Asymmetric Cyclopropanation of Olefins Catalyzed by Chiral Cobalt(II)-Binaphthyl Porphyrins

Simone Fantauzzi,[†] Emma Gallo,*[,†] Eric Rose,*[,‡] Nicolas Raoul,[‡] Alessandro Caselli,[†] Samar Issa,[‡] Fabio Ragaini,[†] and Sergio Cenini[†]

Dipartimento di Chimica Inorganica, Metallorganica e Analitica "Lamberto Malatesta", Università di Milano, and ISTM-CNR, Via Venezian 21, 20133 Milano, Italy, and Laboratoire de Chimie Organique, Equipe Synthèse Organique et Organométallique, Case 181, CNRS UMR 7611, UPMC Univ Paris 06, Tour 44, 1er étage, 4 Place Jussieu, F-75005, Paris, France

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Cobalt(II) complexes of chiral bis-binaphthyl porphyrins were prepared, and their catalytic activity in the asymmetric cyclopropanation of alkenes with ethyl diazoacetate was examined. Good yields and enantioselectivities (up to 90% ee) were observed with *cis/trans* ratios reaching 11:89. UV−vis and ^{1}H NMR studies suggest that the axial nitrogen ligand *N*-methylimidazole could play a role in changing the enantioselectivity of the reaction.

Introduction

Three-membered ring compounds such as cyclopropanes are important building blocks for organic chemistry, and outstanding work has been devoted to the development of catalytic enantio- and diastereoselective olefin cyclopropanation[1] since the first report[2] of chiral induction in cyclopropanation. Up to now, a great number of active catalysts such as Cu(I)/Cu(II)-bis(oxazolidine),[3a,b] Cu(II)-semicorrin complexes,[3c] Pybox-Ru(II)[3d,e] complexes, Co(II)/Co(III)-Schiff bases,[3f,g] *vic*-dioximatocobalt(II),[3h] and Fe(II)/Fe(III) complexes[3i] have been developed, and very good stereo- and enantioselectivities have been achieved.

Metal porphyrin complexes[4] are fascinating molecules, which allow the exploration of the influence of the metal and of the substituents on the porphyrin ring on the outcome of catalytic reactions. Moreover, it should be noted that the robustness of this class of complexes allows excellent turnover numbers to be achieved with metalloporphyrin-based catalysts. Porphyrin complexes of iron,[5a] ruthenium,[5b,c] osmium,[5d,e] and rhodium[5f,g] are well known to catalyze cyclopropanation, and in several cases enantiomeric versions have been reported.[5h]

In spite of the very good catalytic results reported for the use of cobalt−Schiff base complexes in cyclopropanation reactions,[3c,6] other catalytic systems can be valuable, and recently Zhang et al.[7] and some of us[8] have demonstrated the potential of cobalt porphyrin complexes in this class of reactions. The positive catalytic effect of nitrogen promoters, such as *N*-methylimidazole (NMI),[9] on diastereo- and enantioselectivity and the rate of cyclopropanation reactions catalyzed by cobalt complexes has been demonstrated. Moreover, Yamada et al. have reported a theoretical analysis of the axial donor ligand effects in 3-oxobutylideneaminato-cobalt(II)-catalyzed asymmetric cyclopropanation reactions.[10] In this context, an interesting paper related to D_2-symmetrical chiral cobalt porphyrin as

* To whom correspondence should be addressed. E-mail: emma.gallo@unimi.it; eric.rose@upmc.fr.

[†] Università di Milano and ISTM-CNR.

[‡] CNRS UMR 7611, UPMC Univ Paris 06.

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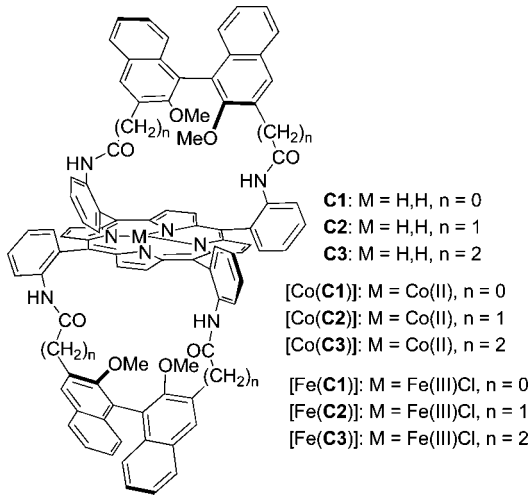


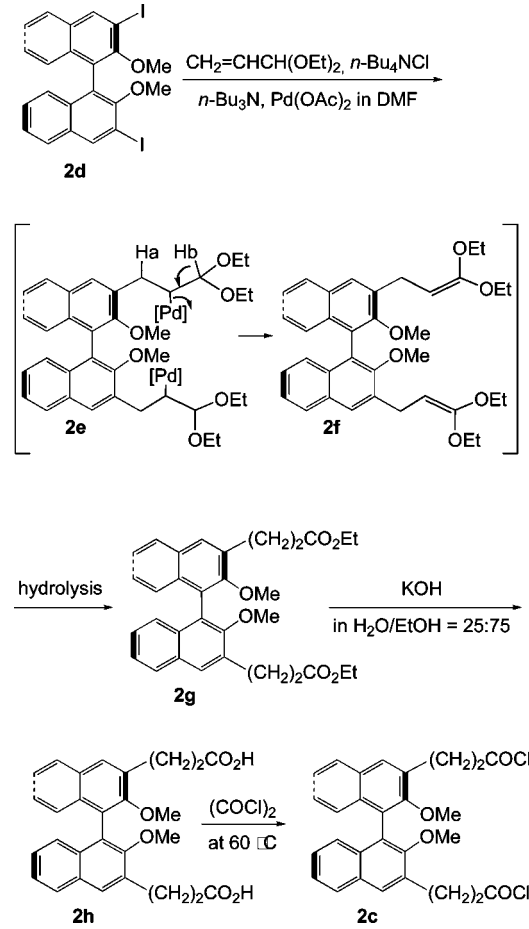
Figure 1. Binaphthyl-handled metal porphyrins.

the catalyst for asymmetric cyclopropanation[7f] prompts us to present our own results in this field.

Some of us have described the synthesis of different chiral porphyrins[11] and recently showed that binaphthyl-strapped iron porphyrins [Fe(**C1**)] and [Fe(**C2**)] (Figure 1) with a C_2 axis of symmetry are good catalysts for asymmetric epoxidation of terminal olefins.[12] Indeed good ee (>97% for the epoxidation of styrene for example) and good turnovers (rate of 2400 turnovers/h) have been obtained. The catalyst [Fe(**C1**)] appeared to be much more efficient for epoxidation than for cyclopropanation.[13]

Herein, we report the synthesis and the catalytic activity in cylopropanations of the new catalyst [Co(**C1**)] and of the homologated compound [Co(**C2**)]. We have also prepared a new, more flexible, free bis-homologated porphyrin, **C3** (Figure 1), and tested the corresponding [Co(**C3**)] complex in several catalytic reactions. The effect of NMI on reaction rate and selectivity has been investigated.

Scheme 1. Synthesis of Diacid Dichloride 2c



Results and Discussion

Synthesis of Catalysts. The porphyrins **C1**−**C3** (Figure 1) have an $\alpha\alpha\beta\beta$ geometry[4a,14] with one pseudo-C_2 axis within the porphyrin plane, which provides open space for substrate access but also steric bulk near the metal center. The main objective for the synthesis of new catalysts is to develop a flexible strategy in order to obtain different catalysts with different strap lengths that can be tested for epoxidation as well as for aziridination, amination,[15] and cyclopropanation of olefins.

