Pergamon

Tetrahedron 54 (1998) 6099–6110

TETRAHEDRON

Chiral Lewis Acid Controlled Diels-Alder Reaction: Factors Affecting the Stereoselective Formation of both Enantiomers in the Bis(Oxazoline)-Magnesium Catalyzed Process.

Paolo Carbone, Giovanni Desimoni,* Giuseppe Faita,* Salvatore Filippone and Pierpaolo Righetti

Dipartimento di Chimica Organica, Università di Pavia, V.le Taramelli 10, 27100 Pavia, Italy

Received 16 February 1998; revised 31 March 1998; accepted 2 April 1998

Abstract

The chiral Lewis acid controlled Diels-Alder (CLAC-DA) reaction between cyclopentadiene and 3-acryloyl- or (*E*)-3-crotonyl-1,3-oxazolidin-2-ones (**2a,b**), to give the *endo* adducts **3a,b** has been studied. The use of magnesium perchlorate (MP) or magnesium triflate (MT), and three chiral bis(oxazolines) (**5-7**) and, eventually, 2 equiv of achiral auxiliary ligands **X** [water or tetramethylurea (TMU)], induces a strong change of the enantioface selectivity. The intermediates are either tetrahedral or octahedral. The MP-based intermediates can be either tetrahedral, giving rise to the *endo (S)* adducts enantioselectively, or, by addition of 2 equiv **X**, octahedral giving rise to the *endo (R)* adducts. The MT-based intermediates always have an octahedral configuration in the presence of two triflate ligands, and the *endo (R)* adducts are obtained enantioselectively. The controlled use of the different reagents to assemble the catalysts gives either (*S*)-**3a** in 94% *ee* from a tetrahedral complex, or (*R*)-**3a** in 93% *ee* from an octahedral one, whereas (*R*)-**3b** can be prepared with *ee* up to 95%.

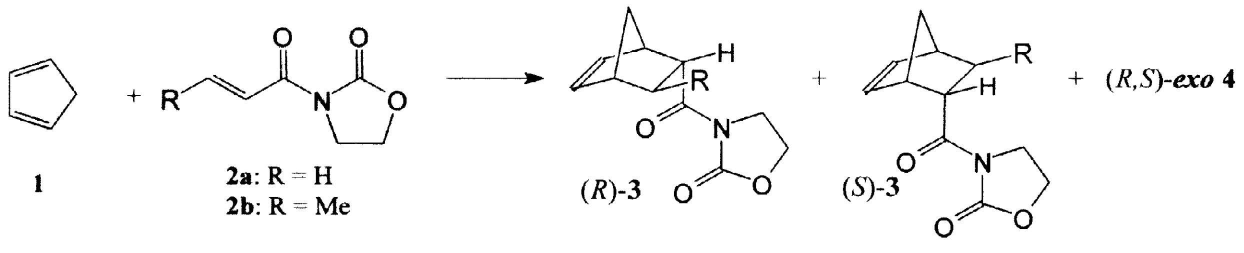
Keywords: Diels-Alder reactions, Catalysis, Asymmetric synthesis, Magnesium and compounds

Introduction

The enantioselective catalysis of the Diels-Alder (DA) reaction has been extensively studied by several groups using chiral Lewis acid complexes. The Lewis acid cores of the catalyst were titanium [1], aluminium [2], boron [3], lanthanium and lantanides [4], ruthenium [5], manganese [6], iron [7], copper [8], magnesium [9], zinc [10], nickel [11], and cobalt [12]. The most used chiral ligands were: TADDOLs [1], binaphthols [4], derivatives of C_2-symmetric diamines, mono and bis(oxazolines).

0040-4020/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(98)00303-2

To test the efficiency of the differing catalytic systems, nearly all groups chose the reactions between cyclopentadiene (**1**) and 3-alkenoyl derivatives of 1,3-oxazolidin-2-one (**2**) that gave (*R*)- and (*S*)-*endo* **3** and *exo* **4** adducts (Scheme 1).



Scheme 1

If the scope of this area of research was only to obtain the best adduct yields, with the best diastereomeric ratios, and the best *ee* of the *endo* adduct, any effort performed after the 1993 Evans study of the Cu(II)-catalyzed DA reaction [8a], could be considered worthless. To break the *ee* records is important, but it is not the sole scope of research, and opportunities for studies devoted to the understanding of the catalytic processes involved and for gaining insight into the structure of the [ligand-metal-reagent] supramolecular device are still open.

One of the major targets of the chiral Lewis acid controlled synthesis (CLAC synthesis) [12] is the preparation of both enantiomers from the same starting materials by designing small controlled modifications of the chiral catalyst. Only a few reports regarding the preparation of both enantiomers of DA adducts are available. A small change in the sulfonamide group of chiral (*R*)-2-sulfonylaminophenyl-4-phenyl-1,3-oxazoline induces a strong change of the enantioface selectivity in the Mg-catalyzed DA reaction [9f]. More important are the reports concerning the catalyzed DA cycloaddition which afford both enantiomers of the same adduct in high *ee* by using the same chiral ligand and a choice of achiral auxiliary ligands. This has been realized either with $Yb(OTf)_3$ and (*R*)-binaphthol [4d,e] using suitably chosen β-dicarbonylic achiral ligands, or with magnesium perchlorate (MP)-bis[(4*R*)-phenyloxazoline] in the presence or absence of hydroxylic achiral ligands [9b,c]. This point deserves attention to further deduce the organization of reagents and ligands around the Mg(II) cation and its influence on the CLAC-DA synthesis.

