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# **α-Diazoacetates as Carbene Precursors: Metallosalen-Catalyzed Asymmetric Cyclopropanation**

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Abstract: Readily available  $\alpha$ -diazo compounds have been shown to be efficient carbene precursors for asymmetric cyclopropanation using ruthenium(NO)–salen and cobalt–salen complexes, as catalysts. The stereoselectivity of the cyclopropanation depends on the metal ion, its valency, the structural and electronic nature of the salen ligand, and the apical ligand of the salen complex used. Both *trans-* and *cis*-selective asymmetric intermolecular cyclopropanation can be realized under mild conditions by using a suitable metallosalen complex. Furthermore, a wide range of alkenyl  $\alpha$ diazoacetates and the related alkenyl diazomethyl ketones undergo intramolecular cyclopropanation in a highly enantioselective manner by using various metallosalen complexes, easily prepared in a modular fashion, as catalyst.

Key words: diazoacetate, asymmetric cyclopropanation, metallosalen, cobalt, ruthenium

Diazo compounds, upon heating, UV-irradiation, or treatment with some transition metal complexs, decompose to highly reactive carbenes, which can undergo addition to a  $\pi$ -bond (cyclopropanation and cyclopropenation), C–H insertion (C-C bond formation), and ylide formation. Most of these carbene transfer reactions are accompanied by the generation of chiral center(s). Although these carbene transfer reactions provide unique tools for organic synthesis, they will become truly useful, if the stereochemistry of the reactions can be controlled at will. Decomposition of diazo compounds under heating or irradiation give free carbenes and control of their reaction stereochemistry is difficult. On the other hand, their decomposition in the presence of a transition-metal complex generally provides a carbene-transition-metal complex (hereafter denoted as a carbenoid) and the stereochemistry of its reaction can be controlled by the ligand coordinated to the transition metal. Thus, much effort has been directed toward the development of transition-metal-mediated carbene transfer reactions (Scheme 1).<sup>1</sup> Of the various diazo compounds known, α-diazo esters are relatively stable but can be decomposed, in the presence of a transitionmetal complex under mild conditions, to give the corresponding carbenoid species, capable of carbene transfer to a range of compounds. Due to the presence of an ester group, the resulting product can be further transformed to other useful compounds. Diazo esters have consequently been extensively studied as carbene precursors.

α-Diazoacetate (ethyl α-diazoacetate) was first synthesized by Curtius<sup>2</sup> in 1883 and, since then, it and its derivatives have been widely used as carbene precursors, especially for cyclopropanations. Asymmetric carbene transfer to olefins poses two stereochemical issues: 1) enantioface selection of a prochiral olefin and 2) diastereoselection in the reaction between a prochiral carbenemetal complex and the prochiral olefin. In 1965, Nozaki et al. for the first time reported transition-metal-mediated stereoselective carbene transfer reactions, cyclopropanation<sup>3a</sup> and oxetane-ring opening,<sup>3b</sup> albeit with modest enantio- and diastereoselectivity. In the wake of this seminal work, much effort has been directed especially toward asymmetric cyclopropanation and various excellent catalysts such as Cu-Schiff base,<sup>3</sup> Co-dioximato,<sup>4</sup> Cu-semicorrin,<sup>5</sup> Cu-bis(oxazoline),<sup>6</sup> Ru-Pybox,<sup>7</sup> Rh-amino carboxylate,<sup>8</sup> and Rh-MEPY,<sup>9</sup> have been developed. Although the enantioselectivities of these reactions are high to excellent, the diastereoselectivities are moderate and mostly trans-selective, except for some examples<sup>7,10</sup> where both high trans-selectivity and high enantioselectivity were observed. On the other hand, cis-selective asymmetric cyclopropanation is limited in number. Cumediated cyclopropanation of some specific substrates shows good *cis*-selectivity<sup>11</sup> and some catalysts show moderate *cis*-selectivity.<sup>12,13</sup> It can thus be seen that, although asymmetric cyclopropanation chemistry has made great advancement in the last three decades, some stereochemical problems remain unresolved.





Recently, metallosalen complexes have been demonstrated to be efficient catalysts for asymmetric oxene and nitrene transfer reactions.<sup>14,15</sup> Since carbene is an isoelectronic species of oxene and nitrene, asymmetric carbene transfer reactions, mainly cyclopropanation, us-

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ing  $\alpha$ -diazoacetates as precursors have been intensively studied with metallosalen complexes as catalyst and it has been found that they show unique catalysis for asymmetric cyclopropanation. In this account, asymmetric cyclopropanation using  $\alpha$ -diazo esters or their related compounds as carbene precursors in the presence of transition-metal complexes, in particular, metallosalen complexes, are briefly described.

As described above, various chiral metal complexes catalyze asymmetric cyclopropanation using  $\alpha$ -diazo esters as carbene precursors. Several metallosalen complexes also catalyze the asymmetric cyclopropanation, and the stereochemistry of the cyclopropanation has been found to strongly depend on the metal ion used, its valency and the structure of the salen ligand. Thus, appropriate choice of a combination of the central metal ion and salen ligand is crucial for achieving high enantio- and diastereoselectivity.

In 1978, the first asymmetric cyclopropanation using  $\alpha$ diazoacetates was examined in the presence of chiral Co(II)-salen complex by the Otsuka and Nakamura group.<sup>16</sup> Although the enantioselectivity of the reaction was modest (<10% ee), this study demonstrated that  $\alpha$ -diazoacetates can be decomposed by a metallosalen complex and an optically active salen ligand can serve as a chiral inducer.

