Catalytic Asymmetric Diels–Alder Reactions†

Henri B. Kagan* and Olivier Riant

Laboratoire de Synthèse Asymétrique, Université Paris-Sud, 91405-Orsay, France

Received November 27, 1991 (Revised Manuscript Received March 23, 1992)

Contents

I. Introduction

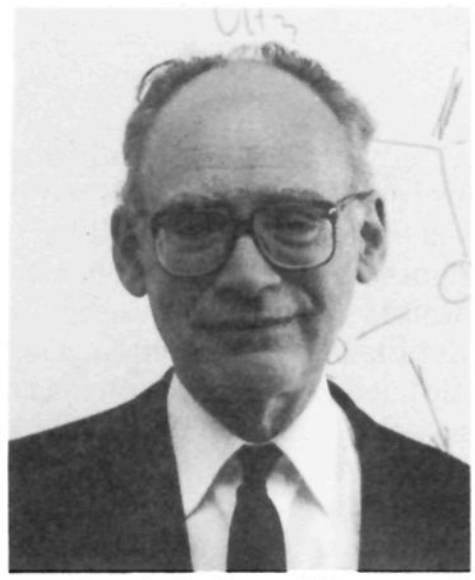
The Diels–Alder reaction is a standard method for six-membered ring formation.[1] It allows in principle the formation of four contiguous asymmetric centers. Relative stereochemistry is usually well defined because of the formation of a cyclic transition state arising from suprafacial–suprafacial interaction, with endo approach.

The asymmetric Diels–Alder reaction was first investigated more than 20 years ago by introducing a *removable chiral auxiliary on the dienophile* (see ref 2 for a review on early attempts and refs 3–5 for more recent reviews).

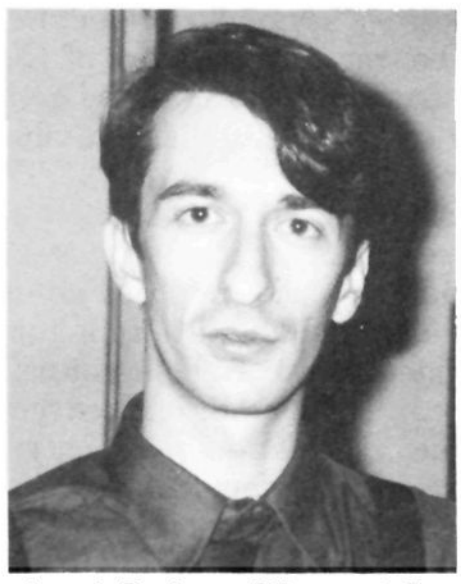
A useful development became possible when it was found that Lewis acids (e.g. $AlCl_3$) catalyze the Diels–Alder reaction, allowing to run it in very mild conditions, often below 0 °C.[6-7] The activation process occurs by coordination of the carbonyl group of dienophile to the Lewis acid.[8,9] The mildness of the catalytic reaction allowed very high levels of diastereomeric excess (<95%) with menthyl acrylate or menthyl fumarate and a diene.[10,11] Corey developed an asymmetric Diels–Alder approach to prostaglandin synthesis.[12] Chiral auxiliaries of various kinds have been subsequently developed for thermal or catalytic Diels–Alder reactions, and some of them are now commercially available.[13] Many natural products can be prepared at an early stage of the synthetic scheme by taking advantage of an asymmetric Diels–Alder reaction. For example loganine has been obtained from a Diels–Alder reaction on a crotonate of a terpene derivative. The cycloadduct was prepared with very high ee.[19] In this efficient reaction the chiral auxiliary is recyclable but a separation step is necessary, and each time only 1 equiv of chiral product is obtained for 1 mol of chiral auxiliary.

In this article we will concentrate on the alternative process where the *chiral auxiliary is part of the catalyst*.

† Dedicated to the memory of Prof. A. Horeau, deceased February 14, 1992.



Henri B. Kagan was born in Boulogne-Billancourt, France, in 1930. He graduated from Sorbonne and Ecole Nationale Supérieure de Chimie de Paris in 1954. He was the first Ph.D. student of the J. Jacques group in Collège de France (Paris), for work on modified steroids. In 1962, he became a research associate with A. Horeau in College de France and became involved in research devoted to stereochemistry and asymmetric synthesis. In 1965, he was also a research associate at the University of Texas, Austin, with T. Mabry. In 1968 he became an assistant professor at the University of Paris-Sud and became a full professor in 1973. In 1991, he was elected to be a member of the French Academy of Sciences. Kagan has been the recipient of various awards of the French Chemical Society, the French Academy of Sciences, and the CNRS. In 1990, he received the Prelog Medal from ETH and in 1991 the August Wilhelm von Hofmann medal from German Chemical Society. His current interests focus on stereochemistry, asymmetric catalysis, asymmetric synthesis, and organic chemistry with divalent lanthanides.



Olivier Riant was born in Boulogne-Billancourt, France, in 1964. He graduated from Ecole Normale Supérieure (Saint-Cloud Lyon) and received a Magistère de Chimie diploma in 1989 at the University of Paris-Sud. In 1988, he got the Agrégation de Chimie diploma. He is currently a teaching assistant at the University of Paris-Sud while preparing his Ph.D. with H. B. Kagan. His research interests include the use of chiral Lewis acids in asymmetric catalysis, asymmetric catalysis of the Diels–Alder reaction with chiral bases, and asymmetric induction in organometallic complexes including ferrocenyl compounds.

0009-2665/92/0792-1007$10.00/0

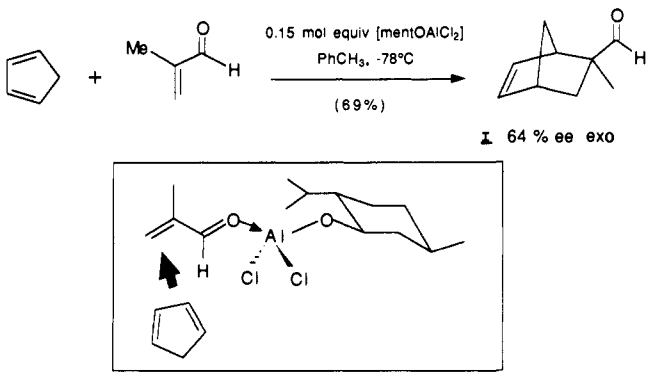


Figure 1.

The potential advantages are multiple: a smaller amount of chiral auxiliary material is required, and the final product is obtained directly. These advantages are counterbalanced by the difficulty to rationally devise the chiral catalyst because of uncertainties of the mechanistic details of the catalytic cycle. The asymmetric catalytic Diels–Alder reaction is a relatively new area, which began in the later 1970's and which is now in rapid development.

The chiral catalyst obviously should be a modification of Lewis acids which have been successfully used in the Diels–Alder reaction (based mainly on boron, aluminum, or titanium). In the following sections will be successively presented results obtained with various chiral Lewis acids. Chiral Lewis acids can act as asymmetric catalysts for various organic transformations, including Diels–Alder reactions (this area has been recently reviewed by Narasaka[20]). Some cases of Diels–Alder reactions where chiral Lewis acids are present in stoichiometric amounts will also be included. In sections VII and VIII are described asymmetric catalysts which are not Lewis acids. This review includes classical Diels–Alder reactions as well as hetero Diels–Alder reactions and homo Diels–Alder reactions.

II. Chiral Aluminum Catalysts

The first positive asymmetric catalytic Diels–Alder reaction can be traced to the work of Koga et al.[22] in 1979. These authors performed the cycloaddition of methacrolein on cyclopentadiene catalyzed by menthoxydichloroaluminum (Figure 1). There was no further report in that area until a new paper in 1987 where the same authors confirmed the results (57% ee) for the cycloadduct I and proposed an interpretation based on the observed absolute configuration.[23]

We investigated the same reaction by using aluminum alcoholates bearing an additional oxygen, hoping to introduce some organization in the chiral complex by chelate effects such as depicted in Figure 2.[24] Such complexes were easily prepared by mixing a chiral alcohol with $EtAlCl_2$ at −78 °C in CH_2Cl_2.

An intensive investigation of monoethers of chiral diols such as **1a,b** and chiral C_2 diols such as **2a,b** gave disappointing results. However quite a high ee was observed for a catalyst prepared from an equimolecular mixture of an unprotected chiral diol and $EtAlCl_2$. Many chiral unsymmetric diols were tested in this reaction (ee <50% for **3b–5**) (Figures 2 and 3). Results with 1,1′-diphenyl-1,2-propanediol (**3a**) are very reproducible (close to 73% ee) if one follows a procedure involving aging of the catalyst for 2 h at room temperature before performing the reaction. Various experimental parameters of the reaction were studied (see for example Figure 4). Increasing the catalytic ratio of the catalyst to 0.5–1 gives a negative effect on the enantioselectivity (catalytic ratio of 1 gives ee of 51% after 20 h). Increase of the ee for the cycloadduct I was observed from 38% (at 5% conversion) to 73% at the end of the reaction. Enantiomeric excess reaches 86% if one decreases temperature to −100 °C. The $\Delta\Delta G^{\ddagger}$ value (−0.74 kcal mol^{-1}) at −78 °C partitions between $\Delta\Delta H^{\ddagger} = -2.46$ kcal mol^{-1} and $-T\Delta\Delta S^{\ddagger} = +1.73$ kcal mol^{-1}. This shows that there is an enthalpic control and that the favored transition state is the more organized one.

The exact nature of the chiral catalyst remains to be established. We tentantively assumed a tetracoordinate or a pentacoordinate aluminum complex, with coordination at carbonyl anti with respect to the C=C bond (Figure 5). This catalyst has also been tested with other dienophiles.[24]

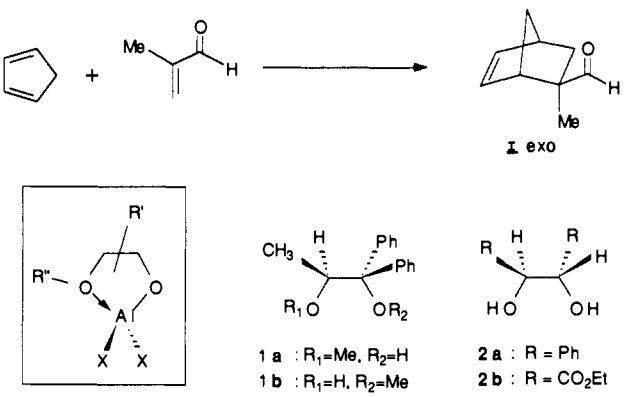


Figure 2.