With the previous results in hand, and having tested the effect of MP-bis(oxazolines) **5-7** (Chart 1) on the DA reaction between **1** and **2a**, eventually in the presence of H_2O, ROH (R = Me, Et, *i*.Pr, and *ter*.Bu) or $(CH_2OH)_2$ [9b,c] some further points were inferred.

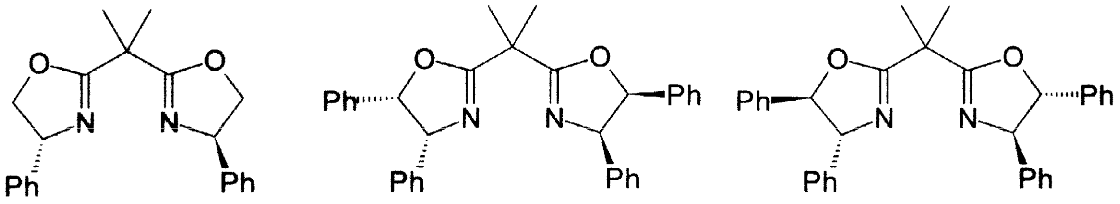

(*R*)-**5** (*R,S*)-**6** (*R,R*)-**7**

Chart 1

Tested were the effect:

a) of further auxiliary ligands differing from hydroxy derivatives;

b) of the different anions of the Mg(II) salt to check their possible behaviour as ligands in the supramolecular device;

c) of a change in the steric hindrance of the dienophile, testing 3-[(*E*)-2'-butenoyl]-1,3-oxazolidin-2-one **(2b)** (the *Z* isomer is unreactive) in addition to **2a**.

Results

All reactions between **1** and **2a** were run at -50 °C in CH_2Cl_2 with a ratio [**2a**]:[catalyst] = 10 (see the experimental section for details) and 12 hours were in general enough to carry to completion the reaction (Table 1).

*DA Reaction of **1** and **2a** with MP, bis(oxazolines) **5-7**, and 2 equiv auxiliary ligands.*

In addition to H_2O, shown to be the best hydroxylic-type ligand [9b,c], some amino and carbonyl compounds were tested.

When the reaction catalyzed by MP-(*R*)-**5** was run in the presence of 2 equiv triethylamine or pyridine, under the previously described conditions (Table 1 - entries 3,4), the yield of adducts was 0%. These ligands strongly bind the cation and inhibit the ligand exchange necessary for the catalytic cycle [13].

The effect of carbonyl compounds was tested by using acetone, dimethylcarbonate (DMC), and tetramethylurea (TMU) (Table 1, entries 5-7). Whereas the presence of 2 equiv acetone did not significantly change the enantiofacial selectivity induced by the tetrahedrally organized catalyst [(*S*)-**3a** was obtained in 67% *ee*], DMC reduced the stereoselectivity and the *ee* of (*S*)-**3a** was 40% only. The effect of TMU was more significant and quite similar to that of H_2O since (*R*)-**3a** was obtained in 51% *ee*. These results can be interpreted in terms of a coordination change from tetrahedral to octahedral around the Mg(II) cation with TMU acting as water does. TMU and water were thus selected as auxiliary ligands of election to change the enantioface selectivity of the catalyst.

When TMU was tested as auxiliary ligand with bis(oxazolines) (*R*,*S*)-**6** and (*R*,*R*)-**7**, the results were those expected if entries 13 and 19 (Table 1) are compared with entries 11, 12 and 17, 18 respectively. The effect of TMU was again to shift the coordination from tetrahedral to octahedral and (*R*)-**3a** became the enantiomer in excess with *cis*-**6** (an effect similar but lower than that of water), whereas (*S*)-**3a** remained the favoured enantiomer with *trans*-**7** (the *ee* was intermediate between those reported in entries 17 and 18, without or with water).

Table 1.

Enantioselectivity of the DA reaction between **1** and **2a** with the catalysts (10 mol %) from **5**-**7**, MP or MT, and the eventual auxiliary ligands (2 equiv), run at -50 °C in CH_2Cl_2.