Since our study on metallosalen-mediated oxene transfer reactions revealed that the stereochemistry of the reaction depends also on the nature of the apical ligand,<sup>17</sup> we were intrigued by the catalysis of Co(III)-salen complexes that carry an apical ligand.<sup>18</sup>

In the asymmetric oxene transfer reaction, the C3- and C3'-substituents of the salen ligand play an important role.<sup>19</sup> Thus, we first examined asymmetric cyclopropanation of styrene with *tert*-butyl  $\alpha$ -diazoacetate in the presence of a Co(III)-salen complex bearing 3,3'-di-tert-butyl groups. However, the Co(III)-salen complex showed no catalytic activity. To our surprise, complex 2, possessing small methyl groups at C3 and C3' was also found to be catalytically inactive (Scheme 2). This result suggested that the olefin approaches along the Co-O bond axis. In accordance with this speculation, the reaction with complexes (1, 3, and 4) bearing no substituent at C3(3') proceeded smoothly and showed high trans-selectivity and moderate enantioselectivity. Introduction of a *tert*-butyl group at C4(4') or C5(5') somewhat improved the enantioselectivity. The reaction with complex 5, bearing an apical bromo-ligand instead of an iodo-ligand, showed further improved enantioselectivity and introduction of an electron-donating methoxy group at C5(5') improved enantioselectivity up to 93% ee without decreasing transselectivity. The effects of the bromo-ligand and the methoxy group have been attributed to a shift of the transition state of the reaction to a more product-like one, due to the weak trans effect of the apical ligand and the electron-donating nature of the methoxy group.

Although the mechanism of Co(III)-salen catalyzed cyclopropanation is unclear at present, we have proposed that olefins approach the putative carbenoid species perpendicularly along the downward Co–O bond and rotate clockwise to give the major *trans*-product. In this proposal, the Co(V)-salen carbenoid species has been considered to have adopted a stepped conformation (Figure 1).<sup>20</sup>



Scheme 2



Figure 1

As mentioned above, most of the asymmetric cyclopropanations are *trans*-selective. This is probably because the incoming olefin rotates to avoid steric repulsion between the olefinic substituent and the carbenoid ester group (Figure 1). Therefore, we expected that cis-selective cyclopropanation should be realized if the olefin is forced to rotate in the opposite direction by some means. Although several moderately cis-selective catalysts and some cisselective cyclopropanation of limited substrates have been reported,<sup>12,13</sup> we wanted to develop an intrinsic and highly cis-selective cyclopropanation. We speculated that the olefin might rotate to give a *cis*-product, if some suitable chiral auxiliaries are positioned on either side of olefins approach, with a space that allows access. Fortunately, we recently found that a Ru(NO)-salen complex served as an excellent catalyst for oxene transfer reaction (epoxidation) under photoirradiation.<sup>21a</sup> Since oxene and carbene are isoelectronic and the Ru-O<sub>eq</sub> bond is ca. 0.2 Å longer than the corresponding  $Co-O_{eq}$ bond,<sup>21b,22</sup> we expected that the Ru(NO)-salen complex 7 or 8 could provide a sufficiently open space for olefins access, between the C3- and the C3'-substituents. We thus





examined the asymmetric cyclopropanation of styrene with the Ru(NO)–salen complexes as catalyst (Table 1).<sup>23</sup>

We examined the cyclopropanation of styrene with complexes 7 and 8 under photo-irradiation, and found that the reaction in the presence of complex 8 showed good *cis*and enantioselectivity (Table 1, entry 2). The solubility of these complexes in less polar solvents is poor, and the heterogeneous reactions in such solvents as hexane showed moderate cis- and good enantioselectivity (entry 3). On the other hand, homogeneous reactions in more polar solvents such as THF, showed excellent cis- and enantioselectivity (entry 4), though the reaction did not proceed in coordinating solvents such as acetonitrile or pyridine (entry 5). It is, however, noteworthy that the sense of asymmetric induction by complex 8 was found to depend on the solvent used and change from a less-polar to a more-polar solvent reversed the sense of asymmetric induction (entries 3 and 4). Although the reason for this reversal is unclear, it is the most likely that complex 8 adopts different conformations in heterogeneous and homogeneous states. The reaction in THF showed excellent enantio- and cis-selectivity but the yield of the product was unsatisfactory because self-coupling of the diazo compound, giving a mixture of fumaric and maleic acid esters, occurred competitively under the reaction conditions (entry 4). The yield was improved to some extent by increasing the olefin concentration, and a moderate yield was achieved without diminishing stereoselectivity, when the reaction was carried out at 1:1 (v/v) substrate-THF ratio (entry 6).<sup>23b,c</sup>

Cobalt(II)–salen complexes are flexible and they adopt various ligand conformations, depending on the ligand substituent and the apical ligand.<sup>24</sup> Furthermore, Yamada et al. reported that the cyclopropanation using a chiral aldiminato cobalt(II) complex as the catalyst showed high enantio- and *trans*-selectivity, and the stereoselectivity and the reaction rate were enhanced by adding *N*-methylimidazole (NMI) to the reaction medium.<sup>25</sup> Although stereoselectivity of the previously reported cyclopropanation using the Co(II)-salen complex was modest, we were intrigued by the catalytic potential of the Co(II) complex of our salen ligands. (Table 2).<sup>26</sup>