For this purpose, we prepared diacid chlorides **2a**[12a] and **2b**[12b−e] and the unknown diacid chloride **2c** using palladium-catalyzed reaction[16a] of 2,2′-dimethoxy-3,3′-diiodo-1,1′-binaphthyl **2d**[16b] with acrolein diethylacetal, *n*-Bu_4NCl, *n*-Bu_3N, and $Pd(OAc)_2$ in dimethylformamide, giving the diester **2g** in 67% yield via hydrolysis of **2f**. The authors showed elegantly that β-elimination of the benzylic hydrogen H_b of intermediate **2e** is favored with respect to the other possible β-elimination of the hydrogen H_a, which would have given the corresponding conjugated aldehyde.[16a] The diester **2g** is then hydrolyzed into the diacid **2h** in a water−ethanol solution of KOH in quantitative yield. Finally the diacid dichloride **2c** is prepared immediately prior to use by quantitative reaction with oxalyl chloride at 60 °C for 12 h (Scheme 1).

The $\alpha\alpha\beta\beta$-tetrakis-(2-aminophenyl)porphyrin ($\alpha\alpha\beta\beta$-TAP-PH_2)[14] and either the diacid chloride **2a** or **2b** in tetrahydrofuran

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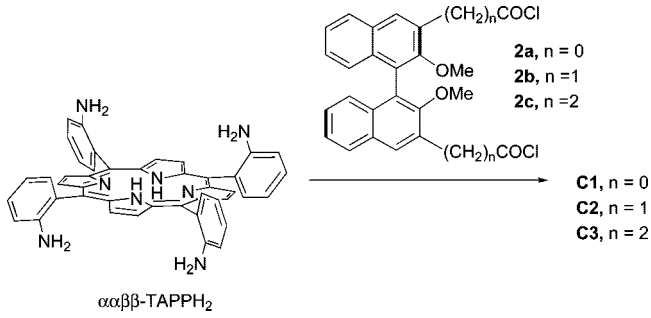
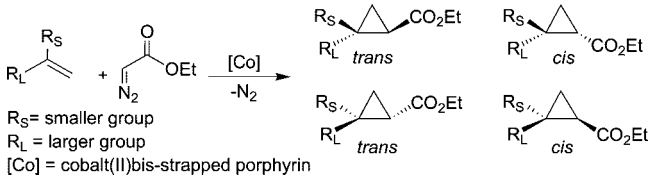
Scheme 2. Synthesis of C1, C2, and C3 Bis-strapped Porphyrins



Scheme 3. Cyclopropanation Reactions Catalyzed by Cobalt-(II) Bis-strapped Porphyrins



in the presence of *N*,*N*-diethylaniline are introduced at 0 °C with a syringe pump to give the free bis-strapped porphyrins **C1**[12a,d] and the homologated porphyrin **C2**.[12c,d] The diacid chloride **2c** and the $\alpha\alpha\beta\beta$-TAPPH$_2$ atropoisomer gave the free bis-homologated porphyrin **C3** in 22% yield (Scheme 2).

In view of the simultaneous formation of two bridges of 12 atoms in this reaction, despite the relatively low yield, the procedure gives convenient access to the desired product. Insertion of the metal with $CoCl_2 \cdot 6H_2O$ in dimethylformamide afforded the cobalt porphyrins [Co(**C1**)], [Co(**C2**)], and [Co(**C3**)] in quantitative yields.

Cyclopropanation Reactions. Cyclopropanation reactions catalyzed by cobalt(II) bis-strapped porphyrin [Co(**C3**)] were examined with EDA (ethyl diazoacetate) as the carbene source and excess olefin substrates (Co/EDA/olefin = 1:200:2000) with and without *N*-methylimidazole (NMI) as promoter (Scheme 3, Table 1).

The cyclopropanations occurred with interesting diastereoselectivity, with good enantioselectivity, and without the formation of fumarate or maleate byproduct from coupling reactions.[17]

As reported in Table 1, several olefins have been tested and the corresponding cyclopropanes were obtained in a good to excellent yields (85−99%). It should be noted that in all the cases there is a *trans*-diastereoselectivity and that the enantiomeric excess of the *cis* isomer is always larger than that of the *trans* one. Experimental data show only a very weak dependence of the reaction efficiency from the electronic/steric characteristics of groups present on the styrene skeleton. In particular, we have obtained almost indistinguishable diastereo- and enantioselectivities using styrene (Table 1, entry 1), 4-chlorostyrene (entry 10), and 4-methylstyrene (entry 13), and the same behavior was observed comparing data relative to α-methylstyrene and 4-chloro-α-methylstyrene (entries 3 and 8).

A general improvement of the stereoselectivity has been observed upon adding 20 equiv of *N*-methylimidazole as promoter, suggesting a *trans* effect of a coordinating ligand, as already reported[5b,6,7c] for similar catalytic systems (entries 2, 5, 9, 11, 14, and 17). Moreover, it can be observed that the ratio between the two diastereomers is almost the same with styrene (entry 2), α-methylstyrene (entry 5), 4-chloro-α-methylstyrene (entry 9), 4-chlorostyrene (entry 11), and 4-methylstyrene (entry 14) in the presence of NMI (20 equiv), showing that again the approach of the olefin with respect to the active site is little altered by electronic factors or by the presence of a α-methyl group. Reactions are generally slower in the presence of NMI. In order to increase the rate of the reaction, several experiments were repeated using 40 °C as reaction temperature. In general this temperature increase always leads to a marked shortening of the reaction time, but to a decrease in the ee of the *trans* cyclopropane (entries 3 vs 4, 5 vs 6, 11 vs 12, and 14 vs 15). There is not an obvious trend in *cis*/*trans* selectivity and ee of the *cis* isomer, but difference are small in most cases.

The cyclopropanation of α-methylstyrene run at RT in the presence of 20 equiv of NMI allowed the isolation of corresponding cyclopropanes with 75% and 80% ee for the *trans* and the *cis* isomer in the ratio *cis*/*trans* = 13:87 (entry 5). It should be noted that this ee is comparable to the value reported by Zhang et al. in the case of a D_2-symmetrical chiral porphyrin.[7d] Then, we repeated the reaction at 40 °C, but the slight improvement of the yield (95% instead of 90%) is coupled with a decrease of the ee (entry 6). As previously observed, NMI is responsible for longer reaction times; therefore, in an attempt to identify the best activity/selectivity conditions, the cyclopropanation of α-methylstyrene has been performed using 5 equiv of NMI instead of 20. The use of a smaller amount of NMI had only a slight positive effect on the time and enantioselectivity of the *cis*-cyclopropane of the reaction run at 40 °C (entry 7).

In order to improve the diastereo-/enantioselectivity of the cyclopropanation of α-methylstyrene, we have repeated the reaction using the experimental conditions reported in entry 5 of Table 1, replacing EDA with ^{t}BDA (*tert*-butyl diazoacetate). Unfortunately, the use of a more hindered diazo reagent did not have a positive effect[7f] and the cyclopropanation of α-methylstyrene was not observed.

It has been reported in the literature[7d] that the addition of 50 equiv of dimethylaminopyridine (DMAP) gives a strong positive effect on cyclopropanations catalyzed by chiral cobalt(II) porphyrin complexes. However, using these experimental conditions, we did not observe any cyclopropanation of α-methylsyrene. This result strongly indicates the crucial role of the nature and quantity of the axial nitrogen ligand employed (see UV−vis studies).

