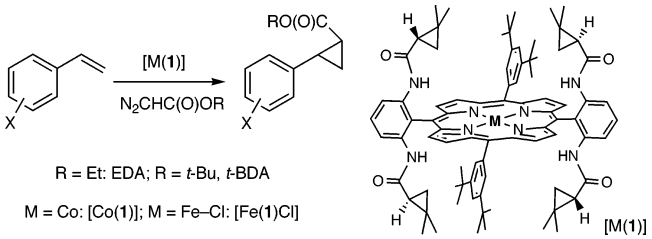
Received May 10, 2007



The cobalt(II) complex of D_2-symmetric chiral porphyrin [Co(**1**)] is an effective catalyst for highly diastereoselective and enantioselective cyclopropanation of a broad range of styrene derivatives under mild conditions. Dimerization of diazo compounds, a common side reaction in metal-mediated carbene transfer processes, is minimized in a cobalt porphyrin-based system, obviating the need to employ excess substrates and slow addition of diazo compounds. The high catalytic activity and selectivity of [Co(**1**)] evidently resulted from the appropriate combination of the cobalt ion and the chiral porphyrin **1** as the use of iron(III) complex of the same ligand [Fe(**1**)Cl] afforded the desired cyclopropane products in low yields and poor enantioselectivity.

Owing to its fundamental and practical importance, transition metal complex-catalyzed cyclopropanation of alkenes has attracted enormous research interest.[1] A number of chiral metal complexes have been developed as effective catalysts for catalyzing asymmetric cyclopropanation, using diazo reagents as carbene sources, with high to excellent enantioselectivity.[2] Despite these considerable advances, several important issues associated with practicality and selectivity of the catalytic process remain to be fully addressed to further expand practical applications of asymmetric cyclopropanation. Of the various combinations of metal ions and supporting ligands,[1] only a limited number of catalytic systems can effectively cyclopropanate alkenes under conditions that are practically desirable: with alkenes as the limiting reagents and without slow addition of diazo reagents while still affording high diastereoselectivity as well as high enantioselectivity.[2]

Inspired by the extraordinary catalytic capabilities of heme-containing enzymes in nature, metalloporphyrins have been recognized as an important class of synthetic catalysts for oxo and related atom/group transfer reactions on account of their unique ligand environment and metal coordination mode.[3] While porphyrin complexes of several Group 8B metals such as Rh, Fe, Ru, and Os have been previously known to catalyze cyclopropanation,[4−6] it was only very recently that we[7] and others[8] revealed the catalytic capability of porphyrin complexes of Co ([Co(Por)]) for cyclopropanation and related carbene transfer processes.[9,10] More importantly, we have shown that [Co(Por)]-based asymmetric cyclopropanation could be operated effectively in a one-pot fashion with alkenes as limiting regents and did not require the slow addition of diazo reagents,[7e−i] a practical protocol that is atypical for previously reported catalytic systems. Furthermore, supported by a new family of D_2-

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10.1021/jo070997p CCC: $37.00 © 2007 American Chemical Society
Published on Web 06/23/2007

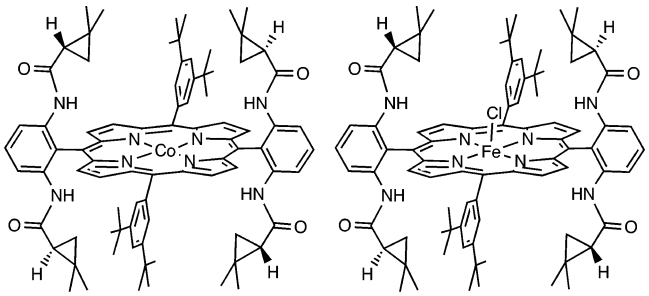


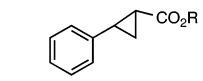
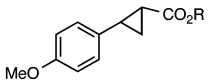
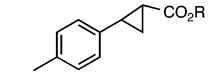
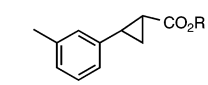
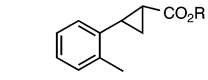
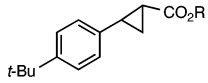
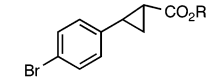
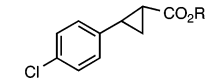
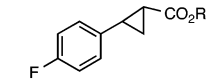
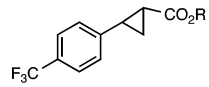
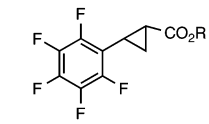
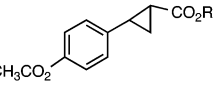
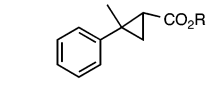
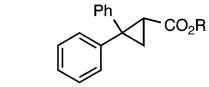
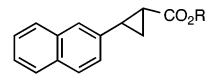
FIGURE 1. Structure of cobalt(II) and Fe(III) complexes of D_2-symmetric chiral porphyrin **1**: [Co(**1**)] and [Fe(**1**)Cl].