Entry	Chiral ligand	Salt	Auxialiry ligand	% yield	*endo* : *exo*	% *e.e. endo* **3a**[a]
1[b]	(*R*)-**5**	MP	---	quant.	92 : 8	72 (*S*)
2[b]	(*R*)-**5**	MP	H_2O	quant.	93 : 7	70 (*R*)
3	(*R*)-**5**	MP	Et_3N	0	---	---
4	(*R*)-**5**	MP	Pyridine	0	---	---
5	(*R*)-**5**	MP	Acetone	quant.	94 : 6	67 (*S*)
6	(*R*)-**5**	MP	DMC	quant.	94 : 6	40 (*S*)
7	(*R*)-**5**	MP	TMU	quant.	96 : 4	51 (*R*)
8	(*R*)-**5**	MT	---	quant.	92 : 8	**88 (*R*)**
9	(*R*)-**5**	MT	H_2O	quant.	92 : 8	86 (*R*)
10	(*R*)-**5**	MT	TMU	quant.	93 : 7	88 (*R*)
11[b]	(*R*,*S*)-**6**	MP	---	quant.	92 : 8	22-43 (*S*)
12[b]	(*R*,*S*)-**6**	MP	H_2O	quant.	95 : 5	82 (*R*)
13	(*R*,*S*)-**6**	MP	TMU	quant.	94 : 6	55 (*R*)
14	(*R*,*S*)-**6**	MT	---	quant.	94 : 6	**93 (*R*)**
15	(*R*,*S*)-**6**	MT	H_2O	quant.	94 : 6	**95 (*R*)**
16	(*R*,*S*)-**6**	MT	TMU	quant.	94 : 6	**95 (*R*)**
17[b]	(*R*,*R*)-**7**	MP	---	quant.	98 : 2	**94 (*S*)**
18[b]	(*R*,*R*)-**7**	MP	H_2O	quant.	95 : 5	49 (*S*)
19	(*R*,*R*)-**7**	MP	TMU	quant.	97 : 3	78 (*S*)
20	(*R*,*R*)-**7**	MT	---	quant.	89 : 11	60 (*R*)
21	(*R*,*R*)-**7**	MT	H_2O	quant.	89 : 11	64 (*R*)
22	(*R*,*R*)-**7**	MT	TMU	quant.	88 : 12	31 (*R*)

[a] The *ee* reported is the average of 2-3 independent experiments; when the variation is larger than 2%, the range is reported. The major enantiomer is in parenthesis.

[b] Data taken from Ref. 9c.

*DA Reaction of **1** and **2a** with MT and bis(oxazolines) **5**-**7**.*

Both iodide (or better I_3^-) and $[Ph_4B]^-$ had been already tested as magnesium counterions in one of the legendary papers [9a] on this topic, and the result was 90% *ee* of the enantiomer resulting from the tetrahedral coordination. The failure of bromide [50% *ee* of (*S*)-**3a**] was expected, less the result of trifluoroacetate (a nearly racemic mixture was obtained).

The result obtained with magnesium triflate (MT) and (*R*)-**5** was interesting since (*R*)-**3a** was obtained as the preferential enantiomer in 88% *ee*. The sense of the asymmetric induction did not change running the reaction in the presence of 2 equiv H_2O or TMU (Table 1 - entries 8-10).

When (*R,R*)-**7** was used as ligand, MT gave 60% *ee* of (*R*)-**3a**, lower in absolute, but opposite in the sense of induction, than MP did (Table 1, entries 20 *vs* 17). Excellent, on the contrary, was the result of MT with the *cis* ligand (*R,S*)-**6**. The enantiofacial selectivity gave (*R*)-**3a** in 93 % *ee* (Table 1, entry 14), that is among the best results reported in the literature [1d,8e,9c] for the DA reaction between **1** and **2a**. The stereoselectivity did not change running the reaction in the presence of 2 equiv H_2O or TMU {Table 1, entries 15, 16, [both gave the (*R*) enantiomer in 95% ee] 21 and 22}. The simplest explanation seems that *the supramolecular device around the Mg(II) core is not influenced by auxiliary ligands in the MT-based chiral catalyst.*

*DA Reaction of **1** and **2b** with MP or MT and bis(oxazolines) **5**-**7**.*

The (*E*)-crotonyloxazolidinone (**2b**) was tested as dienophile. The best results of the DA reaction between this and **1** in terms of enantioselectivity were reported in the literature to be obtained with Ti-TADDOLates [1c-f], Yb-binaphthols [4b], and Cu-*ter.*butyl bis(oxazolines) [8a] with *ee* for the *endo* adduct around or above 90%.

Thus **2b** was made to react with MP or MT, chiral ligands **5-7** and, eventually, H_2O or TMU, at -15 °C in CH_2Cl_2 and the results are reported in Table 2.

The supramolecolar device derived from [MP-**5**-**2b**] was so sensitive to moisture to result useless. Reproducible results [28% *ee* (*S*) - Table 2, entry 1] were obtained by performing the reaction in the presence of molecular sieves, otherwise *ee* of **3b** in the range 27% (*S*) - 30% (*R*) were obtained. This result fits with those obtained running the reaction in the presence of 2 equiv auxiliary ligands: the induced octahedral coordination gave rise to (*R*)-**3b** with *ee* of 62% and 87% for H_2O and TMU respectively (Table 2, entries 2, 3).

Table 2.

Enantioselectivity of the DA reaction between **1** and **2b** with the catalysts (10 mol %) from **5-7**, MP or MT, and the eventual auxiliary ligands (2 equiv), run at -15 °C in CH_2Cl_2.