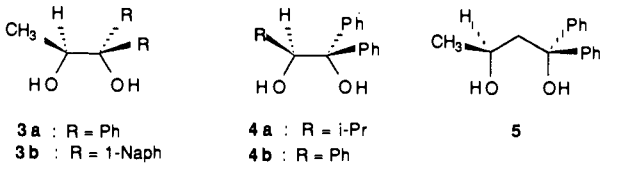


Figure 3.

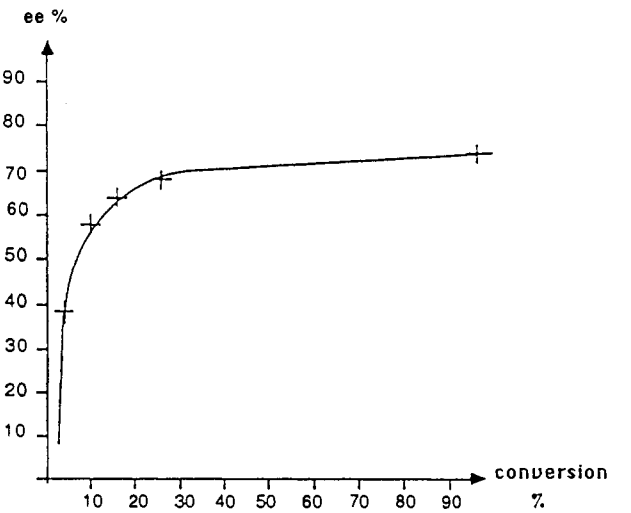


Figure 4. Asymmetric synthesis of (−)-I with a chiral catalyst (0.05 equiv) prepared from $EtAlCl_2$ and (*S*)-**3a** (1:1). Reaction performed in CH_2Cl_2 at −78 °C.

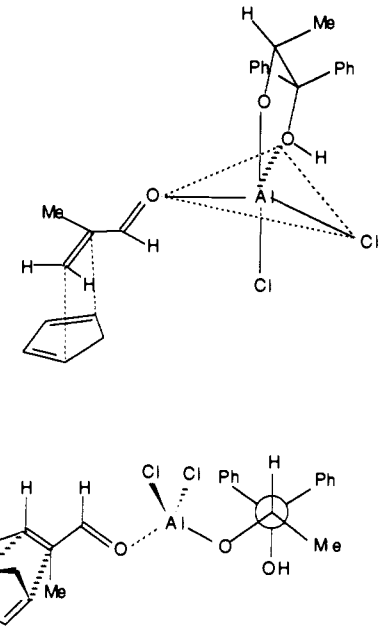


Figure 5.

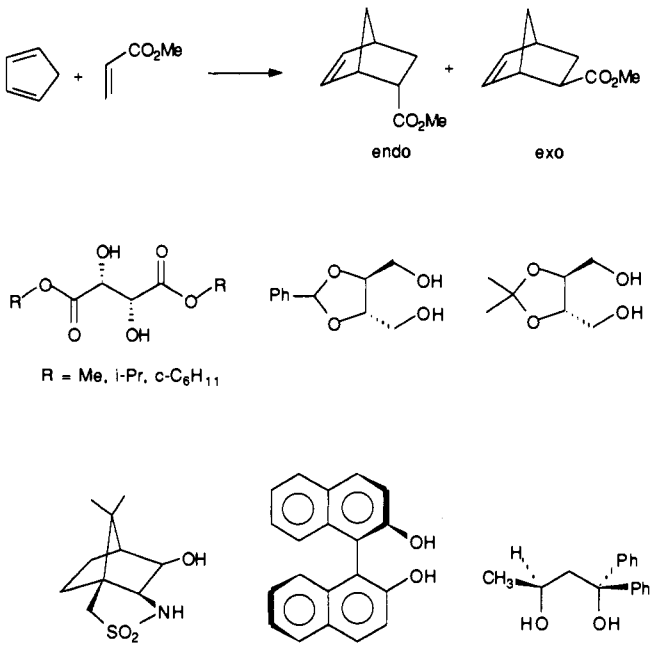


Figure 6.

Many dialkoxychloroaluminum complexes were studied by Herrmann et al.[25] who also showed the influence of the aging time on the composition of the catalytic solution. Reaction of $AlBu^i_2Cl$ and a chiral ligand was studied as a function of time by ^{27}Al NMR and cryoscopic measurements. Formation of a dimer from a monomer was fast at room temperature, but in the presence of a dienophile like methyl acrylate, the dimerization process became very slow. This method allowed the authors to study the catalytic Diels–Alder reaction between methyl acrylate and cyclopentadiene for the different catalytic species, and the best results were obtained for the monomeric ones. An intensive investigation of this reaction was performed for various chiral bidentate ligands (Figure 6) and ee's up to 70% were achieved. In one case, enantiomeric excess could be raised up to 81% if *tert*-butyl acrylate was used as a dienophile.

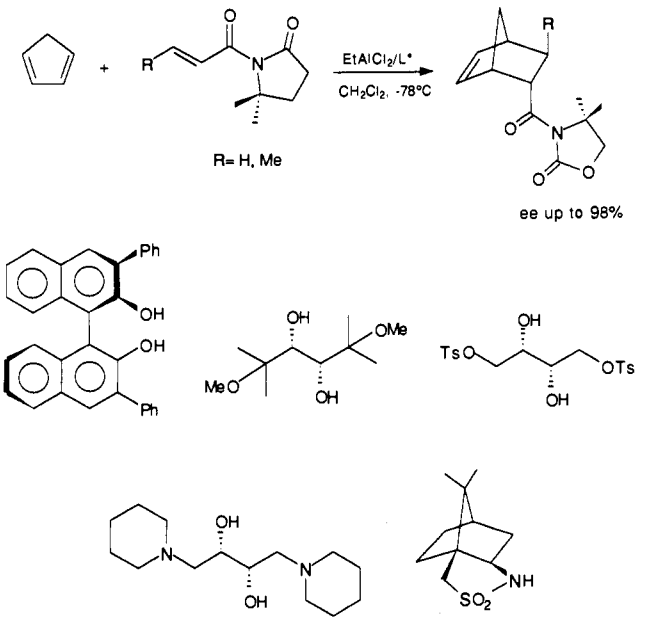
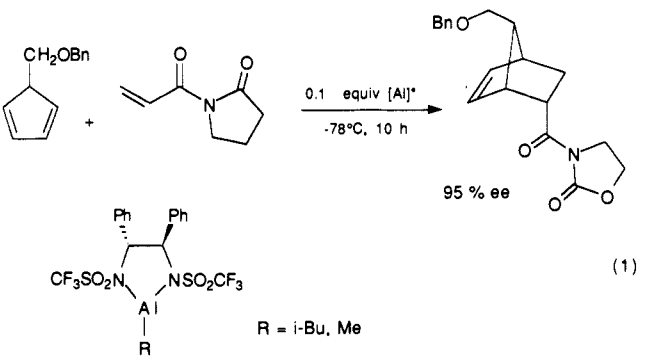


Figure 7.

In a former study, Chapuis et al. described the use of chiral Lewis acids prepared in situ from $EtAlCl_2$ and chiral diols (in a 2:1 ratio) or a sulfonamide (in a 1:1 ratio).[26] Enantiomeric excesses up to 98% for the cycloadduct were achieved when the Diels–Alder reaction was performed with a bidentate dienophile bearing an oxazolidinone moiety (Figure 7). However, there was no report on the possible use of a catalytic amount of chiral complex, and the system was restricted to the bidentate crotonate dienophile (for example, ee drops from 89% to 36% when an acrylate analogue was used as a dienophile).

Corey et al. recently prepared chiral aluminum complexes derived from chiral bis-sulfonamides with C_2 symmetry (eq 1).[27] The aluminum complex (0.1 mol

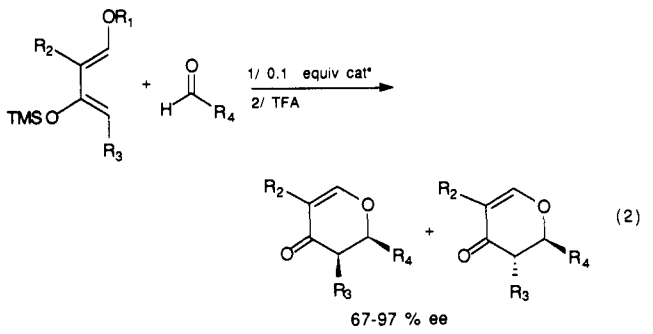


(1)

equiv) acts as a catalyst for cycloaddition between 3-acryloyl-1,3-oxazolidin-2-one and cyclopentadienes. One example is detailed above, giving an intermediate useful for production of optically active prostaglandins.

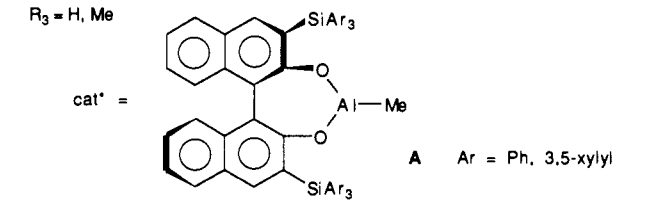
Asymmetric hetero Diels–Alder reaction was investigated by H. Yamamoto et al.[28] A chiral aluminum complex (eqs 2 and 3) with a binaphthyl chirality was found to be very efficient for the condensation of benzaldehyde on some dienes (97% ee). The two silyl moieties were key for the catalytic activity, preventing strong coordination of the aluminum complex to the reaction product.

