

Review

Mixed oxazoline-carbenes as stereodirecting
ligands for asymmetric catalysisLutz H. Gade^{a,*}, Stéphane Bellemin-Laponnaz^{b,**}^a *Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany*^b *Laboratoire de Chimie Organométallique et de Catalyse, Institut Le Bel, Université Louis Pasteur Strasbourg,
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Abstract

Whereas initially the use of chiral *N*-heterocyclic carbene (NHC) ligands in asymmetric catalysis met with very limited success, several novel structural concepts have emerged which have led to a rapid expansion of the field since the beginning of this decade. One concept in the design of new chiral NHC-containing molecular catalysts is the incorporation of oxazolines. These may play a secondary structural role in the design of monodentate chiral NHCs which are either employed as organocatalysts or as stereodirecting spectator ligands in transition metal complexes. Alternatively, oxazolines may be ligating units which are combined with NHCs to give polydentate stereodirecting ligands. Both approaches have been applied successfully and are reviewed in this article.

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1. Introduction

There are several large families of “privileged” chiral ligands which nowadays belong to the basic “tool kit” of asymmetric catalysis, such as chiral diphosphines, salen derivatives and bisoxazolines [1]. These privileged families of ligands possess characteristic properties which lead to the induction of high stereoselectivities in their catalytic reactions. The identification of the key structural elements, which induce high enantioselectivities, will thus lie at the root of a successful design of novel

stereoselecting ligands. During the past 15 years the oxazoline ring has been established as such a “privileged” structural motif in ligand design for asymmetric catalysis [2]. The key features are its rigidity and quasi-planarity as well as its facile accessibility by condensation of an amino-alcohol with a carboxylic acid derivative [3]. In spite of their sensitivity to mineral and Lewis acids, they are remarkably stable towards nucleophiles, bases and radicals. Upon coordination of the oxazoline ring through the N-atom, the stereo directing substituent will be situated in close proximity to the metal centre and will thus directly control the active space available for the substrate(s).

The electronic donor properties of *N*-heterocyclic carbene (NHC) ligands [4] have certain similarities to those of phosphines which is why they are frequently being regarded as their functional analogues. On the other hand, their stereo chemical “topography” is distinctly different from that of diarylphosphine

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units they aim to replace. Whereas phosphines, possessing three substituents at the ligating atom, are generally more or less cone-shaped, the flat heterocyclic structure of NHC ligand may be more appropriately viewed as a structural “wedge” which has to be functionalized and thus molded into a chiral ligand system.


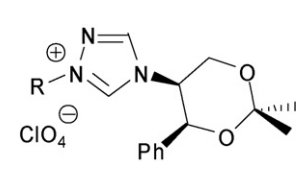
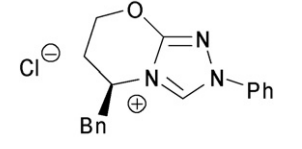
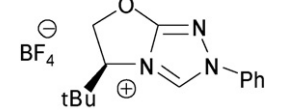
Introducing chirality into NHCs will therefore follow different strategies than those which have proved to be successful in phosphine-based asymmetric catalysis. In a recent review [5], we have already given a comprehensive overview of several large families of chiral *N*-heterocyclic carbene ligands which appear to dominate the ligand design in this field. In this article, we will focus on carbenes incorporating oxazoline units.

2. Oxazoline-NHC and related systems as organocatalysts or monodentate ligands

Organocatalysis which is based on the acceleration of a reaction by a substoichiometric amount of an organic molecule has been investigated with *N*-heterocyclic carbenes [6]. Triazolium salts in the presence of a base are efficient catalysts for the asymmetric addition of an aldehyde to another one [7]. Enders et al. have shown that the chiral triazolium salt **1**, containing one chiral *N*-substituent, is an active catalyst for asymmetric benzoin type condensation reactions. The reaction products are obtained with enantiomeric excesses of up to 86%, which at the time marked a major advance with respect to the previously established catalytic systems (Table 1) [8].

