ELSEVIER

Review

Metal-bis(oxazoline) complexes: From coordination chemistry to asymmetric catalysis[☆]

Ramesh Rasappan, Dominic Laventine, Oliver Reiser[*]

Institut für Organische Chemie, Universität Regensburg, D-93053 Regensburg, Germany

Contents

Abstract

Metal-bis(oxazoline) complexes have proven to be one of the most versatile classes of chiral catalysts being able to promote a large variety of organic transformations. The coordination geometry and electronic properties play an integral role for the asymmetric induction exhibited by these complexes and, aided by X-ray structure analysis and NMR studies, rules have been recognized to understand their function. Based on the most common complex geometries observed, i.e. tri, tetra- (tetrahedral or square-planar), penta- (trigonal-bipyramidal or square-pyramidal), or hexacoordination (octahedral) a mechanistic picture has emerged that allows control of enantioselectivity in reactions in a highly predictable and tunable way, demonstrating the power of combining the knowledge of coordination chemistry and asymmetric catalysis.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Bis(oxazoline) ligands; Metal-bis(oxazoline) complexes; Coordination geometry; Asymmetric catalysis; Stereochemical models

1. Introduction

Bis(oxazoline) (box) ligands have developed into one of the most useful ligand classes for asymmetric catalysis due to their ability to coordinate with a large number of metals [1–4]. The resulting chiral complexes display a C_2-axis (Fig. 1), a feature that has proven most beneficial in designing asymmetric pro-

cesses in general due to the reduction of possible transition states caused by the equivalency of structures upon rotation by 180° [5]. However, unlike for other chiral ligand classes the principles of the function of metal-bis(oxazoline) complexes, especially with respect to chiral discrimination of substrates, have been recognized.

A considerable number of X-ray structure analyses of metal-box and especially metal-box-substrate complexes combined with most insightful interpretations [6,7] have provided a reliable mechanistic picture for many asymmetric transformations, impressively showing the power of combining the knowledge of coordination chemistry and asymmetric catalysis.
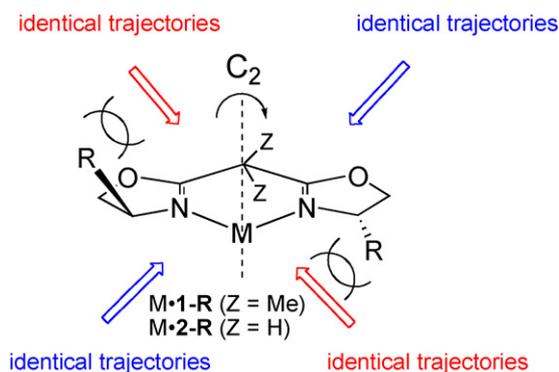
Fig. 1. C_2-symmetrical metal-bis(oxazoline) complexes.

2. Metal-bis(oxazoline) complexes

Complexes with a metal/box stoichiometry of 1:2 have been characterized, however, the decisive intermediates discussed in applications for catalysis generally contain a metal to ligand ratio of 1:1 with two metal sites being occupied by the ligand, leaving typically up to four sites open for substrate interactions. Complexes in which bis(oxazolines) act as a monodentate ligands have been observed [8,9], however such assemblies are not productive to promote asymmetric transformations and moreover, might not represent the structure in solution. Oxazoline ligands [10,11] having three donor atoms (especially pyridine-bis(oxazolines) [12] and tris(oxazolines) [13–15]) have also been most successfully utilized for asymmetric catalysis, while bis(oxazoline) ligands with even more donor atoms are known to display a rich coordination chemistry [16–19], but have found fewer applications [20–27] in promoting organic transformations. This review will focus on metal-bis(oxazoline) complexes with a 1:1 metal/ligand ratio and their implications for asymmetric reactions based on their coordination geometry.

2.1. Tricoordinated metal complexes with bis(oxazoline) ligands

One of the first asymmetric reactions using bis(oxazoline) ligands to be described is the copper(I)-catalyzed cyclopropanation of alkenes with diazoacetates [28–30]. Although copper(I)-carbene complexes had been postulated early on, the characterization of such intermediates has been elusive. Nevertheless, Pfaltz and co-workers put forward a model in 1988 for the related semicorrine ligands that has proven to be the most successful to rationalize the general outcome of this reaction [31].

According to this model, a copper(I)-carbene complex of box ligand 1 is formed in which the substituents on the carbene take positions perpendicular to the plane spanned by the metal-oxazoline moieties (Scheme 1). Since there is no electronic contribution from the copper(I)-center (having d10 configuration) to the carbene ligand, this geometry is most likely a consequence of steric factors, avoiding interactions of the ester with the bulky R groups.
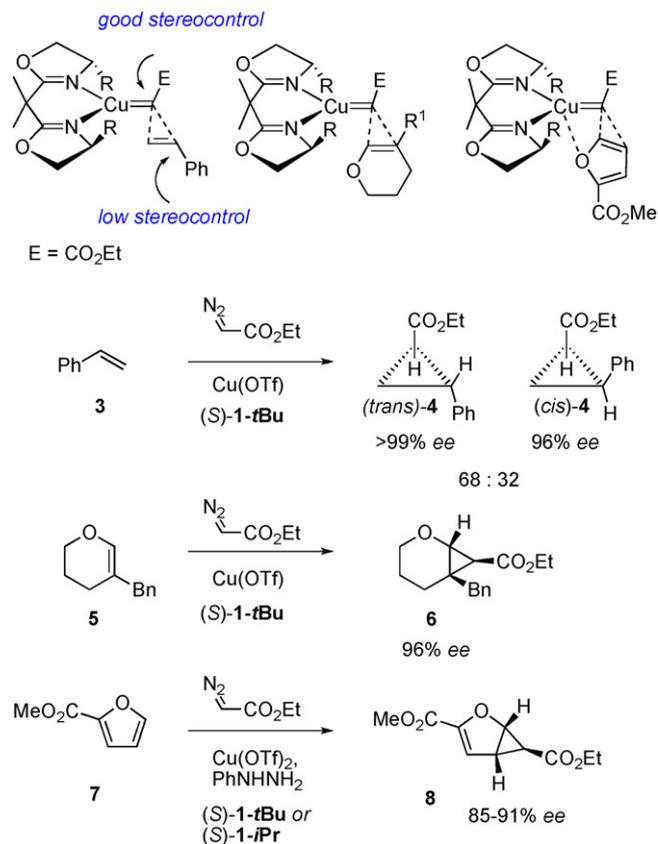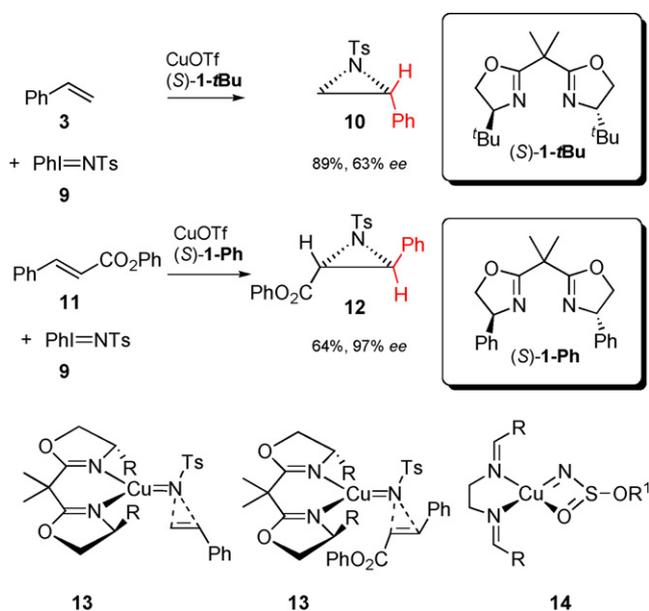

Scheme 1. Asymmetric cyclopropanation with copper(I)-bis(oxazolines).

Hofmann and co-workers provided evidence of such copper carbene species and especially elegantly proved the proposed geometry with respect to the orientation of the substituents on the carbene ligand by NMR [32]. Alkenes approach the carbene complex of Cu·(S)-1-R from the ligand quadrant that best avoids the group R (Scheme 1), placing substituents such as phenyl in 3 [30] or benzyl in 5 [33] away from the ligand. Furthermore, in the forming cyclopropane the ester group of the carbene moves away from the approaching alkene without encountering steric hindrance from the bulky R groups of the ligand.

Acyclic alkenes such as 3 will also place their terminal substituent preferentially away from the ester group E, however, *cis/trans*-selectivity is generally low unless especially bulky esters are employed. With cyclic alkenes such as 5 or 7, *exo*-adducts placing the ester group on the convex face of the bicyclic product are generally obtained with high selectivity. Finally, the high enantiocontrol observed with 7 [34–37], in contrast to results observed with *N*-Boc-pyrrole [27], points to a favorable Lewis acid/Lewis base interaction between copper and the furan oxygen.

In an analogous fashion, copper(I)-catalyzed aziridinations of alkenes were argued to proceed via bis(oxazoline)−Cu=NTs intermediates such as 13 by a concerted pathway [38]. An alternative step-wise mechanism, featuring a square-planar copper complex of type 14 involving coordination of oxygen of the tosyl group in addition to the nitrene moiety has also been proposed (Scheme 2) [39]. Considering a copper-nitrene intermediate as depicted in 13, the stereoselectivity of the reaction can

Scheme 2. Asymmetric aziridination with copper(I)-bis(oxazolines).