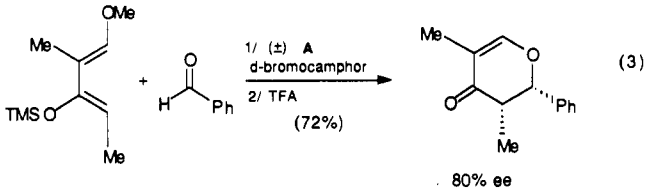
The chiral aluminum complex A as a catalyst gives a quite general method for the generation of function-



(2)

R_1 = Me, TMS R_4 = Ph, (E) Ph=CH-, c-C_6H_{11}, nBu
R_2 = H, OAc
R_3 = H, Me





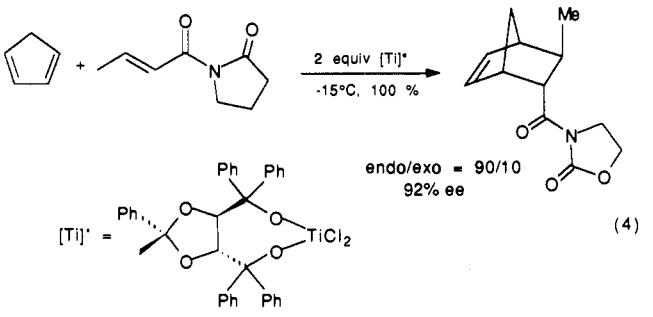
(3)

alized dihydropyrones and has also been employed with success in the asymmetric catalysis of the ene reaction (ee up to 88%)[29] and asymmetric Claisen rearrangement (ee up to 93%).[30] Chiral ketones such as 3-bromocamphor can bind selectively one enantiomer of the complex. Thus if the hetero Diels–Alder reaction is performed in the presence of racemic complex A and (+)-3-bromocamphor (0.3 mol equiv each), *cis*-dihydropyrone is isolated with ee up to 80% (eq 3) (instead of 95% ee with pure (*S*)-A).[31] Previously small ee's in hetero Diels–Alder reaction with menthoxydichloroaluminum as the chiral catalyst had been reported.[32]

III. Chiral Titanium Complexes

Chiral alkoxytitanium complexes prepared from chiral diols have been used as chiral Lewis acids for the Diels–Alder reaction. Stoichiometric amounts of titanium complexes were first utilized. Enantiomeric excesses in the range of 90–95% have been achieved in the condensation of cyclopentadiene and some specific acrylamides or crotonamides.[26,33,34]

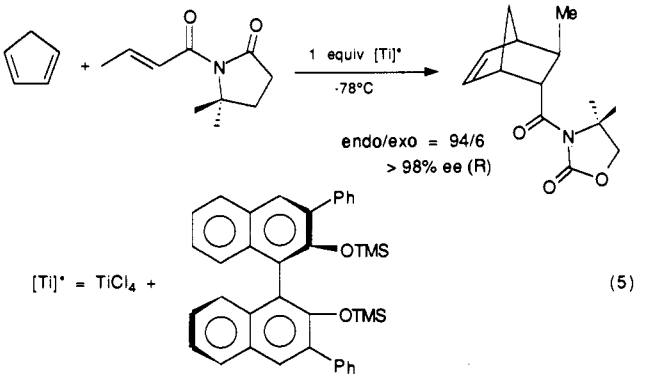
Narasaka et al.[33] found that a class of crotonamides (3-acyl-1,3-oxazolidin-2-ones) reacts with cyclopentadiene to give cycloadducts in presence of some titanium complexes (eq 4). The titanium complexes (2 mol equiv)



(4)

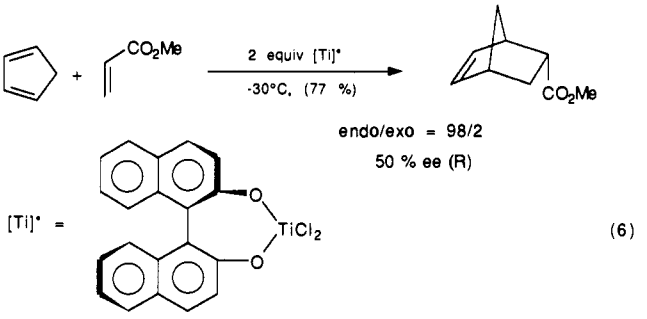
were prepared from equimolar amounts of a chiral diol and $TiCl_2(Oi\text{-}Pr)_2$. The 3-acyl-1,3-oxazolidin-2-ones have been chosen because they should form a bidentate complex with chiral titanium complex, resulting in increased stereoselectivity during the Diels–Alder reaction. Indeed the major product (endo diastereomer) was obtained with 92% ee.

Chapuis and Jurczak[26] used similar chelating crotonamide with cyclopentadiene in presence of 1 mol equiv of a chiral titanium complex (eq 5) yielding a cycloadduct with a very high ee.



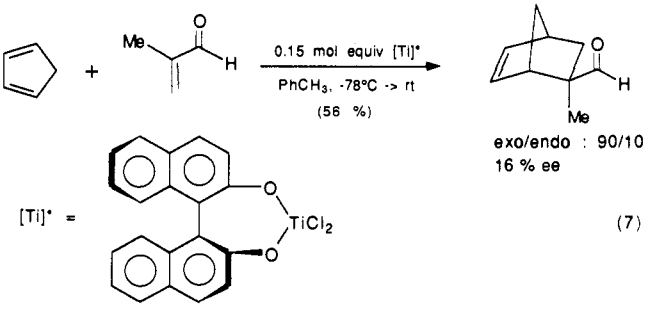
(5)

Seebach et al.[34] also observed asymmetric induction in the condensation of methyl acrylate and cyclopentadiene in the presence of an excess of a chiral Lewis acid (eq 6).



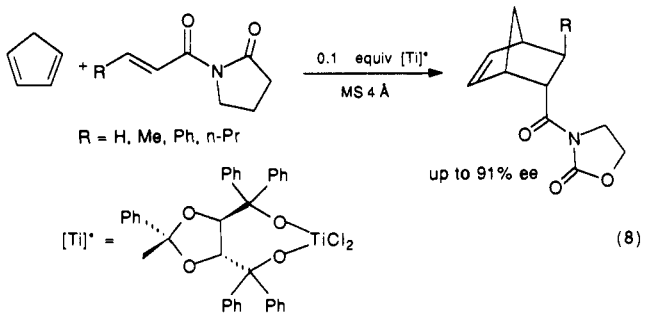
(6)

Catalytic use of titanium complexes is a recent development. Reetz et al.[35] found that 1,1′-binaphthoxydichlorotitanium catalyzed formation of cycloadduct between methacrolein and cyclopentadiene with 16% ee (eq 7).



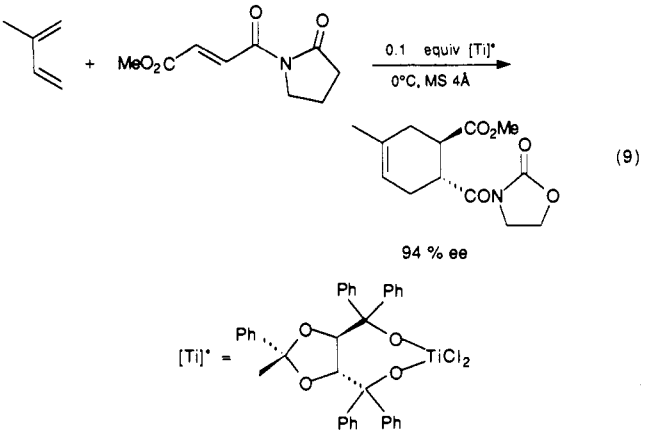
(7)

Narasaka et al.[36–38] made the interesting observation that 4-Å molecular sieves (MS 4Å) allow the use of catalytic amounts of a dialkoxydichlorotitane, keeping the enantioselectivity at the level of 90% (close to ee of the stoichiometric reaction) (eq 8).



(8)

The beneficial effect of molecular sieves was ascribed at least in part to the removal of water from the reaction mixture. The same authors found that 1,3,5-trialkylbenzenes are excellent solvents for enhancing the enantioselectivity of the cycloadducts. A detailed study of solvent effect has been performed in the case of the fumarate derivative of eq 9.[38]



(9)

The solvent effect was discussed taking into account its donor and acceptor abilities. In order to give the best chance of complexation to titanium by the acyloxazolidinone moiety it is necessary to avoid solvent interaction with the two fragments. The alkyl groups on the benzene ring tend to reduce molecular interactions due to the steric repulsion. Some data for reaction in eq 9 are listed in Table I.

It is inconvenient to use mesitylene since it is difficult to remove during workup. A mixed solvent such as toluene–petroleum ether (1:1) is as beneficial as mesitylene. Cycloaddition described in eq 9 has been performed in 45 mmol scale in the mixed solvent with only 5 mol % of the chiral titanium complex. Cycloadduct was produced in 94% yield with 94% ee. The reaction has been extended to a diene containing a sulfur atom such as 2-(ethylthio)-1,3-butadiene, affording the Diels–Alder adduct in 91% ee.[39a] A transition-state model has been proposed for all Diels–Alder reactions using acyloxazolidinones (assumed to react as a six-membered chelate to titanium).

Narasaka et al. studied the structure of the titanium complex involved in eqs 8 and 9.[40] A ^{1}H NMR investigation gave some structural information on the single species formed by the mixing of the chiral diol and $TiCl_2(O\textit{i}\text{-}Pr)_2$. However it could not be decided if the complex is monomeric or dimeric. The chiral titanium complex is in equilibrium with the chiral diol, $TiCl_2(O\textit{i}\text{-}Pr)_2$ and 2-propanol. It could be seen that addition of molecular sieves (MS 4 Å) shifts the equilibrium to the side of the chiral titanium complex. The simultaneous increase in enantioselectivity comes from a decreased concentration of $TiCl_2(O\textit{i}\text{-}Pr)_2$ which can by itself catalyze the Diels–Alder reaction. It was also found that the dienophile (3-acyl-1,3-oxazolidin-2-one) and the chiral titanium complex form a 1:1 complex in solution; this complex has been isolated and seems to be the key intermediate in the cycloaddition. The reaction has been modified into an intramolecular Diels–Alder reaction. In this way, a bicyclic compound with ee >95% has been obtained and was transformed into the hydronaphthalene moieties of mevinic acid[39b] (Figure 8). Corey et al. investigated modified titanium catalysts for elucidating the origin of the high enantioselectivity observed in reaction of eqs 8 and 9.[80] A strong influence of groups in meta position of aromatic rings led the authors to propose the transition state represented in Figure 9. Attractive π–π interactions between a donor aromatic group and the double bond of the dienophile (s-trans geometry) protects one face and provides high ee.