The Co(II) complex 9, carrying the same salen ligand as complex 8, also catalyzed the cyclopropanation of styrene

 
 Table 1
 Asymmetric Cyclopropanation of Styrene with Ru(NO)– Salen Complex as Catalyst

| Ph    | Ru(NC | )–salen complex (5<br>N <sub>2</sub> CHCO <sub>2</sub> <sup>t</sup> Bu | mol%)<br>Ph'''' +Ph |                                 |  |  |
|-------|-------|--|---------------------|---------------------------------|--|--|
|       |       | solvent, hv, N <sub>2</sub> , r.t.                                     | cis                 | ČO <sub>2</sub> <sup>t</sup> Bu | ČO <sub>2</sub> <sup>t</sup> Bu<br>trans |  |
| Entry | Cat.  | Solvent  | Yield (%)           | cis:trans                       | % ee ( <i>cis</i> )                      |  |
| 1     | 7     | _  | 12                  | 37:63                           | 12 (1 <i>S</i> , 2 <i>R</i> )            |  |
| 2     | 8     | -  | 53                  | 80:20                           | 81 (1 <i>S</i> , 2 <i>R</i> )            |  |
| 3     | 8     | Hexane   | 10                  | 68:32                           | 83 (1 <i>R</i> , 2 <i>S</i> )            |  |
| 4     | 8     | THF  | 18                  | 96:4                            | 99 (1 <i>S</i> , 2 <i>R</i> )            |  |
| 5     | 8     | MeCN   | 0                   | -                               | -  |  |
| 6     | 8     | THF–styrene (1:1)  | 45                  | 93:7                            | 97 (1 <i>S</i> , 2 <i>R</i> )            |  |

with high enantio- and *cis*-selectivity (entry 1). In contrast to the reaction with 8, self-coupling of the diazo ester was slow in the reaction with 9 and only a trace amount of fumaric and maleic acid ester (<1%) was detected. Enantioand cis-selectivity was further improved to 98% ee and 98:2 respectively, by addition of NMI (entry 2). Another advantage of the reaction was that excellent cis- and enantio-selectivity could be attained even with commercial ethyl  $\alpha$ -diazoacetate (entry 3).<sup>26b</sup> It is noteworthy that complexes 8 and 9, bearing the same ligand, showed the opposite sense of enantioface selection to each other (Tables 1 and 2). These results suggested that the access route of the substrate to a carbenoid center is strongly affected by the nature of the metal ion (vide infra). The reaction with complex 10 also showed high cis- and enantio-selectivity; however, the catalytic activity of 10 was low and its sense of asymmetric induction was opposite to that of **9** (entries 2 and 5).

The cyclopropanation of other styrene derivatives also showed excellent *cis*- and enantioselectivity, except for the reaction of  $\alpha$ -methylstyrene, in which *cis*-selectivity was somewhat diminished (Table 3).





Table 2 Asymmetric Cyclopropanation of Styrene with Co(II)-Salen Complex as Catalyst

| Ph             | Co(II)–salen complex (5 mol<br>N <sub>2</sub> CHCO <sub>2</sub> R, NMI (10 mol%<br>THF, N <sub>2</sub> , r.t. | $(5)$ Ph $CO_2R$ + Ph $CO_2R$ | cO <sub>2</sub> R<br>trans |           |           |  |
|----------------|---|-------------------------------|----------------------------|-----------|-----------|--|
| Entry          | Cat.  | THF/Styrene                   | R                          | Yield (%) | cis:trans | % ee ( <i>cis</i> )                        |
| 1 <sup>a</sup> | 9   | 100/1                         | <i>t</i> -Bu               | 88        | 92:8      | 96 (1 <i>R</i> , 2 <i>S</i> )              |
| 2              | 9   | 100/1                         | <i>t</i> -Bu               | 89        | 98:2      | 98 (1 <i>R</i> , 2 <i>S</i> )              |
| 3              | 9   | 10/6                          | Et                         | quant     | 99:1      | 96 (1 <i>R</i> , 2 <i>S</i> )              |
| 4              | 9   | 10/1                          | <i>t</i> -Bu               | 90        | 98:2      | 98 (1 <i>R</i> , 2 <i>S</i> )              |
| 5              | 10  | 100/1                         | <i>t</i> -Bu               | 18        | 97:3      | 99 (1 <i>S</i> , 2 <i>R</i> )              |
| 6              | 11  | 10/1                          | <i>t</i> -Bu               | 25        | 97:3      | 2 (1 <i>S</i> , 2 <i>R</i> )               |
| 7              | 12  | 10/6                          | <i>t</i> -Bu               | 91        | 27:73     | 95 $(1R, 2R)^{b}$                          |
| 8              | 12  | 10/6                          | Et                         | quant     | 31:69     | 95 (1 <i>R</i> , 2 <i>R</i> ) <sup>b</sup> |

<sup>a</sup> The reaction was carried out in the absence of NMI.

<sup>b</sup> The ee of the *trans*-isomer.