Entry	Chiral ligand	Salt	Auxiliary ligand	% conversion (time, days)	*endo* : *exo*	% *e.e. endo* **3b**[a]	e.r. *exo*[b]
1	(*R*)-**5**	MP	---	quant. (2)	85 : 15	28 (*S*)[c]	n.d.
2	(*R*)-**5**	MP	H_2O	quant. (4)	83 : 17	62 (*R*)	19 : 81
3	(*R*)-**5**	MP	TMU	93 (6)	84 : 16	87 (*R*)	11 : 89
4[d]	(*R*)-**5**	MT	---	94 (2)	81 : 19	84 (*R*)	12 : 88
5	(*R*)-**5**	MT	H_2O	92 (2)	81 : 19	84 (*R*)	11 : 89
6	(*R*)-**5**	MT	TMU	88 (2)	81 : 19	84 (*R*)	11 : 89
7	(*R,S*)-**6**	MP	---	quant. (3)	83 : 17	38 (*R*)[c]	n.d.
8	(*R,S*)-**6**	MP	H_2O	84 (2.5)	85 : 15	85 (*R*)	10 : 90
9	(*R,S*)-**6**	MP	TMU	quant. (2)	87 : 13	**95 (*R*)**	n.d.
10	(*R,S*)-**6**	MT	---	97 (2)	84 : 16	**92 (*R*)**	7 : 93
11	(*R,S*)-**6**	MT	H_2O	quant. (2.5)	83 : 17	**90 (*R*)**	10 : 90
12	(*R,S*)-**6**	MT	TMU	quant. (2.5)	84 : 16	**91 (*R*)**	10 : 90
13	(*R,R*)-**7**	MP	---	quant. (2)	88 : 12	72 (*S*)[c]	75 : 25
14	(*R,R*)-**7**	MP	H_2O	95 (2)	88 : 12	46 (*S*)	n.d.
15	(*R,R*)-**7**	MP	TMU	quant. (3)	85 : 15	24 (*S*)	n.d.
16	(*R,R*)-**7**	MT	---	35 (7)	75 : 25	60 (*R*)	10 : 90
17	(*R,R*)-**7**	MT	H_2O	42 (7)	74 : 26	70 (*R*)	10 : 90
18	(*R,R*)-**7**	MT	TMU	73 (7)	75 : 25	50 (*R*)	20 : 80

a)The ee reported is the average of 2-3 independent experiments. The major enantiomer is in parenthesis.

b)The absolute configuration of the *exo*-adduct is unknown, the ratio refers to the order of elution (see experimental part).

c)Reaction run in the presence of MS 4Å pellets (50 mg).

d)Ref. 10: the reaction run at room temperature gave [*endo*] : [*exo*] = 77:24 and the *ee* of **3b** was 73% (*R*).

The change of the anion of Mg(II) from perchlorate to triflate resulted in the formation of the (*R*) enantiomer (in analogy to **2a**) either in the absence or in the presence of H_2O or TMU and the *ee* was always 84% (Table 2, entries 4-6).

The (*R,S*)-**6** ligand gave unsatisfactory results with MP [the *ee* of **3b** was 38% (*R*) in the presence of MS 4A]. As previously observed for **2a**, the addition of 2 equiv H_2O strongly influenced the enantiofacial selectivity of the catalyst and the (*R*) enantiomer was obtained in 87% *ee*. A significant improvement of the performance of the catalyst was obtained with TMU and the *ee* [95% (*R*)] was one of the best results reported in the literature [1c-f,4a,8a] for this DA reaction (Table 2, entries 7-9).

Excellent results were also obtained with the MT-derived catalyst and the *ee* of the (*R*) enantiomer was in the range 90-92%, either with or without auxiliary ligands (Table 2, entries 10-12).

The results with ligand (*R,R*)-**7** were comparable to those obtained with **2a**. The (*S*) enantiomer was preferentially formed with MP (72% *e.e.* - Table 2, entry 13) and this selectivity was reduced in the presence of H_2O or TMU (46 and 24% respectively - Table 2, entries 14 and 15). The enantioselectivity was strongly changed by using MT, since the (*R*) enantiomer was obtained in 50-70% *ee,* with or without auxiliary ligands (Table 2, entries 16-18).

Discussion and Conclusions

The above reported results illustrate a good example of CLAC DA reactions. The enantiofacial selectivity of the reaction between **1** and **2a,b** can be modulated keeping unchanged the chirality of the ligand and the cationic core of the catalyst. The variations involve either the counterion of Mg(II) (perchlorate or triflate) or the addition of two equivalents of auxiliary achiral ligands, the best ones being water or TMU.

The reason of the change of the enantiofacial selectivity seems to be the different coordinations around the metal of chiral ligand, dienophile, and auxiliary ligands.