The chiral titanium complex previously used in Diels–Alder reactions[34,35] was recently found by Mikami et

Table I. Solvent Effect for the Catalytic Reaction of Eq 9

solvent	ee (%)
benzene	41
toluene	36–68
mesitylene	96
CH_2Cl_2	45
$CHCl_3$	52
CCl_4	75

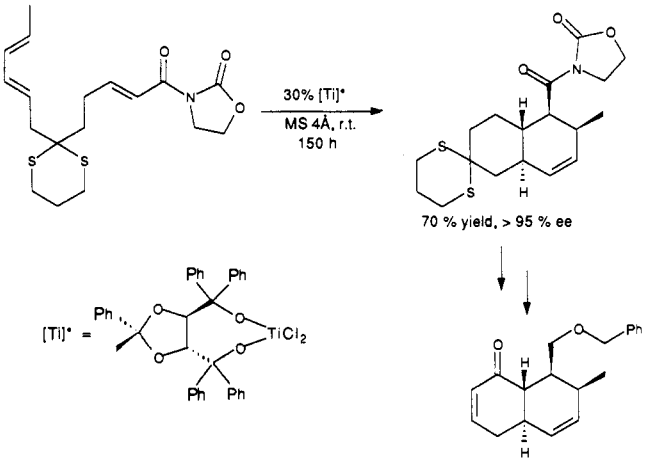


Figure 8.

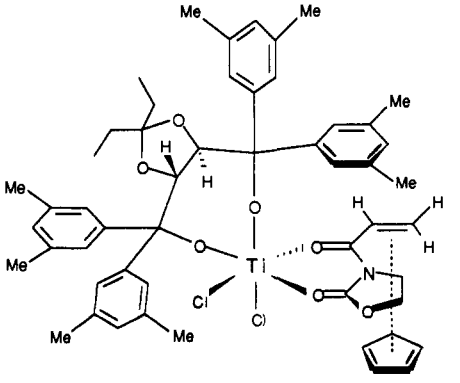
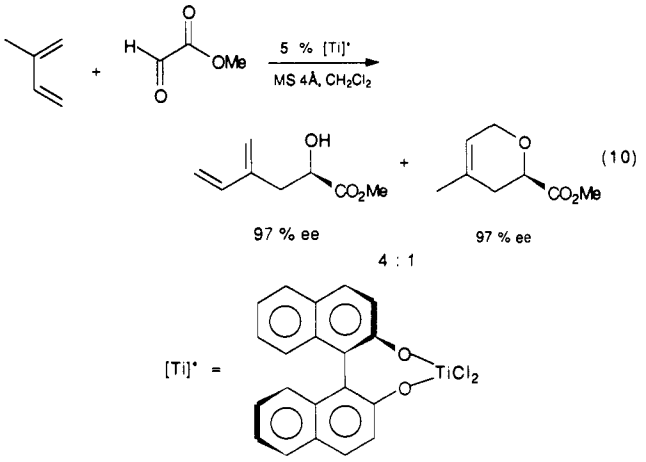


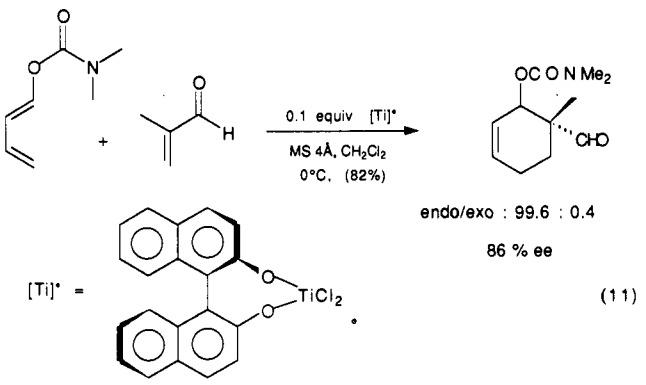
Figure 9.

al.[41] to be an excellent catalyst in reaction between isoprene and methyl glyoxylate. Ene product and a hetero Diels–Alder product were produced, both in very high ee (eq 10).



(10)

The use of this chiral catalyst has been extended to Diels–Alder reaction between 1,3-dienol derivatives and methacrolein or 1,4-naphthoquinone. Endo selectivity is very high in most cases. One example of this process is described in eq 11.



(11)

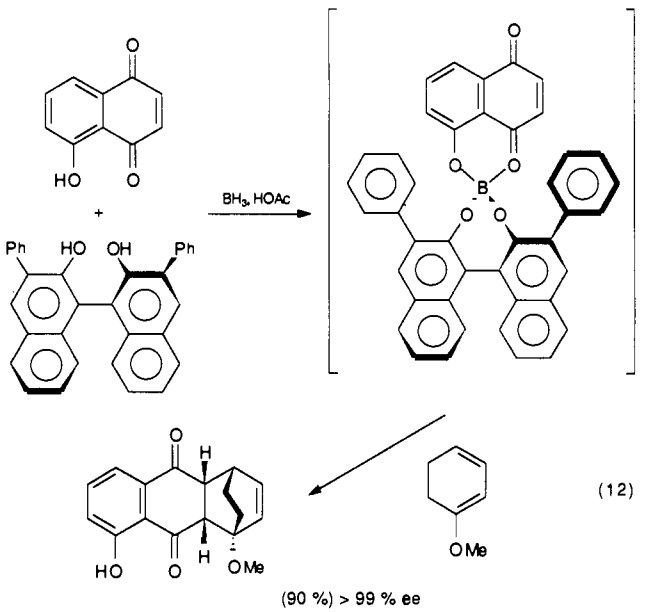
The authors proposed that the steric course of the reaction is the result of complexation of methacrolein under its transoid conformation, the titanium catalyst being complexed in an anti fashion.

IV. Chiral Boron Catalysts

Chiral boron compounds have been explored as promoters (stoichiometric amounts) for the Diels–Alder reaction.

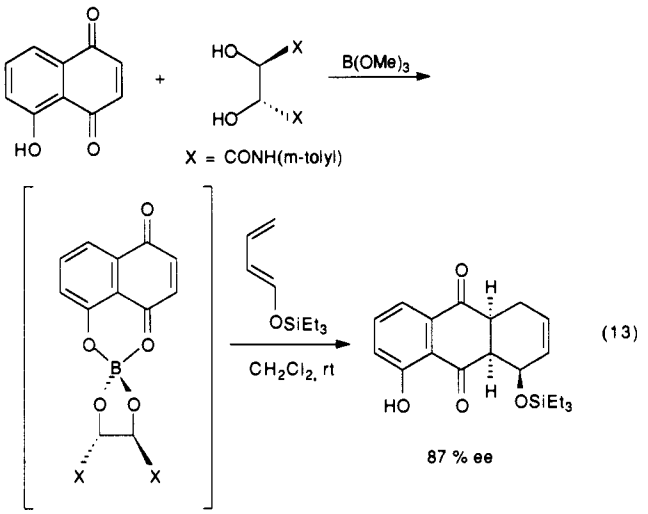
A chiral boron complex prepared by Kelly et al. from juglone and a disubstituted 1,1′-binaphthol stoichiometrically reacts with various dienes to give Diels–Alder adducts with ee's up to 98%[42] (eq 12). It is interesting to see that because of the C_2 symmetry of the chiral binaphthol, only one transient chelated borate is formed (boron is not an asymmetric center). Steric differentiation of the two faces of the C=C double bond of juglone occurs because of its shielding by one of the two ortho phenyl groups. In the case of eq 12 the diene will attack the double bond back side. A similar approach has been studied by H. Yamamoto et al.[43] (eq 13).

The chiral boron reagent has been prepared from juglone, trimethyl borate, and various (*R,R*)-tartaric



(12)

acid diamides. It reacts with 1-(trimethylsiloxy)-1,3-butadiene to give a cycloadduct with complete regioselectivity (eq 13) and very high enantioselectivity.

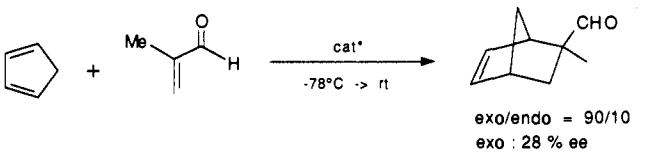


(13)

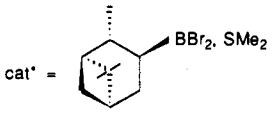
The good properties of tartramides with X = CONHR were ascribed to a hydrogen bond between amide-hydrogen and the naphthoquinone carbonyl bonded to boron.

More recently *catalytic* use of boron derivatives was investigated.[44] Compound of type $RBBr_2$ (R = pinanyl) catalyzes at −78 °C the Diels–Alder reaction with low ee[46] (eq 14). Modified isopinocampheyldibromoborane was later synthesized and gave better results in the reaction of cyclopentadiene and methyl acrylate (eq 15).[47]

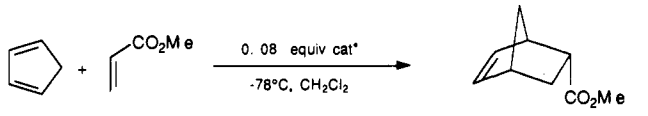
Kaufmann greatly improved his results by using a boron compound derived from 1,1-binaphthol[48] (eq 16). This compound has been unexpectedly obtained from monobromoborane dimethyl sulfide and 1,1′-binaphthol. The diborate structure with a propellerlike shape has been established by X-ray analysis. The reaction between methacrolein and cyclopentadiene was catalyzed at −78 °C in dichloromethane by 3 mol % of the chiral diborate, the exo cycloadduct was obtained with high exo selectivity (97.4:2.6) and 90% ee. Mechanistic details and scope of the reaction are still missing.