Finally, we have used a conjugated diene such as 2,3-dimethyl-1,3-butadiene, to explore the scope of the reaction. Cyclopropanation gave the products in 90% yield, giving the monocyclic compounds in the *cis*/*trans* ratio of 16:84 and respectively in 5% and 60% ee (entry 18). Surprisingly, the cyclopropanation of this olefin was not observed in the presence of NMI, indicating a different mechanism for nonaromatic olefins.

The reaction did not occur using an aliphatic olefin such as 1-octene as well as with very electron-deficient pentafluorostyrene or with sterically hindered *cis*-stilbene as substrates.

Next, we changed the length of the bridge of the porphyrin and used the shorter [Co(**C2**)] complex as catalyst. To examine the activity and selectivity of this catalyst, cyclopropanation reactions of selected olefins with varied electronic and steric

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Table 1. Cyclopropanation Reactions Catalyzed by Complex [Co(C3)][a]

entry	olefin	yield[b] (%)	time[c] (h)	*cis*/*trans*[d] (%)	ee *cis* (%)	ee *trans* (%)
1	styrene	92	36	27:73	60[e](1*R*,2*S*)	10[e](1*R*,2*R*)
2	styrene[f]	89	60	16:84	50[e](1*R*,2*S*)	26[e](1*R*,2*R*)
3	α-methylstyrene	95	20	27:73	76[g](1*S*,2*R*)	31[g](1*S*,2*S*)
4	α-methylstyrene[h]	98	6	33:67	80[g](1*S*,2*R*)	26[g](1*S*,2*S*)
5	α-methylstyrene[f]	90	48	13:87	80[g](1*S*,2*R*)	75[g](1*S*,2*S*)
6	α-methylstyrene[f,h]	95	12	18:82	61[g](1*S*,2*R*)	45[g](1*S*,2*S*)
7	α-methylstyrene[h,i]	96	10	28:72	71[g](1*S*,2*R*)	40[g](1*S*,2*S*)
8	4-chloro-α-methylstyrene	99	16	26:74	70[j]	23[j]
9	4-chloro-α-methylstyrene[f]	95	40	18:82	52[j]	48[j]
10	4-chlorostyrene	90	24	29:71	61[k](1*R*,2*S*)	8[l](1*R*,2*R*)
11	4-chlorostyrene[f]α	94	24	16:84	51[k](1*R*,2*S*)	38[l](1*R*,2*R*)
12	4-chlorostyrene[f,h]	99	3	14:86	58[k](1*R*,2*S*)	30[l](1*R*,2*R*)
13	4-methylstyrene	90	36	27:73	62[k](1*R*,2*S*)	10[l](1*R*,2*R*)
14	4-methylstyrene[f]	99	48	14:86	58[k](1*R*,2*S*)	38[l](1*R*,2*R*)
15	4-methylstyrene[f,h]	95	16	11:89	61[k](1*R*,2*S*)	33[l](1*R*,2*R*)
16	1,1-diphenylethylene	93	72			56[m](1*R*)
17	1,1-diphenylethylene[f]	85	48			70[m](1*R*)
18	2,3-dimethyl-1,3-butadiene	90	48	16:84	5[n]	60[n]

[a] General procedure for the reaction: [Co(**C3**)] (2.0 mg, 1.27×10^{-3} mmol) in benzene (10 mL) at RT; mol ratios [Co(**C3**)]/EDA/olefin = 1:200:2000. [b] Determined by ^{1}H NMR (2,4-dinitrotoluene as the internal standard). [c] Time required to reach complete conversion of the starting EDA. [d] Determined by ^{1}H NMR. [e] Determined by GC analysis using chiral column (Cyclodex B fused silica, 50 m × 0.25 mm, DF = 0.25 μm, isothermal at 140 °C). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[9c] data. [f] NMI (20 equiv) was added to the reaction mixture. [g] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, IB, *n*-hexane/*i*-PrOH = 99.75:0.25). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[9c] data. [h] T = 40 °C. [i] NMI (5 equiv) was added to the reaction mixture. [j] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, OD-H, *n*-hexane/*i*-PrOH = 99.5:0.5). The absolute configuration was not determined. [k] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, IB, *n*-hexane/*i*-PrOH = 99.75:0.25). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[3h] data. [l] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, OJ, *n*-hexane/*i*-PrOH = 99:1). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[3h] data. [m] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, OD-H, *n*-hexane/*i*-PrOH = 99.8:0.2). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[5c] data. [n] Determined by ^{1}H NMR using chiral shift reagent ((+)Eu(hfc)$_3$). The absolute configuration was not determineted.

Table 2. Cyclopropanation Reactions Catalyzed by Complex [Co(C2)][a]

entry	olefin	yield[b] (%)	time[c] (h)	*cis*/*trans*[d] (%)	ee *cis* (%)	ee *trans* (%)
1	styrene	96	48	25:75	57[e](1*R*,2*S*)	42[e](1*R*,2*R*)
2	styrene[f]	93	60	18:82	66[e](1*R*,2*S*)	31[e](1*R*,2*R*)
3	α-methylstyrene	94	16	28:72	39[g](1*S*,2*R*)	22[g](1*S*,2*S*)
4	α-methylstyrene[h]	90	6	25:75	37[g](1*S*,2*R*)	25[g](1*S*,2*S*)
5	α-methylstyrene[f]	85	48	34:66	90[g](1*S*,2*R*)	71[g](1*S*,2*S*)
6	α-methylstyrene[f,h]	88	14	30:70	60[g](1*S*,2*R*)	50[g](1*S*,2*S*)
7	α-methylstyrene[h,i]	90	9	28:72	52[g](1*S*,2*R*)	37[g](1*S*,2*S*)
8	4-chloro-α-methylstyrene	99	48	26:74	42[j]	46[j]
9	4-chloro-α-methylstyrene[f]	93	60	18:82	74[j]	40[j]
10	4-chlorostyrene	85	24	17:83	8[k](1*R*,2*S*)	21[l](1*R*,2*R*)
11	4-chlorostyrene[f]α	96	48	23:77	65[k](1*R*,2*S*)	32[l](1*R*,2*R*)
12	4-chlorostyrene[f,h]	98	10	26:74	65[k](1*R*,2*S*)	38[l](1*R*,2*R*)
13	1,1-diphenylethylene	93	72			22[m](1*R*)
14	1,1-diphenylethylene[f]	86	60			57[m](1*R*)
15	2,3-dimethyl-1,3-butadiene	90	24	16:84	60[n]	12[n]

[a] General procedure for the reaction: [Co(**C2**)] (2.0 mg, 1.32×10^{-3} mmol) in benzene (10 mL) at RT; mol ratios [Co(**C2**)]/EDA/olefin = 1:200:2000. [b] Determined by ^{1}H NMR (2,4-dinitrotoluene as the internal standard). [c] Time required to reach complete conversion of the starting EDA. [d] Determined by ^{1}H NMR. [e] Determined by GC analysis using chiral column (Cyclodex B fused silica, 50 m × 0.25 mm, DF = 0.25 μm, isothermal at 140 °C). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[9c] data. [f] NMI (20 equiv) was added to the reaction mixture. [g] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, IB, *n*-hexane/*i*-PrOH = 99.75:0.25). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[9c] data. [h] T = 40 °C. [i] NMI (5 equiv) was added to the reaction mixture. [j] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, OD-H, *n*-hexane/*i*-PrOH = 99.5:0.5). The absolute configuration was not determineted. [k] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, IB, *n*-hexane/*i*-PrOH = 99.75:0.25). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[3h] data. [l] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, OJ, *n*-hexane/*i*-PrOH = 99:1). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[3h] data. [m] Determined by HPLC analysis using chiral column (DAI-CEL CHIRALCEL, OD-H, *n*-hexane/*i*-PrOH = 99.8:0.2). The absolute configuration was determined by comparison of $[\alpha]_D$ with reported[5c] data. [n] Determined by ^{1}H NMR using chiral shift reagent ((+)Eu(hfc)$_3$). The absolute configuration was not determined.

properties were carried out again using ethyl diazoacetate as carbene source and alkene in excess (Table 2).