Fig. 2. Preferred trajectory (solid arrow) of a substrate S for the attack of a prochiral group Y forming a tetrahedral (left) or a square-planar (right) environment with a metal-bis(oxazoline) complex.

be explained by primarily minimizing steric interactions of the approaching alkene with the bis(oxazoline) ligand, and secondarily with the *N*-tosyl group. As a consequence of this rational, the selection of the enantiotopic faces should be reversed upon variation of the substrate from a terminal alkene such as **3** to a *trans*-substituted alkene such as **11**, which is indeed the observed experimental result [40]. However, by varying the copper source, the nitrene precursor, or the solvent the opposite stereoselectivity has been reported, indicating that other factors must also play a role [41,42].

2.2. Tetra-, penta-, and hexacoordinated complexes with bis(oxazoline) ligands

The most common total number of ligands in bis(oxazoline) complexes is four to six, i.e. in addition to the two point coordination of the bis(oxazoline) ligand two to four coordination sites can be occupied by substrates, solvent molecules or counter anions, the latter stemming from the metal salt employed for complexation. Which species will be present in solution is dependent on subtle factors and has very significant consequences for the stereochemical outcome of a given reaction. The coordination geometry can be especially affected, which might result in a complete reversal of the absolute stereoinduction, thus allowing the access of either enantiomer of a product with the same catalyst.

2.2.1. Tetracoordinated complexes with bis(oxazoline) ligands

The two principle geometries possible for tetracoordinated bis(oxazoline) complexes are square-planar and tetrahedral. These are indeed widely found for such complexes with varying degrees of distortion. Interestingly, complexes residing in either of these geometries show opposite selectivity, since rotation of a coordinated substrate by 90° moves its accessible face
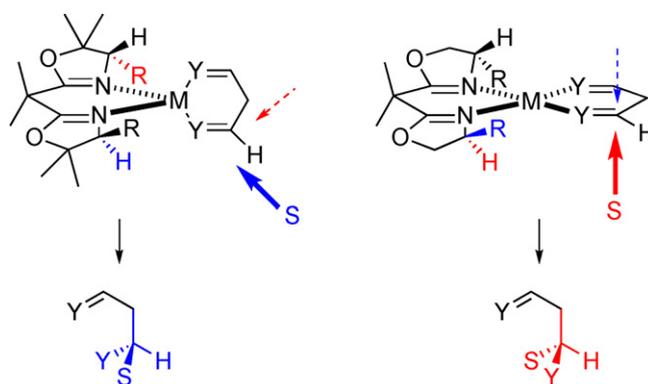
from the shielded into the unshielded region of the ligand and vice versa (Fig. 2). Consequently, switching between these two geometries by the appropriate choice of the metal opens the possibility to access either enantiomer of a product with the same bis(oxazoline) ligand stereochemistry.

2.2.1.1. Tetrahedral bis(oxazoline) complexes. Zinc(II) [43], nickel(II) [44] and iron(II) chloride [45] have been proven by X-ray structure analysis to form only slightly distorted tetrahedral complexes with bis(oxazoline) ligands (*R*)-**1-Ph** and (*S*)-**1-*t*Bu** (Fig. 3).

Copper(II)-halide complexes with bis(oxazolines) are considerably more distorted towards a square-planar geometry (Fig. 4), therefore, such complexes can also be described as distorted square-planar.

Quite obviously, the chlorine ligands orient themselves away from the ligand quadrants blocked by the sterically demanding substituents. Comparing the copper complexes (Fig. 4; Table 1), for example the copper complexes of the *tert*-butyl substituted bis(oxazoline) (*S*)-**1-*t*Bu** and the isopropyl substituted azabis(oxazoline) [46,47] (*S*)-**15-*i*Pr** it also becomes evident that the degree of distortion away from the ideal tetrahedral geometry is increasing with the steric bulk of the R groups.
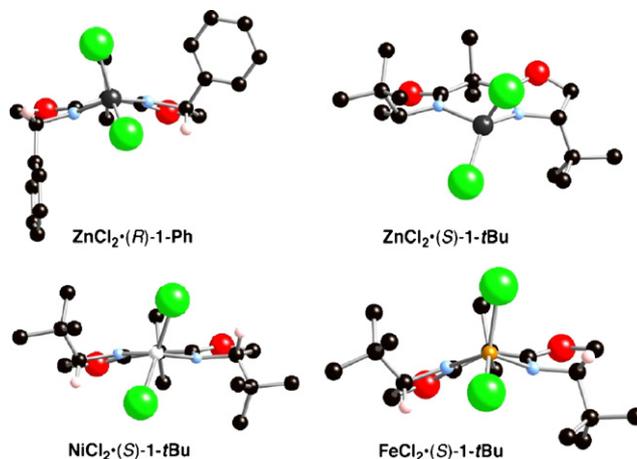
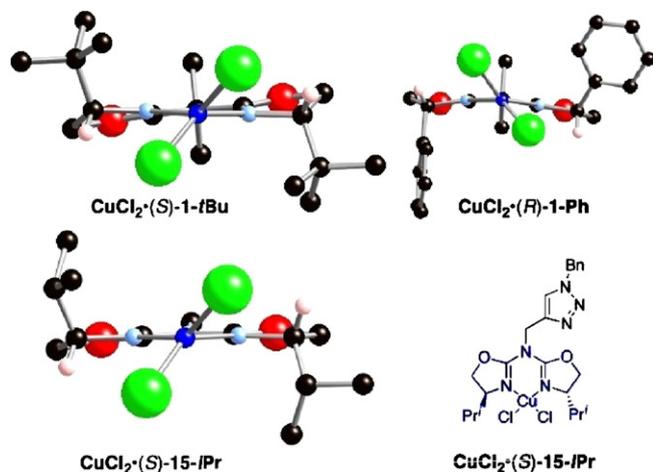Fig. 3. X-ray structures of **1-R** with ZnCl$_2$, NiCl$_2$, and FeCl$_2$.

Fig. 4. X-ray structures of copper(II)-chloride complexes of bis(oxazolines) (S)-**1-tBu** and (R)-**1-Ph**, and of azabis(oxazoline) (S)-**15-iPr** (triazole moiety omitted for clarity).

Therefore, it cannot always be assumed that increasing the steric bulk of the groups R in bis(oxazolines) will also enhance selectivity. The latter is reversed upon changing from a tetrahedral to a square-planar geometry (Fig. 2), and sterically demanding substituents R will not only more effectively block approaching substrates but also cause distortion of tetrahedral complexes towards square-planar ones. Indeed, quite a number of examples are known in which **1-Ph** leads to higher selectivities than **1-tBu** [43,50–54], which might also be attributed to the special features of a phenyl group as a π-shield, providing a "flat wand" to block incoming substrates. However, there are also cases known in which isopropyl has proven superior against *tert*-butyl substitution in bis(oxazoline) ligands, for example in the asymmetric benzoylation of α-hydroxycarbonyl compounds (Scheme 3) [55] or in conjugate reductions of α,β-unsaturated carbonyl compounds [56].

Magnesium-bis(oxazoline) complexes have been widely employed in Diels–Alder reactions (Section 2.2.4). Although no X-ray structures of such complexes are available, from the

Table 1
Degree of distortion in tetrahedral metal(II)-bis(oxazoline) complexes

Metal	Box	Anion	θ_1/θ_2	Ref.
Zn	(R)-**1-Ph**	Cl	17/13	[43]
Zn	(S)-**1-tBu**	Cl	32/22	[43]
Ni	(S)-**1-tBu**	Cl	23/23	[44]
Fe	(S)-**1-tBu**	Cl	18/15	[45]
Cu	(R)-**1-Ph**	Cl	45/38	[43]
Cu	(S)-**1-tBu**	Cl	45/45	[43,48]
Cu	(S)-**15-iPr**	Cl	31/25	[49]
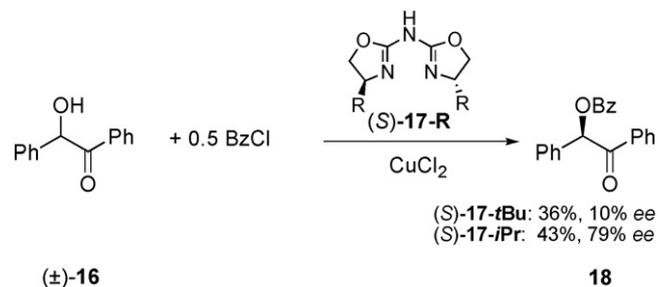
Scheme 3. Kinetic resolution of (±)-2-hydroxy-1,2-diphenylethanone (±)-**16** by asymmetric benzoylation.

Table 2
Degree of distortion in square-planar metal-bis(oxazoline) complexes

Metal	Box	$(X)_2$	θ_1/θ_2	Ref.
Cu	(S)-**1-Ph**	$(H_2O)_2$	79/66	[57]
Cu	(S)-**1-tBu**	$(H_2O)_2$	52/50	[58]
Cu	(S)-**1-Ph**	$PhCH=C(CO_2Me)_2$	90/85	[63]
Cu	(S)-**1-tBu**	$PhCH=C(CO_2Me)_2$	79/75	[62]
Pd	(S)-**1-iPr**	Me/Cl	20/8	[64]
Pd	(S)-**19-iPr**	Me/Cl	12/5	[64]
Pd	(R)-**1-tBu**	PhCHCHCHPh	84/71	[65]

selectivities observed in such reactions it could be concluded that tetrahedral species are formed as the decisive intermediates in the absence of coordinating solvents or anions.