A new type of triazolinyldene with a bicyclic molecular structure has been developed more recently by Leeper's group and found to be an effective catalyst for benzoin condensa-

Table 1
The asymmetric benzoin condensation catalyzed by 1–3

	
Catalyst	ee
1 	86
2 	82
3 	99

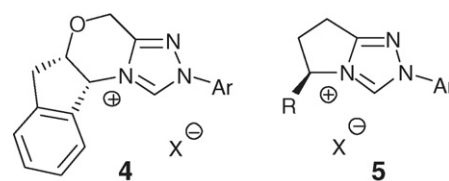


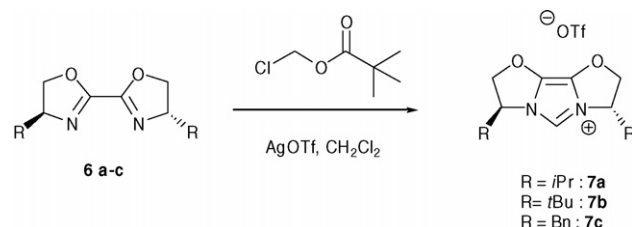
Fig. 1. Triazolium salts that have shown efficient activity and enantioselectivity in organocatalysis.

tion reactions (catalyst **2**, ee's up to 82%) [9]. In the precursor salt the internal rotation around the N–C (substituent) axis is blocked by annelation of a six-membered heterocycle (oxazine) and therefore the sterically demanding substituent has the same orientation as the ligating atom which potentially favours a high asymmetric induction. In 2002, Enders and Kallfass [10] demonstrated that the use of a more conformationally rigid bicyclic carbene leads to an even better chiral induction (catalyst **3**, ee's up to 99%). In system **3**, the five-membered heterocycle (oxazoline) is almost planar and possesses the rigidity for the construction of a well-defined chiral environment. Moreover, this compound is easily obtained in a three-step synthesis from the corresponding oxazolidinone.

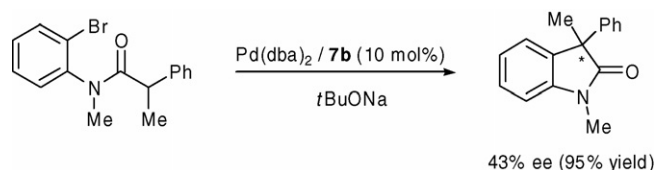
The utility of triazolium salts of type **2** or **3** as carbene precatalysts, but also of other related derivatives such as **4** and **5** (Fig. 1), has been subsequently demonstrated in a large variety of catalytic reactions including the intramolecular Stetter reaction [11], the intramolecular crossed-benzoin reaction [12], the synthesis of α -chloroesters by enantioselective protonation [13] or the desymmetrization of meso diols [14] and cyclohexadienones [15].

Chiral monodentate *N*-heterocyclic carbene ligands that contain a bisoxazoline unit have been reported. Glorius et al. [16] described the synthesis of the imidazolium salts **7** by cyclizing the corresponding bisoxazolines **6** (Scheme 1).

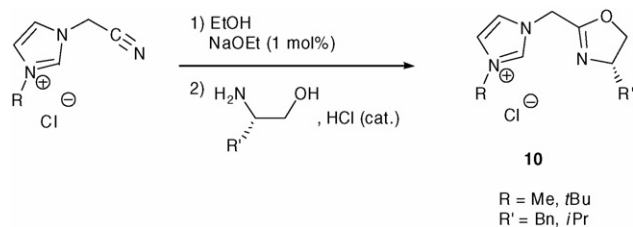
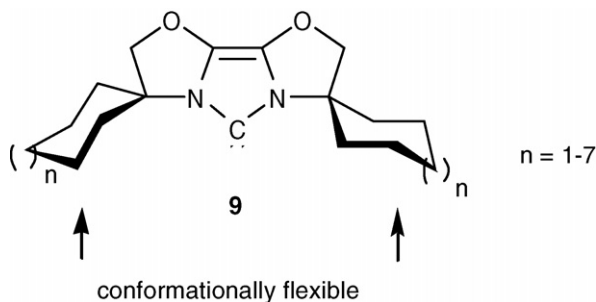
The key step is the introduction of a C_1 synthon which links the two oxazoline-N atoms. The combination of chloromethyl pivalate and silver triflate generates a highly electrophilic reagent undergoing double nucleophilic substitution at its central carbon atom and thus giving the desired imidazolium salt **7**. A major advantage of this strategy is the facile accessibility of the bisoxazolines along with the modularity of their synthesis. The imidazolium salts **7** have been employed in Pd-catalyzed asymmetric α -arylations (Scheme 2) albeit with only moderate results (ee's up to 43%).



Scheme 1. Synthesis of imidazolium salts **7a–7c** from the corresponding bisoxazolines **6a–6c**.



Scheme 2. Asymmetric catalytic oxindole synthesis.

Scheme 4. Synthesis of the imidazolium precursor **10** of Herrmann's oxazolinyl-carbene ligand.Fig. 2. Highly efficient ligand **9** for Suzuki-Miyaura cross-coupling.