Table 3 Asymmetric Cyclopropanation of Styrene Derivatives with Co(II)–Salen Complex 9 as Catalyst

| Ar Co(II)-sale | n complex <b>9</b> (5 mol%)<br>ای 2 <sup>R<sup>2</sup>, NMI (10 mol%)<br/>FHF, N<sub>2</sub>, r.t.</sup> | $R_{1}^{1}$ $CO_{2}R^{2}$ $R_{1}^{1}$ $R_{1}^{1}$ $R_{1}^{1}$ $R_{2}^{1}$ $R_{1}^{1}$ $R_{2}^{1}$ $R_{1}^{1}$ $R_{2}^{1}$ $R_$ | CO <sub>2</sub> R <sup>2</sup> |           |           |                     |
|----------------|--|--|--------------------------------|-----------|-----------|---------------------|
| Entry          | Ar   | <b>R</b> <sup>1</sup>  | R <sup>2</sup>                 | Yield (%) | cis:trans | % ee ( <i>cis</i> ) |
| 1              | p-ClC <sub>6</sub> H <sub>4</sub>  | Н  | <i>t</i> -Bu                   | 85        | 97:3      | 96                  |
| 2              | <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>   | Н  | t-Bu                           | 84        | 97:3      | 97                  |
| 3              | Ph   | Me   | t-Bu                           | 39        | 83:17     | 99                  |
| 4              | p-ClC <sub>6</sub> H <sub>4</sub>  | Н  | Et                             | quant     | 97:3      | 96                  |
| 5              | <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>   | Н  | Et                             | quant     | 95:5      | 93                  |
| 6              | Ph   | Me   | Et                             | quant     | 85:15     | 94                  |

Although sufficient structural information on complexes **9** and **10** is not yet available, we assumed that the Co(IV)carbenoid species derived from them have a stepped conformation. Furthermore, the sense of salen ligand folding seems to be dictated by the chirality of the ethylenediamine moiety, since **9** and **10** show the opposite sense of asymmetric induction to each other. We also assumed that olefins would approach the carbenoid center derived from **9** along the Co–N(a) bond beyond the downward naphthalene ring and the equatorial substituent at the diamine moiety and rotate counterclockwise to show the observed *cis*- and enantioselectivity (Figure 4; top). It is noteworthy that complex **11**, with no chirality at its ethylenediamine moiety, showed almost no enantioselectivity but high *cis*selectivity. This result also supports the suggestion that olefins approach along the Co(II)–N bond axis (Table 2, entry 6). When the phenyl group on the naphthalene ring of **9** is replaced by a small methyl group, the ester alkoxy group of the carbenoid species derived from **12** shifts backward and, therefore, olefins approach the carbenoid species with reversed orientation and show good *trans*-selectivity with excellent enantioselectivity (Figure 4; bottom, Table 2; entry 7). The carbenoid species derived from **10** is also considered to adopt a stepped conformation; however, the sense of the folding should be opposite to that of the carbenoid species derived from **9** and olefins presumably approach along the Co–N(b) bond axis, resulting in high *cis*- and enantioselectivity. In this case, however, the 2"-phenyl group protrudes over this access route and the reaction with **10** is slow.



Figure 4

Since Stork and Ficini reported the first intramolecular cyclopropanation in 1968,<sup>27</sup> its asymmetric version has been extensively studied. Doyle et al. have introduced a series of chiral dirhodium(II) carboxamidate complexes and achieved excellent enantioselectivity for intramolecular cyclopropanations of various types of alkenyl diazoacetates.<sup>28</sup> On the other hand, Pfaltz et al. have revealed that copper-bis(oxazoline) complexes are excellent catalysts for intramolecular cyclopropanation of alkenyl diazo ketones.<sup>29</sup> Later, Doyle et al. further demonstrated that copper-bis(oxazoline) complexes serve as catalysts for macrocyclization of alkenyl diazo esters.<sup>30</sup> Pérez-Pietro et al. introduced a dirhodium complex with a unique orthometalated arylphosphine ligand and demonstrated that its rhodium complex was an excellent catalyst for cyclization of alkenyl diazo ketones.<sup>31</sup> Davies et al. reported highly enantioselective cyclization of alkenyl α-vinyl-α-diazoactates.<sup>32</sup> As these results indicate, although high enantioselectivity has been achieved for a range of intramolecular cyclopropanations, the scope of each reaction is rather narrow, because the transition states of the intramolecular cyclopropanations strongly depend on the substrate structure, olefinic substitution pattern, etc. We thought that the use of catalysts readily assembled from modules would provide a solution to this problem. Salen ligands can be synthesized by condensation of salicyl aldehyde with ethylenediamine and various derivatives are commercially available or readily synthesized. Thus, we expected that cyclization of a wide range of unsaturated diazo compounds could be performed in a highly enantioselective manner using a metallosalen complex as catalyst.

We examined the cyclization with Ru(NO)–salen and Co(II)–salen complexes as catalyst (Scheme 3).<sup>33</sup> The cyclization of *E*-cinnamyl  $\alpha$ -diazoacetate was first studied with Ru(NO)–salen complex **8** as catalyst, but the enantioselectivity of the reaction was only moderate (70% ee). However, the configuration of the product suggested that the cyclization proceeded through a transition state described in Figure 5.<sup>33a</sup> This transition-state model suggested that a bulky 2"-substituent would disturb the desired transition state and reduce enantioselectivity due to steric

repulsion between the substituent and the ester unit of the carbenoid. Thus, we examined the cyclopropanation with complex **13** and **14** and found that the latter showed considerably improved enantioselectivity. Encouraged by these results, we next examined the cyclization with Co(II)–salen complexes: though the reaction with complex **9** was slow and only moderately enantioselective was observed, those with complex **12** or **15** bearing no or small substituent at C2" showed high enantioselectivity with acceptable yields.