Three main types of coordination (in Chart 2 are illustrated those involving **2a** and **5**) can be assumed: one tetrahedral (**A**) with [chiral ligand - Mg(II) - **2**] in the ratio [1:1:1], and two octahedral whose supramolecular devices require [chiral ligand - Mg(II) - **2** - **X**] in the ratio [1:1:1:2]; the only difference is the respective positions of the auxiliary ligands **X**: either *cis* or *trans* (Chart 2 - **B** and **C** respectively). Three further variables should be considered, but previous ^{1}H-NMR investigations [9c] suggested the *s-cis* conformation of the dienophile in **A**-**C** and the stereochemistry of the **B** complex with both the oxazolidinone ring close to the phenyl group and the oxazolidinone carbonyl group *trans* to **X**.

If the above complexes are involved in the catalytic process, can **A-C** rationalize the different results reported in Tables 1 and 2?

When MP is made to react with chiral ligands **5-7** in the presence of **2a,b**, the tetrahedral complex **A** is formed (the suitable modifications of the structure in Chart 2 can be easily assumed if **2b** and **6** or **7** are involved). The diastereoface better accessible to **1** should be the *Re* one and (*S*)-**3a,b** is expected to be obtained. The only exception to this is the reaction reported in Table 2 - entry 7, whereas the results reported in Table 1 (entries 1, 11 and 17) and Table 2 (entries 1 and 13), even with different degrees of enantioselection, fit this model.

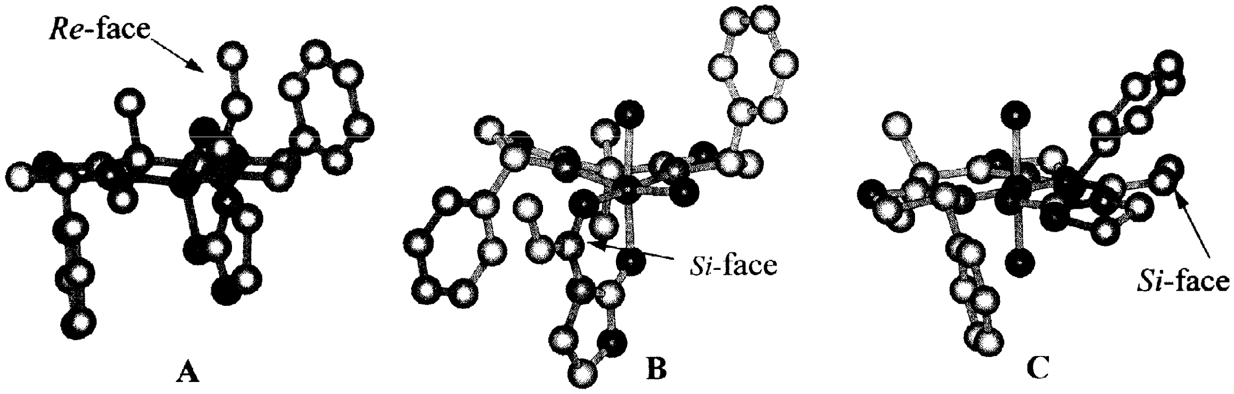


Chart 2

When 2 equiv of auxiliary ligands are added to the tetrahedral complex, the *cis* octahedral complex (**B**) is expected to be formed [9c]. This requires ligands with suitable nucleophilicity that is not the case of the experiments described in Table 1, entries 3 and 4. When (**B**) is involved in the catalytic cycle, the enantiomer (*R*) is expected if the addition occurs on the *Si* face preferentially. The results described in Table 1 (entries 2, 7, 12, 13, 18 and 19) and Table 2 (entries 2, 3, 8, 9, 14 and 15) show that, when this occurs, either the (*R*) enantiomer becomes the main product of the reaction, or the *ee* of the (*S*) enantiomer is strongly reduced.

When the catalyst is builded from MT, something different must happen if the (*R*) enantiomer is preferentially obtained and its *ee* does not change in the presence of 2 equiv auxiliary ligands (Table 1: entries 8-10, 14-16 and 20-22; Table 2: entries 4-6, 10-12 and 16-18). Since the complex must have an octahedral configuration which is not modified by addition of the auxiliary ligands, this requires that two electronegative triflate ligands are involved in the coordination, a model which has been already proposed by Takacs [10]. The octahedral complex could be either (**B**) or (**C**), but the results obtained with the triflate-based catalysts are too different from those obtained with the (perchlorate/auxiliary ligands)-based catalysts to involve an identical configuration (see *e.g.* in Table 1 entry 19 *vs* 20 and in Table 2 entry 15 *vs* 16). If (**B**) is the intermediate in the presence of MP-auxiliary ligands [9c], it seems reasonable to propose (**C**) as the intermediate for the MT-catalyzed processes.

If an homegeneous octahedral complex like (**C**) is involved in the catalytic cycle of the DA reaction between **1** and **2a** to give (*R*)-**3a** enantioselectively, a linear relationship is expected to be obtained by plotting ee_{product} *vs* ee_{ligand}. The results, illustrated in Figure 1, were determined on mixtures of (*R*)-**5** having enantiomeric purities of 75, 50, and 25% and gave (*R*)-**3a** with *ee* of 62, 38, and 18% respectively.