Data reported in Table 2 showed that when cyclopropanations are catalyzed by [Co(**C2**)], the effect of NMI on the diastereoselectivity is in some cases opposite that observed for the [Co(**C3**)]-catalyzed reactions (compare entries 3 with 5 and 10 with 11 of Table 1 with the same entries of Table 2). In general, the effect on reaction enantioselectivity is more noticeable when NMI is added to the reaction catalyzed by [Co(**C2**)] than by [Co(**C3**)] (Table 2, entries 3 vs 5, 8 vs 9, and 10 vs 11) even at 40 °C (entries 4 and 6). In fact, by adding 20 equiv of NMI to the cyclopropanation of α-methylstyrene (entry 5) 90% ee of the *S*,*R* diastereoisomer and 71% ee of the *S*,*S* diastereoisomer with a *cis*/*trans* ratio of 34:66 were observed. It should be noted that this 90% ee represents the best ee obtained in this work. If the reaction was performed with only 5 equiv of NMI at 40 °C, the ee of both *trans*- and *cis*-cyclopropanes diminished (entry 7), indicating again the active role of the additive. The cyclopropanation of a diene occurred with a good diastereoselectivity and acceptable enantioselectivity of the *cis*-isomer, and, as in the case of [Co(**C3**)], no reaction was observed when NMI was added to the reaction.

Table 3. ^{1}H NMR Values of C1, C2, and C3 Bis-strapped Porphyrins and Their Zinc Complexes in Different Deuterated Solvents

entry	compound	distal O*Me*[a] $CDCl_3$	distal O*Me*[a] Py-d_5	distal O*Me*[a] C_6D_6	proximal O*Me*[a] $CDCl_3$	proximal O*Me*[a] Py-d_5	proximal O*Me*[a] C_6D_6
1	**C1**	2.96	2.86	2.81	−0.65	−0.42	−0.53
2	**C2**	1.98[b]	2.37	1.81	−0.51[b]	0.47	−0.42
3	**C3**	2.41	2.18	1.92	1.81	1.69	1.63
4	[Zn(**C1**)]	2.21	3.05	2.69	−0.34	−0.60	0.03
5	[Zn(**C2**)]	2.04[b]	2.64[b]	2.05	1.97[b]	1.40[b]	1.93
6	[Zn(**C3**)]	2.32	2.60	2.09	1.90	2.15	1.81
7	[Zn(**C1**)$(NMI)_2$]			2.97			−0.24
8	[Zn(**C2**)$(NMI)_2$]			2.18			1.51
9	[Zn(**C3**)$(NMI)_2$]			2.12			1.86
10	[Fe(**C2**)]		2.21[b]			1.97[b]	

[a] δ (ppm). [b] Ref 12c.

Finally, we tried the cyclopropanation reactions of olefins with the metalloporphyrin with a very short handle [Co(**C1**)], but unfortunately, no reaction occurred.

NMR and UV−vis Studies. In order to investigate some mechanistic aspects of the reactions such as the role of the axial ligand on the selectivity of the reaction and the importance of the concentration of all the species present in the catalytic mixture, we have performed NMR and UV−vis studies.

First of all, we synthesized and spectroscopically investigated the zinc complex of the **C3** bis-strapped porphyrin, [Zn(**C3**)], which is inactive for the cyclopropanation, by the reaction of $Zn(OAc)_2$ in refluxing dimethylformamide using the same method described for the preparation of Zn(**Ci**), i = 1, 2.[12c] We decided to employ zinc complexes to perform our initial studies for two reasons: (i) the complexes are diamagnetic and the effect of a central metal on the conformation of the porphyrin ligand can be easily observed because the methoxy groups play the role of spectators of the environment and represent a fingerprint of the system; (ii) the zinc atom can coordinate two axial ligands to mimic the behavior of the cobalt atom during the catalytic reaction. Inspection of molecular models shows that the handles of porphyrins **Ci** (i = 1−3) exhibit conformations ranging from rigid to flexible depending on the nature of the axial ligand. The special conformation imparted to the handles of the metalloporphyrin can be observed by comparing the chemical shifts of the proximal OMe groups.

The ^{1}H NMR spectrum of the free **C1** porphyrin in benzene showed two methoxy groups of the binaphthyl handles (Figure 1) at 2.81 (distal OMe) and −0.53 ppm (proximal OMe) (Table 3, entry 1). For the **C2** porphyrin, the OMe groups resonated at 1.81 and −0.42 ppm in C_6D_6 (Table 3, entry 2). The ^{1}H NMR spectrum of the new free **C3** porphyrin in the same solvent showed two distal and proximal methoxy groups with chemical shifts at 1.92 and 1.63 ppm, in good agreement with the presence of a more flexible handle (Table 3, entry 3). This phenomenon is directly related to the position of these OMe groups with respect to the core of the porphyrin. A slight shift to higher frequencies, with characteristic values for an aromatic OMe group, is recorded for distal OMe groups that point outward from the tetrapyrrolic core, while proximal methoxy groups, which point toward the tetrapyrrolic core, gave the signals at lower frequencies due to the anisotropic effect of the porphyrin ring.[18]

The insertion of the zinc atom into **C3** did not produce a significant variation in the chemical shifts of the proximal OMe groups: 1.90−1.81 = 0.09 ppm in $CDCl_3$ (Table 3, entries 6 and 3). This is also true for the proximal OMe groups of [Zn(**C1**)]: −0.34 − (−0.65) = 0.31 ppm (Table 3, entries 4 and 1). However, the metalation of the free base **C2** with $Zn(OAc)_2$ caused a huge shift [1.97 − (−0.51) = 2.44 ppm in $CDCl_3$ (Table 3, entries 5 and 2)] toward higher frequencies of the proximal methoxy group.[19]

Thus, only one unexpected chemical shift of the proximal methoxy group of **C2** and [Zn(**C2**)] is observed in three solvents. How can the methoxy group of [Zn(**C2**)] be shifted to such a high frequency? *We suggest an average conformation of the binaphthyl handle away from the porphyrin plane by metalation of the free* **C2** porphyrin. However, the effects of the coordination of the *N*-methylimidazole ligand NMI by adding 20 equiv of this nitrogen ligand to the Zn complexes [Zn(**C2**)] in C_6D_6 are interesting to compare. The proximal OMe groups of the diamagnetic symmetrical [Zn(**C2**)$(NMI)_2$] derivative are shielded unexpectedly by 0.42 ppm (Table 3, entries 5 and 8) and resonate at a lower frequency at 1.51 ppm, in good agreement with a preferential conformation of the NMI ligand with respect to the proximal OMe group eclipsing the N_1 and N_3 nitrogen atoms of the porphyrin (Scheme 4, Figure 2).[20]

Obviously the same NMR study cannot be performed using cobalt(II) porphyrin complexes since the paramagnetism of the metal center prevented the full characterization of cobalt(II) complexes by NMR. However, the ^{1}H NMR spectrum of catalyst [Co(**C2**)] revealed the presence of typical paramagnetic signals[8a,21] of the pyrrolic unit at 16.4 and 15.4 ppm.