Scheme 3





Based on these results, we further examined the reaction of various allyl  $\alpha$ -diazoacetates with complexes **12** and **15** (Table 4). The reactions of most  $\alpha$ -diazoacetates proceeded with high enantioselectivity, except for 2-methylpropenyl  $\alpha$ -diazoacetate (entry 10). This is in accord with the model (Figure 5), where the presence of a geminal substituent (R<sup>3</sup>) causes steric repulsion with the salen ligand and reduces enantioselectivity.

Cyclization of 3-alkenyl diazomethyl ketones were also examined (Scheme 4). In contrast to the reaction of alkenyl  $\alpha$ -diazoacetates, Co(II)–salen complexes showed no catalytic activity for this reaction, however, the Ru(NO)– salen complex **8** was found to be effective.<sup>33c</sup> The reason why complex **8** is the best catalyst is not very clear at present, but it has been proposed that, in the cyclization of alkenyl diazoketones, the alkenyl moiety approaches the carbenoid center away from the chiral auxiliary.<sup>34</sup> This proposal could explain why the 2"-phenyl group of compound **8** seems to be essential for the cyclization.

Table 4 Asymmetric Cyclopropanation of Allyl α-Diazoacetate Derivatives with Co(II)–Salen Complexes as Catalyst

| $R_{+}^{3} \xrightarrow{O_{+} CHN_{2}} \underbrace{Co(II)-salen \ complex \ (5 \ mol\%), \ NMI}_{THF, \ N_{2}, \ r.t.} \xrightarrow{R_{+}^{2}, \dots, A_{+}} \underbrace{R_{+}^{2}, \dots, A_{+}}_{R^{3}} \xrightarrow{O_{+} CHN_{2}} \underbrace{Co(II)-salen \ complex \ (5 \ mol\%), \ NMI}_{R^{3}}$ |      |  |                |                       |           |        |  |
|---|------|--|----------------|-----------------------|-----------|--------|--|
| Entry   | Cat. | <b>R</b> <sup>1</sup>                      | R <sup>2</sup> | <b>R</b> <sup>3</sup> | Yield (%) | ee (%) |  |
| 1   | 12   | p-ClC <sub>6</sub> H <sub>4</sub>          | Н              | Н                     | 72        | 98     |  |
| 2   | 12   | p-BrC <sub>6</sub> H <sub>4</sub>          | Н              | Н                     | 70        | 97     |  |
| 3   | 12   | <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> | Н              | Н                     | 70        | 98     |  |
| 4   | 12   | PhC≡C                                      | Н              | Н                     | 32        | 93     |  |
| 5   | 12   | PhCH <sub>2</sub> CH <sub>2</sub>          | Н              | Н                     | 10        | 91     |  |
| 6   | 15   | <i>i</i> -Pr                               | Н              | Н                     | 34        | 75     |  |
| 7   | 15   | Ph   | Me             | Н                     | 47        | 91     |  |
| 8   | 12   | Ph   | Ph             | Н                     | 35        | 81     |  |
| 9   | 12   | Н  | Ph             | Н                     | 16        | 74     |  |
| 10  | 15   | Ph   | Н              | Me                    | 12        | 38     |  |



### $R^1 = CH_3, R^2 = CH_3$ 8: 65%, 87% ee

### Scheme 4

 $\alpha$ -Diazoacetate esters are useful carbene precursors and, in this study, it has been demonstrated that they are also useful precursors for metallosalen-catalyzed asymmetric cyclopropanation. It was also found that the stereochemistry of this cyclopropanation depends on the metal ion, its valency, the structure of the salen ligand, its electronic nature, and the nature of the apical ligand. Both highly cisand trans-selective asymmetric cyclopropanations have been achieved by an appropriate combination of these factors. Although cyclopropanation competes with the selfcoupling of diazoacetate, the self-coupling can be suppressed using an appropriate metallosalen complex. Furthermore, metallosalen complexes have been successfully applied to the intramolecular cyclopropanation of unsaturated diazo esters and ketones. The scope of known intramolecular cyclopropanation reactions is generally narrow; however, the modular nature of these metallosalen complexes enables the cyclization of a wide range of unsaturated diazo compounds.

We believe that the synthetic value of  $\alpha$ -diazoacetates as a carbene precursor has been remarkably enhanced by the use of appropriate metallosalen complexes as catalyst.

<sup>1</sup>H NMR spectra were recorded at 400 MHz on a Jeol JNM-AL-400 instrument. All signals are expressed as ppm down field of TMS, used as an internal standard, in CDCl<sub>3</sub>. IR spectra were obtained with a Shimadzu FTIR-8400 instrument. Optical rotations were measured with a Jasco P-1020 polarimeter. Column chromatography was conducted on silica gel 60N (spherical, neutral), 63–210  $\mu$ m, available from Kanto Chemical Co., Inc. Preparative thin layer chromatography was performed on 0.5 mm × 20 cm × 20 cm E. Merck silica gel plate (60 F-254). Enantiomeric excesses were determined by HPLC analysis using Shimadzu LC-10AT-VP with an appropriate optically active column. Solvents were dried and distilled shortly before use. Reactions were carried out under nitrogen or argon, if necessary.