SCHEME 1. Cyclopropanation of Styrenes with Diazo Reagents

symmetric chiral porphyrins,[7g] which can be straightforwardly prepared from bromoporphyrin synthons via palladium-catalyzed carbon−heteroatom cross-coupling reactions,[11] it was demonstrated that the [Co(Por)]-based system can efficiently catalyze the cyclopropanation reaction in high diastereo- and enantioselectivity. In particular, under the practical one-pot conditions in the presence of a substoichiometric amount of 4-(dimethylamino)pyridine (DMAP),[7i] the cobalt complex of chiral porphyrin **1** ([Co(**1**)], Figure 1) could cyclopropanate styrene in high yields with excellent enantioselectivity (98% ee) as well as diastereoselectivity (>98% de).[7g] In addition to styrene, we report herein that [Co(**1**)] is an effective catalyst for highly diastereo- and enantioselective cyclopropanation of a broad range of styrene derivatives (Scheme 1). On the basis of comparative studies with [Fe(**1**)Cl] (Figure 1),[12] we wish to further illustrate the unique attributes of the cobalt center and its superiority over iron in metalloporphyrin-based asymmetric cyclopropanation.

To examine the substrate scope of the [Co(**1**)]-based catalytic system, cyclopropanation reactions of a series of styrene derivatives with varied electronic and steric properties were carried out, along with styrene, using both ethyl diazoacetate (EDA) and *tert*-butyl diazoacetate (*t*-BDA) as carbene sources (Table 1). Under the one-pot protocol with alkenes as the limiting reagents, the employment of 1 mol % [Co(**1**)] in the presence of 0.5 equiv of DMAP could effectively cyclopropanate styrene and its various derivatives at room temperature or lower. For example, cyclopropanation reactions of styrene (Table 1, entries 1−4) and its neutral derivatives with substituents at different positions (Table 1, entries 8−20) could be performed in high yields with excellent diastereoselectivity and enantioselectivity. Similar results were also obtained for a derivative with an electron-donating substituent (Table 1, entries 5−7). In addition, the catalytic system appeared suitable for styrene derivatives with electron-withdrawing substituents such as

TABLE 1. Diastereo- and Enantioselective Cyclopropanation of Styrenes Catalyzed by [Co(1)][a]

entry	product	R	temp (°C)	yield[b] (%)	trans:cis[c]	ee (%)[d] trans
1		Et	RT	82	97:3	78
2		Et	–20	86[e]	98:2	80
3		*t*-Bu	RT	84	>99:1	95
4		*t*-Bu	–20	85[e]	>99:1	98
5		Et	RT	82	93:7	84
6		*t*-Bu	RT	86	98:2	96
7		*t*-Bu	–20	76[e]	99:1	98
8		Et	RT	71	96:4	70
9		*t*-Bu	RT	91	99:1	94
10		*t*-Bu	–20	66[e]	>99:1	92
11		Et	RT	87[c]	97:3	79
12		Et	–20	82[e]	99:1	87
13		*t*-Bu	RT	92	99:1	94
14		*t*-Bu	–20	54[e]	99:1	98
15		Et	RT	61	97:3	79
16		*t*-Bu	RT	84	>99:1	94
17		*t*-Bu	–20	76[e]	>99:1	97
18		Et	RT	95	96:4	89
19		*t*-Bu	RT	92	99:1	93
20		*t*-Bu	–20	86[e]	>99:1	91
21		Et	RT	81	95:5	73
22		*t*-Bu	RT	92	99:1	93
23		*t*-Bu	–20	78[e]	>99:1	97
24		Et	RT	71	93:7	68
25		*t*-Bu	RT	69	98:2	91
26		*t*-Bu	–20	52[e]	98:2	96
27		Et	RT	60	93:7	72
28		*t*-Bu	RT	88	98:2	86
29		*t*-Bu	–20	29[e]	97:3	94
30		Et	RT	79	95:5	77
31		*t*-Bu	RT	64	99:1	92
32		*t*-Bu	–20	65[e]	99:1	87
33		Et	RT	49	93:7	65
34		*t*-Bu	RT	74[f]	97:3	84
35		*t*-Bu	–20	75[e,f]	99:1	90
36		Et	40	63	92:8	72
37		*t*-Bu	40	87	98:2	88
38		Et	RT	83[c]	94:6	75
39		Et	0	69[c]	96:4	82
40		Et	–20	67[e]	98:2	87
41		*t*-Bu	RT	31[c]	96:4	nr[h]
42		Et	RT	46[c]	nd[g]	nr[h]
43		Et	RT	85[f]	nd[g]	nr[h]
44		*t*-Bu	RT	10[c]	nd[g]	nr[h]
45		Et	RT	72	96:4	85
46		*t*-Bu	RT	84	99:1	95
47		*t*-Bu	–20	58[e]	99:1	98