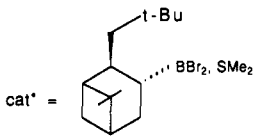
exo/endo = 90/10
exo : 28 % ee



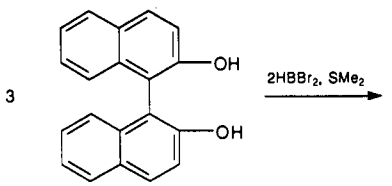
(14)

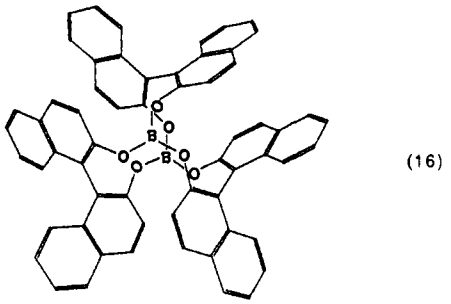


endo/exo = 99.3/0.7
endo : 48 % ee



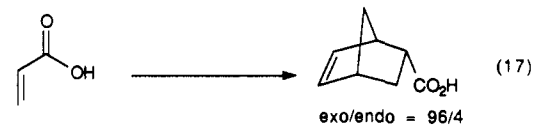
(15)





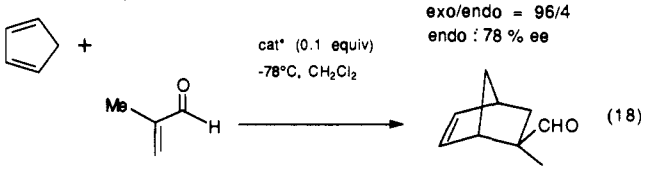
(16)

Another promising approach has been devised by H. Yamamoto et al.[49] These authors found that action of a controlled amount of diborane on a carboxylic acid leads to a boron compound (presumably an (acyloxy)-borane RCO–O–BR′$_2$) which behaves as a Lewis acid. The boron complex in situ formed from monoacyl tartaric acid and diborane is an excellent asymmetric catalyst for the Diels–Alder reaction of cyclopentadiene and acrylic acid (78% ee)[49] (eq 17) or of cyclopentadiene and methacrolein (96% ee)[50] (eq 18).



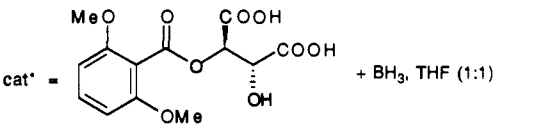
(17)

exo/endo = 96/4
endo : 78 % ee

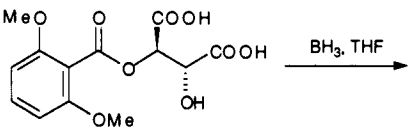


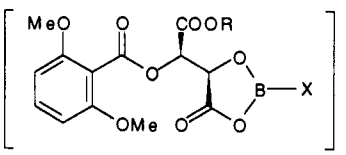
(18)

exo/endo = 89/11
exo : 96 % ee



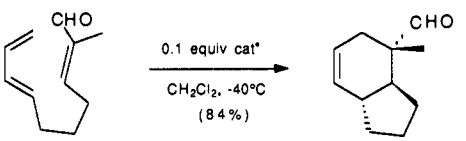
The reaction with acrylic acid deserves special attention, since usually it is not a good component in Diels–Alder reactions. The fact that the reaction proceeded catalytically and with high ee indicates the facile exchange of the (acyloxy)borane of the cycloadduct with carboxylic group of unreacted acrylic acid, the monoacylated tartaric acid remaining bound to boron. The process is quite general for simple dienes and aldehydes. For example acrolein and cyclopentadiene, cyclohexadiene or 2,3-dimethyl-1,3-butadiene gave cycloadducts with about 80% ee (and endo selectivity). When there is a β-substitution in the dienophile as in crotonaldehyde the cycloadduct is almost racemic, but for a substrate having substituents at both α- and β-positions, high ee's were observed as in case of 2-methylcrotonaldehyde and cyclopentadiene (90% ee, exo/endo = 97:3). The active boron catalyst is believed to have the structure shown in eq 19, with a five-membered ring and a free carboxylic group. This later seems to be not crucial for the enantioselectivity since comparable results are obtained when the carboxylic group is transformed into an ester.





(19)

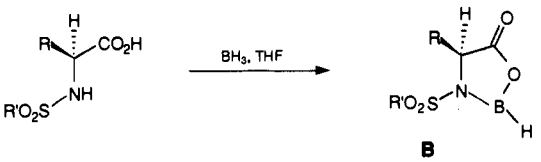
The Yamamoto catalyst (eq 19) was applied to asymmetric intramolecular Diels–Alder reaction (eq 20).[51] The same aldehyde devoid of a methyl group in the α-position affords the adduct with 46% ee. An α-substituent is essential for high ee, as observed in the intermolecular reaction.



(20)

endo/exo = 99/1
92 % ee

Helmchen et al.[52] and Yamamoto et al.[53] found that N-sulfonyl derivatives of α-amino acids react with diborane, giving complexes formulated as B (eq 21). These complexes catalyze various asymmetric cycloadditions.

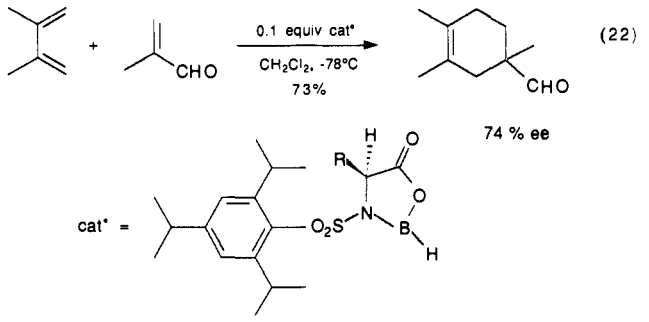


(21)

B

Takasu and Yamamoto[53] selected 2,4,6-triisopropylbenzenesulfonamide of α-amino acids (B, R = Et, R′ = 2,4,6-triisopropylphenyl) as catalyst.

The best result is indicated in eq 22. The new catalyst is easily available in both enantiomeric forms; it is of broad applicability, but ee's are not very high. Helmchen et al.[52] independently found similar results with



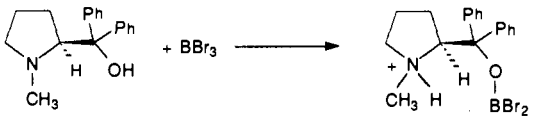
(22)

catalysts of type B derived from valine (R = *i*-Pr). When R′ = 2,4,6-trimethylphenyl the cycloaddition of crotonaldehyde on cyclopentadiene occurs with 72% ee (endo/exo = 97:3) in presence of 0.2 equiv of chiral catalyst. More recently the same authors made a systematic investigation of the influence of various experimental parameters on the enantioselectivity.[54] Improvement was obtained in THF or by addition of some THF (ee up to 86%). A transition-state model (Figure 10) was proposed to predict the absolute configuration of adducts. In this model the R^1 group directs the R^2SO_2 group to the opposite side of the ring, the latter group orientates attack on boron again in trans. The s-cis conformation of complexed enal has been chosen as well as coordination of carbonyl to born syn to H. This model correctly predicts all the examples studied.

A very recent report of Hawkins and Loren[55] described a simple and efficient catalyst for Diels–Alder reaction based on a chiral alkyldichloroborane (Figure 11).

A molecular complex between methyl crotonate and the chiral catalyst could be isolated for the first time. A crystal structure study of the complex allowed the authors to propose a model to predict the approach of the diene on one of the faces of methyl crotonate because of protection of the other face by π–π donor–acceptor interactions. This secondary attractive substrate–catalyst interaction is the key to the stereocontrol. A similar effect was also published a few months later by Corey et al. for chiral oxazaborolidinone catalysts.[81] Especially efficient is the asymmetric catalysis of cycloaddition between 2-bromoacrolein and various dienes (ee >90–95%). The transition state is believed to be as represented in Figure 12. Attractive interactions between the indolyl moiety and the π-acidic dienophile protect one face of the dienophile. This effect is well supported by the discovery that the replacement of the indole group by a cyclohexyl or a cyclopropyl group gives the cycloadduct with opposite configuration (and 70% ee).

Prolinol derivatives combined to BBr_3 were found by Mukaiyama et al. to produce promising catalysts for some Diels–Alder reactions.[56] For example methacrolein and cyclopentadiene afford exo adduct (exo/endo > 99:1) in 97% ee (reaction at −78 °C in dichloromethane with 0.2 mol equiv of catalyst). The chiral catalyst is believed to be the HBr adduct salt of the amino boron derivative (see eq 23).



(23)

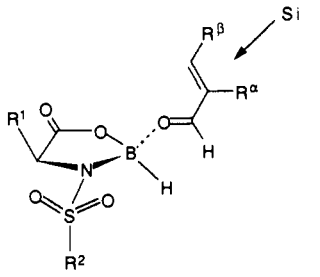


Figure 10.

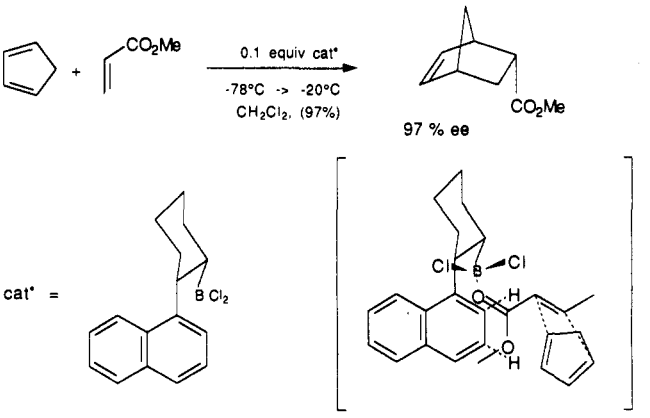


Figure 11.

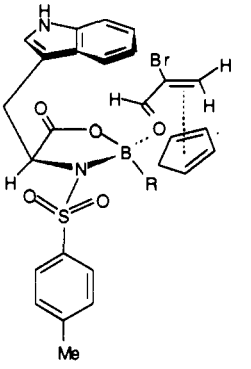


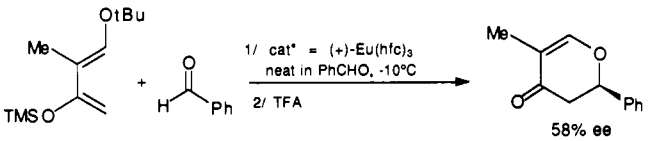
Figure 12.