2.2.1.2. Square-planar complexes with bis(oxazoline) ligands. A great number of copper(II)-bis(oxazoline) complexes with additional oxygen ligands have been characterized [43,57–63], reflecting the great importance such complexes play in the promotion of many asymmetric transformations. In comparison to copper(II)chloride complexes described in Section 2.2.1.1, complexes with hydroxyl as well as with carbonyl ligands exhibit a marked preference for square-planar geometries (Table 2; Figs. 4–7), reflecting the larger d orbital splitting the latter groups should cause.
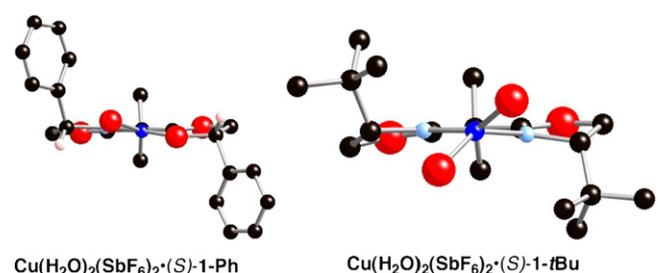

Fig. 5. X-ray structures of $Cu(H_2O)_2(SbF_6)\cdot$(S)-**1-R** complexes (outer sphere SbF_6 ligands omitted for clarity).
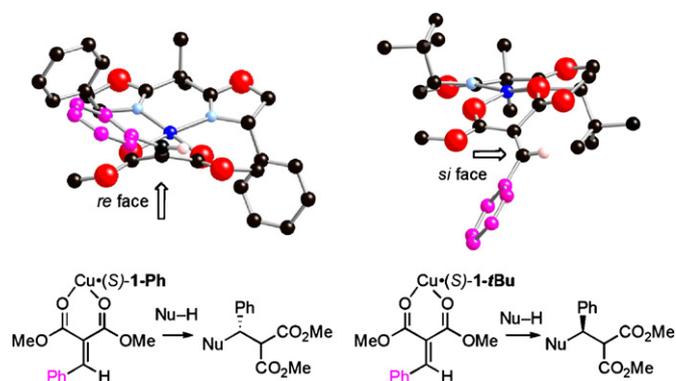
Fig. 6. X-ray structures of copper(II)-phenylbenzylidene complexes (outer sphere SbF$_6$ ligands omitted for clarity).

Again, the distortion in the copper(II)-aquo complex of the *tert*-butyl substituted bis(oxazoline) **1-tBu** (Fig. 5, right) is large [57], orienting the water molecules away from the *tert*-butyl groups into the open quadrants of the box-ligands. In contrast, distortion of the analogous complex with **1-Ph** is small (Fig. 5, left), and quite unexpectedly, the water molecules are even oriented towards the phenyl groups [58].

The same trend can also be seen in the X-ray structures of the phenylbenzylidene complexes depicted in Fig. 6, representing a milestone in the analysis of copper-bis(oxazoline) complexes since for the first time a substrate being relevant for subsequent transformations could be characterized in the solid state while being coordinated to a metal-box-complex [62,63]. Notably, the distortion away from a square-planar geometry is much smaller with **1-Ph** than with **1-tBu**, but also the phenyl group of phenyl-benzylidene is oriented *towards* the proximal phenyl group of **1-Ph** while it is *bent away* in **1-tBu**. Keeping in mind that extrapolation from solid state structures to reactions proceeding in solution is problematic, the X-ray structures shown nevertheless provide a rational as to why **1-Ph** gives rise to *opposite* enantioselection with this substrate in nucleophilic additions: The upward bend of the malonate seen with **1-Ph** causes the prox-

imal phenyl group to tower on top of the malonate making the *si* face inaccessible, while the downward bend in combination with the tilt by approximately 10–15° out of the coordination plane (Table 2) of the metal-bis(oxazoline) causes shielding of the *re* face by the *tert*-butyl group pointing down in **1-tBu**.

The solid state structures of the palladium(II) complexes PdMeCl·(*S*)-**1-iPr** and PdMeCl·(*S*)-**19-iPr**, being catalyst precursors for alkene/CO copolymerization reactions, have been reported [64]. In both complexes palladium is coordinated in a square-planar environment, however, the metal-bis(oxazoline) chelate ring adopts a boat conformation, while the palladium-azabis(oxazoline) chelate is almost perfectly flat due to the central sp^2 hybridized nitrogen. Therefore, the azabis(oxazoline) ligand is more electron rich, which is reflected by a shorter oxazoline–N palladium bond. In turn, the palladium methyl–C bond was found to be longer for the azabis(oxazoline) system.

As a consequence, PdMeCl·(*S*)-**19-iPr** was found not only to be more stable (as judged by slower palladium black formation in the course of the reaction) in CO/styrene copolymerizations but also more active, reflected in higher turnover frequencies with respect to PdMeCl·(*S*)-**1-iPr**, since dissociation of alkyl groups from palladium is necessary for the catalysis to proceed.

The determination of X-ray structures of palladium(II)-bis(oxazoline) ligands with allyl substituents [65], being decisive intermediates in allylic substitution reactions [66,67], has been another landmark in deducing rules for the function of bis(oxazolines) as asymmetric promoters (Fig. 8) [68,69]. It is quite apparent that, the bis(oxazoline) ligand is even more strongly bent in this complex, caused by the six-membered palladacycle residing in a boat conformation. This is most likely a consequence of minimizing steric interactions of the phenyl group in the allyl ligand with the proximal benzyl group of the bis(oxazoline) ligand. The palladium is coordinated in a distorted square-planar geometry by the allyl termini and the oxazoline nitrogens, with the allyl group being more strongly rotated out of the plane on the side where the phenyl and benzyl groups are close. This is also reflected in the larger palladium–carbon bond to further reduce steric strain between
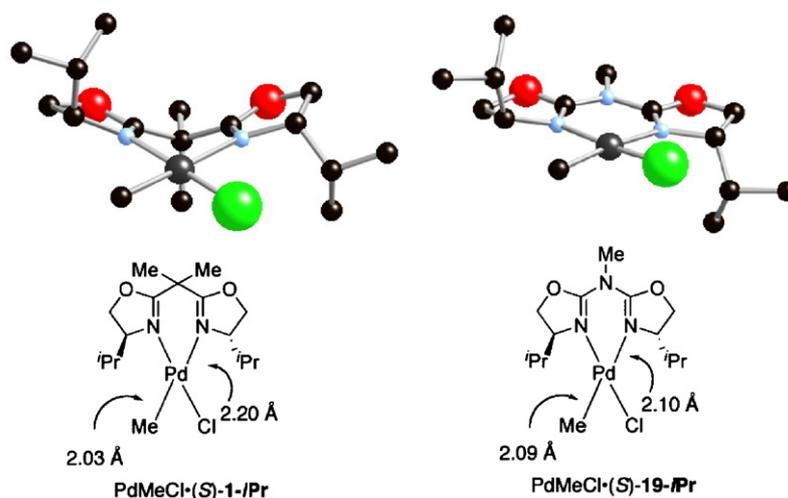

Fig. 7. X-ray structures of bis(oxazoline) and -azabis(oxazoline) palladium(II) complexes.
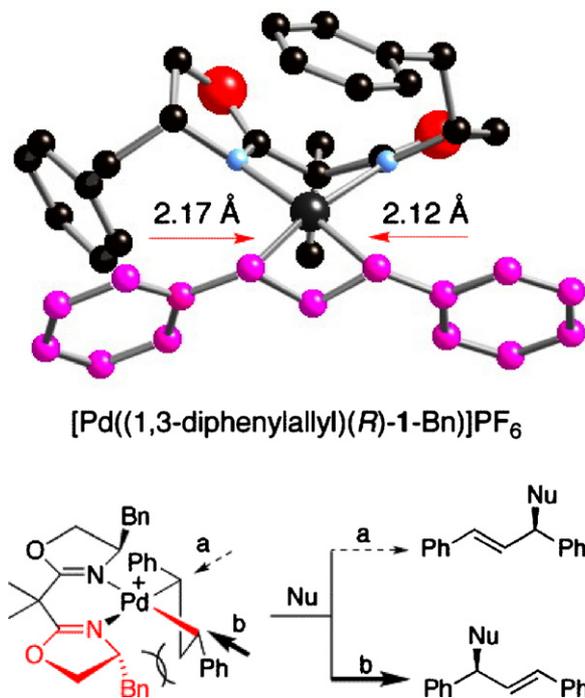
[Pd((1,3-diphenylallyl)(*R*)-1-Bn)]PF$_6$

Fig. 8. X-ray structure of palladium(II)-bis(oxazoline) complex with 1,3-diphenylallyl ligand.

Fig. 9. (a) Trigonal-bipyramidal versus (b–d) square-pyramidal complexes with bis(oxazoline) and bis(oxazolinyl)pyridine ligands.

these groups, and as a consequence a nucleophile will attack preferentially that weaker bond, which explains the excellent selectivities for nucleophilic allylic substitutions.

2.2.2. Pentacoordinated complexes with bis(oxazoline) ligands

The two principle possibilities for pentacoordinated complexes with bis(oxazolines) are trigonal-bipyramidal and square-pyramidal (Fig. 9), and indeed both types of geometries have been observed. If in such complexes a bidentate substrate coordinates orthogonal to the metal-bis(oxazoline) plane (Fig. 9a), the prediction for stereochemical induction is similar as discussed for tetrahedral complexes (cf. Fig. 2). However, due to the additional ligand X, one of the groups Y in the substrate is rotated backward in comparison to the tetrahedral geometry making the front-side accessible as well. Consequently, switching from a tetrahedral to a trigonal-bipyramidal geometry by coordination of an additional ligand such as a solvent molecule might lead to an erosion of stereochemistry in the products. However, no catalytically active intermediates with such coordination geometry have been encountered so far.