[a] Performed in toluene for 20 h under N_2 with 1.0 equiv of alkene, 1.2 equiv of EDA or *t*-BDA, and 1 mol % [Co(**1**)] in the presence of 0.5 equiv of DMAP. [alkene]: 0.25 M. [b] Isolated yields. [c] Determined by GC. [d] Determined by chiral GC or chiral HPLC. [e] Carried out for 8 h. [f] Used 5 mol % [Co(**1**)]. [g] No diastereomers. [h] Not resolved.

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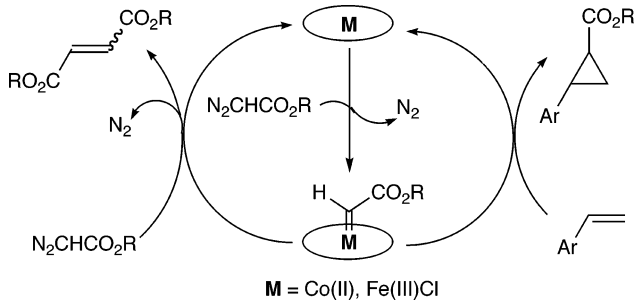
SCHEME 2. Possible Mechanism for Cyclopropanation of Alkenes and Dimerization of Diazo Reagents Catalyzed by [M(1)]

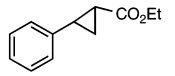
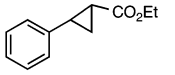
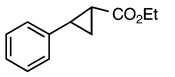
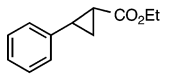
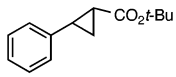
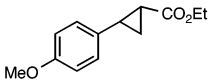
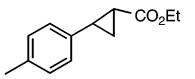
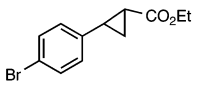
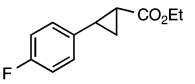
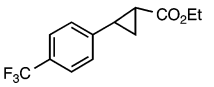


halogens and the trifluoromethyl group (Table 1, entries 21−35). Functional substituents such as the acetoxy group could be tolerated in the catalytic reaction (Table 1, entries 36 and 37). While 2-vinylnaphthalene was a suitable substrate (Table 1, entries 45−47), higher catalyst loadings were required to cyclopropanate some of the α-substituted styrenes with good yields (Table 1, entries 38−44).

It is noteworthy that even the extremely electron-deficient pentafluorostyrene could be cyclopropanated, albeit in relatively lower yields (Table 1, entries 33−35). To the best of our knowledge, these represent the first examples of the catalytic cyclopropanation of pentafluorostyrene. In most of the above cases (Table 1), corresponding *trans*-cyclopropane esters were produced with excellent diastereo- and enantioselectivity. In general, better stereoselectivities were observed with *t*-BDA than EDA and lowering the reaction temperature could further improve enantioselectivity. Although the catalytic reactions were carried out with styrenes as the limiting reagents and without slow addition of EDA or *t*-BDA, it is notable that little to no dimerization side products from the diazo reagents were observed (Scheme 2).