Ab initio calculations have been performed by Houk et al. to define the transition state in Diels–Alder reactions catalyzed by boron derivatives.[57] As a model, authors studied the reaction between butadiene and acrolein complexed with BH_3. Endo addition of anti complex of s-syn acrolein has been found to be the preferred one.

V. Chiral Lanthanide Complexes

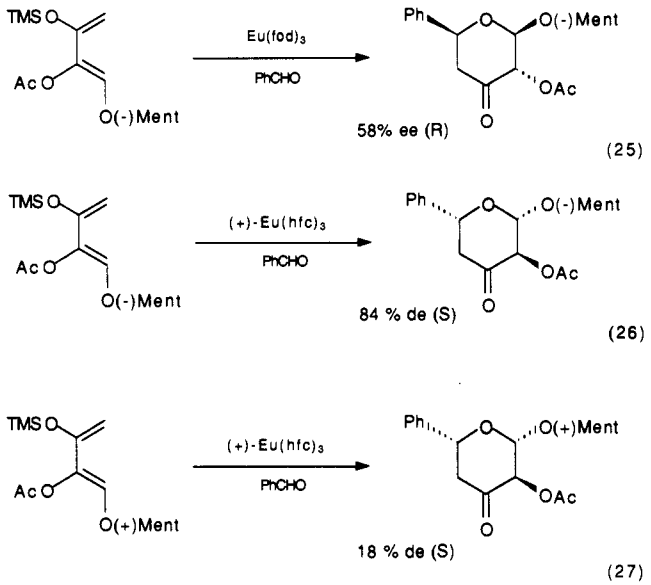
It is well known that various lanthanide complexes act as shift reagents because of their ability to coordinate to donor atoms. This property has been used to catalyze hetero Diels–Alder reactions through activation of an aldehyde function. Chiral europium complexes catalyze some asymmetric hetero Diels–Alder reactions but they are not active in the usual Diels–Alder reaction. Danishefsky and Bednarski used highly functionalized 1,3-dienes in an hetero Diels–Alder reaction with benzaldehyde.[58] They found that a chiral shift reagent (+)-$Eu(hfc)_3$ is an asymmetric catalyst for this reaction with ee's in the range of 20–40%. The reactions are performed in chloroform at room temperature with 1 mol % of the catalyst. Significant improvement was

obtained in absence of solvent at reduced temperature (see eq 24).



(24)

The combined action of chiral catalyst (+)-Eu(hfc)$_3$ and of a chiral auxiliary in the silyloxy diene has also been developed.[59] For example when an achiral catalyst (Eu(fod)$_3$) is used with *O*-menthoxy diene (derived from (−)-menthol) the pyranose derivative has 10% de (*R* configuration at the benzylic position) (eq 25). A similar experiment with (+)-Eu(hfc)$_3$ and *O*-*tert*-butoxy diene gives 34% ee (*S* configuration). By combining both the chiral auxiliaries (from (+)- and (−)-menthol) in diene and catalyst ((+)-Eu(hfc)$_3$) one expects a product with *S* configuration and de lower than 34% (mismatched pair) (eqs 26 and 27). Actually the product has *S* configuration with a very high de (eq 26). This unexpected amplification was called "specific interactivity" of chiral catalyst and chiral auxiliary and seems promising for stereoselective control.

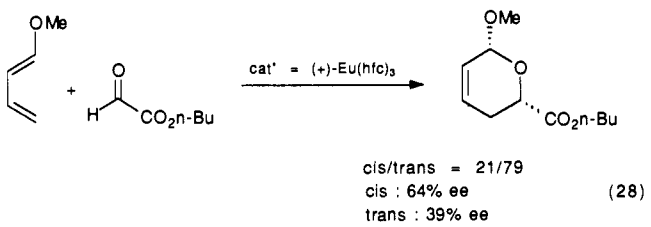


(25)

(26)

(27)

A hetero Diels–Alder reaction on butyl glyoxylate catalyzed by Eu(hfc)$_3$ gives a mixture of *cis*- and *trans*-dihydropyran compounds, with quite good ee's (eq 28).[32]



(28)

Eu(hfc)$_3$ gave no asymmetric induction in hetero Diels–Alder reactions[60] between ketones and Brassard's diene, but this catalyst is sometimes beneficial for achieving high diastereoselectivity in hetero Diels–Alder reactions between α-alkoxy aldehydes or N-protected α-amino aldehydes and Brassard's diene.[61] In the example of eq 29 Eu(hfc)$_3$ gives 90% de while catalysis by Et_2AlCl affords 84% de. A chelation involving the alkoxy group has been established in the case of Eu(hfc)$_3$ and α-alkoxy aldehydes.[62]

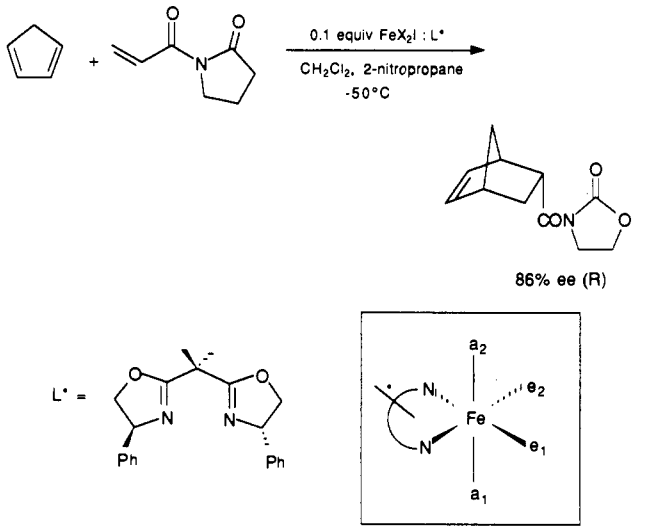
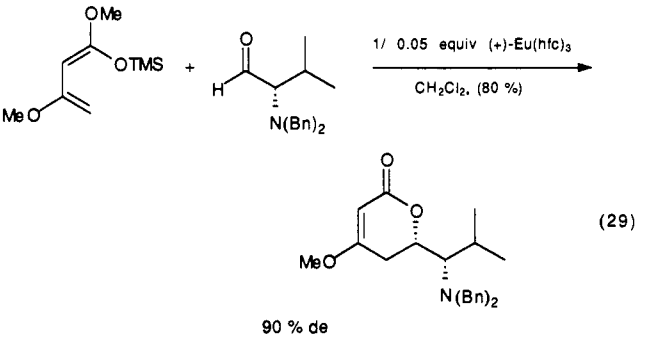


Figure 13.

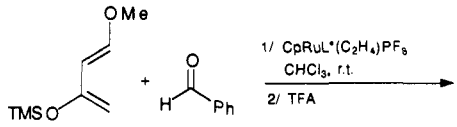


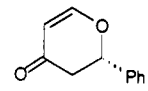
(29)

VI. Transition-Metal Complexes

In this section, we will consider transition metals (except titanium) which can give rise to catalytic systems for the Diels–Alder reaction. Chiral bis-oxazolines with C_2 symmetry have recently found some applications in asymmetric catalysis with various transition metals.[63] A new chiral iron(III) Lewis acid L*FeX_2I was thus prepared in situ by treatment of anhydrous FeX_2 (X = halogen) and ligand L* followed by oxidation of iron(II) complex with iodine. Iron(III) complex catalyzes the Diels–Alder reaction between cyclopentadiene and bidentate dienophile, the cycloadduct is isolated with 86% ee and 99/1 endo/exo diastereoselectivity (Figure 13).[64] An octahedral structure is proposed for the active complex, and rationalization of the stereochemistry was deduced from the absolute configuration of the cycloadduct. Chelation of the dienophile (through a s-cis form for the C=C/C=O bonds) occurs on the a_1, e_1 sites of the chiral complex, thus giving a rigid structure favorable in high enantioselectivity.

Some achiral ruthenium complexes such as [(η_5-Cp)Ru(PPh_3)$_2$(CH_2=CH_2)]$^+PF_6^-$ have been shown by Faller et al. to catalyze the hetero Diels–Alder reaction between Danishefsky diene and benzaldehyde.[65] When triphenylphosphine is replaced by a chiral bidentate phosphine such as Diop or Chiraphos (eq 30), ee's up to 25% were achieved.



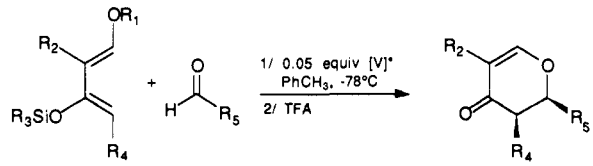


(30)

L* = (R,R)-Diop : 16% ee

L* = (S,S)-Chiraphos : 25% ee

In a recent paper of Togni et al. fair to good ee's were obtained in the asymmetric catalysis of the hetero Diels–Alder reaction by oxovanadium(IV) complexes bearing camphor-derived 1,3-diketonato ligands[66] (eqs 31 and 32).

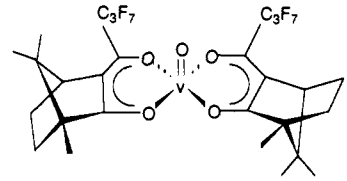


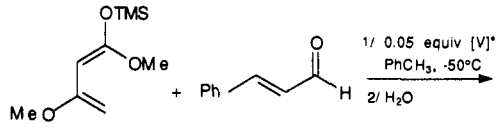
(31)

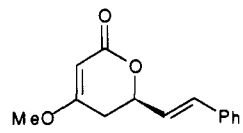
de up to 99%

ee up to 85%

[V]* =







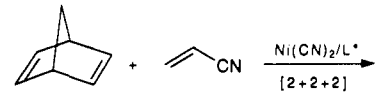
(32)

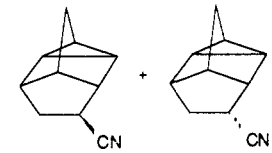
(73%) 13% ee

In the same conditions, Brassard's diene and cinnamaldehyde furnished the kaiwain lactone with a rather low optical yield, and no reaction was observed if imines are used as heterodienophiles.

