Zinc(II)-catalysed asymmetric hetero-Diels–Alder reactions of conjugated dienes with glyoxylate

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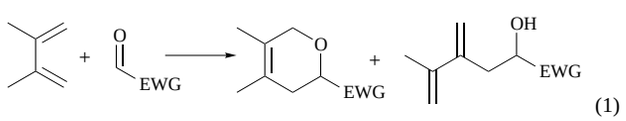
The zinc(II)-catalysed hetero-Diels–Alder reaction of the conjugated dienes 2,3-dimethylbuta-1,3-diene and cyclohexa-1,3-diene with ethyl glyoxylate has been studied in the presence of different C_2-symmetric bisoxazolines. The zinc(II)-catalysed reaction of 2,3-dimethylbuta-1,3-diene with ethyl glyoxylate gives both the hetero-Diels–Alder and ene products, the former being the major product with an enantiomeric excess up to 87%. The hetero-Diels–Alder : ene ratio is relatively independent of the catalytic system and the solvent and is in the range 1 : 0.5–1 : 0.8. For the zinc(II)-catalysed reaction of cyclohexa-1,3-diene with ethyl glyoxylate, the hetero-Diels–Alder product is formed in up to 84% isolated yield and with an enantiomeric excess up to 65%. The enantiomeric excess for this reaction is very dependent on the solvent, with $MeNO_2$ generally lowering the enantiomeric excess compared with CH_2Cl_2. Based on the absolute stereochemistry of the hetero-Diels–Alder products and semi-empirical calculations on different bisoxazoline–zinc(II)–ethyl glyoxylate intermediates the mechanism for the reaction is discussed.

Introduction

The metal-catalysed hetero-Diels–Alder (HDA) reaction of conjugated dienes with carbonyl compounds has been of considerable interest in recent years since it allows the formation of heterocyclic compounds in a highly regio- and stereo-selective manner.[1] For conjugated dienes having an allylic C–H bond such as 2,3-dimethylbuta-1,3-diene **1a** the metal-catalysed reaction with electron-deficient aldehydes **2** can take two paths, giving either the HDA-product **3** or the hetero-ene product **4** [eqn. (1)].

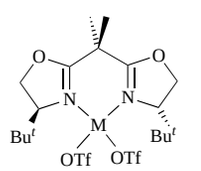


(1)

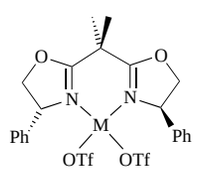
1a **2** **3** **4**

The course of the metal-catalysed reaction of conjugated dienes **1** with electron-deficient aldehydes **2** is dependent on the catalyst. Mikami *et al.* and Nakai *et al.* have found that by the use of TiX_2–BINOLate as the catalyst the reaction gives predominantly the ene product with a high enantiomeric excess (ee).[2] By the use of Cu-bisoxazolines† we were able to change the reaction path from an ene-reaction path to an HDA-reaction path, with a slight excess of the HDA-product relative to the ene-product.[3] The ee's of the HDA-product were in several cases >80%.[3] The HDA : ene ratio has been further improved using AlMe–BINOLate complexes as the catalyst for these reactions and the HDA : ene ratio was increased to more than 7 : 1 with ee >95% of the HDA product.[4] Several other metal complexes have also been found to catalyse the HDA reaction of conjugated dienes with carbonyl compounds.[5]

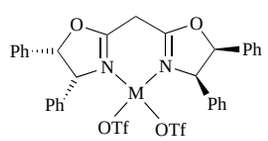
The HDA reaction of **1a** with **2** catalysed by bisoxazoline–copper complexes proceeds with some interesting stereochemical results since the use of (*S*)-**5a** (M = Cu) and (*R*)-**5b** (M = Cu) both gave rise to an HDA product with the same absolute stereochemistry.[3a] The HDA : ene ratio is dependent on the solvent and the anion; it has also been found that $MeNO_2$ increases both the reaction rate, chemoselectivity (HDA : ene ratio) and, in some cases, the enantioselectivity of the reaction.[3b,6] For the reaction of cyclohexa-1,3-diene **1b** with **2**, it was observed that the absolute stereochemistry of the HDA product is dependent on the solvent since CH_2Cl_2 and $MeNO_2$ gave enantiomers of opposing stereochemistry using (*R*)-**5b** (M = Cu) as the catalyst.[3b,6] It has been proposed that the change in absolute stereochemistry in these copper-catalysed HDA reactions may be a result of the catalyst–glyoxylate intermediate having two different structures.[3] For the bisoxazoline having *tert*-butyl substituents a planar structure accounts for the stereochemical outcome of the reaction, while for the bisoxazoline having phenyl substituents, a tetrahedral intermediate may be operating in CH_2Cl_2 as the solvent.[3] Others have also observed a similar change in the stereochemical outcome of these HDA reactions.[5]