Nevertheless, we can presume that, during the cyclopropanation, the coordination of NMI to the cobalt center of the catalyst causes the same effect discussed above for Zn/NMI complexes on porphyrin binaphthyl units. According to all data reported up to now, we propose that the positive effect on the enantioselectivity of the reaction observed when the catalysis was run in the presence of NMI (Table 2) is a consequence of

(18) The magnetic inequivalences of the two OMe groups diminish with increasing length of the handle. By defining $\Delta = \delta_{(\text{distal OMe})} - \delta_{(\text{proximal OMe})}$ (see Table 3) we observed in C_6D_6: Δ = 3.34, 2.23, and 0.29, respectively, for **C1**, **C2**, and **C3**. Similarly, in $CDCl_3$ Δ = 3.61, 2.49, and 0.60 for **C1**, **C2**, and **C3**, respectively. Finally, in Py-d_5 Δ = 3.28 for **C1**, 1.90 for **C2**, and 0.49 ppm for **C3**.

(19) In C_6D_6, these shifts at higher frequencies are equal to 0.56 ppm (Table 3, entries 4 and 1) and 0.18 ppm (entries 6 and 3) for the **C1**/[Zn(**C1**)] and **C3**/[Zn(**C3**)] couples, respectively, but again equal to a large value of 2.35 ppm (entries 5 and 2) for the **C2**/[Zn(**C2**)] compounds. A similar trend in the shift of the proximal OMe groups is observed even in a coordinated solvent such as Py-d_5: 0.18 ppm (entries 4 and 1), 0.46 ppm (entries 6 and 3), and 0.93 ppm (entries 5 and 2) for the [Zn(**C1**)]/**C1**, [Zn(**C3**)]/**C3**, and [Zn(**C2**)]/**C2** couples, respectively.

(20) This is in contrast with the [Zn(**C3**)]/[Zn(**C3**)$(NMI)_2$] compounds, entries 6 and 9, Table 3, for which the chemical shifts of the proximal and distal OMe groups are almost identical. For the [Zn(**C1**)]/[Zn(**C1**)$(NMI)_2$] couple (Table 3 entries 4 and 7) the proximal OMe groups resonate respectively at 0.03 and−0.24 ppm. These data cannot be compared with those of [Zn(**Ci**)] in pyridine. In the three cases, i = 1−3, the porphyrins are diamagnetic, hexacoordinated with two axial pyridine coordinated to the zinc atom.

(21) Ragaini, F.; Penoni, A.; Gallo, E.; Tollari, S.; Gotti, C. L.; Lapadula, M.; Mangioni, E.; Cenini, S. *Chem.−Eur. J.* **2003**, *9*, 249–259.

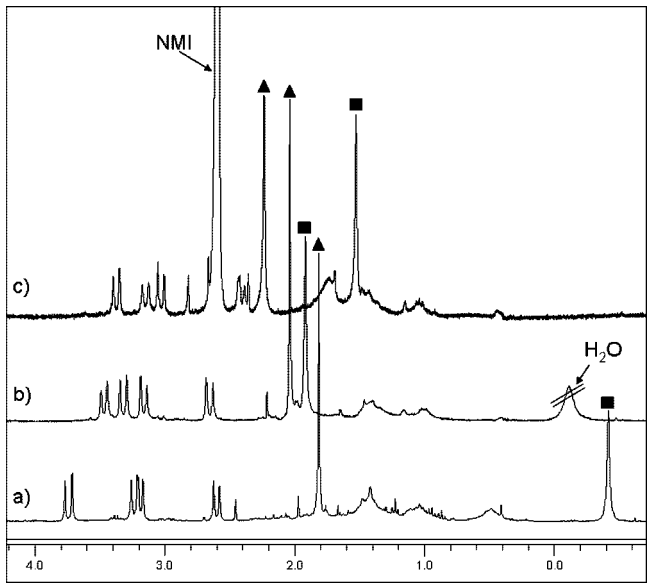
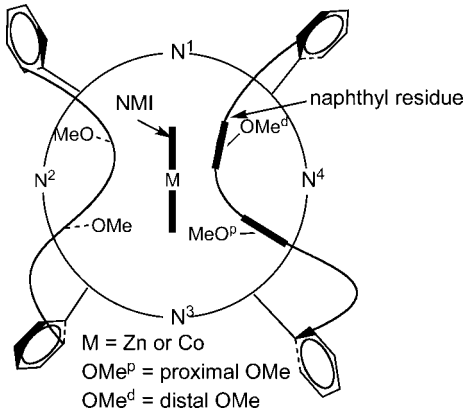


Figure 2. ^{1}H NMR spectra in C_6D_6 of (a) **C2**, (b) [Zn(**C2**)], and (c) [Zn(**C2**)$(NMI)_2$]. ■ = proximal methoxy groups. ▲ = distal methoxy groups.

Scheme 4. Proposed Conformation of the NMI Cobalt Complex

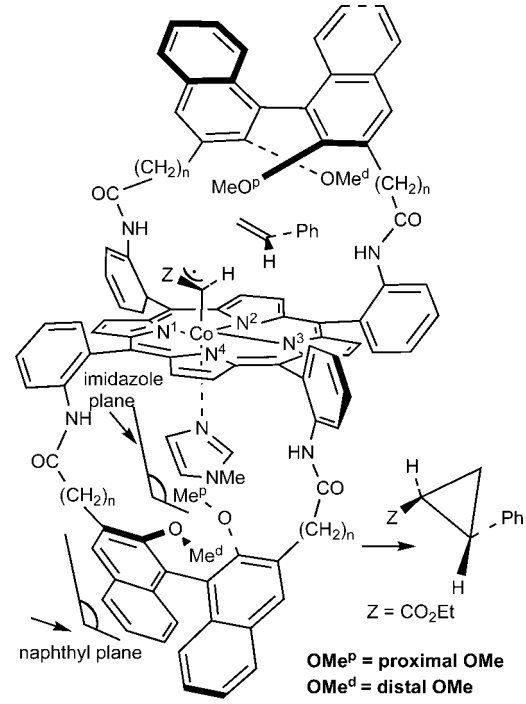


the coordination of the NMI as a ligand. The nitrogen ligand and the proximal naphthyl handle could render the whole system more efficient (Schemes 4 and 5).

We suggest a special conformation of the NMI toward the binaphthyl handle, eclipsing the N_1 and N_3 nitrogen atoms of the porphyrin, but unfortunately, up to now we cannot prove it. Indeed the imidazole ring cannot be perpendicular to the distal naphthyl residue but instead is almost parallel to it for steric and electronic reasons (Scheme 5). Thus the proximal OMe group of [Zn(**C2**)$(NMI)_2$] resonating at 1.51 ppm is probably shielded by 0.42 ppm (Table 3, entry 5 vs entry 8) by the nearby imidazole ring, whereas the proximal OMe group of [Zn(**C3**)$(NMI)_2$], less influenced by the imidazole ring and the porphyrin macrocycle, is very slightly deshielded by 0.05 ppm (Table 3, entry 6 vs entry 9).

In order to better compare zinc and cobalt complexes, we have performed a UV−vis spectroscopic study of reactions between zinc or cobalt complexes and a large excess of NMI ([M(**Ci**)]/NMI = 1:50) in benzene. All of the reactions showed isosbestic points on both Soret and Q-bands (for [Zn(**C2**)] at 432 and 559 nm, respectively; [Zn(**C3**)] at 431 and 559 nm; [Co(**C2**)] at 424 and 541 nm; [Co(**C3**)] at 427 and 543 nm), which indicates that the conversion of the starting [M($\mathbf{C_i}$)] complex (M = Zn, Co; i = 2, 3) into the corresponding [M($\mathbf{C_i}$)$(NMI)_2$] occurs without the accumulation of any long-lived intermediate (Figure 3).