These examples show the high potential of transition-metal complexes as chiral Lewis acids. Some achiral Lewis acid complexes such as ferricinium hexafluorophosphate,[67] $[W(Me_3P)(NO)(CO)_3](FSbF_5)$,[68] or $[(\eta_5\text{-Cp})Fe^+(CO)(P(OMe)_3)](THF)(BF_4^-)$[69] have been shown to efficiently catalyze the Diels–Alder reaction, and a crystal structure of an acrolein tungsten complex (catalytically active) reveals coordination of carbonyl oxygen to tungsten.[68a]

The homo Diels–Alder reaction (a [2 + 2 + 2] cycloaddition) between norbornadiene and an olefin (or a monosubstituted acetylene) can be performed with the help of nickel or cobalt catalysis.[70] This method gives an entry to deltacyclane (or deltacyclene) skeleton with formation in a single step of up to six new stereocenters. An asymmetric modification of these catalysts has been independently reported by the groups of Lautens et al. and Brunner et al., and high enantiomeric excesses were achieved in both cases.[71,72] A first investigation using chiral-modified nickel catalyst (a combination of nickel(II) cyanide and chiral diphosphines)[72a] in the reaction between norbornadiene and acrylonitrile gave disappointingly low enantioselectivity (eq 33). Good results were finally obtained with a cobalt catalyst prepared from $Co(acac)_3$, a chiral diphosphine, and excess of $EtAlCl_2$ (based on cobalt). This method proved to be quite general for various monosubstituted acetylenes, and ee in the range of 55–100% could be obtained (eq 34). Among the various phosphines studied, chiraphos, prophos, and norphos gave the best results.

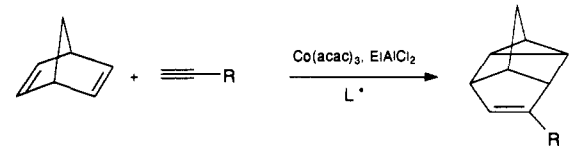




(33)

L* = DIOP : 100%, de = 20%, ee = 4 and 3%

L* = Norphos : 10%, de = 10%, ee = 12 and 15%



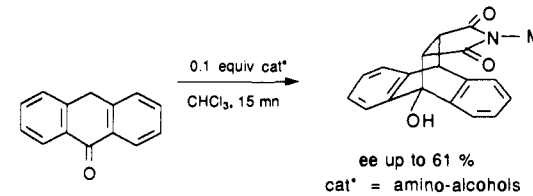
(34)

Lautens et al. R = Bu, L* = (S,S)-chiraphos : 91 % ee

Brunner et al. R = Ph, L* = (S,S)-norphos : 98.4 % ee

VII. Base-Catalyzed Diels–Alder Reactions

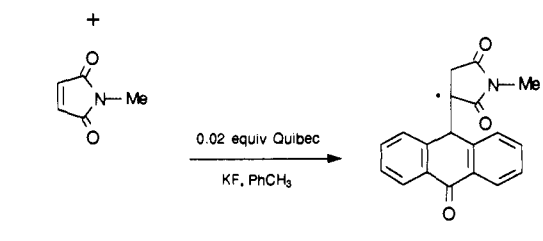
The first evidence for a base-catalyzed Diels–Alder reaction was given by Rickborn et al. in 1989, a full paper was later published.[73,74] Anthrone reacts with various dienophiles in chloroform after addition of a small amount of triethylamine. This has been ascribed to an oxyanion acceleration (via the enolate of anthrone). This report encouraged us to try to set up conditions allowing chiral bases to be used as catalysts of the Diels–Alder reaction. We succeeded in this unique case of asymmetric catalysis and published a preliminary note.[75] We found that a fast reaction occurs at room temperature when 1–10% mol equiv of an alkaloid is added to a chloroform solution of equimolar amounts of anthrone and *N*-methylmaleimide (eq 35).



(35)

ee up to 61 %

cat* = amino-alcohols

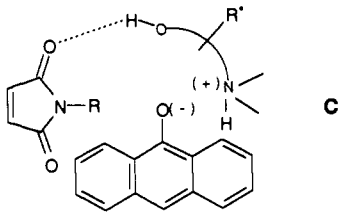


(36)

16 % ee

Table II. Some Efficient Asymmetric Catalytic Systems for the Diels–Alder Reaction (with ee's > 90%)

chiral catalyst (mol equiv)	reactants	ee max (%)	ref(s)
methylaluminum binaphtholate A (eq 2)	hetero Diels–Alder reaction	97	28
dichlorotitanium diolate + MS 4 Å (eq 8)	3-Acyl-1,3-oxazolidin-2-ones + Cp or isoprene	94	36–38
diborate from binaphthol (eq 16)	Cp + acrylate or methacrolein	90	48
acyloxy-borane (eq 18)	dienes + acrylic acid or α,β-unsaturated aldehydes	96	49, 50
alkyldichloroborane (Figure 11)	dienes + α,β-unsaturated esters	97	55
oxazaborolidinone (Figure 12)	dienes + 2-bromoacrolein	95	81
BBr_3 + *N*-methylprolinol (eq 23)	Cp + α,β-unsaturated aldehydes	97	56
Co complex with chiral diphosphines	homo Diels–Alder reaction	98	71, 72



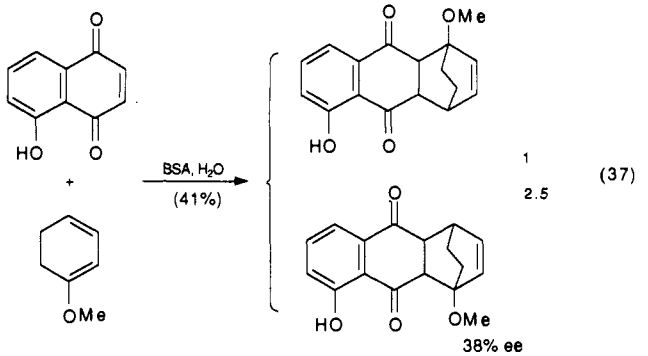
C

Figure 14.

Cycloadduct is isolated in excellent yield and is optically active. Enantiomeric excesses were measured by chiral HPLC on Sumipax OA-2000. By decreasing the temperature to −50 °C, ee of 61% could be achieved using quinidine as a catalyst. A competitive reaction, especially when rising temperature, is the formation of Michael adduct (eq 36). This is the main product formed (16% ee) if one uses KF (1 equiv) and quibec (*N*-benzylquininium chloride) (0.02 equiv) in conditions of phase-transfer catalysis in toluene. Mechanism of the asymmetric cycloaddition is under investigation. Enantioselectivity vanishes when OH of β-amino alcohols has been protected. Complex C has been proposed for explaining chiral recognition (Figure 14).

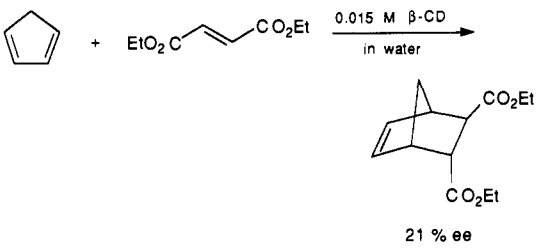
VIII. Miscellaneous

BSA (bovine serum albumin, 5% equiv) in water is a catalyst for the Diels–Alder reaction between juglone and 1-methoxycyclohexadiene.[76a] While regiochemistry of the reaction is not affected by the use of the protein of the catalyst, an enantioselectivity of 38% is observed for the major regioisomer (eq 37). Interaction between juglone and BSA can be shown by circular dichroism. If the hydroxy group of juglone is protected as an *n*-octyl ether, the interaction with the protein becomes impossible and the Diels–Alder reaction occurs without enantioselectivity. Bakers' yeast has also been shown to catalyze Diels–Alder reaction between cyclopentadiene and fumarate derivatives.[76b] However no report was made about a possible asymmetric induction in this reaction.



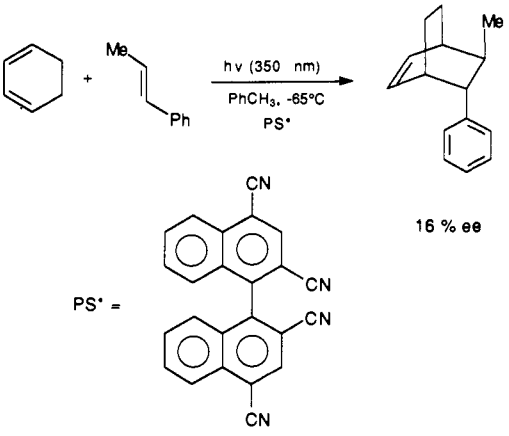
(37)

Molecular recognition between a dienophile and a macromolecule has also been shown in the work of Schneider and Sangwan.[77] Catalysis of the Diels–Alder reaction in water by β-cyclodextrin (β-CD) is clearly shown by the change in diastereoselectivity of the cycloadducts (compared with the uncatalyzed reaction in water). In the case of the cycloaddition between cyclopentadiene and diethyl fumarate, an enantiomeric excess of 21 ± 5.5% was obtained (eq 38).



(38)

A phenomenon of chirality transfer has been observed in the photosensitized Diels–Alder reaction between cyclohexadiene and a electron-rich dienophile (*trans*-β-methylstyrene) (eq 39).[78] The chiral electron-deficient sensitizer used can form diastereomeric exciplexes with the electron-rich dienophile and asymmetric induction arises from the capture of these diastereoisomeric complexes by the diene.



(39)

IX. Conclusion

Catalysis of Diels–Alder reactions by chiral Lewis acids including early transition-metal Lewis acids is now well known. One can expect to see in the future more examples of catalysis involving transition-metal complexes (for leading references, see refs 67–69). The catalytic asymmetric Diels–Alder reaction will benefit from all progresses obtained with achiral catalysts. Structural studies of complexes between Lewis acids and carbonyl compounds are of considerable interest for discussing the steric course of catalytic asymmetric

Diels–Alder reactions. A survey on this topic can be found in the excellent review article of Schreiber et al.[82] Calculations on transition states involved in the Lewis acid catalyzed Diels–Alder reaction show a significant zwitterionic character.[57] Another direction where one can hope for new developments for catalytic Diels–Alder reactions is the use of supramolecular catalysis[83] or macromolecules of biological origin (proteins, monoclonal antibodies, etc.). The first examples of antibody catalysis of the Diels–Alder reaction has been published;[79] it remains to tailor "Diels–Alderases" antibodies for asymmetric reactions.