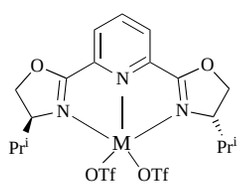
(*S*)-**5a**



(*R*)-**5b**



(*4R,5S*)-**5c**



(*S*)-**5d**

Copper complexes are known to have the ability to exist in different geometrical arrangements which give rise to interesting properties, but also cause troubles in the prediction of properties. In an attempt to develop further catalysts for HDA reactions and to obtain insight into the intermediates we have turned our attention to the complexes of the closely related metal zinc. Zinc(II) complexes can have different geometries: thus, four-coordinated zinc(II) complexes are mainly tetrahedral,[7] but if other coordinating ligands are present octahedral

† Throughout, isoxazoline refers to 4,5-dihydrooxazole.

Table 1 The hetero Diels–Alder (HDA) reaction between 2,3-dimethylbuta-1,3-diene and ethyl glyoxylate **2** catalysed by (*S*)-**5a**, (*R*)-**5b**, (4*R*,5*S*)-**5c** and (*S*)-**5d** (M = Zn^{II}) in CH_2Cl_2 and CH_3NO_2 as the solvents

				HDA product **3**		Ene product **4**		
Entry	Catalyst	Solvent	Reac. time (h)	Yield (%)[a]	Ee (%)[b] [config.]	Yield (%)[a]	Ee (%)[b,c]	**3**:**4** Ratio
1	(*S*)-**5a**	CH_2Cl_2	50	41	23 [*S*]	25	31	1:0.6
2	(*S*)-**5a**	$MeNO_2$	25	21	25 [*S*]	15	11	1:0.7
3	(*R*)-**5b**	CH_2Cl_2	50	42	81 [*S*]	25	68	1:0.6
4	(*R*)-**5b**	CH_2Cl_2[d]	50	26	87 [*S*]	18	72	1:0.7
5	(*R*)-**5b**	$MeNO_2$	50	46	~0	26	17	1:0.6
6	(4*R*,5*S*)-**5c**	CH_2Cl_2	25	42	79 [*S*]	33	61	1:0.8
7	(4*R*,5*S*)-**5c**	$MeNO_2$	25	34	46 [*S*]	21	45	1:0.6
8	(*S*)-**5d**	CH_2Cl_2	60	32	25 [*S*]	21	47	1:0.7
9	(*S*)-**5d**	$MeNO_2$	90	44	~0	21	17	1:0.5

[a] Isolated yield. [b] Ee determined by GC on a Chrompack Chirasil-DEX CB column. [c] Absolute stereochemistry not assigned. [d] Reaction temperature −25 °C.

Table 2 The hetero Diels–Alder (HDA) reaction between cyclohexa-1,3-diene **1b** and ethyl glyoxylate **2** catalysed by (*S*)-**5a**, (*R*)-**5b**, (4*R*,5*S*)-**5c** and (*S*)-**5d** (M = Zn^{II}) in CH_2Cl_2 and $MeNO_2$ as the solvents

Entry	Catalyst	Reac. time (h)	Solvent	HDA product **6** Yield (%)[a] [ee][b]
1	(*S*)-**5a**	40	CH_2Cl_2	57 [23][c]
2	(*S*)-**5a**	40	$MeNO_2$	46 [~0]
3	(*R*)-**5b**	25	CH_2Cl_2	62 [35][c]
4	(*R*)-**5b**	25	$MeNO_2$	84 [27][d]
5	(4*R*,5*S*)-**5c**	35	CH_2Cl_2	84 [65][c]
6	(4*R*,5*S*)-**5c**	35	$MeNO_2$	83 [45][c]
7	(*S*)-**5d**	100	CH_2Cl_2	19 [7][c]
8	(*S*)-**5d**	40	$MeNO_2$	64 [~0]

[a] Isolated yield. [b] Determined by HPLC using a CHIRALCEL OD column. [c] Absolute configuration (1*R*,3*S*,4*S*). [d] Absolute configuration (1*S*,3*R*,4*R*).