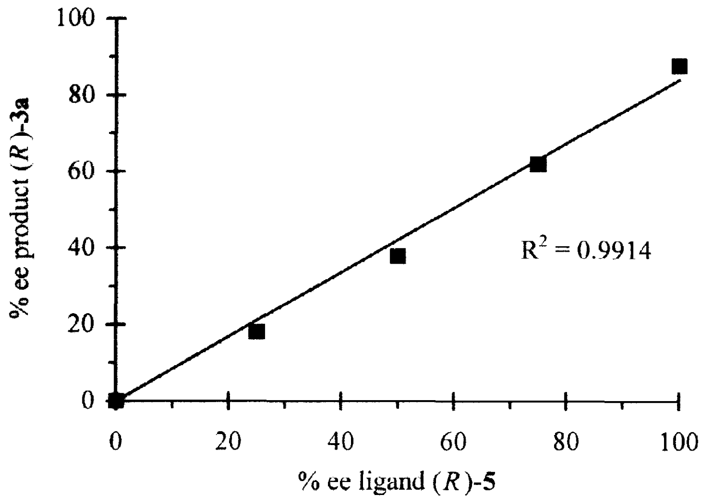


Figure 1. Linear relationship between the *ee* of the *endo* product (*R*)-**3a** and that of the ligand (*R*)-**5**.

In conclusion, the above reported results illustrate the excellent flexibility of Mg(II) as cationic core of a chiral catalyst for a DA reaction. It can easily change its coordination number from 4 to 6 assuming either a tetrahedral or an octahedral configuration, and this can be done either with auxiliary ligands (water or TMU) or with the anions deriving from the Mg(II) salt.

Since the tetrahedral or octahedral configuration, at least in the DA reaction between **1** and **2a,b**, have opposite enantiofacial selectivity, it becomes easy to obtain excellent *ee* of both enantiomers.

From the results reported in Table 1, (*S*)-**3a** can be obtained in 94% *ee* using the tetrahedral catalyst derived from MP and ligand **7**; (*R*)-**3a** can be obtained in 93-95% *ee* using the octahedral catalyst derived from MT and ligand **6**.

From the results reported in Table 2 it seems difficult to run the DA reaction between **1** and **2b** with a tetrahedrally organized Mg catalyst, whereas the octahedral catalyst derived from MP, (**6**) and 2 equiv TMU gives (*R*)-**3b** with 95% *ee*. The way to have (*S*)-**3b** in 87% *ee* requires MP, 2 equiv TMU and the commercially available chiral ligand (*S*)-**5**.

Whereas the *trans* bis(oxazoline) (*R,R*)-**7** proved best for **2a** and MP [9c], the ligand of election for MT and **2a,b** was the *cis* (*R,S*)-**6** one. Furthermore, when compatible with the desired results, MT was found to be superior to the corresponding MP since traces of moisture did not changed the efficiency of the deriving catalyst.

Experimental Section

Dichloromethane was the hydrocarbon-stabilized Aldrich ACS grade, distilled on calcium hydride and immediately used. Magnesium perchlorate and magnesium triflate were the anhydrous Aldrich ACS reagents. 2,2-Bis{2-[4(*R*)-phenyl-1,3-oxazolinyl]}propane **5** and its 4(*S*) isomer were commercially available by Aldrich; whereas 2,2-bis{2-[4(*R*),5(*S*)- and [4(*R*),5(*R*)-diphenyl-1,3-oxazolinyl]}propanes (**6** and **7** respectively) were prepared as described in the literature [13]. The *endo* : *exo* ratios were measured by HPLC and confirmed by ^{1}H NMR; the enantiomer compositions were determined by HPLC (Daicel Chiralcel OD and Chiralpak AD columns).

3-Acryloyl-1,3-oxazolidin-2-one (**2a**) was prepared following the literature method [14].

3-(E)-2'-butenoyl-1,3-oxazolidin-2-one (**2b**) was prepared following the literature method [15]. The reaction mixture was column chromatographed (eluant, cyclohexane-ethyl acetate = 85 : 15) to give as first fraction 3-(*Z*)-2'-butenoyl-1,3-oxazolidin-2-one (10% yield) as white crystals, m.p. = 41-42 °C (from diethyl ether). ^{1}H NMR, δ ($CDCl_3$): 7.01 (1H, dq, *J* = 1.5 and 11.5 Hz, α-vinylic proton), 6.47 (1H, dq, *J* = 7.5 and 11.5 Hz, β-vinylic proton), 4.42 (2H, t, H_5), 4.05 (2H, t, H_4), and 2.15 (3H, dd, *J* = 1.5 and 7.5 Hz, Me). **2b** was isolated as second fraction (75% yields) as white crystals, m.p. = 46-47 °C (from diethyl ether). ^{1}H NMR, δ: 7.25-7.07 (2H, m, vinylic protons), 4.41 (2H, t, H_5), 4.07 (2H, t, H_4), and 1.98 (3H, dd, *J* = 1 and 6.5 Hz, Me).