Scheme 5. Suggested Role of the NMI Ligand for the Cyclopropanation



Present results suggest that the reaction of [Co(**C2**)] or [Co(**C3**)] complexes with NMI during the catalytic cycle allowed the formation of a bis-coordinated complex and that the cyclopropanation reaction can occur only after the loss of one NMI ligand. According to UV−vis data, the inhibiting effect of NMI during the catalysis can be due to the formation of a coordinatively saturated cobalt complex that is favored at high concentration of the nitrogen ligand. To prove that the coordination of NMI to the cobalt center is a reversible process, we have monitored by UV spectroscopy the reaction between [Co(**C2**)$(NMI)_2$] and EDA (20 equiv). The Soret band at 438 nm, attributed to [Co(**C2**)$(NMI)_2$], shifted to 424 nm after the addition of EDA, indicating that NMI is easily displaced by EDA to form, in the absence of olefin, a cobalt(III) complex (*vide infra*). In order to explain the observed negative effect on the catalytic activity of DMAP, we have treated [Co(**C2**)] with 6 equiv of DMAP, and then 20 equiv of EDA was added to the resulting solution. The reaction was monitored by UV spectroscopy. The Soret band was shifted from 414 to 447 nm, indicating the coordination of DMAP to the cobalt center, and then no shifts were observed after the addition of EDA. These data support the hypothesis that DMAP is a stronger ligand than NMI for [Co(**C2**)]. Therefore DMAP, rather than being a promoter in our catalytic system, is a strong inhibitor.

It should also be noted that the EDA concentration plays an important role in the catalytic efficiency of our system. In fact, when the reaction between α-methystyrene and EDA is carried out in the presence of [Co(**C2**)] and with a molar ratio Co/EDA/olefin/NMI = 1:120:100:20, as reported for other cobalt−porphyrin-catalyzed systems,[7d] no reaction was observed. We propose that, as already reported by some of us in a mechanistic study of cyclopropanation reactions catalyzed by Co(TPP) (TPP = dianion of tetraphenylporphyrin),[8a] the use of a great excess of EDA is responsible of the formation of a

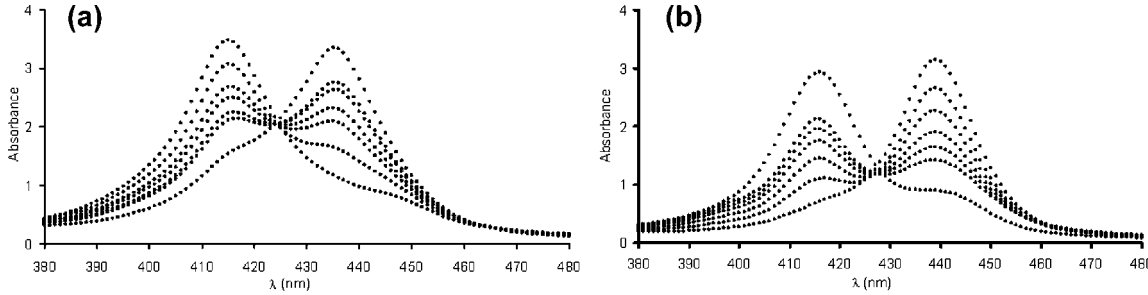
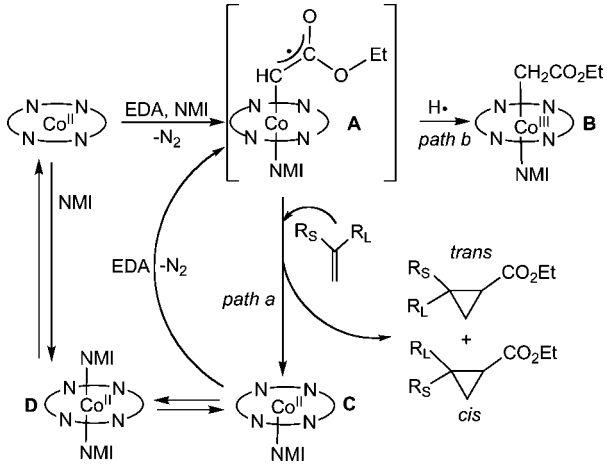


Figure 3. UV−vis spectra of the reactions [Co(**Ci**)] (a, $i = 2$; b, $i = 3$) with a molar ratio Co/NMI = 1:50.

Scheme 6. Suggested Catalytic Cycle for Cyclopropanation



catalytically inactive cobalt(III) derivative. Unfortunately, up to now any attempts to isolate in a pure form the product of the stoichiometric reaction between [Co(**C2**)] and EDA failed, but the diamagnetism of the reaction mixture and the presence of a new Soret band at 424 nm in the UV−vis spectrum indicate a chemical modification of the catalyst. It is important to emphasize that in order to avoid the deactivation of the catalytic species, the cyclopropanation reaction must be carried out with EDA as limiting agent and with an excess of the olefin.

All the data, reported up to now, are in agreement with the reaction pathway shown in Scheme 6.

We propose that the cobalt catalyst can coordinate one or two molecules of NMI,[8a,22] giving complex **C** or **D**, and the subsequent reaction of **C** with EDA yields a radical active species **A**, already proposed by Yamada on the basis of theoretical and spectroscopic studies.[10b,c] This species, depending on olefin concentration, can transfer the carbene unit to the olefin (*path a*) or can be deactivated by forming the cobalt(III) complex **B** (*path b*). The cyclopropanation of the olefin is responsible for the formation of complex **C** that re-enters in the catalytic cycle. As reported in Tables 1 and 2, catalytic reactions run in the presence of NMI are slower than those performed in the absence of any coordinating ligand. We suggest that this effect can be due to the presence of an equilibrium between complexes **C** and **D** because only the coordinatively unsaturated complex **C** can react with EDA and be catalytically active. This hypothesis is also supported by the decrease of the reaction time observed when the cyclopropanation of α-methylstyrene was performed with 5 equiv of NMI instead of 20 equiv.

(22) All mechanistic investigations were carried out using the [Co(**C2**)] complex because the *trans* effect observed using NMI with this catalyst is more evident of that caused by the addition of the nitrogen ligand to the reaction catalyzed by [Co(**C3**)].

Finally, the radical nature of the reaction mechanism is supported by the strong inhibiting effect of the addition of TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxide) to the cyclopropanation reactions of α-methylstyrene. This experimental result is in accord with those previously obtained by us while investigating the mechanism of the benzylic amination of olefins mediated by Co(porphyrin) complexes,[21] which was also shown to proceed through the formation of radical species. Moreover, to exclude that the observed inhibiting effect of TEMPO is due to its coordination to the cobalt center, a mixture of [Co(**C2**)] and 20 equiv of TEMPO in benzene was analyzed by UV spectroscopy. We did not observe any shift of [Co(**C2**)] UV absorptions after the addition of TEMPO to support the hypothesis that TEMPO does not coordinate to the cobalt center.

Conclusion

In summary, we have shown that [Co(**C2**)] and [Co(**C3**)] are effective catalysts for diastereo- and enantioselective cyclopropanation of mono- and diolefins. Data reported in the paper allow also to suggest a mechanism for this reaction in which an important role is played by the concentration of *N*-methylimidazole and ethyl diazoacetate. In particular, we suggest the formation of an intermediate rigidifying the proximal side by coordination of the NMI ligand, which is stabilized by the presence of the naphthyl residue as well as the whole system. We are currently working to expand the scope of these catalysts to other olefins and to probe further the origin of the selectivity.