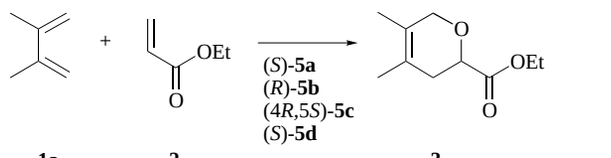
complexes have been observed.[8] Furthermore, zinc(II) has a Lewis acid character slightly different from that of copper(II). The catalytic properties of the zinc(II) complexes have been compared with those of copper(II) complexes to evaluate the properties of the Lewis acid for the HDA reaction. Furthermore, we have studied the intermediates by semi-empirical calculations in an attempt to obtain insight into the structure of the intermediate. Recently, Evans *et al*. have compared zinc(II) and copper(II) complexes for the Diels–Alder reactions and found that the properties of the latter were superior for this purpose.[7e]

Results and Discussion

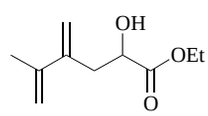
Synthetic aspects

The reactions of the two different conjugated 1,3-dienes, 2,3-dimethylbuta-1,3-diene **1a** and cyclohexa-1,3-diene **1b** with ethyl glyoxylate **2** in the presence of various catalysts [(*S*)-**5a**, (*R*)-**5b**, (4*R*,5*S*)-**5c** and (*S*)-**5d** (M = Zn^{II}); eqns. (2) and (3)] have been studied in CH_2Cl_2 and $MeNO_2$ as the solvents. The reason for studying the former reaction is to investigate the influence of zinc(II), chiral ligands and solvent on the HDA:ene ratio, as well as, the ee and absolute stereochemistry of the HDA product. The results are given in Table 1 and Table 2, respectively.

The results of the zinc(II)-catalysed reaction of 2,3-dimethylbuta-1,3-diene **1a** with ethyl glyoxylate **2** in the presence of (*S*)-**5a**, (*R*)-**5b**, (4*R*,5*S*)-**5c** and (*S*)-**5d** (M = Zn^{II} in all reactions of Tables 1,2) presented in Table 1 show that the HDA product **3** is the major product formed rather than the ene product **4**. The HDA:ene ratio, which varies in the range 1:0.5–1:0.8, is more or less independent of the different catalysts and the solvents studied, whereas the ee of **3** is very dependent on both the catalyst and solvent. For (*S*)-**5a** as the catalyst the *S*-enantiomer of **3** is formed, but the ee is low since only 23 and 25% are



1a **2** **3** (2)



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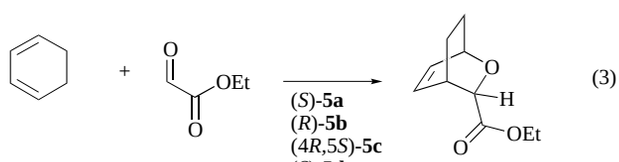


1b **2** **6** (3)

obtained in CH_2Cl_2 and $MeNO_2$, respectively (Table 1, entries 1, 2). The catalyst (*R*)-**5b** gives the highest ee of **3** as 81% is obtained at room temperature and 87% at −25 °C in CH_2Cl_2 (entries 3, 4), while it is notable that using $MeNO_2$ as the solvent leads to a racemic HDA product **3** (entry 5). The HDA product is formed as the *S*-enantiomer using (*R*)-**5b** as the catalyst; *i.e.* changing the substituent from *tert*-butyl to phenyl and changing the absolute stereochemistry of the chiral carbon atom in the bisoxazoline ligand lead to the same absolute induction in **3**. The catalyst (4*R*,5*S*)-**5c** gives also a relatively high ee of **3** in CH_2Cl_2 (79%) compared with that obtained in $MeNO_2$ (46%) (entries 6, 7); in both reactions the *S*-enantiomer of **3** is formed. The catalyst (*S*)-**5d** gives a low ee of **3** in both solvents (entries 8, 9). The ene product **4** is also formed with ee's dependent on the catalyst and the solvent used in these reactions; the highest ee is 72% using (*R*)-**5b** as the catalyst in CH_2Cl_2 while it is only 11% with (*S*)-**5a** in $MeNO_2$ (entries 2, 4).

