Optically Active Aldiminato Cobalt(II) Complexes as Efficient Catalysts for Enantioselective Cyclopropanation of Styrenes with Diazoacetates

Tohru Yamada, Taketo Ikeno, Hiroyuki Sekino, and Mitsuo Sato
Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223-8522

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The optically active cobalt(II) complex, MPAC, has proved to be efficient enantioselective catalyst for the cyclopropanation of styrenes with diazoacetates. The addition of a catalytic amount of *N*-methylimidazole remarkably accelerated the cyclopropanation reaction to improve both the chemical and optical yields of the product.

Since the catalytic enantioselective cyclopropanation of olefins with diazoacetates was reported in 1966,[1] various transition-metals and many varieties of optically active ligands have been subjected to this bench-mark test reaction and applied to the industrial synthesis of pyrethroides.[2] For example, chiral (dioximato)cobalt(II)[3] and chiral Schiff-base copper(II)[4] complex catalysts were originally proposed for the enantioselective cyclopropanation and, recently, copper(I) complexes with semicorrin,[5] bis(oxazoline)[6] or bipyridine[7] ligands, ruthenium(II) complexes with bis(oxazolinyl)pyridine[8] ligands, and rhodium(III) complexes with proline derivative[9] ligands were developed as effective catalysts to provide an extremely high level of enantioselectivity. It was very recently reported that optically active (salen)cobalt(III) bromide complexes[10] were efficient catalysts for the asymmetric cyclopropanation of styrene derivatives, and much effort has been devoted to developing more effective catalysts.[11]

The optically active aldimines derived from the corresponding 1,3-dicarbonyl compounds and optically active 1,2-diaryl-1,2-ethylenediamine have been reported to form a new class of effective ligands for catalytic enantioselective reactions; manganese(III) complexes with optically active aldiminato ligands employed as effective catalysts for the aerobic and enantioselective epoxidation of unfunctionalized olefins[12] and asymmetric oxidation of sulfides to the corresponding optically active sulfoxides.[13] The corresponding cobalt(II) complexes, for example, MPAC (Figure 1), effectively catalyzed the enantioselective borohydride reduction of prochiral aryl ketones,[14] phosphinyl imines,[15] and α,β-unsaturated carboxamides.[16] In the present communication, we wish to report that the optically active aldiminato cobalt(II) complex, MPAC, has proved to be an efficient catalyst for the enantioselective cyclopropanation of styrene with diazoacetates and that *N*-methylimidazole can be employed as an effective additive to accelerate the reaction and also to improve the enantioselectivity of the cyclopropanecarboxylates.

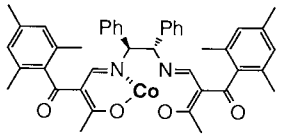

Figure 1. (*S*)-MPAC.

A preliminary investigation suggested that THF was an appropriate solvent to allow the cyclopropanation using the cobalt(II) complex catalyst, MPAC, therefore, it was expected that THF would act as an axial donor ligand to activate the cobalt(II) complex. It was found that the addition of a catalytic amount of *N*-methylimidazole as an axial donor ligand remarkably accelerated the cyclopropanation reaction to improve both the chemical and optical yields of the product.[17] In the presence of 2.0 equivalents of *N*-methylimidazole vs. the Co(II) complex, the cyclopropanation of styrene with *tert*-butyl diazoacetate was immediately initiated and diazoacetate was