Experimental Section

General Procedures. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere using Schlenk tube techniques. Benzene, tetrahydrofuran, and diethyl ether were dried over sodium benzophenone ketyl and distilled. CH_2Cl_2 was dried over calcium hydride and distilled. Infrared spectra were measured on a Perkin-Elmer 1420 spectrometer and on a Varian Scimitar FTS 1000 spectrophotometer as Nujol mulls or using Perkin-Elmer CaF_2 cells. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on Bruker AC200, 300-DRX, ARX400, or DRX500 spectrometers. Chemical shifts (ppm) are reported relative to TMS. The ^1H NMR signals of compounds described in the following have been attributed by COSY and NOESY techniques. Assignments of the resonances in ^{13}C NMR were made using the APT pulse sequence and HSQC and HMQC techniques. GC-MS analyses were performed on a Shimadzu GCMS-QP5050A instrument. GC analyses were performed on a Varian CP3380 instrument, equipped with a Cyclodex B fused silica column (50 m × 0.25 mm). HPLC analyses were performed on a Hewlett-Packard 1050 instrument. UV/vis spectra were recorded on an Agilent 8453E and on an Uvikon 923 instrument. Mass spectra were recorded in the analytical laboratories of Milano University. Elemental analyses were performed by Le Service de Microanalyses de l'Université Pierre et Marie Curie and analytical laboratories of the University of Milano.

All starting materials were commercial products and were used as received, unless otherwise reported.

Synthesis of Bis-strapped Porphyrin C3. Porphyrin **C3** was synthesized by using the same procedure reported for the preparation of the related bis-strapped porphyrin **C2**. A 500 mL two-neck, round-bottom flask equipped with a nitrogen inlet and a rubber septum was charged with 120 mL of tetrahydrofuran freshly distilled on sodium. Freshly dried *N*,*N*-diethylaniline (230 μL, 2.64 mmol) was added. In a separate flask under nitrogen α,α,*β*,*β*-tetraaminophenylporphyrin (226 mg, 0.335 mmol) and *N*,*N*-diethylaniline (115 μL, 1.32 mmol) were dissolved in 20 mL of tetrahydrofuran, and the resulting solution was transferred into two 10 mL syringes. In parallel, freshly synthesized **2c** (326 mg, 0.66 mmol) (see Supporting Information) was dissolved in 10 mL of tetrahydrofuran and charged in a third well by a dry 10 mL syringe. A syringe pump was equipped with the three syringes, and the reactants were simultaneously added in the three-necked flask over 3 h at 0 °C. Then the red solution was allowed to stir at room temperature for an additional 3 h. The solvent was then removed under vacuum, and the purple residue purified by flash chromatography on silica gel (SiO_2 15−40 μm, eluent dichloromethane). The bis-strapped porphyrin was eluted with a mixture of dichloromethane/methanol (99.5:0.5) as a red-purple compound (21.6%). Anal. Calcd for $C_{100}H_{78}N_8O_8$: C, 79.03; H, 5.17; N, 7.37. Found: C, 79.35; H, 5.32; N, 7.49. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 8.79−8.76 (m, 4H), 8.73−8.69 (m, 4H), 8.62−8.60 (m, 2H), 8.21−8.18 (m, 2H), 7.94−7.90 (m, 6H), 7.85 (s, 2H), 7.78−7.72 (m, 4H), 7.65−7.63 (m, 2H), 7.55−7.50 (m, 8H), 7.39−7.36 (m, 2H), 7.25−7.21 (m, 2H), 7.06−7.00 (m, 4H), 6.94−6.92 (m, 2H), 6.80−6.77 (m, 2H), 6.39 (s, 2H), 3.05−3.00 (m, 2H), 2.69−2.60 (m, 4H), 2.45−2.40 (m, 2H), 2.41 (s, 6H, OCH_3), 2.28−2.20 (m, 2H), 2.05−1.94 (m, 4H), 1.81 (s, 6H, OCH_3),1.53−1.46 (m, 2H), −2.67 (s, 2H, NH_{pyrr}). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 171.98 (C), 171.73 (C), 155.71 (C), 155.05 (C), 138.81 (C), 138.76 (C), 136.65 (CH), 135.68 (CH), 134.15 (C), 133.97 (C), 133.73 (C), 133.31 (C), 132.42 (C), 131.95 (C), 131.43 (CH), 131.25 (C), 131.14 (C), 130.57 (CH), 130.48 (CH), 129.65 (CH), 128.47 (CH), 128.05 (CH), 126.65 (CH), 126.45 (CH), 126.32 (CH), 125.93 (CH), 125.51 (CH), 125.17 (C), 124.41 (C), 124.08, 123.23, 115.98 (C), 115.51 (C), 59.93 (OCH_3), 59.51 (OCH_3), 38.84 (CH_2), 36.94 (CH_2), 28.46 (CH_2), 27.03 (CH_2). UV/vis (CH_2Cl_2): λ_{max}/nm (log ε_M) 424 nm (5.63), 517 (4.36), 552 (3.81), 592 (3.80), 650 (3.35). MS (MALDI-TOF): *m*/*z* 1519.7 [M^+].

Synthesis of [Zn(C3)]. To a 50 mL two-neck, round-bottom flask charged with 10 mL of dry dimethylformamide were added **C3** (30.0 mg, 19.8×10^{-2} mmol), $Zn(OAc)_2$ (18.0 mg, 82.0×10^{-2} mmol), and AcONa (10 mg, 12.2×10^{-2} mmol). The red solution was brought to reflux and stirred under nitrogen for 1 h. A UV−vis control revealed that the reaction had reached completion. Dimethylformamide was evaporated under reduced pressure, and the residue was taken up in a mixture of dichloromethane (25 mL) and water (25 mL). After separation of the two phases, the aqueous layer was extracted with dichloromethane (2 × 10 mL), and the organic layers were then collected, dried on Na_2SO_4, filtered, and evaporated to dryness, affording clean [Zn(**C3**)] without any further purification (98%). Anal. Calcd for $C_{100}H_{76}N_8O_8Zn$: C, 75.87; H, 4.84; N, 7.08. Found: C, 75.64; H, 4.52;. N, 7.23. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 8.79 (s, 4H, H_β), 8.77 (s, 4H, H_{pyrr}), 8.74−8.71 (m, 2H, H_{Ar}), 8.16−8.13 (m, 2H, H_{Ar}), 8.03−8.01 (m, 2H, H_{Ar}), 7.88−7.80 (m, 6H, H_{Ar}), 7.71−7.68 (m, 4H, H_{Ar}), 7.61−7.58 (m, 2H, H_{Ar}), 7.49−7.44 (m, 8H, H_{Ar}), 7.39−7.34 (m, 2H, H_{Ar}), 7.23−7.18 (m, 2H, H_{Ar}), 7.09−6.99 (m, 4H, H_{Ar}), 6.89−6.86 (m, 2H, H_{Ar}), 6.77−6.74 (m, 2H, H_{Ar}), 6.48 (s, 2H), 2.98−2.85 (m, 2H, CH_2), 2.65−2.52 (m, 2H, CH_2), 2.50−2.40 (m, 4H, CH_2), 2.32 (s, 6H, OCH_3), 2.09 (s, 6H, OCH_3), 2.07−1.97 (m, 2H, CH_2), 1.86−1.71 (m, 4H, CH_2), 1.35−1.22 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 171.01 (C), 170.55 (C), 154.83 (C), 154.11 (C), 151.35 (C), 150.80 (C), 151.58 (C), 150.15 (C), 138.57 (C), 138.28 (C), 135.88 (CH), 135.06 (CH), 133.58 (C), 133.36 (C), 133.24 (C), 133.14 (CH), 132.84 (CH), 132.66 (C), 132.42 (CH), 132.37 (C), 132.04 (CH), 131.45 (CH), 130.97 (C), 130,75 (C), 129.82 (CH), 129.66 (CH), 129.33 (CH), 128.13 (CH), 127.70 (CH), 126.41 (CH), 126.19 (CH), 125.83 (CH), 125.56 (CH), 125.30 (CH), 124.64 (C), 124.33 (C), 123.64 (CH), 123.35 (CH), 123.00 (CH), 121.93 (CH), 115.77 (C), 60.29 (OCH_3), 59.73 (OCH_3), 39.12 (CH_2), 36.88 (CH_2), 28.54 (CH_2), 27.87 (CH_2). UV/vis (CH_2Cl_2): λ_{max}/nm (log ε_M) 428 nm (5.25), 554 (3.93), 592 (3.07). MS (MALDI-TOF): *m*/*z* 1581.9 [M^+].