The results in Table 2 for the reaction of cyclohexa-1,3-diene **1b** with ethyl glyoxylate **2** in the presence of the various catalysts (*S*)-**5a**, (*R*)-**5b**, (4*R*,5*S*)-**5c** and (*S*)-**5d** (M = Zn^{II}) [eqn. (3)] show that reasonable yields of the HDA product **6** are obtained; the highest, 84%, is obtained with (*R*)-**5b** and (4*R*,5*S*)-**5c** as the catalysts. Unfortunately, the ee of **6** obtained is relatively low, except for (4*R*,5*S*)-**5c** as the catalyst where a 65% ee is obtained (Table 2, entry 5). The absolute stereochemistry of **6** also shows some remarkable changes. The reactions catalysed by (*S*)-**5a** and (*R*)-**5b** in CH_2Cl_2 give the same absolute stereochemistry of **6** (1*R*,3*S*,4*S*) (entries 1, 3), whereas

for (*R*)-**5b** as the catalyst and $MeNO_2$ as the solvent the (1*S*,3*R*,4*R*) enantiomer of **6** is mainly formed (entry 4). However, use of (4*R*,5*S*)-**5c** as the catalyst for the reaction leads to formation of the (1*R*,3*S*,4*S*) enantiomer of **6** both in CH_2Cl_2 and $MeNO_2$ (entries 5, 6). For (*S*)-**5d** as the catalyst a low ee of **6** is formed in both solvents (entries 7, 8).

It is notable that for the reaction of 2,3-dimethylbuta-1,3-diene **1a** and cyclohexa-1,3-diene **1b**, the ee of the HDA products is generally significantly lower, and in some cases even racemic, for the reactions performed in $MeNO_2$, compared with CH_2Cl_2 as the solvent.

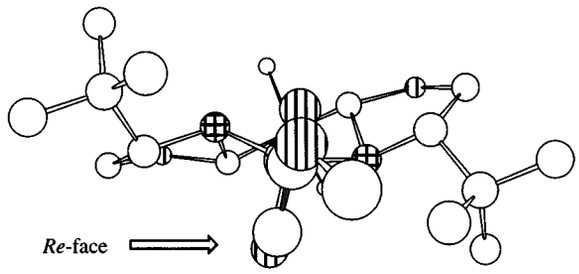
Theoretical calculations for bisoxazoline–zinc(II)–methyl glyoxylate intermediates

In an attempt to get some insight into the geometry of the intermediate(s) and to account for the stereochemical outcome in the bisoxazoline–zinc(II)-catalysed HDA reactions, the bisoxazoline–zinc(II)–methyl glyoxylate intermediates (we have used methyl glyoxylate in the calculations instead of ethyl glyoxylate to save computing time) have been investigated by semi-empirical calculations using the AM1 method.[9] In the calculations it is assumed that the two triflate anions are dissociated from the metal and that methyl glyoxylate is bidentate, being coordinated to the zinc metal by the two carbonyl oxygen atoms. Two possible geometries have been investigated: one in which the geometry at the zinc atom is tetrahedral and one in which the geometry is planar. These two geometries have been chosen in an attempt to account for the experimentally observed absolute stereochemistry of the HDA products, and, furthermore, to see whether a planar intermediate is closely related to an octahedral intermediate since it gives the same absolute induction. It has also been assumed that only the chiral ligand and methyl glyoxylate are coordinated to zinc(II) in the intermediate. The two structural possibilities, tetrahedral and planar, of (*S*)-**5a**, (*R*)-**5b** and (4*R*,5*S*)-**5c** (M = Zn) coordinated to methyl glyoxylate have been optimised by AM1 calculations.