With the aim of understanding the origin of the practicality and selectivities associated with [Co(**1**)]-based cyclopropanation, comparative catalytic reactions using the iron(III) complex of the same chiral porphyrin **1** ([Fe(**1**)Cl], Figure 1) as the catalyst were carried out (Table 2). Under the same conditions in the presence of 0.5 equiv of DMAP, the cyclopropanation of styrene with EDA by [Fe(**1**)Cl] gave essentially no formation of the desired product (Table 2, entry 1). The same negative result was obtained even when a 10-fold excess of styrene was used (Table 2, entry 2). In both cases, however, no dimerization products were detected in the presence of DMAP. Instead, formation of white precipitates was observed in both reactions.[13] In the absence of DMAP, the desired cyclopropane was produced in a low yield with almost no asymmetric induction, albeit with good diastereoselectivity (Table 2, entry 3). The observed formation of significant amounts of side dimerization products was likely responsible for the low yield of the desired cyclopropanation products (Scheme 2). In the absence of DMAP, the use of large excess amounts of styrene reduced the formation of dimerization products, giving an improved yield of the desired product but still poor enantioselectivity (Table 2, entry 4). Similar results were obtained with *t*-BDA (Table 2, entry 5) and for styrene derivatives with different substituents, including electron-donating (Table 2, entry 6), -neutral (Table 2, entry 7), and -withdrawing (Table 2, entries 8−10) groups.

TABLE 2. Diastereo- and Enantioselective Cyclopropanation of Styrenes Catalyzed by [Fe(1)Cl][a]

entry	product	alkene :diazo	DMAP	yield[b] (%)	trans:cis[c]	ee (%)[d] trans
1		1.0:1.2	yes	01[c]	nd[e]	nd[e]
2		10:1.0	yes	03[c]	nd[e]	nd[e]
3		1.0:1.2	no	41[c]	93:7	03
4		10:1.0	no	77	92:8	04
5		10:1.0	no	63	94:6	24
6		10:1.0	no	75	91:9	15
7		10:1.0	no	72	93:7	11
8		10:1.0	no	60	93:7	20
9		10:1.0	no	64	93:7	28
10		10:1.0	no	35	92:8	11

[a] Performed in toluene for 20 h at rt under N_2 with 1 mol % [Fe(**1**)Cl]. [b] Isolated yields. [c] Determined by GC. [d] Determined by chiral GC or chiral HPLC. [e] Not determined.

Control experiments in the absence of alkene substrate and DMAP showed that both [Fe(**1**)Cl] and [Co(**1**)] could lead to the dimerization of EDA (data not shown). But [Fe(**1**)Cl] catalyzed the dimerization process much more efficiently than [Co(**1**)]. Additionally, it was found that addition of DMAP stalled the [Fe(**1**)Cl]-catalyzed dimerization process as a result of the formation of white precipitates,[13] which were also observed in the presence of the alkene substrate (Table 2, entries 1 and 2). Importantly, the limited catalytic activity of [Co(**1**)] toward EDA dimerization was completely inhibited with the addition of DMAP without formation of other observable products such as the white precipitates.[13] While significant amounts of dimerization of diazo reagents occurred in [Fe(**1**)-Cl]-catalyzed reactions even with the use of excess amounts of the alkene substrates (Table 2), no dimer formation was observed in [Co(**1**)]-catalyzed cyclopropanation of styrenes regardless of the presence or absence of DMAP (Table 1).[7e−i] Together with the results from the above catalytic reactions (Tables 1 and 2), these control experiments illustrate the distinctive capability of cobalt in discriminating the desired cyclopropanation from the undesired dimerization, two competitive processes that are

(13) Preliminary NMR data suggest the white precipitates consisted of a mixture of two related compounds that contain both DMAP and ethyl acetate units, presumably resulting from carbene transfer from the iron center to DMAP. In the absence of either DMAP or EDA, no white precipitates were observed.

presumably catalyzed by the same metalloporphyrin carbene intermediate (Scheme 2).

In summary, we have shown [Co(**1**)] is an effective catalyst for highly diastereoselective and enantioselective cyclopropanation of a broad range of styrene derivatives under the one-pot practical protocol with alkene substrates as the limiting reagents and without slow addition of diazo reagents. Through comparative studies, we have demonstrated the unique characteristics of cobalt and its superiority over iron in metalloporphyrin-catalyzed asymmetric cyclopropanation. We are currently working to expand the scope of the [Co(**1**)]-based catalytic system to include non-styrene substrates. Continuing efforts are underway to further understand the origin of the practicality and selectivity associated with [Co(**1**)]-catalyzed asymmetric cyclopropanation.