In contrast, square-pyramidal coordinated metal-bis(oxazoline) complexes as catalytically active intermediates have been discussed for a number of processes. If coordination of a bidentate substrate occurs with both groups equatorial (in the plane of the metal-bis(oxazoline) chelate) the situation is the same as discussed for square-planar coordination with respect to the stereochemical outcome of a reaction. However, the bidentate substrate might be coordinated in the metal-box plane (equatorial) with the first, and orthogonal to it (apical) with the second group Y. The most well-known of this type of coordi-
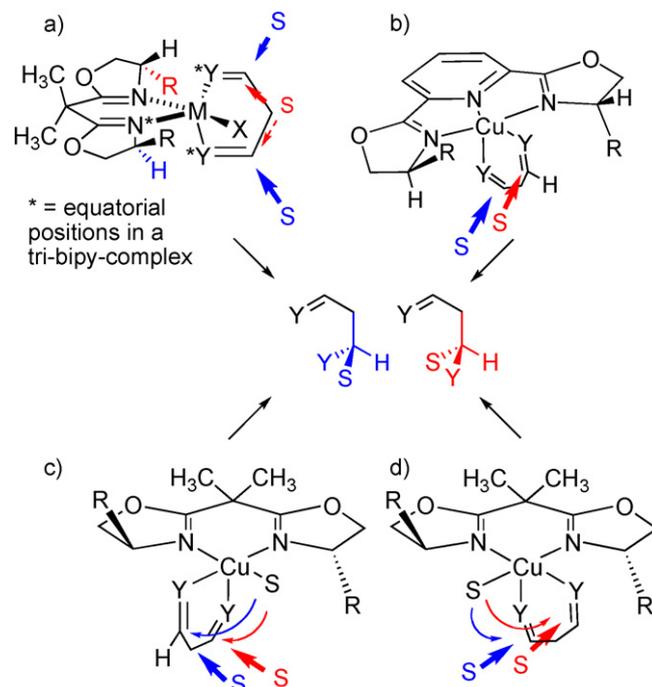
nation is for bis(oxazolinyl)pyridine ligands (Fig. 9b) [12], but examples for bis(oxazoline) ligands have also been disclosed [43,49,58,61]. In such cases the equatorial positions are not identical, and it can be argued that coordination of a bidentate substrate occurs in a way that best avoids steric interactions with the groups R (Fig. 9c). However, there is also evidence that coordination might occur as shown in Fig. 9d, and the proximity of the group Y with the adjacent group R might benefit for electronic reasons, e.g. π-stacking effects. Importantly, it should be noted that attack of a reagent from the same trajectory either to an equatorial or to an axial coordinated group Y leads to *opposite* selectivity, suggesting that only if one group is activated preferentially over the other a productive reaction will be possible.

2.2.2.1. Trigonal-bipyramidal complexes with bis(oxazoline) ligands.
Very few examples for trigonal-bipyramidal complexes with bis(oxazoline) ligands are known. Hanessian and co-workers have described bis(oxazoline) ligands to which thioalkyl side chains are attached [70]. Some promising results were obtained with these ligands in the addition of organolithium reagents to aldimines, however, it appears likely that these reactions proceeded through tetracoordinated lithium-bis(oxazoline) complexes [71,72]. X-ray structure analysis of the corresponding copper complexes (Fig. 10), nevertheless, revealed the ability of the side chains to coordinate with the metal center to form trigonal-bipyramidal complexes, having one thioalkyl and one oxazoline nitrogen in axial positions, with different degrees of distortion toward a square-pyramidal geometry. Unfortunately, despite their unique structures these complexes could not be utilized as catalysts in many representative model reactions.
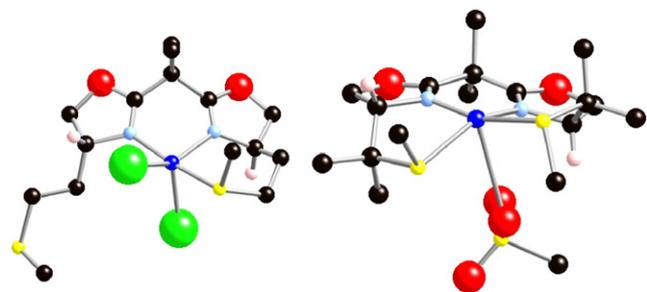
Fig. 10. X-ray structures of CuCl$_2$·(*R*)-**1**-(CH$_2$)$_2$SMe (left) and CuOTf$_2$·(*R*)-**1**-(CMe$_2$)SMe (right; fluorides and non-coordinating triflate omitted for clarity).

2.2.2.2. Square-pyramidal complexes with bis(oxazoline ligands). Square-pyramidal metal complexes play an important role as intermediates in catalysis with pyridine-bis(oxazoline ligands), and were therefore thoroughly studied. Although this ligand class is beyond the scope of this review, a short summary on the principles for inducing stereoselectivity for this system will be given, which is also meaningful for corresponding bis(oxazoline) complexes.

As already discussed above (Fig. 9b), the selective activation of either an equatorial or axial group coordinated to square-planar metal-box complex appears to be a prerequisite for achieving a selective process. Comparing X-ray structures of various copper(II)-bis(oxazolinyl)pyridine complexes, it was revealed that equatorially coordinated ligands are bound more tightly, judged by the shorter bond lengths, than the corresponding axial ligands [73]. Consequently, from the former, e.g. carbonyl oxygens, electron density should be withdrawn more effectively, resulting in their greater activation for reactions with nucleophiles. Responsible for this effect could be the electronic properties exhibited by the pyridine moiety, being transmitted especially strongly to the *trans* positioned ligand (so called *trans* influence) in the complex. Furthermore, an X-ray structure of a copper(II)pybox complex having 2-(benzyloxy)acetaldehyde coordinated [73], a substrate that is applied in aldol reactions, was obtained with equatorial position of the carbonyl group and apical position of the benzyloxy group (Fig. 11, right). Even if this preference is not observed in solution but rather a dynamic equilibrium of equatorial/apical coordinated species, only equatorial carbonyl coordination might lead to a productive substrate turnover.

Two structurally very different types of square-pyramidal complexes with bis(oxazoline) ligands have been reported (Fig. 12). The nickel complex Ni(OTf)$_2$(H$_2$O)$_2$·(*S*)-**1***t*Bu was found to contain one triflate group in addition to the box ligand and two water molecules [44], resulting in a square-pyramidal complex with one oxazoline unit as the apical ligand. No significant difference in nickel–oxygen bond length between the water molecule being bound in the metal-bis(oxazoline) plane or orthogonal to it is observed. In comparison, in the square-pyramidal complex [Cu(ClO$_4$)$_2$(CH$_3$CN)$_2$·(*S*)-**15-*iPr***]$_n$ the equatorially bound acetonitrile ligand shows a distinctively shorter copper–nitrogen bond than the axially bound one, probably benefiting again from the *trans*-influence of one of the oxazoline moieties [49].
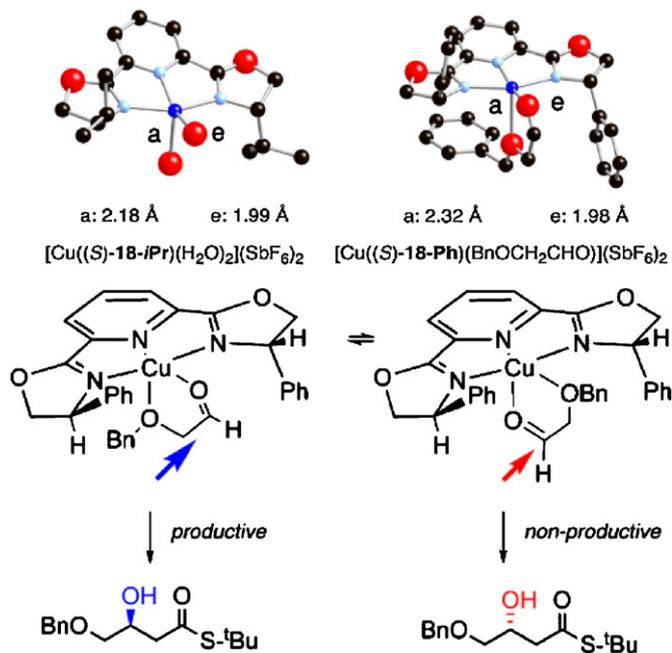

Fig. 11. X-ray structures of copper(II)-pyridine(bisoxazoline) complexes.

Square-pyramidal copper(II) complexes could also be characterized for tris(oxazoline) ligand **20** [74]. Interestingly, it was found that in [Cu(MeCOC(Me)CO$_2$Et)·(*S*)-**20**]$^+$(BF$_4$$^-$) only two oxazoline moieties participate in the coordination of the metal (Fig. 13), while it was also shown for related zinc [75] and scandium [76] complexes that all three oxazolines are interacting with the metal center. These findings are very significant since they provide a rational for the high efficiency of copper-tris(oxazoline) complexes as Lewis acid catalysts observed in some processes [49,77]. While a catalytically active species most likely involves copper(II) coordinated by two oxazolines, the third oxazoline might act as a hemilabile ligand that can stabilize the resting state of the catalyst by additional coordination. It should be noted that here as well as in the X-ray structure of the analogous square-pyramidal complex of Cu(OTf)$_2$·**1-*tBu*** and 2,4-dioxobutanoic acid ethyl ester (not shown) [78]

Fig. 12. X-ray structures of Ni(OTf)$_2$(H$_2$O)$_2$·(*S*)-**1-*tBu*** (left, non-coordinating triflate omitted for clarity) and of one unit of the coordination polymer [Cu(ClO$_4$)$_2$(CH$_3$CN)$_2$·(*S*)-**15-*iPr***]$_n$ (right, benzyl groups and perchlorates omitted for clarity).