In a remarkable example of asymmetric organocatalysis, Burstein and Glorius [17] have investigated the formation of γ -butyrolactone from α,β -unsaturated aldehydes with aromatic aldehydes or ketones using NHCs (Scheme 3). This reaction is a conjugate umpolung of α,β -unsaturated aldehydes. In their search for a catalytic enantioselective formation of γ -butyrolactones, they found that the imidazolium **8**, derived from a bisoxazoline, proved to be effective, whereas triazolium salts **3** or **4** did not give any product. Although enantiomeric excesses are still low, this result clearly illustrates the potential of that ligand family **7**.

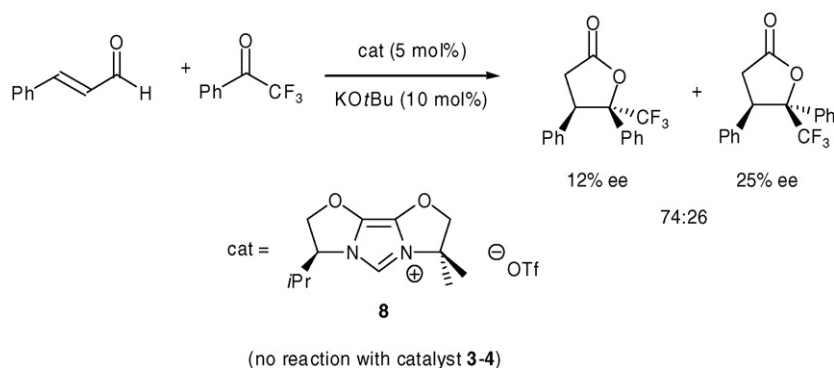
We also note that nonchiral and sterically demanding versions of these ligands have been developed (Fig. 2) and have been successfully applied in Suzuki-Miyaura cross-coupling of sterically hindered aryl chlorides and boronic acids to give tetra-*ortho*-substituted biaryl compounds [18]. This type of ligands exhibits flexible steric bulk and can be adjusted to aid oxidative addition in an open position or to enhance reductive elimination in the sterically more demanding conformation during the palladium-catalyzed cross-coupling.

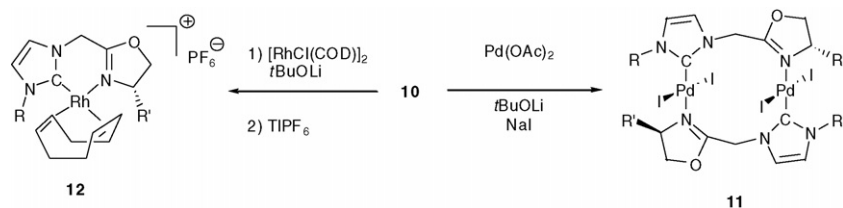
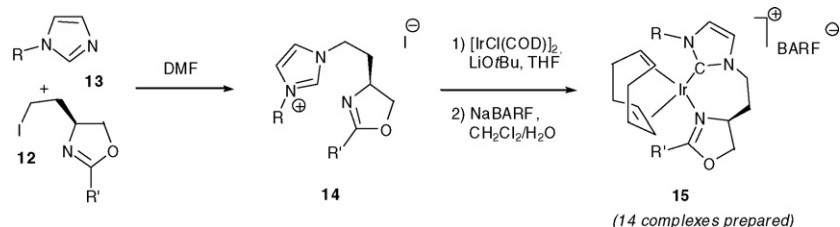
3. Bidentate *N*-heterocyclic carbenes ligands incorporating oxazoline units

In 1998, Herrmann et al. reported the synthesis of the first chiral carbene containing an oxazoline unit. In this bidentate ligand the oxazoline ring is linked in its 2-position to the imidazole ring via a methylene bridge [19]. The key step in the synthesis of the imidazolium precursor is the acid-catalyzed cyclization of the oxazoline by reaction of an iminoester, formed in situ from a nitrile function, with the amino-alcohol (Scheme 4).

Compound **10** was subsequently coordinated as a carbene-oxazoline ligand to rhodium(I) and palladium(II) (Scheme 5). The carbene of **10** acts as a bidentate chelating ligand in the rhodium(I) complex and the six-membered metallacycle thus formed adopts a boat conformation. On the other hand, the palladium complex **11** is dinuclear with two oxazoline-carbenes acting as bridging ligands. The rhodium complex **12** was employed in the hydrosilylation of ketones giving the secondary alcohols in moderate enantioselectivity (ee's up to 70%) [20].