### (*R*,*R*)-[*N*,*N*'-Bis(5-methoxysalicylidene)-1,2-diphenylethylenediaminato]cobalt(II)

(1R,2R)-l,2-Diphenylethylenediamine (102 mg, 0.48 mmol) was added to a solution of 2-hydroxy-5-methoxybenzaldehyde (145 mg, 0.96 mmol) in EtOH (2 mL) and stirred at r.t. overnight. The mixture was concentrated in vacuo and to the residue were added degassed EtOH (8 mL) and a freshly prepared ethanolic solution of  $Co(OAc)_2$  (0.5 M, 0.96 mL, 0.48 mmol) under nitrogen. The mixture was refluxed for 9 h, and then allowed to cool to r.t.. The resulting brown precipitate was separated from the solution by filtration, washed with degassed ethanol under a nitrogen atmosphere, and dried under vacuum to give the corresponding Co(II)–salen complex (198 mg, 0.37 mmol, 77%).

IR (KBr): 3028, 3001, 2943, 2905, 2833, 1595, 1533, 1462, 1421, 1362, 1302, 1256, 1219, 1167, 1030, 824, 698 cm<sup>-1</sup>.

Anal. Calcd for  $C_{30}H_{26}N_2O_4Co: C, 67.04; H, 4.88; N, 5.21.$  Found: C, 66.98; H, 4.90; N, 5.20.

# Asymmetric Cyclopropanation Using Complex 6; General Procedure

To a CH<sub>2</sub>Cl<sub>2</sub> solution of the Co(II)–salen complex (8.4 mM, 0.5 mL) was added a CH<sub>2</sub>Cl<sub>2</sub> solution of Br<sub>2</sub> (17  $\mu$ L, 0.12 M, 2.1  $\mu$ mol) and the mixture was stirred for 1 h at r.t. to give the Co(III)–salen complex **6**. Styrene (49  $\mu$ L, 0.42 mmol) was then added followed, after 10 min stirring at r.t., by *tert*-butyl  $\alpha$ -diazoacetate (11.9  $\mu$ L, 85  $\mu$ mol). The reaction was stirred at r.t. for 24 h then concentrated in vacuo. The residue was passed through a short silica gel column (hexane–AcOEt, gradient from 1:0 to 9:1) to give a 96:4 mixture of *trans*- and *cis-tert*-butyl 2-phenylcyclopropane-l-carboxylates, respectively, in a combined yield of 80%.

### (15,2S)-tert-Butyl 2-Phenylcyclopropane-1-carboxylate

 $[a]_D^{20}$  +253.3 (*c* 0.73, CHC1<sub>3</sub>); ee = 93% (HPLC; Daicel Chiralcel OD-H; hexane).

The configuration was determined by chemical correlation.<sup>18b</sup>

HRMS–FAB: m/z [M + H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>19</sub>O<sub>2</sub>: 219.1385; found: 219.1385.

### (*R*,*R*)-{*N*,*N*'-Bis[(*R*)-2-hydroxy-2'-phenyl-1,1'-binaphthyl-3-ylmethylene]-1,2-cyclohexanediaminato}ruthenium(nitrosyl) Chloride (8)

To a solution of (1R,2R)-1,2-diaminocyclohexane (0.17 g, 1.5 mmol) in EtOH (20 mL) was added (a*R*)-3-formyl-2-hydroxy-2'-phenyl-1,1'-binaphthyl (1.1 g, 3.0 mmol) and the mixture was stirred at r.t. for 6 h. The resulting light-yellow precipitate was separated from the solution by filtration, and dried under vacuum. This precipitate was dissolved in DMF (30 mL) and added to a stirred suspension of washed (hexane,  $3 \times 1.0$  mL) NaH (60% dispersion in mineral oil, 0.13 g, 3.3 mmol). Hydrogen evolved and the mixture turned to a clear red solution. After 1 h, Ru(NO)Cl<sub>3</sub>·H<sub>2</sub>O (0.42 g, 1.6 mmol) was added and the mixture was stirred at 110 °C for 48 h. The reaction mixture was cooled, concentrated under vacuum and the residue was purified directly by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>–acetone, 50:1) to give Ru(NO)–salen complex **8** as redbrown crystals (892 mg, 0.9 mmol, 60%).

IR (KBr): 3051, 2937, 2860, 1824, 1707, 1639, 1614, 1577, 1546, 1490, 1446, 1423, 1384, 1346, 1319, 1296, 1274, 1246, 1226, 1190, 1169, 1145, 1124, 1091, 1072, 1028, 951, 864, 818, 793, 775, 760, 696, 667, 640, 582, 548, 499, 470, 428 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.25$  (d, J = 2.0 Hz, 1 H), 8.22 (d, J = 1.5 Hz, 1 H), 8.16 (d, J = 8.0 Hz, 1 H), 8.03 (d, J = 8.5 Hz, 1 H), 7.99 (d, J = 8.5, 1 H), 7.87–7.82 (m, 3 H), 7.67 (d, J = 8.0 Hz, 1 H), 7.63–7.58 (m, 3 H), 7.45–7.34 (m, 3 H), 7.29–6.95 (m, 9 H), 6.59–6.55 (m 2 H), 6.30 (pseudo-d, J = 7.5 Hz, 2 H), 6.20–6.10 (m, 6 H), 3.99 (br t, J = 10.4 Hz, 1 H), 3.03 (br t, J = 10.4 Hz, 1 H), 2.68 (br d, J = 12.0 Hz, 1 H), 2.60 (br d, J = 11.0 Hz, 1 H), 2.05–1.98 (br m, 2 H), 1.71–1.63 (br m, 1 H), 1.53–1.33 (br m, 3 H).