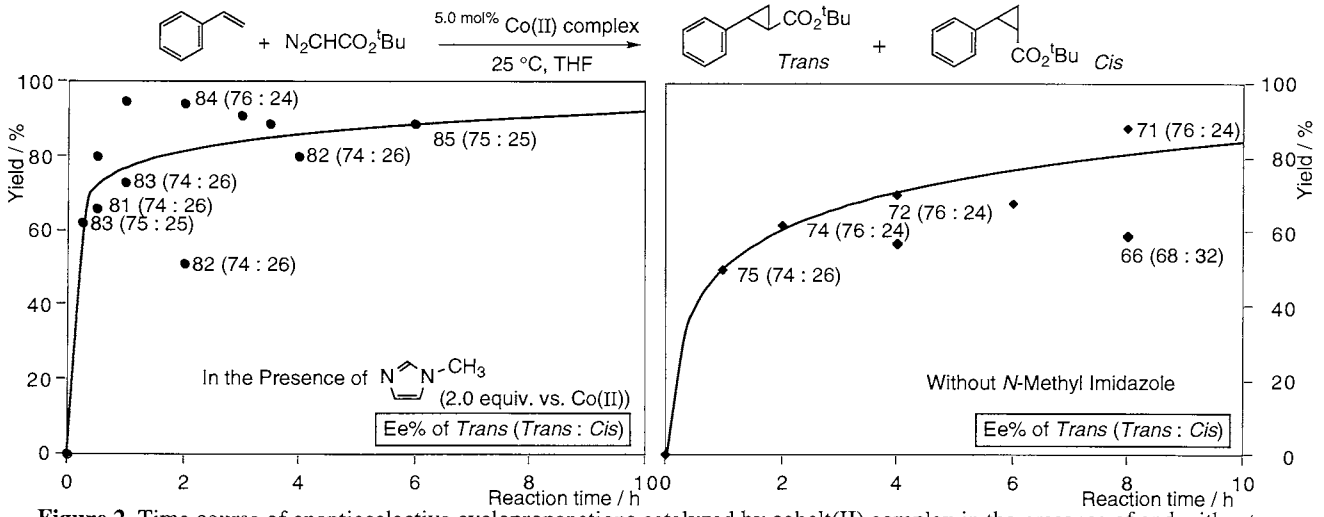

Figure 2. Time course of enantioselective cyclopropanations catalyzed by cobalt(II) complex in the presence of and without *N*-methylimidazole.

completely consumed in 2 h to afford the corresponding cyclopropanecarboxylates (Figure 2). The *trans:cis* isomer ratio was about 75:25 and the enantiomeric excess of the *trans* isomer ranged between 81% and 85% ee for each reaction time. On the contrary, the rate of the cyclopropanation catalyzed by the cobalt(II) complex without *N*-methylimidazole was much slower than that in the presence of *N*-methylimidazole. The optical yield of the *trans* isomer ranged between 66% and 75% ee.

Several nitrogen-containing cyclic compounds were then screened as axial ligands in the present cyclopropanation. Chemical yields were improved by the addition of the *N*-alkylimidazoles (Entries 1-3) compared to that without additives (Entry 9), while 4-methyl- or 2-methyl-imidazole, 2,6-lutidine, and quinoline, are less effective to improve the chemical yields, respectively (Entries 4, 6, 7 and 8). The optically active cyclopropanecarboxylate with high enantioselectivities (80-85% ee) were produced during the cobalt(II)-catalyzed cyclopropanation with diazoacetate by the addition of *N*-methyl-, *N*-benzyl-, *N*-phenyl- or 4-methyl-imidazole (Entries 1-4) and pyridine[18] (Entry 5 in Table 1). On the contrary, the optical yields of cyclopropanecarboxylate were much lower when 2-methyl-*1H*-imidazole, 2,6-lutidine or quinoline was added (Entries 6-8) and without such additives (Entry 9). These results could be explained as follows. These heterocycles as the axial donor ligand would coordinate to the opposite carbenoid site of the cobalt complex to accelerate the addition step of the carbenoid with styrene. Imidazoles or pyridines having alkyl groups attached to the carbon next to the nitrogen atom such as 2-methylimidazole, 2,6-lutidine, and quinoline would restrict the coordination to the cobalt(II) complexes because of their steric hindrance.[19] However, *N*-alkylimidazoles such as *N*-methyl-, *N*-benzyl-, and *N*-phenyl-imidazole could coordinate the cobalt-carbenoid complex as the opposite axial ligand and, therefore, the symmetry of the complex was totally retained[20] in order to achieve high enantioselection and high yield in the cyclopropanation reaction.