Fig. 13. X-ray structure of [Cu(MeCOC(Me)CO$_2$Et)·(*S*)-**20**]$^+$(BF$_4$$^−$).
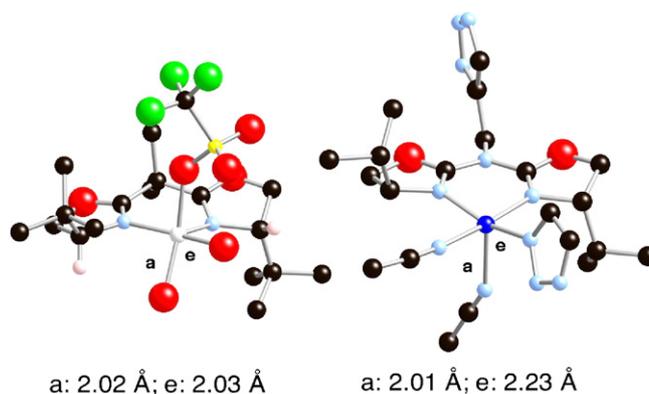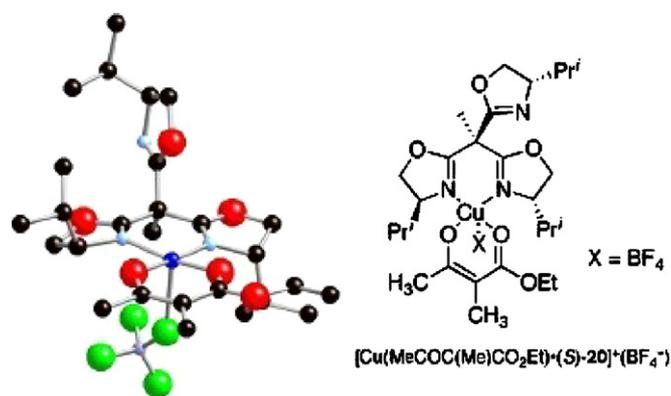
the stronger coordinating carbonyl groups obviously take the equatorial positions in the metal bis(oxazoline) plane, while the weaker coordinating triflate anion is found in the apical position.

2.2.3. Hexacoordinated complexes with bis(oxazoline) ligands

The principle geometry for hexacoordination, also found in bis(oxazoline) complexes, is octahedral. If such intermediates are involved in a catalytic process, the stereochemical models are analogous as discussed already for square-planar (cf. Section 2.2.2.1) and square-pyramidal (cf. Section 2.2.2.2) complexes.

Based on the assumption that the group being placed in the plane of the metal-bis(oxazoline) chelate will preferably be activated for a reaction, Fig. 14 depicts the preferred trajectories for an incoming substrate for the three possible octahedral complexes having a bidentate reagent coordinated.

Octahedral complexes with bis(oxazoline) ligands of copper [70], tungsten [79] and ruthenium [80] have been characterized, the two last have found applications as catalysts. Notably, in W(CO)$_4$·(*S*)-**2-*i*Pr** (Fig. 15, left) the bonds to carbonyl groups being coordinated in the plane of the metal-bis(oxazoline) chelate are again significantly elongated with respect to those that are orthogonally bound. Along these lines,
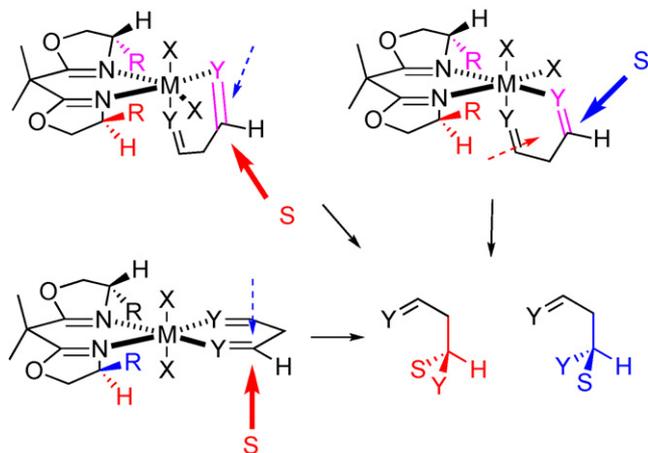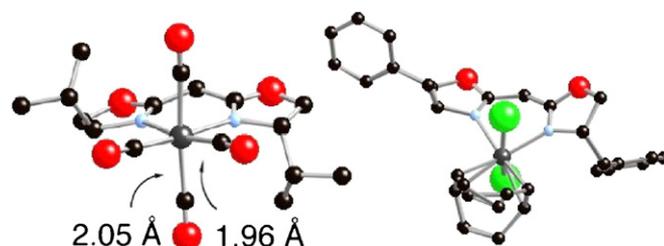

Fig. 14. Preferred trajectory (solid arrow) of a substrate S for the attack of a prochiral group Y forming an octahedral environment with a metal-bis(oxazoline) complex.

Fig. 15. X-ray structures of W(CO)$_4$·(*S*)-**2-*i*Pr** and RuCl$_2$(COD)·(*S*)-**2-Bn**.

in the RuCl$_2$(COD)·(*S*)-**2-Bn** the π-ligand COD was found to be coordinated in the metal-bis(oxazoline) plane.

2.2.4. Selected applications in catalysis: the interplay between tetra-, penta- and hexacoordinated complexes with bis(oxazoline) ligands

A great number of organic reactions can be catalyzed by metal-bis(oxazoline) complexes. The most broadly investigated are Diels–Alder and Aldol reactions, which can be used to clearly illustrate and compare the concepts discussed in Section 2.2.

For the Diels–Alder reaction between cyclopentadiene and the dienophile **21** (Table 3 and Fig. 16) a wide variety of metal-bis(oxazolines) under different reaction conditions have been tested. Based on the discussion above it is assumed that the acryloyl group is most effectively activated when coordinated in the metal-bis(oxazoline) plane rather than orthogonal to it: consequently, in the following discussion octahedral transition

Table 3
Metal-bis(oxazoline) catalyzed Diels–Alder reaction between cyclopentadiene (**20**) and 3-acryloyloxazolidin-2-one (**21**)
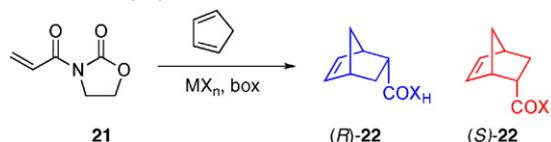
Entry	Box (*S*)[a]	Metal M	Anion X	Additive	ee (%)	cg[b]	Ref.
1	**1-Ph**	Cu(II)	OTf		30(*S*)	**B**	[61]
2	**1-Ph**	Cu(II)	ClO$_4$	6H$_2$O	41(*S*)	**B/E**	[83]
3	**1-*t*Bu**	Cu(II)	OTf		98(*S*)	**B**	[61]
4	**1-*t*Bu**	Cu(II)[c]	OTf		58(*S*)	**B/D**	[61]
5	**1-*t*Bu**	Cu(II)	ClO$_4$	6H$_2$O	6(*S*)	**B/E**	[83]
6	**1-Ph**	Mg(II)	ClO$_4$		73(*R*)	**A**	[84]
7	**1-Ph**	Mg(II)	ClO$_4$	2H$_2$O	73(*S*)	**E**	[84]
8	**1-Ph**	Mg(II)	OTf		88(*S*)	**C**	[85]
9	**1-Ph**	Mg(II)	OTf[c]	2H$_2$O	86(*S*)	**C**	[85]
10	**1-*t*Bu**	Ni(II)	OTf		40(*S*)	**A/C**	[61]
11	**1-*t*Bu**	Zn(II)	OTf		38(*S*)	**A/C**	[61]
12	**1-Ph**	Zn(II)	ClO$_4$	6H$_2$O	20(*S*)	**A/E**	[86]
13	**1-Ph**	Zn(II)	ClO$_4$[d]		73(*R*)	**A**	[86]
14	**1-Ph**	Zn(II)	SbF$_6$		92(*R*)	**A**	[61]
15	**1-Ph**	Fe(III)	I	I$_2$	82(*R*)	**E**	[87]

[a] For clarity, all results are given as if the (*S*)-configured bis(oxazoline) ligand was used, even though in the original paper the enantiomeric (*R*)-ligand might have been employed; reactions were carried out in CH$_2$Cl$_2$ unless otherwise stated.

[b] cg: coordination geometry, see Fig. 16.

[c] In CH$_3$CN.

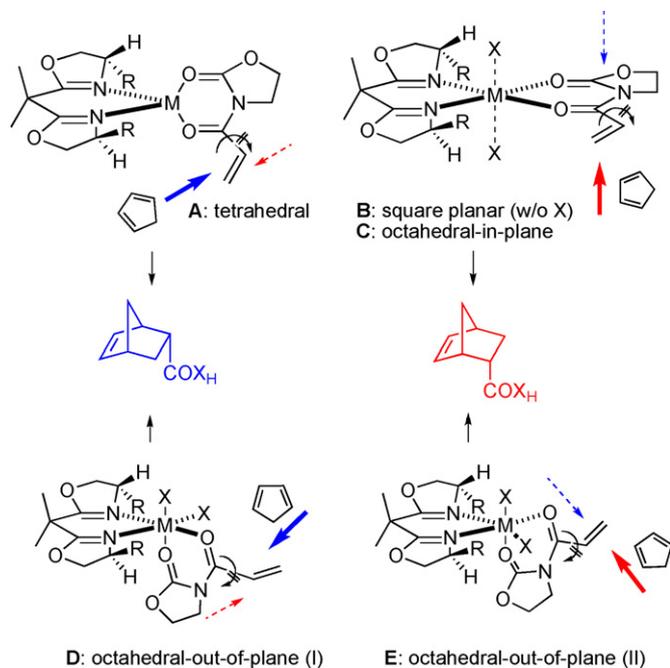[d] Addition of molecular sieves 4 Å.

Fig. 16. Possible transition states for the Diels–Alder reaction between cyclopentadiene and 3-acryloyloxazolidin-2-one (**21**) catalyzed by metal-bis(oxazoline) complexes.

states are only considered that fulfill this requirement. Moreover, the *s-cis* conformation of the vinyl group in **21** should be strongly preferred over the *trans*-conformation based on 1,3-allylic strain arguments [81]. High *endo* selectivity is observed in all cases, therefore, the minor *exo* diastereomers are not being discussed.