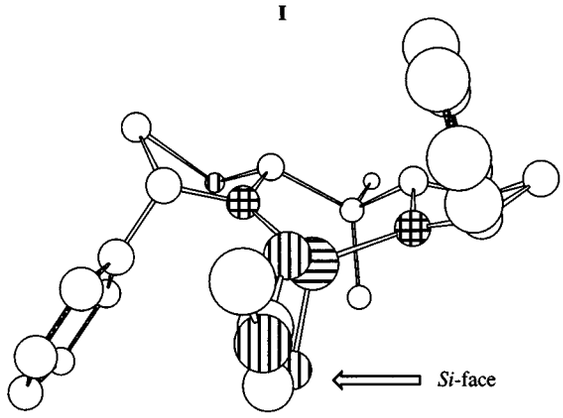
In Scheme 1, **I** the lowest energy structure of methyl glyoxylate coordinated to (*S*)-**5a** is presented. The geometry at the zinc(II) centre is tetrahedral and the total energy for this intermediate is calculated to be 158 kJ more stable than the related planar one. With the lowest energy intermediate for methyl glyoxylate coordinated to (*S*)-**5a** (−4743.765 eV) as outlined in **I** (Scheme 1) the diene can approach the carbonyl from the *Re*-face to give *R* as the absolute stereochemistry at the former carbonyl carbon atom in the HDA-product, which is the reverse of the experimentally observed stereochemistry.

The total energies of (*R*)-**5b** and (4*R*,5*S*)-**5c** (M = Zn) coordinated to methyl glyoxylate have also been calculated: for (*R*)-**5b**-coordinated to methyl glyoxylate the tetrahedral geometry (total energy −5147.273 eV) is 18 kJ more stable than the planar geometry, while for (4*R*,5*S*)-**5c**-coordinated to methyl glyoxylate the tetrahedral geometry (total energy −6791.216 eV) is 75 kJ more stable than the planar geometry. The energy differences for the two different structures of (*R*)-**5b** and (4*R*,5*S*)-**5c** (M = Zn) coordinated to methyl glyoxylate show that the tetrahedral complexes are the most stable. Only the complexes consisting of (*R*)-**5b** coordinated to methyl glyoxylate is outlined as **II** (Scheme 1) as the two optimised structures of (*R*)-**5b** and (4*R*,5*S*)-**5c** (M = Zn) coordinated to methyl glyoxylate are very similar. The zinc(II)-nitrogen (bisoxazoline) bond lengths (2.02 Å) calculated in **II** (Scheme 1) correspond well to the same bond lengths in (*S*)-**5b**–$ZnCl_2$ (2.035 Å and 2.047 Å).[7e] The intermediate **II** in Scheme 1 has the *Si*-face of the glyoxylate carbonyl functionality available for approach of the diene. The theoretical calculations for the structure of (*R*)-**5b** and (4*R*,5*S*)-**5c** (M = Zn) coordinated to methyl glyoxylate gives thus an intermediate, **II** (Scheme 1) which accounts for the absolute stereochemistry of the HDA product in the reactions performed in CH_2Cl_2.

The theoretical results show thus that there is a preference



I



II

Scheme 1

for a tetrahedral intermediate. However, for methyl glyoxylate coordinated to (*S*)-**5a** the absolute stereochemistry of the HDA product obtained from such an intermediate does not agree with the experimental results, whereas for (*R*)-**5b** and (4*R*,5*S*)-**5c** (M = Zn) coordinated to methyl glyoxylate, the intermediate accounts for the experimental results.

Mechanistic considerations

The activation of ethyl glyoxylate by the bisoxazoline–zinc(II) complexes is less effective than that induced by the corresponding bisoxazoline–copper(II) complexes since, generally, longer reaction times are necessary for the former reactions. However, the bisoxazoline–zinc(II)-catalysed HDA reaction of 2,3-dimethylbuta-1,3-diene with ethyl glyoxylate shows higher HDA-chemoselectivity than the corresponding copper complexes,[3] but lower HDA-chemoselectivity than the AlMe–BINOLate complexes.[4] Although the theoretical calculations fail to explain why the zinc(II) catalytic system leads to a slower HDA reaction than the corresponding copper(II) system, lower reactivity for zinc(II) complexes has been observed in both Diels–Alder reactions using related complexes as catalysts[7e] and in ene and HDA reactions of trifluoroacetaldehyde with dienes.[10] Finally, since the theoretical calculations fail to explain why the bisoxazoline–zinc(II) complexes are more HDA-chemoselective than the bisoxazoline–copper(II) complexes but less selective than the AlMe–BINOLate system, we shall leave for the future further attempts to explain the catalytic activity and HDA : ene selectivity of the bisoxazoline–zinc(II) complexes.