It is noted that the optically active aldiminato cobalt(II) complex was employed as an efficient catalyst for the asymmetric cyclopropanation of styrene with *tert*-butyl diazoacetate and that the addition of a catalytic amount of *N*-alkylimidazole or pyridine remarkably accelerated the reaction and improved the enantioselectivity. To expand the application of the present reaction system using the cobalt(II) complex catalyst plus *N*-alkylimidazole, the screening and design of various optically active aldiminato cobalt(II) complexes are under way. The detailed studies on the mechanism of the effect of *N*-alkylimidazole upon both the reaction rate and enantioselectivity are also currently ongoing.

Table 1. Various additives for enantioselective cyclopropanation

Entry[a]	Additive	Yield / %[b]	*Trans* : *Cis*[c]	Optical yield / %ee[d] *Trans*
1		94	76 : 24	84
2		83	75 : 25	85
3		85	77 : 23	84
4		27	73 : 27	80
5		50	72 : 28	82
6		34	72 : 28	75
7		36	73 : 27	71
8		37	73 : 27	70
9	None	62	76 : 24	74

[a]Reaction conditions : 5 mol% of (*S*) or (*R*)-MPAC, 5.0 mmol of styrene, 1.0 mmol of *tert*-butyl diazoacetate and 10 mol%(2.0 equiv. vs. Co(II) complex) of additive in THF at 25 °C under a N_2 atmosphere for 2 h. [b]Isolated yield based on *tert*-butyl diazoacetate. [c]Determined by GC and/or NMR analysis. [d]Determined by HPLC analysis after reduction of the isolated products into the corresponding alcohols (*Trans* : Daicel Chiralcel OD-H and/or OB-H, *Cis* : OB-H, hexane / 2-propanol). Absolute configuration of the *trans* isomer : (+)-(*1S*, *2S*) corresponding to (*S*)-MPAC.

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17 Typical procedure: To a solution of (*S*)-MPAC (35 mg, 0.05 mmol) in THF (1.0 ml) was added styrene (0.57 ml, 5.0 mmol) and *tert*-butyl diazoacetate (148 µl, 1.0 mmol) at 25 °C under a N_2 atmosphere, and then *N*-methylimidazole (8 µl, 0.1 mmol) was added to the solution. GC analysis after 2 h showed that the diazoacetate had been completely consumed and that the corresponding phenylcyclopropanecarboxylate was produced in a 75 : 25 ratio of *trans:cis* isomers. The reaction mixture was purified with silica-gel column chromatography to obtain the product in 94% yield. The mixture of *trans* and *cis* phenylcyclopropanecarboxylates was treated with $LiAlH_4$ to convert it to the corresponding mixture of alcohols and then HPLC analysis of the mixture revealed 84% ee for the *trans* isomer (Daicel Chiralcel OB-H and/or OD-H) and 85% ee for the *cis* isomer (Chiralcel OB-H), respectively.
18 When 3-fluoro-, 4-cyano-, 4-(*N,N*-dimethylamino)-, and 4-amino-pyridines were used as additives, the cyclopropanecarboxylates were obtained in 40% yield with 76% ee (*trans*), 38% yield with 74% ee, 36% yield with 79% ee, and 31% yield with 78% ee, respectively.
19 A similar effect of *N*-alkylimidazole or pyridine derivatives on the enantioselection was observed during the enantioselective aerobic epoxidation catalyzed by the optically active aldiminato manganese(III) complex. T. Yamada, K. Imagawa, T. Nagata, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **67**, 2248 (1994). Recently, it was reported that a donor ligand, such as 2-methylimidazole or pyridine *N*-oxide improved the enantioselection in the salen-manganese(III)-catalyzed epoxidation when iodosylbenzene was used as the terminal oxidant. R. Irie, Y. Ito, and T. Katsuki, *Synlett*, **1991**, 265.
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