Employing Cu(OTf)$_2$ in the non-coordinating solvent dichloromethane, the reaction is likely to proceed via a square-planar intermediate **B** (cf. Section 2.2.1.2), hence, the sterically more bulky ligand **1-*t*Bu** gives superior results with respect to **1-Ph** (entries 1 and 3) [61,82]. Performing the reaction in acetonitrile (entry 4) or using CuClO$_4$·6H$_2$O (entry 2) [83], thus having a coordinating solvent or water molecules present, led to an erosion of stereochemistry. A possible explanation could be a competing reaction pathway via the transition state **D**, which could be preferred over **E** due to avoiding steric interactions of the downward pointing acroylo group of **21** and the R group in the box-ligand. In contrast, the selectivity upon switching from Cu(OTf)$_2$ to CuClO$_4$·6H$_2$O improves when **1-Ph** is employed as the ligand (entries 1 and 2). A (competing) reaction pathway via the octahedral transition state **E** would be in line with these results, which indeed might be favored over **D** due to a favorable π-stacking effect between the acryloyl group of **21** and the proximal phenyl group of the box ligand **1-Ph**.

A very insightful analysis of the above reaction was provided for different magnesium(II)-box catalysts [84,85,88]. Using magnesium perchlorate, the reaction should proceed via the tetrahedral transition state **A**, which is in agreement with the sense of asymmetric induction obtained (entry 6). Addition of two molecules of water per catalyst molecule caused a complete reversal of enantioselectivity (entry 7), obviously calling for a change of the coordination geometry in the catalyst. The

observed results are in agreement with the octahedral complex of type **E**, and indeed experimental evidence by NMR studies for such a species could be obtained. Moreover, the formation of an octahedral complex of type **D** could be ruled out as unlikely since use of ethylene glycol as an additive instead of water, for which a species **A** would not be possible, gave the same sense of optical induction. However, using Mg(OTf)$_2$ as catalyst precursor also gave rise to (*S*)-**22**, but based on reactivity data a complex **E** was argued to be unlikely in favor of **A**. A similar competition between tetrahedral and octahedral species also seems to operate for nickel and zinc complexes (entries 10–14) [61,86,89,90], and good results could only be obtained for the latter when potentially coordinating molecules other than the ligand or the oxazolidinone were excluded. Following this line of argument the beneficial effects of adding molecular sieves (entries 12 and 13) for the selectivity of a metal catalyzed reaction becomes evident, an effect that has been noted for other transition metal catalyzed processes as well. Last but not least, iron(III)-bis(oxazoline) complexes have been found early on to be excellent promoters for the process discussed (entry 15) [87]. An octahedral iron(III)-complex of type **E** seems to be most likely the decisive intermediate. Many more examples for Diels–Alder and Hetero-Diels–Alder reactions have been successfully developed that follow the principles applied here [2].

While for Diels–Alder reactions tetra- and hexacoordinated metal-bis(oxazoline) are discussed as intermediates, the development of enantioselective Mukaiyama aldol reactions revealed the importance of pentacoordinated complexes as well.

(Benzyloxy)acetaldehyde (**24**) was one of the first substrates being recognized as suitable for a Mukaiyama aldol reaction due to its ability to undergo a bidentate coordination with a metal complexes. While metal-bis(oxazolinyl)pyridine complexes have proved to be even more effective than metal-bis(oxazoline) complexes, the latter nevertheless showed good selectivities with silyketene acetal (**23**) and moreover provided valuable insights into the reaction mechanism (Table 4; Fig. 17).

Based on the complex geometries found in various X-ray structures (cf. Section 2.2.1) and reflected in the outcome of Diels–Alder reactions (cf. Table 3; Fig. 16) tetracoordinated

Table 4

Metal-bis(oxazoline) catalyzed Mukaiyama aldol reaction between silylketene acetal (**23**) and (benzyloxy)acetaldehyde (**24**)

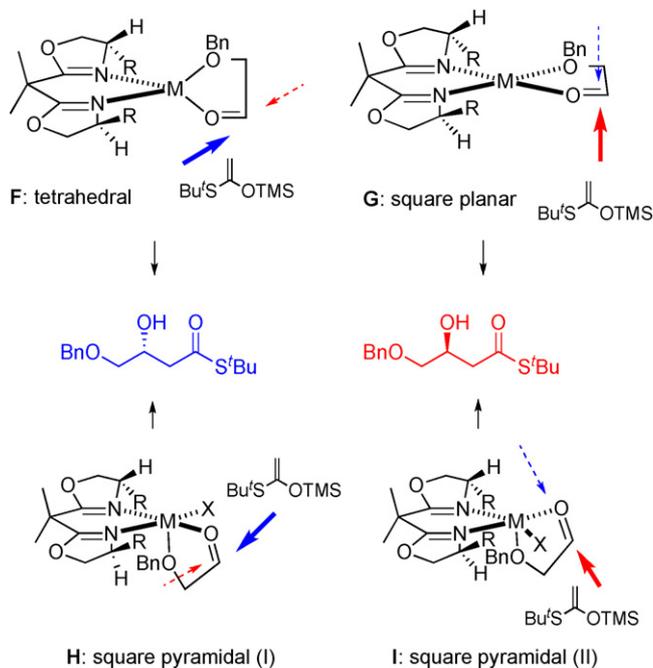| Entry	Box (*S*)	Metal M	Anion X	ee (%)	cg[a]	Ref.
1	**1-Ph**	Zn(II)	SbF$_6$	85(*S*)	**G**(?)	[91]
2	**1-*t*Bu**	Cu(II)	SbF$_6$	64(*S*)	**G**	[73]
2	**1-Ph**	Cu(II)	OTf	9(*R*)	**H/I**	[73]
3	**1-*i*Pr**	Cu(II)	OTf	9(*S*)	**H/I**	[73]
4	**1-Bn**	Cu(II)	OTf	88(*R*)	**H**	[73]
5	**1-*t*Bu**	Cu(II)	OTf	91(*R*)	**H**	[73]

[a] cg: coordination geometry, cf. Fig. 17.

Fig. 17. Possible transition states for the Mukaiyama aldol reaction between silylketene acetal **23** and (benzyloxy)acetaldehyde (**24**).

Fig. 18. Possible transition states for the Mukaiyama aldol reaction between silylketene acetals and α-carbonyl esters.

zinc(II) and copper(II) intermediates should show complementary results to each other also in the reaction between **23** and **24**. Therefore, the formation of (*S*)-**25** using $Zn(SbF_6)_2$ in combination with **1-Ph**, calling for a square-planar transition state, is surprising (Table 4, entry 1) [91]. Using $Cu(SbF_6)_2$ as precursor, (*S*)-**25** is predominantly formed (entry 2), being consistent with a square-planar intermediate. However, the relatively low selectivity observed might reflect the considerable distortion towards a tetrahedral geometry of Cu(II)-bis(oxazoline) complexes that is observed in certain cases (cf. Section 2.2.1.2). With $Cu(OTf)_2$ it was concluded that the metal anion must also be involved in the transition state of the reaction, leading to the proposal of square-pyramidal intermediates with an equatorially coordinated triflate [73]. With the further assumption that only a carbonyl group coordinated in equatorial rather than in apical position (cf. Section 2.2.1.2) will undergo the reaction, intermediates **H** and **I** (Fig. 17) must be considered. Very notably, the success of the reaction is highly dependant on the group R in the bis(oxazoline) ligand: Both the phenyl and *iso*-propyl substituted ligand gave virtually racemic product, suggesting that both **H** and **I** both are accessible. With the sterically more bulky *tert*-butyl and benzyl substituted ligands high enantioselectivity in agreement with transition state **H** is observed, which might be preferred to **I** by avoiding sterical interactions between the downward-pointing **24** and the likewise oriented R-group.

Mukaiyama aldol reactions with substrates having two coordinating carbonyl groups such as α-keto-esters that are catalyzed by copper(II)-bis(oxazoline) complexes give results consistent with (distorted) square-planar intermediates of type **J** (Fig. 18), independent of which copper salt is used as precursor [92,93]. Most likely the greater nucleophilicity of carbonyl with respect to ether groups is responsible for this observation. If an anion like
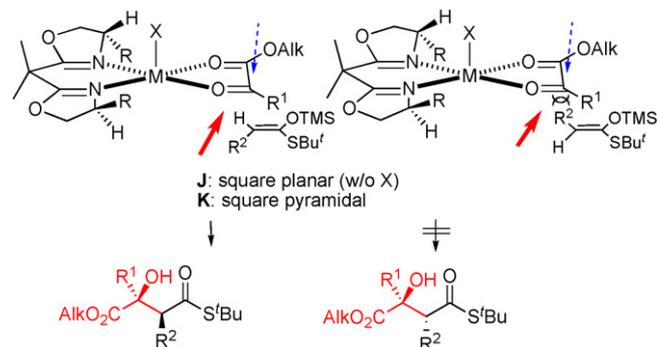
triflate is also coordinating to the copper(II) complex, it consequently might occupy the apical position giving rise to **K**, being in perfect agreement with the X-ray structure reported for the copper(II)tris(oxazoline) complex with ethyl 3-oxobutanoate depicted in Fig. 13.

In agreement with this model, $Cu(OTf)_2$·**1-*t*Bu** was found to be an excellent catalyst for aldol reactions, giving high enantioselectivities in the reaction of silylketene acetals and pyruvates (Table 5, entries 2–4). Using $Cu(SbF_6)$ instead (entry 1) gave a more reactive, but less selective complex, reflecting most likely a square-planar coordinated complex **J** (Fig. 18) in comparison to a square-pyramidal intermediate **K** with an apical coordinated triflate anion attenuating the Lewis acidity of the complex. The copper(II) complexes were found to be highly *syn*-selective, which can be explained by pointing the group R^2 in the transition state away from the metal coordinated ester group (Fig. 18, left) rather than toward it (Fig. 18, right).