DA Reaction of cyclopentadiene (1) and 3-acryloyl-1,3-oxazolidin-2-one (2a) catalyzed by magnesium perchlorate or magnesium triflate and bis(oxazolines) 5-7. General procedure.

Anhydrous magnesium perchlorate (11 mg - 0.05 mmol) or magnesium triflate (16 mg - 0.05 mmol), bis(oxazoline) **5-7** (0.05 mmol) and 3-acryloyl-1,3-oxazolidin-2-one (**2a**) (72 mg - 0.5 mmol) were added to anhydrous CH_2Cl_2 (0.3 mL) under stirring at ambient temperature in a rubber septum sealed vial. Within one hour the inorganic salt dissolved and a dusty white solid can precipitate. At this stage, *when required,* the auxiliary ligand [water or tetramethylurea (0.1 mmol)] was added with a microsyringe and stirring was continued for two additional hours. The vial was chilled at -50 °C and after 20 minutes cyclopentadiene (0.1 mL - about 1.5 mmol) was added. Stirring was continued overnight, then the reaction was decomposed in water, extracted with CH_2Cl_2 and dried . In at least one experiment for each reaction, a portion of the crude mixture was monitored by ^{1}H NMR and the *endo* : *exo* ratio was determined. The standard analysis of the reaction mixture was performed by HPLC analysis using a Diacel OD column with 10% 2-propanol in hexane as eluant [1 mL/min; average retention times: 19.9 and 20.7 min for *exo* enantiomers, 21.9 min for (*S*)-**3** and 24.6 min for (*R*)-**3**]. The *exo* : *endo* ratio, determined by HPLC, was identical to that determined by ^{1}H NMR.

*DA Reaction of cyclopentadiene (**1**) and 3-(E)-2'-butenoyl-1,3-oxazolidin-2-one (**2b**) catalyzed by magnesium perchlorate or magnesium triflate and bis(oxazolines) **5-7**. General procedure*

The reactions were run under the same experimental condtions reported above for **2a,** but the temperature was -15 °C and the time required is reported in Table 2. A portion of the crude mixture was monitored by ^{1}H NMR to determine the amount of unreacted **2b** and the *endo* : *exo* ratio. The standard analysis of the reaction mixture was performed by HPLC analysis using a Chiralpak AD column with 5% 2-propanol in hexane as eluant [0.5 mL/min; average retention times: 24.8 and 27.0 min for *exo* enantiomers, 25.8 min for (*S*)-**3b** and 29.6 min for (*R*)-**3b**].

Acknowledgment.

Financial support for this work was provided by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and by the Consiglio Nazionale delle Ricerche (CNR).

References

[1] (a)Narasaka K, Inoue M, Okada N. Chem. Lett. 1986; 1109. (b)Narasaka K, Inoue M, Yamada T. Chem. Lett. 1986; 1967. (c)Narasaka K, Iwasawa N, Inoue M, Yamada T, Nakashima M, Sugimori J. J. Am. Chem. Soc. 1989; 111: 5340. (d)Corey EJ, Matsumura Y, Tetrahedron Lett. 1991; 32: 6289. (e)Haase C, Sarko CR, DiMare M. J. Org. Chem. 1995; 60: 1777. (f)Seebach D, Dahinden R, Marti RE, Bek AK, Plattner DA, Kühnle NM. J. Org. Chem. 1995; 60: 1788. (g)Gothelf KV, Hazell RG, Jørgensen KA. J. Am. Chem. Soc. 1995; 117: 4435. (h)Gothelf KV, Jørgensen KA. J. Org. Chem. 1995; 60: 6847. (i)Seebach D, Marti RE, Hintermann T. Helv. Chim. Acta 1996; 79: 1710. (j)Altava B, Burguete MA, Fraile JM, Garcia JI, Luis SV, Mayoral JM, Royo AJ, Vicent MJ. Tetrahedron: Asymmetry 1997; 8: 2561. (k)Tietze LF, Ott C, Frey U. Liebigs Ann. Chem. 1996; 63. (l)Narasaka K, Yamamoto I. Tetrahedron 1992; 48: 5743.

[2] (a)Rebiere F, Riant O, Kagan HB. Tetrahedron: Asymmetry 1990; 1: 199. (b)Corey EJ, Imai N, Pikul S. Tetrahedron Lett. 1991; 32: 7517. (c)Corey EJ, Sarshar S, Bordner J. J. Am. Chem. Soc. 1992; 114: 7938. (d)Corey EJ,Sarshar S,Lee DH. J. Am. Chem. Soc. 1994;116:12089. (e)Maruoka K, Oishi M, Shiohara K, Yamamoto H. Tetrahedron 1994; 50: 8983. (f)Fraile JM, Mayoral JM, Royo AJ, Royo AJ, Salvador RV, Luis SV, Burguete MA. Tetrahedron 1996; 52: 9853.