Let us now turn our attention to the enantioselectivity and absolute induction observed in these HDA additions as well as related systems. Evans *et al*. found that in the Diels–Alder reaction of acryloyloxazolidinone and cyclopentadiene catalysed by (*S*)-**5b** ($M = Zn^{II}$) a tetrahedral intermediate could account for the absolute stereochemistry of the Diels–Alder product.[7e] Use of (*S*)-**5a** ($M = Zn^{II}$) as catalyst, however, only gave poor results in the same reaction.[7e] In contrast, they observed that when the related copper complexes were used as the Lewis acid, the (*S*)-*tert*-butyl derived catalyst gave high enantioselectivity, whereas

the phenyl ligand gave poor results.[7e,10] Recently Davies *et al*. found that the indane-derived ligand, which can be regarded as a rotationally fixed phenyl ligand, gave high enantioselectivity in the same reaction.[11] All these results can be rationalised on the basis of a square planar or an octahedral intermediate.

In summary, it seems that depending on whether the bisoxazoline ligand has *tert*-butyl or phenyl substituents dictates whether the outcome of the reaction can be rationalised in terms of a planar/octahedral or tetrahedral intermediate, respectively, irrespective of whether the central metal is zinc, copper or magnesium. In support of this conclusion, Porter *et al*. observed that in a bisoxazoline–Lewis acid ($M = Mg^{II}$) and Zn^{II}-catalysed radical addition to crotonyl- and cinnamoyloxazolidinone an (*S*)-*tert*-butyl or isopropyl substituted chiral ligand gave the (*R*)-product, while an (*S*)-phenyl substituted chiral ligand gave the (*S*)-product.[12] Moreover, we recently observed in the glyoxylate HDA-reaction catalysed by copper complexes that the (*S*)-*tert*-butyl and (*R*)-phenyl derived ligands gave the same absolute induction. This observation has recently been confirmed by Ghosh *et al*. using the highly active Danishefsky's diene in the glyoxylate HDA reaction.[5d] In this paper we report that use of zinc(II) as the Lewis acid in the HDA reaction of glyoxylate with non-activated dienes, such as cyclohexa-1,3-diene and 2,3-dimethylbuta-1,3-diene, the observed absolute stereochemistry can again be rationalised on the basis of a tetrahedral intermediate using the phenyl-substituted ligand, and a square planar or octahedral intermediate when using the *tert*-butylbisoxazoline ligand. Apart from these observations there have been two reports on a magnesium-catalysed reaction with the phenyl-substituted ligand, where the outcome of the reaction was rationalised on the basis of a tetrahedral complex.[13] It appears, therefore, that it is the ligand which determines the selectivity in the magnesium-, copper- and zinc-catalysed reactions, irrespective of which of the metals is involved. In the case of a phenyl-substituted bisoxazoline ligand a tetrahedral intermediate may be involved, whereas for the corresponding *tert*-butyl substituted ligand a square planar or octahedral intermediate is possible.