A major step forward in the development of asymmetric catalysis with chiral *N*-heterocyclic carbene complexes has been the work of Burgess and co-workers [21] on the asymmetric hydrogenation of alkenes using iridium(I) catalysts containing NHC-oxazolines such as **14**. Their design was inspired by the chiral bidentate phosphine-oxazoline ligands (*Phox*) developed by Helmchen and Pfaltz which had proved to be highly selective in the enantioselective hydrogenation of non-functionalized trisubstituted alkenes [22]. Furthermore, Burgess and co-workers had previously studied a novel family of P,N-ligands, dubbed *JM-Phos* [23], and were thus guided by the analogy between phos-

Scheme 3. Synthesis of γ -butyrolactone catalyzed by **8**.

Scheme 5. Coordination of the imidazolium **10** to rhodium(I) and palladium(II).

Scheme 6. Synthesis of an iridium(I) complex bearing Burgess's chiral oxazoline-imidazolyldiene ligand.

phanes and NHCs in the design of the new class of oxazoline-carbenes represented by **14** (Scheme 6).

In the imidazolium salts **14**, obtained by way of a nucleophilic substitution of the iodo-derivative **12** by an imidazole **13**, the oxazoline is linked by the carbon atom in 4-position.

Coordination of the bidentate ligand to the {Ir(COD)}⁺ complex fragment is then achieved by in situ deprotonation (Scheme 6). This modular design allows facile and rapid access to a large ligand library by variation of the substituents in 2-position of the oxazoline and at the “terminal” N-atom of the heterocyclic carbene.

Complexes **15** have been tested in the asymmetric hydrogenation of *E*-1,2-diphenylpropene, and adamantyl derivative **15d** proved to be the most active and selective for this reaction. Some results of the catalyst screening are summarized in Table 2, illustrating the importance of the modular ligand design.

The authors have put forward an explanation for the high selectivity of catalyst **15d** and pointed out the key structural features leading to an efficient chiral induction with this class of

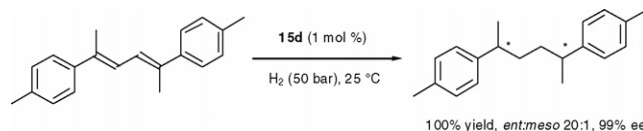
complexes. Ligand from **15d**, in particular, displays high efficiency since the bulky 2,6-(*i*Pr)₂-C₆H₃ group effectively blocks one of the quadrants of the active space in the catalyst, allowing good control of the geometry of the coordination sphere around the metal. A DFT study of the hydrogenation reaction of trisubstituted alkenes with catalyst **15** revealed that an Ir(III)/Ir(IV) pathway is probably involved. Excellent correlation was obtained between theoretical and experimental data. They also pointed out that the alkene is coordinated in *trans* disposition to the carbene, where it interacts with the oxazoline substituent [24].