Complementary to $Cu(OTf)_2$·**1-*t*Bu**, the analogous tin(II) complex $Sn(OTf)_2$·**1** was found to be *anti*-selective in such aldol reactions with both pyruvates (Table 5, entry 5) and glyoxylates (Table 6), following again the models put forward in Fig. 18 with respect to the newly formed stereocenter bearing the hydroxy group. However, the pronounced *anti*-selectivity of this catalyst remains unclear at this time.

$Cu(OTf)_2$·**1-*t*Bu** has been also found to be a most efficient catalyst in nitroaldol reactions between nitromethane and various α-ketoesters [95,96]. Based on the stereochemical outcome

Table 5

Mukaiyama aldol reaction between silylketene acetals **26** and methyl pyruvate (**27**)

Entry	Box (*S*)	Metal M	Anion X	R^2	**28**[a] (ee, %)	Ref.
1	**1-*t*Bu**	Cu(II)	SbF_6	H	75	[93]
2	**1-*t*Bu**	Cu(II)	OTf	H	99	[93]
3	**1-*t*Bu**	Cu(II)	OTf	Me (*E*)	98 (*syn*)	[93]
4	**1-*t*Bu**	Cu(II)	OTf	Me (*Z*)	96 (*syn*)	[93]
5	**1-Bn**	Sn(II)	OTf	Me (*Z*)	94 (*anti*)	[94]

[a] Diastereomeric ratio > 90:10 as indicated.

Table 6

Mukaiyama aldol reaction between silylketene acetals (**29**) and ethyl glyoxylate (**30**)

Entry	Box (S)	Metal M	Anion X	R^2	(anti)-**31**[a] (ee, %)	Ref.
1	**1-Bn**	Sn(II)	OTf	H	98	[94]
2	**1-Ph**	Sn(II)	OTf	H	91	[94]
3	**1-iPr**	Sn(II)	OTf	iBu	96	[94]
4	**1-Bn**	Sn(II)	OTf	Me	95	[94]

[a]Anti/syn ratio ≥ 90:10.

of the reaction, transition states in analogy to those depicted in Fig. 18, having the ketoester coordinated in plane with the metal-bis(oxazoline) chelate, can be ruled out. A valid proposal can be made however with the reacting carbonyl group and nitromethane being coordinated to copper(II) in equatorial positions, while the ester carbonyl oxygen adopts the apical position. Following this line of argument it can be assumed that in contrast to the triflate anion (cf. Fig. 18) the more nucleophilic nitronate anion can successfully compete with a carbonyl group for an equatorial position being decisive in the product formation (Fig. 19; Table 7).

The investigation of nitroaldol reactions using simple aldehydes with copper(II)-bis(oxazoline) complexes [97] brought, besides the significant achievement of successfully carrying out such a reaction enantioselectively with monodentate substrates, yet another mechanistic proposal into the picture: The outcome of the reaction is again consistent with a square-pyramidal copper intermediate, having the aldehyde in equatorial position
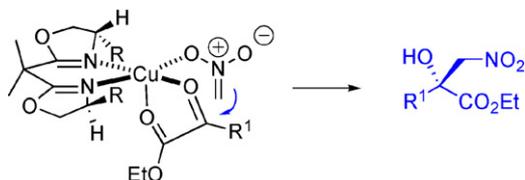

Fig. 19. Possible transition states in the nitroaldol reaction between α-ketoesters and nitromethane catalyzed by Cu(OTf)$_2$·**1-tBu**.

Table 7

Enantioselective nitroaldol reaction between α-ketoesters and nitromethane catalyzed by Cu(OTf)$_2$·**1-tBu** [95,96]

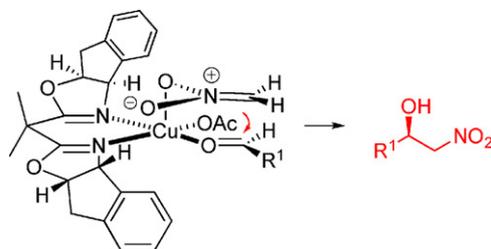| Entry	R^1	**34** (ee, %)
1	Me	92
2	Et	87
3	PhCH$_2$CH$_2$	77
4	CH$_2$=CHCH$_2$CH$_2$	94
5	CH$_3$CH=CH	60
6	Ph	86
7	p-NO$_2$Ph	93

Fig. 20. Possible transition state in the nitroaldol reaction between aldehydes and nitromethane catalyzed by Cu(OAc)$_2$·**36**.

Table 8

Nitroaldol reaction between aldehydes and nitromethane catalyzed by Cu(OAc)$_2$·**35** [97]

Entry	R^1	**37** (ee %)
1	Ph	94
2	p-NO$_2$Ph	81
3	o-MeOPh	93
4	1-Naphthyl	87
5	iPr	94
6	nBu	93
7	tBu	94

placing its group R away and the hydrogen adjacent to the neighboring acetate group (Fig. 20; Table 8). The nitronate however is coordinated in the apical position pointing away from the sterically blocking indane groups of the bis(oxazoline) ligand **36**. Ligands **1-tBu** or **1-Ph** have proven to be by far less effective, suggesting the necessity of sterically especially demanding box ligands when using monodentate substrates. Equally important, Cu(OAc)$_2$ instead of Cu(OTf)$_2$ as the copper source has to be employed, since only acetate is basic enough to deprotonate nitromethane.

In conclusion, this review has shown only a very small fraction of reactions than can be successfully catalyzed by bis(oxazoline) ligands in order to illustrate the stereochemical models involving their tri-, tetra-, penta- and hexacoordinated metal complexes. Although not understood in all details, a consistent mechanistic edifice is emerging that should allow the rational design of many more asymmetric transformations with this ligand class in the future.

References

[1] S. Dagorne, S. Bellemin-Laponnaz, A. Maisse-François, Eur. J. Inorg. Chem. (2007) 913.

[2] G. Desimoni, G. Faita, K.A. Jørgensen, Chem. Rev. (2006) 3561.

[3] H.A. McManus, P.J. Guiry, Chem. Rev. 104 (2004) 4151.

[4] A.K. Ghosh, P. Mathivanan, J. Cappiello, Tetrahedron: Asymmetry 9 (1998) 1.

[5] J.K. Whitesell, Chem. Rev. 89 (1989) 1581.

[6] J.S. Johnson, D.A. Evans, Acc. Chem. Res. 33 (2000) 325.

[7] T. Rovis, D.A. Evans, Prog. Inorg. Chem. 50 (2001) 1.

[8] S. Ma, S. Wu, New J. Chem. 25 (2001) 1337.

[9] D.A. Evans, K.A. Woerpel, M.J. Scott, Angew. Chem. Int. Ed. 31 (1992) 430.

[10] H. Brunner, U. Obermann, P. Wimmer, J. Organomet. Chem. 316 (1986) C1.

[11] H. Brunner, U. Obermann, Chem. Berl. 122 (1989) 499.

[12] G. Desimoni, G. Faita, P. Quadrelli, Chem. Rev. 103 (2003) 3119.

[13] J. Zhou, Y. Tang, Chem. Soc. Rev. 34 (2005) 664.

[14] K. Kawasaki, S. Tsumura, T. Katsuki, Synlett (1995) 1245.

[15] C. Foltz, M. Enders, S. Bellemin-Laponnaz, H. Wadepohl, L.H. Gade, Chem. Eur. J. 13 (2007) 5994.

[16] M. Seitz, A. Kaiser, D.R. Powell, A.S. Borovik, O. Reiser, Adv. Synth. Catal. 346 (2004) 737.

[17] M. Seitz, A. Kaiser, S. Stempfhuber, M. Zabel, O. Reiser, J. Am. Chem. Soc. 126 (2004) 11426.

[18] M. Seitz, A. Kaiser, S. Stempfhuber, M. Zabel, O. Reiser, Inorg. Chem. 44 (2005) 4630.

[19] M. Seitz, S. Stempfhuber, M. Zabel, M. Schutz, O. Reiser, Angew. Chem. Int. Ed. 44 (2005) 242.

[20] N. End, L. Macko, M. Zehnder, A. Pfaltz, Chem. Eur. J. 4 (1999) 818.

[21] G. Chelucci, Tetrahedron: Asymmetry 8 (1997) 2667.

[22] C. Bolm, N. Hermanns, M. Kesselgruber, J.P. Hildebrand, J. Organomet. Chem. 624 (2001) 157.

[23] M. Gómez, S. Jansat, G. Muller, D. Panyella, P.W.N.M. Van Leeuwen, P.C.J. Kamer, K. Goubitz, J. Fraanje, Organometallics 18 (1999) 4970.

[24] Y. Imai, S. Matsuo, W. Zhang, Y. Nakatsuji, I. Ikeda, Synlett (2000) 239.

[25] S.-g. Lee, C.W. Lim, C.E. Song, I.O. Kim, Tetrahedron: Asymmetry 8 (1997) 4027.

[26] I.M. Pastor, H. Adolfsson, Tetrahedron Lett. 43 (2002) 1743.

[27] M. Schinnerl, C. Böhm, M. Seitz, O. Reiser, Tetrahedron: Asymmetry 14 (2003) 765.

[28] R. Lowenthal, A. Abiko, S. Masamune, Tetrahedron Lett. 31 (1990) 6005.

[29] R.E. Lowenthal, S. Masamune, Tetrahedron Lett. 32 (1991) 7373.