[3] (a)Furuta K, Shimizu S, Miwa Y, Yamamoto H. J. Org. Chem. 1989; 54: 1481. (b)Corey EJ, Loh TP. J. Am. Chem. Soc. 1991; 113: 8966. (c)Corey EJ, Loh TP, Roper TD, Azimioara MD, Noe MC. J. Am. Chem. Soc. 1992; 114: 8290. (d)Ishihara K, Yamamoto H. J. Am. Chem. Soc. 1994; 116: 1561. (e)Loh TP, Wang RB, Sim KY. Tetrahedron Lett. 1996; 37: 2989. (f)Hayashi Y, Rohde JJ, Corey EJ. J. Am. Chem. Soc. 1996; 118: 5502. (g)Corey EJ, Lee TW. Tetrahedron Lett. 1997; 38: 5755.

[4] (a)Kobayashi S, Hachiya I, Araki M, Ishitani H. Tetrahedron Lett. 1993; 34: 3755. (b)Kobayashi S, Hachiya I, Ishitani H, Araki M. Tetrahedron Lett. 1993; 34: 4535. (c)Kobayashi S, Araki M, Hachiya I. J. Org. Chem. 1994; 59: 3758. (d)Kobayashi S, Ishitani H, Hachiya I, Araki M. Tetrahedron 1994; 50: 11623. (e)Kobayashi S, Ishitani H. J. Am. Chem. Soc. 1994; 116: 4083. (f)Kobayashi S, Ishitani H, Araki M, Hachiya I. Tetrahedron Lett. 1994; 35: 6325. (g)Hawarth J, Gillespie K. Tetrahedron Lett. 1996; 37: 6011.

[5] Carmona D, Cativiela C, Garcia-Correas R, Lahoz FJ, Lamata MP, Lopez JA, Lopez-Ram de Viu MP, Oro LA, San Josè E, Viguri F. J. Chem. Soc., Chem. Commun. 1996; 1247.

[6] Yamashita Y, Katsuki T. Synlett 1995; 829.

[7] (a)Corey EJ, Imai N, Zhang HY. J. Am. Chem. Soc. 1991; 113: 728. (b)Khiar N, Fernandez I, Alcudia F. Tetrahedron Lett. 1993; 34: 123.

[8] (a)Evans DE, Miller SJ, Lectka T. J. Am. Chem. Soc. 1993; 115: 6460. (b)Evans DE, Lectka T, Miller SJ. Tetrahedron Lett. 1993; 34: 7027. (c)Evans DE, Murry JA, von Matt P, Norcross RD, Miller SJ. Angew. Chem. Int., Ed. Engl. 1995; 34: 798. (d)Davies IW, Senanayake CH, Larsen RD, Verhoeven TR, Reider PJ. Tetrahedron Lett. 1996; 37: 1725. (e)Evans DA, Kozlowski MC, Tedrow JS. Tetrahedron Lett. 1996; 37: 7481. (f)Davies IW, Gerena L, Castonguay L, Senanayake CH, Larsen RD, Verhoeven TR, Reider PJ. J. Chem. Soc., Chem. Commun. 1996; 1753. (g)Takaks JM, Quincy DA, Shay W, Jones BE, Ross CR. Tetrahedron: Asymmetry 1997; 8: 3079. (h)Davies IW, Gerena L, Cai D, Larsen RD, Verhoeven TR, Reider PJ. Tetrahedron Lett. 1997; 38: 1145. (i)Evans DA, Barnes DM. Tetrahedron Lett. 1997; 38: 57. (j)Evans DA, Barnes DM. Tetrahedron Lett. 1997; 38: 3193. (k)Knol J, Meetsuna A, Feringa BL. Tetrahedron: Asymmetry 1995; 6: 1069.

[9] (a)Corey EJ, Ishihara K. Tetrahedron Lett. 1992; 33: 6807. (b)Desimoni G, Faita G, Righetti PP. Tetrahedron Lett. 1996; 37: 3027. (c)Desimoni G, Faita G, Gamba Invernizzi A, Righetti P. Tetrahedron 1997; 53: 7671. (d)Ordonez M, Guerrero-de la Rosa V, Labastida V, Llera JM. Tetrahedron: Asymmetry 1996; 7: 2675. (e)Honda Y, Date T, Hiramatsu H, Yamauchi M. J. Chem. Soc., Chem. Commun. 1997; 1411. (f)Ichiyanagi T, Shimizu M, Fujisawa T. J. Org. Chem. 1997; 62: 7937.

[10] Takacs JM, Lawson EC, Reno MJ, Youngman MA, Quincy DA. Tetrahedron: Asymmetry 1997; 8: 3073.

[11] (a)Kanemasa S, Oderaotoshi Y, Yamamoto H, Tanaka J, Wada E, Curran DP. J. Org. Chem. 1997; 62: 6454.

[12] Kobayashi S, Horibe M. Chem. Eur. J. 1997; 3: 1472.

[13] Desimoni G, Faita G, Mella M, Ricci M, Righetti PP. Tetrahedron 1997; 53: 13495.

[14] Pikul S, Corey EJ. Org. Synth. 1993; 71: 30

[15] Evans DA, Chapman KT, Bisaha J. J. Am. Chem. Soc. 1988; 110: 1238.