HRMS–FAB: m/z [M]<sup>+</sup> calcd for C<sub>60</sub>H<sub>44</sub>ClO<sub>3</sub>N<sub>3</sub>Ru: 991.2128; found: 991.2114.

Anal. Calcd for  $C_{60}H_{44}ClO_3N_3Ru \cdot H_2O$ : C, 71.38; H, 4.59; N, 4.16. Found: C, 71.24; H, 4.59; N, 4.13.

### Intermolecular Asymmetric Cyclopropanation Using Ru(NO)– Salen Complex 8 as Catalyst; Typical Procedure

To a solution of complex **8** (4.9 mg, 5  $\mu$ mol) in THF (0.12 mL) was added styrene (0.12 mL) under N<sub>2</sub>. *tert*-Butyl  $\alpha$ -diazoacetate (14  $\mu$ L, 0.1 mmol) was then added and the mixture was stirred for 48 h under incandescent light (100 V, 57 W). The reaction mixture was then concentrated in vacuo and the residue was passed through a short silica gel column (hexane–*i*-Pr<sub>2</sub>O, 1:0 to 4:1) to give a 7:93 mixture of *tert*-butyl *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates (9.8 mg, 45  $\mu$ mol, 45%). Their enantiomeric excesses and configuration were determined by HPLC (Daicel Chiralcel OD-H, hexane, 0.5 mL/min). Further purification by preparative TLC (silica gel, hexane–*i*-Pr<sub>2</sub>O, 4:1) gave *tert*-butyl *cis*-2-phenylcyclopropane-1-carboxylate as a single isomer (9.1 mg, 42  $\mu$ mol, 42%).

# (1*S*,2*R*)-*tert*-Butyl 2-Phenylcyclopropane-1-carboxylate $[\alpha]_{D}^{24}$ +18.0 (*c* 0.73, CHC1<sub>3</sub>); ee = 97%.

The configuration was determined by chemical correlation.<sup>18b</sup>

Anal. Calcd for  $C_{14}H_{18}O_2$ : C, 77.03; H, 8.31. Found: C, 77.00; H, 8.37.

# $(R,R) - \{N,N'-Bis[(R)-2-hydroxy-2'-phenyl-1,1'-binaphthyl-3-yl-methylene] - 1,2-cyclohexanediaminato \} cobalt(II) (9)$

Complex **9** was prepared in a manner similar to that described for (R,R)-[N,N'-bis(5-methoxysalicylidene)-1,2-diphenylethylenediaminato]cobalt(II).

IR (KBr): 3443, 3051, 2934, 2860, 2363, 1603, 1547, 1491, 1450, 1331, 1298, 1225, 1186, 1148, 1028, 952, 870, 822, 758, 700, 581, 544  $\rm cm^{-1}$ .

Anal. Calcd for  $C_{60}H_{44}O_2N_2Co\cdot 0.5~H_2O;~C,~80.7;~H,~5.08;~N,~3.14.$  Found: C, 80.86; H, 5.08; N, 3.09.

### (*R*,*R*)-{*N*,*N*'-Bis[(*S*)-2-hydroxy-2'-methyl-1,1'-binaphthyl-3-ylmethylene]-1,2-cyclohexanediaminato}cobalt(II) (12)

IR (KBr): 3439, 3049, 3007, 2932, 2858, 1591, 1553, 1445, 1421, 1337, 1227, 1190, 1148, 1123, 955, 887, 860, 806, 781, 746, 567, 430  $\rm cm^{-1}.$ 

Anal. Calcd for  $C_{50}H_{40}O_2N_2Co: C$ , 79.04; H, 5.31; N, 3.69. Found: C, 79.03; H, 5.35; N, 3.79.

### (*R*,*R*)-{*N*,*N'*-Bis[(*S*)-2-hydroxy-1,1'-binaphthyl-3-ylmethylene]-1,2-cyclohexanediaminato}cobalt(II) (15)

IR (KBr): 3443, 3049, 2932, 2856, 1595, 1551, 1423, 1352, 1329, 1227, 1188, 1150, 1123, 1043, 1018, 955, 891, 858, 797, 777, 748, 567, 503, 426 cm<sup>-1</sup>.

Anal. Calcd for  $C_{48}H_{36}O_2N_2Co\cdot0.5$   $H_2O$ : C, 77.83; H, 5.03; N, 3.78. Found: C, 78.03; H, 5.08; N, 3.79.

# Asymmetric Cyclopropanation with Co(II)–Salen Complex 9 and Styrene; General Procedure

To a solution of complex **9** (44 mg, 50 µmol) in THF (5 mL) was added a THF solution of *N*-methylimidazole (0.5 M, 0.2 mL, 0.1 mmol) and the mixture was stirred for 2 min. Styrene (550 µL, 4.8 mmol) was added to this solution and the mixture was stirred for another 3 min before being treated with *tert*-butyl *a*-diazoacetate (140 µL, 1.0 mmol). The mixture was stirred for 24 h at r.t. and then concentrated in vacuo. The residue was chromatographed on silica gel (hexane–EtOAc, 1:0 to 9:1) to give a 2:98 mixture of *trans*- and *cis*-products (194 mg, 0.89 mmol, 89%). An aliquot of the mixture was submitted to preparative TLC (silica gel, hexane–*i*-Pr<sub>2</sub>O, 4:1) to yield the *cis*-product which was used to determination the enantiomeric excess by HPLC analysis (Daicel Chiralcel OD-H, hexane, 0.5 mL/min). The configuration was determined by comparison of the sign of optical rotation.<sup>35</sup>

# (1*R*,2*S*)-*tert*-Butyl 2-Phenylcyclopropane-1-carboxylate $[\alpha]_D^{24}$ –18.4 (*c* 0.34, CHC1<sub>3</sub>); ee = 98%.