[30] D.A. Evans, K.A. Woerpel, M.M. Hinman, M.M. Faul, J. Am. Chem. Soc. 113 (1991) 726.

[31] H. Fritschi, U. Leutenegger, A. Pfaltz, Helv. Chim. Acta 71 (1988) 1553.

[32] B.F. Straub, P. Hofmann, Angew. Chem. Int. Ed. 40 (2001) 1288.

[33] O. Temme, S.-A. Taj, P.G. Andersson, J. Org. Chem. (1998) 6007.

[34] C. Böhm, O. Reiser, Org. Lett. 3 (2001) 1315.

[35] B. Nosse, R.B. Chhor, W.B. Jeong, C. Boehm, O. Reiser, Org. Lett. 5 (2003) 941.

[36] E. Jezek, A. Schall, P. Kreitmeier, O. Reiser, Synlett (2005) 915.

[37] S. Kalidindi, W.B. Jeong, A. Schall, R. Bandichhor, B. Nosse, O. Reiser, Angew. Chem. Int. Ed. 46 (2007) 6361.

[38] Z. Li, R.W. Quan, E.N. Jacobsen, J. Am. Chem. Soc. 117 (1995) 5889.

[39] P. Brandt, M.J. Södergren, P.G. Andersson, P.O. Norrby, J. Am. Chem. Soc. 122 (2000) 8013.

[40] D.A. Evans, M.M. Faul, M.T. Bilodeau, B.A. Anderson, D.M. Barnes, J. Am. Chem. Soc. 115 (1993) 5328.

[41] D. Ryan, P. McMorn, D. Bethell, G. Hutchings, Org. Biomed. Chem. 2 (2004) 3566.

[42] H.-L. Kwong, D. Liu, K.-Y. Chan, C.-S. Lee, K.-H. Huang, C.-M. Che, Tetrahedron Lett. 45 (2004) 3965.

[43] J. Thorhauge, M. Roberson, R.G. Hazell, K.A. Jørgensen, Chem. Eur. J. 8 (2002) 1888.

[44] D.A. Evans, C.W. Downey, J.L. Hubbs, J. Am. Chem. Soc. 125 (2003) 8706.

[45] S.C. Bart, E.J. Hawrelak, A.K. Schmisseur, E. Lobkovsky, P.J. Chirik, Organometallics 23 (2004) 237.

[46] M. Glos, O. Reiser, Org. Lett. 2 (2000) 2045.

[47] H. Werner, R. Vicha, A. Gissibl, O. Reiser, J. Org. Chem. 68 (2003) 10166.

[48] D.A. Evans, S.J. Miller, T.v.M.P. Lectka, J. Am. Chem. Soc. 121 (1999) 7559.

[49] R. Rasappan, M. Hager, A. Gissibl, O. Reiser, Org. Lett. 8 (2006) 6099.

[50] S. Yao, M. Johannsen, K.A. Jørgensen, J. Chem. Soc., Perkin Trans. 1 (1997) 2345.

[51] M.P. Sibi, H. Matsunaga, Tetrahedron Lett. 45 (2004) 5925.

[52] M.P. Sibi, J. Ji, J.H. Wu, S. Gürtler, N.A. Porter, J. Am. Chem. Soc. 118 (1996) 9200.

[53] K. Juhl, N. Gathergood, K.A. Jørgensen, Angew. Chem. Int. Ed. 40 (2001) 2995.

[54] L. Bernardi, W. Zhuang, K.A. Jørgensen, J. Am. Chem. Soc. 127 (2005) 5772.

[55] A. Gissibl, M.G. Finn, O. Reiser, Org. Lett. 7 (2005) 2325.

[56] C. Geiger, P. Kreitmeier, O. Reiser, Adv. Synth. Catal. 347 (2005) 249.

[57] D.A. Evans, G.S. Peterson, J.S. Johnson, D.M. Barnes, K.R. Campos, K.A. Woerpel, J. Org. Chem. 63 (1998) 4541.

[58] D.A. Evans, T. Rovis, J.S. Johnson, Pure Appl. Chem. 71 (1999) 1407.

[59] D.A. Evans, J.S. Johnson, C.S. Burgey, K.R. Campos, Tetrahedron Lett. 40 (1999) 2879.

[60] D.A. Evans, J.S. Johnson, E.J. Olhava, J. Am. Chem. Soc. 122 (2000) 1635.

[61] D.A. Evans, S.J. Miller, T. Lectka, P. von Matt, J. Am. Chem. Soc. 121 (1999) 7559.

[62] D.A. Evans, T. Rovis, M.C. Kozlowski, C.W. Downey, J.S. Tedrow, J. Am. Chem. Soc. 122 (2000) 9134.

[63] D.A. Evans, T. Rovis, M.C. Kozlowski, J.S. Tedrow, J. Am. Chem. Soc. 121 (1999) 1994.

[64] A. Schätz, A. Scarel, E. Zangrando, L. Mosca, C. Carfagna, A. Gissibl, B. Milani, O. Reiser, Organometallics 25 (2006) 4065.

[65] M. Zehnder, M. Neuburger, P. von Matt, A. Pfaltz, Acta Crystallogr. C Cryst. Struct. 51 (1995) 1109.

[66] B.M. Trost, D.L. Van Vranken, Chem. Rev. 96 (1996) 395.

[67] O. Reiser, Angew. Chem. Int. Ed. Engl. 32 (1993) 547.

[68] U. Leutenegger, G. Umbricht, C. Fahrni, P. Von Matt, A. Pfaltz, Tetrahedron 48 (1992) 2143.

[69] A. Pfaltz, Acc. Chem. Res. 26 (1993) 339.

[70] S. Hanessian, E. Jnoff, N. Bernstein, M. Simard, Can. J. Chem. 82 (2004) 306.

[71] S.E. Denmark, N. Nakajima, O.J.C. Nicaise, J. Am. Chem. Soc. 116 (1994) 8797.

[72] S.E. Denmark, C.M. Stiff, J. Org. Chem. 65 (2000) 5875.

[73] D.A. Evans, M.C. Kozlowski, J.A. Murry, C.S. Burgey, K.R. Campos, B.T. Connell, R.J. Staples, J. Am. Chem. Soc. 121 (1999) 669.

[74] C. Foltz, B. Stecker, G. Marconi, S. Bellemin-Laponnaz, H. Wadepohla, L.H. Gade, Chem. Commun. (2005) 5115.

[75] C. Dro, S. Bellemin-Laponnaz, R. Welter, L.H. Gade, Angew. Chem. Int. Ed. Engl. 34 (2004) 4479.

[76] B.D. Ward, S. Bellemin-Laponnaz, L.H. Gade, Angew. Chem. Int. Ed. 44 (2005) 1668.

[77] J. Zhou, Y. Tang, J. Am. Chem. Soc. 124 (2002) 9030.

[78] H. Audrain, J. Thorhauge, R.G. Hazell, K.A. Jørgensen, J. Org. Chem. 65 (2000) 4487.

[79] G.C. Lloyd-Jones, A. Pfaltz, Z. Nat. B Chem. Sci. 50 (1995) 361.

[80] S. Bennett, S.M. Brown, G. Conole, M. Kessler, S. Rowling, E. Sinn, S. Woodward, J. Chem. Soc. Dalton Trans. (1995) 367.

[81] R.W. Hoffmann, Chem. Rev. 89 (1989) 1841.

[82] I.W. Davies, L. Gerena, D. Cai, R.D. Larsen, T.R. Verhoeven, P.J. Reider, Tetrahedron Lett. 38 (1997) 1145.

[83] A.K. Ghosh, H. Cho, J. Cappiello, Tetrahedron: Asymmetry 9 (1998) 3687.

[84] G. Desimoni, G. Faita, A. Gamba Invernizzi, P. Righetti, Tetrahedron 53 (1997) 7671.

[85] P. Carbone, G. Desimoni, G. Faita, S. Filippone, P. Righetti, Tetrahedron 54 (1998) 6099.

[86] S. Crosignani, G. Desimoni, G. Faita, S. Filippone, A. Mortoni, P. Righetti, M. Zemat, Tetrahedron Lett. 40 (1999) 7007.

[87] E.J. Corey, N. Imai, H.Y. Zhang, J. Am. Chem. Soc. 113 (1991) 728.

[88] G. Desimoni, G. Faita, P.P. Righetti, Tetrahedron Lett. 37 (1996) 3027.

[89] J.M. Takacs, E.C. Lawson, M.J. Reno, M.A. Youngman, D.A. Quincy, Tetrahedron: Asymmetry 8 (1997) 3073.

[90] S. Kanemasa, Y. Oderaotoshi, S.-i. Sakaguchi, H. Yamamoto, J. Tanaka, E. Wada, D.P. Curran, J. Am. Chem. Soc. 120 (1998) 3074.

[91] D.A. Evans, M.C. Kozlowski, J.S. Tedrow, Tetrahedron Lett. 37 (1996) 7481.

[92] D.A. Evans, M.C. Kozlowski, C.S. Burgey, D.W.C. MacMillan, J. Am. Chem. Soc. 119 (1997) 7893.

[93] D.A. Evans, C.S. Burgey, M.C. Kozlowski, S.W. Tregay, J. Am. Chem. Soc. 121 (1999) 686.

[94] D.A. Evans, D.W.C. MacMillan, K.R. Campos, J. Am. Chem. Soc. 119 (1997) 10859.

[95] C. Christensen, K. Juhl, K.A. Jørgensen, Chem. Commun. (2001) 2222.

[96] C. Christensen, K. Juhl, R.G. Hazell, K.A. Jørgensen, J. Org. Chem. 67 (2002) 4875.

[97] D.A. Evans, D. Seidel, M. Rueping, H.W. Lam, J.T. Shaw, C.W. Downey, J. Am. Chem. Soc. 125 (2003) 12692.