Experimental Section

Synthesis of Free-Base Chiral Porphyrin 1.[7g] 5,15-Bis(2,6-dibromophenyl)-10,20-bis[3,5-di(*tert*-butyl)phenyl]porphyrin (0.231 g, 0.2 mmol), (*S*)-(+)-2,2-dimethylcyclopropanecarboxamide (0.362 g, 3.2 mmol), $Pd(OAc)_2$ (0.018 g, 0.08 mmol), Xantphos (0.093 g, 0.16 mmol), and Cs_2CO_3 (1.045 g, 3.2 mmol) were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and THF (4 mL) was added via syringe. The tube was purged with nitrogen for 2 min, and then the septum was replaced with the Teflon screwcap. The tube was sealed, and its contents were heated with stirring. The reaction was conducted at 100 °C for 48 h. The resulting mixture was cooled to room temperature, taken up in ethyl acetate, and concentrated in vacuo. The crude product was then purified by flash chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as purple solids (0.217 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (d, J = 4.8 Hz, 4H), 8.87 (d, J = 4.8 Hz, 4H), 8.44 (br, 4H), 8.04 (d, J = 1.5 Hz, 4H), 7.83 (m, 4H), 6.50 (br, 4H), 1.53 (s, 36H), 0.87 (s, 12H), 0.69 (br, 4H), −0.05−0.14 (m, 20H), −2.34 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 149.3, 139.8, 139.2, 133.6, 130.3, 129.8, 122.7, 121.8, 117.4, 35.0, 31.7, 29.0, 26.3, 22.3, 20.2, 18.3. UV−vis (CH_2Cl_2), λ_{max} nm (log ϵ) 422 (5.46), 517 (4.17), 552 (3.77), 591 (3.66), 646 (3.53). HRMS-EI ($[M]^+$) calcd for $C_{84}H_{98}N_8O_4$ 1282.7711, found 1282.7715 with an isotope distribution pattern that is the same as the calculated one.

Synthesis of Chiral Cobalt Porphyrin [Co(1)].[7g] Free base chiral porphyrin **1** (0.100 g) and anhydrous $CoCl_2$ (0.080 g) were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and 2,6-lutidine (0.027 mL) and dry THF (5 mL) were added via syringe. The tube was purged with nitrogen for 2 min, and then the septum was replaced with the Teflon screwcap. The tube was sealed, and its contents were heated with stirring. The reaction mixture was heated at 70 °C for 9 h. The resulting mixture was cooled to room temperature, taken up in ethyl acetate, and transferred to a separatory funnel. The mixture was washed with water 3 times and concentrated in vacuo. The pure compound was obtained after flash column chromatography (silica gel, ethyl acetate:hexanes (v/v) 1:4) as a red solid (0.099 g, 91%). UV−vis (CH_2Cl_2), λ_{max} nm (log ϵ) 414 (5.37), 529 (4.14), 549 (3.84). HRMS-EI ($[M]^+$) calcd for $C_{84}H_{96}CoN_8O_4$ 1339.6887, found 1339.6909 with an isotope distribution pattern that is the same as the calculated one.

Synthesis of Chiral Iron Porphyrin [Fe(1)Cl]. Free base chiral porphyrin (0.043 g) and anhydrous $FeCl_2$ (0.030 g) were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and 2,6-lutidine (0.020 mL) and dry DMF (4 mL) were added via syringe. The tube was purged with nitrogen for 2 min, and then the septum was replaced with the Teflon screwcap. The tube was sealed, and its contents were heated at 160 °C with stirring. The resulting mixture was cooled to room temperature, taken up in CH_2Cl_2, and transferred to a separatory funnel. The mixture was washed with 0.1 M HCl, then washed with water 3 times and concentrated in vacuo. The pure compound was obtained as a red solid (0.043 g, 93%). UV−vis (CH_2Cl_2), λ_{max} nm (log ϵ) 419 (5.34), 508 (4.36), 580 (4.08). HRMS-EI ($[M]^+$) calcd for $C_{84}H_{96}ClFeN_8O_4$ 1371.6592, found 1371.6650.

Representative Procedure for Cyclopropanation Reactions. Catalyst (1 mol %) and DMAP (50 mol %) were placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and toluene (0.5 mL) and 1.0 equiv of styrene (0.25 mmol) were added via syringe, followed by 1.2 equiv of diazo compound and toluene again (0.5 mL). The tube was purged with nitrogen for 1 min and its contents were stirred at room temperature. After the reaction finished, the resulting mixture was concentrated and the residue was purified by flash silica gel chromatography to give the product. See the Supporting Information for all characterizations.

Acknowledgment. We are grateful for financial support of this work from the University of Tennessee and the University of South Florida for Startup Funds, the American Chemical Society for a PRF-AC grant, and the National Science Foundation for a CAREER Award. Funding for the USF Department of Chemistry Mass Spectrometry Facility has been furnished in part by the NSF (CRIF:MU-0443611).

Supporting Information Available: Analytical data and NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070997P