Anal. Calcd for  $C_{14}H_{18}O_2$ : C, 77.03; H, 8.31. Found: C, 77.01; H, 8.32.

### (1R,2S)-Ethyl 2-Phenylcyclopropane-1-carboxylate

 $[\alpha]_D^{24}$  –19.3 (*c* 0.48, CHC1<sub>3</sub>); ee = 96% (Daicel Chiralcel OB-H). HRMS–FAB: *m*/*z* [M + H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>15</sub>O<sub>2</sub>: 191.1057; found: 191.1058.

# Intramolecular Cyclopropanation of 2-Alkenyl $\alpha$ -Diazoacetates with Co(II)–Salen Complex (12 or 15) as Catalyst; General Procedure

2-Alkenyl  $\alpha$ -diazoacetate (0.1 mmol) was placed in a Schlenk tube and purged with nitrogen. A solution of *N*-methylimidazole (0.5 M, 0.2 mL) in THF followed by Co(II)–salen complex (5 mol%) was then added and the reaction mixture was stirred for 24 h at 25 °C. The solvent was removed in vacuo and the residue was chromatographed on silica gel using an appropriate eluent to afford the corresponding bicyclic lactone.

### (1S,5R,6R)-6-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one

Enantiomeric excess was determined by GLC analysis using a chiral column (Supelco Chiral BETA-DEX column operated at 160  $^{\circ}$ C).

Mp 104 °C;  $[\alpha]_D^{22}$  -127 (*c* 0.25, CHCl<sub>3</sub>) {Lit.<sup>28b</sup>  $[\alpha]_D^{23}$  +130 (*c* 0.29, CHCl<sub>3</sub>) for 1*R*,5*S*,6*S*-isomer}; ee = 97%.

### 6-Methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one

Enantiomeric excess was determined by HPLC analysis using chiral column (Daicel Chiralcel OB-H, hexane–*i*-PrOH, 15:1, 0.5 mL/ min).

 $[\alpha]_{D}^{22}$  -92 (*c* 0.25, CHCl<sub>3</sub>); ee = 90%.

IR (KBr): 1762, 1440, 1357, 1188, 1070, 1045, 995, 968, 866, 833, 758, 698 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.35–7.23 (m, 5 H), 4.54 (dd, J = 10.0, 5.6 Hz, 1 H), 4.36 (ddd, J = 10.0, 1.2, 0.8 Hz, 1 H), 2.54 (ddd, J = 6.6, 5.6, 1.2 Hz, 1 H), 2.46 (dd, J = 6.6, 0.8 Hz, 1 H), 1.49 (s, 3 H).

# Intramolecular Cyclopropanation of 3-Alkenyl Diazomethyl Ketones Using Ru(NO)-Salen Complex 8; General Procedure

Ru(NO)–salen complex **8** (4.9 mg, 5 mmol) was dissolved in THF (4 mL) under  $N_2$  and the mixture was irradiated with incandescent light whilst a solution of 3-alkenyl diazomethyl ketone (0.1 mmol) in THF (1 mL), was added dropwise over a period of 12 h using a syringe pump. The reaction mixture was stirred for a further 4 h then concentrated in vacuo. The residue was chromatographed on silica gel (hexane–AcOEt, 11:1) to yield the corresponding [3.1.0]bicyclic ketone.

### 6-Phenylbicyclo[3.1.0]hexan-2-one

Enantiomeric excess was determined by HPLC analysis using chiral column (Daicel Chiralcel OD-H, hexane–*i*-PrOH, 9:1, 0.5 mL/min).

Mp 101 °C;  $[\alpha]_D^{22}$  –95 (*c* 0.275, CHCl<sub>3</sub>); ee = 94%.

Anal. Calcd for  $C_{12}H_{12}O$ : C, 83.69; H, 7.02. Found: C, 83.42; H, 7.04.

### 6-Methyl-6-(4-methyl-3-penten-1-yl)bicyclo[3.1.0]hexan-2-one

Enantiomeric excess was determined by GLC analysis using chiral column (Supelco Chiral BETA-DEX column operated at 180  $^\circ$ C).

 $[\alpha]_D^{24}$  +27 (*c* 0.46, CHCl<sub>3</sub>); ee = 93%.

IR (KBr): 2935, 2858, 1720, 1652, 1600, 1494, 1296, 1267, 1190, 1078, 1026, 968, 875, 802  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.05 (tt, *J* = 7.1, 1.5 Hz, 1 H), 2.34–2.18 (m, 2 H), 2.09–2.00 (m, 3 H), 1.95–1.86 (m, 2 H), 1.68 (m, 4 H), 1.60 (s, 3 H), 1.33–1.20 (m, 2 H), 1.14 (s, 3 H).

HRMS–EI: m/z [M]<sup>+</sup> calcd for C<sub>13</sub>H<sub>20</sub>O: 192.1514; found: 192.1529.

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