Synthesis of [Co(C3)]. Free base chiral porphyrin **C3** (20 mg, 13.2×10^{-2} mmol) and $CoCl_2 \cdot 6H_2O$ (15 mg, 63.0×10^{-2} mmol) were dissolved under an inert atmosphere in dried dimethylformamide (10 mL). The resulting mixture was degassed, placed under nitrogen, and heated at 150 °C for 2 h. TLC and UV monitoring after this time showed no presence of residual porphyrin. The solvent was then evaporated under vacuum, and the dark residue was taken up in a dichloromethane (10 mL)/water (10 mL) mixture. After phase separation the aqueous layer was washed with dichloromethane (2 × 10 mL). Organic layers were collected, dried on Na_2SO_4, filtered, and evaporated to dryness, affording [Co(**C3**)] (98%). Anal. Calcd for $C_{100}H_{76}CoN_8O_8$: C, 76.18; H, 4.86; N, 7.11. Found: C, 76.40; H, 5.01; N, 7.34. UV/vis (CH_2Cl_2): λ_{max}/nm (log ε_M) 414 nm (5.05), 535 (3.80). MS (MALDI-TOF): *m*/*z* 1576.0 [M^+].

General Procedure for Cyclopropanation Reactions. In a typical experiment, the olefin (2.5 mmol), ethyl diazoacetate (26 μL, 0.25 mmol), *N*-methylimidazole (see Table 1 and 2), and the catalyst (0.5 mol % relative to ethyl diazoacetate) were dissolved in this order in 10 mL of benzene. The reaction was followed by IR spectroscopy, measuring the diazo characteristic absorbance at 2110 cm^{-1}. The reaction was considered to be finished when the absorbance of the EDA was below 0.03 (by using a 0.5 mm thick cell). The solution was then evaporated to dryness and analyzed by ^{1}H NMR with 2,4-dinitrotoluene as an internal standard. The residue was purified by flash chromatography on silica gel. The collected analytical data for *cis*- and *trans*-ethyl-2-phenylcyclopropanecarboxylate,[7d] *cis*- and *trans*-ethyl 2-methyl-2-phenylcyclopropanecarboxylate,[7d] *cis*- and *trans*-ethyl-2-(4-chlorophenyl)cyclopropanecarboxylate,[7d] *cis*- and *trans*-ethyl-2-*p*-tolylcyclopropanecarboxylate,[7d] and ethyl-2,2-diphenylcyclopropanecarboxylate[7d] are in agreement with those reported in the literature.

***trans*-Ethyl-2-(4-chlorophenyl)-2-methylcyclopropanecarboxylate.** Anal. Calcd (%) for $C_{13}H_{15}ClO_2$: C 65.41, H 6.33. Found: C 65.26, H 6.27. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 7.28−7.21 (m, 4H, Ar*H*), 4.20 (q, J = 7.3 Hz, 2H, OCH_2CH$_3$), 1.95−1.90 (m, 1H, C*H*), 1.50 (s, 3H, CH_3), 1.47−1.41 (m, 1H, C*H*), 1.40−1.35 (m, 1H, C*H*), 1.30 (t, J = 7.3 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 170.5 (COO), 145.1 (C), 133.0 (C), 129.4 (CH), 129.2 (CH), 61.3 (*C*H$_2$CH$_3$), 30.6 (C), 28.5 (CH), 21.4 (CH_2), 20.5 (CH_3), 15.0 (CH_3). MS (EI): *m*/*z* 238 [M^+].

***cis*-Ethyl-2-(4-chlorophenyl)-2-methylcyclopropanecarboxylate.** Anal. Calcd (%) for $C_{13}H_{15}ClO_2$: C 65.41, H 6.33. Found: C 65.30, H 6.24. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 7.24−7.18 (m, 4H, Ar*H*), 3.87 (q, J = 7.3 Hz, 2H, OCH_2CH$_3$), 1.91 (dd, J = 7.8, 5.2 Hz, 1H, C*H*), 1.74 (dd, J = 7.8, 5.2 Hz, 1H, CH_2), 1.44 (s, 3H, CH_3), 1.16 (pst, J = 5.2 Hz, 1H, CH_2), 1.01 (t, J = 7.3 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 171.7 (COO), 141.1 (C), 133.0 (C), 130.8 (CH), 129.0 (CH), 60.6 (*C*H$_2$CH$_3$), 32.0 (C), 28.9 (CH), 28.7 (CH_3), 19.9 (CH_2), 14.4 (CH_3). MS (EI): *m*/*z* 238 [M^+].

***cis*-Ethyl-2-methyl-2-(prop-1-en-2-yl)cyclopropanecarboxylate..**[23] Anal. Calcd (%) for $C_{10}H_{16}O_2$: C, 71.39, H, 9.59. Found: C 71.76, H 9.30. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 4.89 (s, 2H, CH_2), 4.09 (q, J = 7.4 Hz, 2H, OCH_2CH$_3$), 1.71 (s, 3H, CH_3), 1.66−1.62 (m, 1H), 1.53−1.49 (m, 1H), 1.26 (s, 3H, CH_3), 1.23 (t, J = 7.4 Hz, 3H, OCH$_2$CH_3), 0.95 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 171.5 (COO), 144.4, 113.5, 60.3, 33.5, 27.8, 25.3, 20.7, 20.4, 14.4. MS (EI): m/z 168 [M^+].

***trans*-Ethyl-2-methyl-2-(prop-1-en-2-yl)cyclopropanecarboxylate.**[23] Anal. Calcd (%) for $C_{10}H_{16}O_2$: C, 71.39, H, 9.59. Found: C 71.65, H 9.25. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 4.81 (s, 1H, CH_2), 4.76 (s, 1H, CH_2), 4.14 (q, J = 7.4 Hz, 2H, OCH_2CH$_3$), 1.75 (s, 3H, CH_3), 1.74−1.69 (m, 1H), 1.30 (s, 3H, CH_3), 1.26 (t, J = 7.4 Hz, 3H, OCH$_2$CH_3), 1.20−1.16 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 172.6 (COO), 148.5, 111.0, 60.6, 32.0, 26.4, 20.3, 20.1, 17.0, 14.6. MS (EI): m/z 168 [M^+].

(23) (a) Analytical data are not reported in ref 23b. (b) Yeung, C.-T.; Yeung, H.-L.; Tsang, C.-S.; Wong, W.-Y.; Kwong, H.-L. *Chem. Commun.* **2007**, 5203–5205, c).

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Supporting Information Available: Synthesis of **2g**, **2h**, **2c**, [Co(**C2**)], and [Co(**C1**)]; spectra illustrating sample purity, GC/HPLC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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