In this paper we report that in the reaction of cyclohexa-1,3-diene **1b** with ethyl glyoxylate in the presence of (*R*)-**5b** as the catalyst, the absolute stereochemistry of the HDA product **6** is changed from (1*R*,3*S*,4*S*) to (1*S*,3*R*,4*R*) when the solvent is changed from CH_2Cl_2 to $MeNO_2$; this is similar to the bisoxazoline–copper(II)-catalysed HDA-reactions.[3b] This change in absolute stereochemistry can be accounted for by a change in the geometry of the intermediate, a change of the solvent from CH_2Cl_2 to CH_3NO_2 leading to a change of the intermediate from a tetrahedral to an octahedral geometry, in which two ligand molecules are coordinated at the axial positions of zinc(II). This intermediate has now the *Re*-face of the glyoxylate carbonyl available for approach of the diene. Another change of absolute induction using the same ligand was observed in the bisoxazoline–magnesium(II)-catalysed Diels–Alder reaction with magnesium perchlorate as the metal salt.[13a] It was observed that the reaction of acryloyloxazolidinone with cyclopentadiene in the presence of (*R*)-**5b**–magnesium perchlorate gave the *S*-enantiomer of the Diels–Alder product, while the addition of 2 equivalents of water to the same catalyst gave the *R*-enantiomer.[13a] The outcome can be explained in terms of an initial four-coordinated tetrahedral intermediate, which after the addition of water, changes to a six-coordinated octahedral magnesium intermediate.

Finally, it should be mentioned that the enantioselective Mukaiyama–Michael reaction of 2-methoxycarbonylcyclopentenone catalysed by bisoxazoline–copper(II) complexes (*R*)-**5b** and (4*R*,5*S*)-**5c** ($M = Cu^{II}$) gives the same absolute induction in the product.[14] This reaction is also very sensitive to the anion used since upon exchange of triflate for antimonate the absolute stereochemistry of the product is changed.[14]

Since the theoretical calculations for the (*S*)-**5a** ($M = Zn^{II}$)–methyl glyoxylate intermediate do not account for the absolute stereochemistry of the HDA products, we conclude that the intermediate in the present HDA reactions is probably very sensitive to the chiral ligands and reaction conditions.

Experimental

General

$Zn(OTf)_2$, cyclohexa-1,3-diene, 2,3-dimethylbuta-1,3-diene, 2,2′-isopropylidenebis[(4*S*)-4-*tert*-butyl-4,5-dihydrooxazole], (*R*)-(+)-2,2′-isopropylidenebis(4-phenyl-4,5-dihydrooxazole), 2,2′-methylenebis[(4*R*,5*S*)-4,5-diphenyl-4,5-dihydrooxazole] and 2,6-bis[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]pyridine were purchased from Aldrich Chemical Co. and used without further purification. $Zn(OTf)_2$ was stored under N_2. Ethyl glyoxylate, prepared as described in the literature[6,15] and stored at −18 °C, was distilled under reduced pressure (water pump) prior to use. Solvents were dried according to standard procedures.

Standard procedure for the HDA reactions: reaction of 2,3-dimethylbuta-1,3-diene 1a and cyclohexa-1,3-diene 1b with ethyl glyoxylate 2 catalysed by the various catalysts (*S*)-5a, (*R*)-5b, (4*R*,5*S*)-5c and (*S*)-5d ($M = Zn^{II}$)

A dry flask was charged with $Zn(OTf)_2$ (36 mg, 0.1 mmol) and the ligand [0.105 mmol: (*S*)-**5a** (31 mg), (*R*)-**5b** (35 mg), (4*R*,5*S*)-**5c** (48 mg) or (*S*)-**5d** (32 mg) ($M = Zn^{II}$)] under a stream of N_2. Dry CH_2Cl_2 or $MeNO_2$ (1–2 ml) was added to the mixture which was then stirred at room temperature for 2 h. Ethyl glyoxylate **2** (0.102 g, 1.0 mmol) dissolved in the same solvent (1–2 ml) was added to the mixture, followed by addition of 2,3-dimethylbuta-1,3-diene **1a** (170 μl, 1.5 mmol) or cyclohexa-1,3-diene **1b** (140 μl, 1.5 mmol). The reaction mixture was then stirred at room temperature (except for entry 4, Table 2 which took place at −25 °C) for the time given in the Tables. After evaporation of the solvent, the crude products were purified by flash chromatography on silica gel [EtOAc–light petroleum (1:9) as the eluent for **3** and **4**, and EtOAc–light petroleum (2:8) as the eluent for **6**]. The enantioselectivities were determined on a chiral GC, Chrompack Chirasil-DEX CB column 25 m * 0.25 mm, oven temperature was 120 °C for **3** and **4**, and 130 °C for **6**. The results are given in Tables 1 and 2. Spectral data are consistent with those previously published.[3,4]

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