In conclusion, catalytic Diels–Alder reaction has been in fast evolution for several years; it has arrived at the point where it can be considered as a useful tool in organic synthesis. In Table II are listed some of the most efficient and useful catalytic systems for asymmetric Diels–Alder reactions. It is also expected to see more developments in the direction of cycloadditions involving polyfunctional dienes and dienophiles, which will need a new generation of asymmetric catalysts.

Acknowledgments. One of us acknowledges the Ministery of Education for a fellowship (O.R.).

References

(1) (a) *Organic Reactions*; Vol. IV, Chapters 1 and 2; Vol. V, Chapter 3. (b) Carruthers, W. In *Cycloaddition Reactions in Organic Synthesis*. Tetrahedron Organic Chemistry Series Vol. 8; Pergamon Press: Elmsford, NY, 1990.

(2) (a) Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*; Prentice Hall: Engelwood Cliffs, NJ, 1971; p 252. (b) For the first example of asymmetric Diels–Alder reaction using a chiral dienophile, see: Walborsky, H. M.; Barash, L.; Davis, T. C. *J. Org. Chem.* **1961**, *26*, 4478.

(3) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3B, p 455.

(4) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876.

(5) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods 1986*; Sheffold, R., Ed.; Springer Verlag: New York, 1986; Vol. 4, p 262.

(6) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436.

(7) Although Lewis acid catalysis proved to give the best de in the asymmetric Diels–Alder reaction, some chiral dienophiles also give high selectivity in the uncatalyzed reaction; for an example, see ref 15.

(8) For isolated complexes between carbonyl groups and Lewis acids, see for example ref 9.

(9) (a) Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405. (b) Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 112.

(10) Walborsky, H. M.; Barash, L.; Davis, T. C. *Tetrahedron* **1963**, *19*, 2333.

(11) Sauer, J.; Kredel, J. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 989.

(12) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908.

(13) For leading references on the use of chiral dienophiles in the asymmetric Diels–Alder reaction, see refs 12 and 14–28. For examples on use of chiral dienes, see ref 21.

(14) Oppolzer, W. In Camphor derivatives as chiral auxiliaries in asymmetric synthesis. *Tetrahedron* **1987**, *43*, 1969.

(15) Hartmann, H.; Hady, A. F. A.; Sartor, K.; Weetman, J.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1143.

(16) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238.

(17) Furuta, K.; Iwagana, K.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 4507.

(18) Arai, Y.; Kuwayama, S.; Takeuchi, Y.; Koizumi, T. *Tetrahedron Lett.* **1985**, *26*, 6205.

(19) Vandewalle, M.; Van der Eycken, J.; Oppolzer, W.; Vullioud, C. *Tetrahedron* **1986**, *42*, 4035.

(20) Narasaka, K. *Synthesis* **1991**, 1.

(21) (a) Trost, B. M.; O'Krongly, D.; Belletire, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7595. (b) Tripathy, R.; Carroll, P. J.; Thorton, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 7630 and references therein.

(22) Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437.

(23) Takemura, H.; Komeshima, M.; Takahashi, I.; Hashimoto, S.; Ikota, N.; Tomioka, K.; Koga, K. *Tetrahedron Lett.* **1987**, *28*, 5687.

(24) Rebiere, F.; Riant, O.; Kagan, H. B. *Tetrahedron: Asymmetry* **1990**, *1*, 199.

(25) Ketter, A.; Glahsl, G.; Herrmann, R. *J. Chem. Res. (S)* **1990**, 278–79; *(M)*, 2118–56.

(26) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 437.

(27) (a) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493. (b) Corey, E. J.; Imai, N.; Pikul, S. *Tetrahedron Lett.* **1991**, *32*, 7517.

(28) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.

(29) Maruoka, K.; Hoshino, Y.; Shirasaka, T.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 3967.

(30) (a) Maruoka, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 7791. (b) Maruoka, K.; Banno, H.; Yamamoto, H. *Tetrahedron: Asymmetry* **1991**, *2*, 647.

(31) Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 789.

(32) Quimpère, M.; Jankowski, K. *J. Chem. Soc., Chem. Commun.* **1987**, 676.

(33) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109.

(34) Seebach, D.; Beck, A. K.; Imwinkelried, R.; Roggo, S.; Wonnacott, A. *Helv. Chim. Acta* **1987**, *70*, 954.

(35) Reetz, M. T.; Kyung, S. H.; Bolm, C.; Zierke, T. *Chem. Ind. (London)* **1986**, 824.

(36) Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967.

(37) Narasaka, K.; Inoue, M.; Yamada, T.; Sugimori, J.; Ywasawa, N. *Chem. Lett.* **1986**, 2409.

(38) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340.

(39) (a) Narasaka, K.; Tanaka, H.; Kanai, F. *Bull. Soc. Chem. Jpn.* **1991**, *64*, 387. (b) Narasaka, K.; Saitou, M.; Iwasawa, N. *Tetrahedron: Asymmetry* **1991**, *2*, 1305.

(40) Iwasawa, N.; Hayashi, Y.; Sakurai, H.; Narasaka, K. *Chem. Lett.* **1989**, 1581.

(41) Mikami, K.; Terada, M.; Motoyama, Y.; Nakai, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 643.

(42) Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *J. Am. Chem. Soc.* **1986**, *108*, 3510.

(43) Maruoka, K.; Sakurai, M.; Fujiwara, J.; Yamamoto, H. *Chem. Lett.* **1986**, 4895.

(44) The first example of an asymmetric catalytic Diels–Alder reaction is the report in 1976 of cycloaddition between methyl acrylate and cyclopentadiene.[45] The catalyst was BF_3 complexed to (−)-methyl menthyl ether. Enantiomeric excess was very small (3%), it seems unlikely that catalysis occurred by a chiral catalyst (e.g. the undissociated complex).

(45) Guseinov, M. M.; Akhmedov, M. I.; Mamedov, E. G. *Azer. Khem. Zh.* **1976**, *1*, 46; *Chem. Abstr.* **1976**, *85*, 176295z.

(46) Kauffman, D.; Bir, G. *Tetrahedron Lett.* **1987**, *28*, 777.

(47) Bir, G.; Kaufmann, D. *J. Organometal. Chem.* **1990**, *390*, 1.

(48) Kauffman, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545.

(49) Furuta, K.; Miwa, Y.; Iwanaga, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 6254.

(50) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481.

(51) Furuta, K.; Kanematsu, A.; Yamamoto, H.; Takaoka, S. *Tetrahedron Lett.* **1989**, *30*, 7231.

(52) Sartor, D.; Saffrich, J.; Helmchen, G. *Synlett* **1990**, 197.

(53) Takasu, M.; Yamamoto, H. *Synlett* **1990**, 194.

(54) Sartor, D.; Saffrich, J.; Helmchen, G.; Richards, C. J.; Lambert, H. *Tetrahedron: Asymmetry* **1991**, *2*, 639.

(55) Hawkins, J. M.; Loren, S. *J. Am. Chem. Soc.* **1991**, *112*, 7794.

(56) Kobayashi, S.; Murakami, M.; Harada, T.; Mukaiyama, T. *Chem. Lett.* **1991**, 1341.

(57) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127.

(58) Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451.

(59) (a) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 6968. (b) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1986**, *108*, 7060.

(60) Middland, M. M.; Graham, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 4294.

(61) Middland, M. M.; Afonso, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 4368.

(62) Middland, M. M.; Koops, R. W. *J. Org. Chem.* **1990**, *55*, 4647.

(63) See for example: Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726.

(64) Corey, E. J.; Imai, N.; Zhang, H. Y. *J. Am. Chem. Soc.* **1991**, *113*, 728.

(65) Faller, J. W.; Smart, C. J. *Tetrahedron Lett.* **1989**, *30*, 1189.

(66) (a) Togni, A. *Organometallics* **1990**, *9*, 3106. (b) Togni, A.; Pastor, S. T. *Chirality* **1991**, *3*, 331.

(67) Kelly, T. R.; Maity, S. K.; Meghani, P.; Chandrakumar, N. S. *Tetrahedron Lett.* **1989**, *30*, 1357.

(68) (a) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, *52*, 5293. (b) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070.

(69) Olson, A. S.; Seitz, W. J.; Hossain, M. M. *Tetrahedron Lett.* **1991**, *32*, 5299.

(70) (a) Schrauzer, G. N.; Glockner. *Chem. Ber.* **1964**, *97*, 2451. (b) Lautens, M.; Crudden, C. M. *Organometallics* **1989**, 8, 2733 and references therein.
(71) Lautens, M.; Lautens, J. C.; Smith, A. C. *J. Am. Chem. Soc.* **1990**, *112*, 5627.
(72) (a) Brunner, H.; Muschiol, M.; Prester, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 652. (b) Brunner, H.; Prester, F. *J. Organometal. Chem.* **1991**, *414*, 401.
(73) Koerner, M.; Rickborn, B. *J. Org. Chem.* **1989**, *54*, 6.
(74) Koerner, M.; Rickborn, B. *J. Org. Chem.* **1990**, *55*, 2662.
(75) Riant, O.; Kagan, H. B. *Tetrahedron Lett.* **1989**, *30*, 7403.
(76) (a) Colonna, S.; Manfredi, A.; Annunziata, R. *Tetrahedron Lett.* **1988**, *29*, 3347. (b) Rama Rao, K.; Srinivasan, T. N.; Bhanumathi, N. *Tetrahedron Lett.* **1990**, *31*, 5959.
(77) Sangwan, N. K.; Schneider, H. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 896.
(78) Kim, J. I.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 9636.
(79) (a) Hilvert, D.; Hill, K. W.; Nared, K. D.; Auditor, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 9261. (b) Braisted, A. C.; Schultz, P. G. *J. Am. Chem. Soc.* **1990**, *112*, 7430.
(80) Corey, E. J.; Matsumara, Y. *Tetrahedron Lett.* **1991**, *32*, 6289.
(81) Corey, E. J.; Loh, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 8966.
(82) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.
(83) Hirst, S. C.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 382.