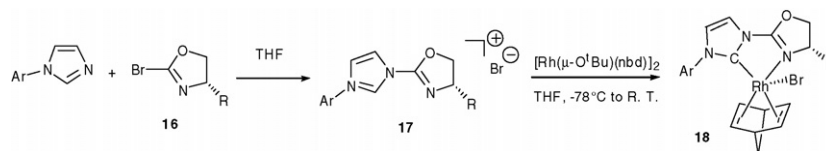
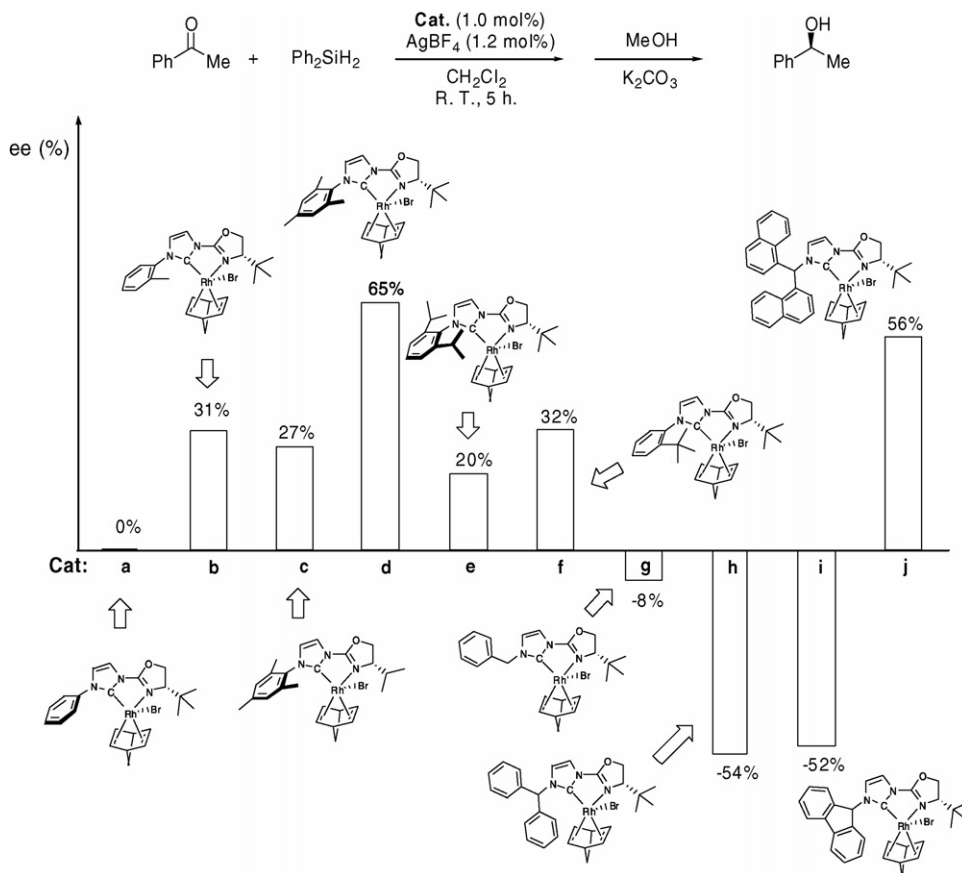
Remarkably, complex **15d** has also been successfully employed in the stereoselective hydrogenation of dienes yielding the reduced products with up to 20:1 diastereoselectivity and 99% ee (Scheme 7) [25]. These results mark a real progress in that field since 1,3-dienes are difficult to hydrogenate with high catalyst activity and enantioselectivity. It should be noted that Crabtree's (achiral) catalyst Ir(py)(PCy₃)(COD)PF₆, which is the most important homogeneous catalyst for the hydrogenation of unfunctionalized hindered alkenes, generally displays low activity for such substrates [26]. The mechanism of the iridium-catalyzed hydrogenation of dienes has been investigated in detail by an investigation of the reaction kinetics together with DFT computational studies. Here again, the results indicate that an Ir(III)/Ir(IV) mechanism is most likely involved [27].

Gade and co-workers reported the synthesis of an oxazolinyl-carbene which is obtained by direct linkage of the two heterocycles. The new ligand system was obtained by reacting the 2-bromooxazoline **16** [28] with an imidazolium precursor in

Table 2
Catalytic hydrogenation of *E*-1,2-diphenylpropene with complexes **15a–15d**
15 (0.6 mol %)

	R'	ee (%)	Yield (%)	
	15a	Ph	13	25
	15b	CHPh ₂	25	12
	15c	<i>t</i> Bu	50	81
	15d	1-Ad	98	99

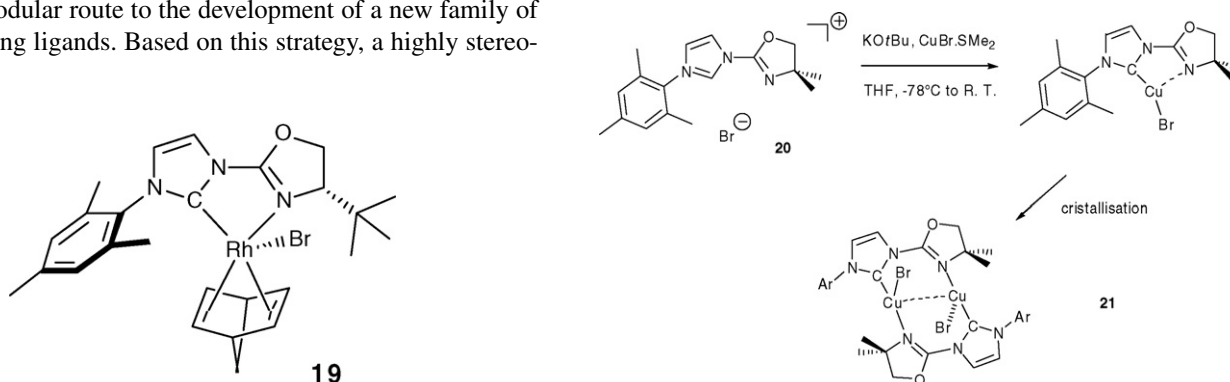
Scheme 7. Catalytic hydrogenation of a diene with complex **15d**.

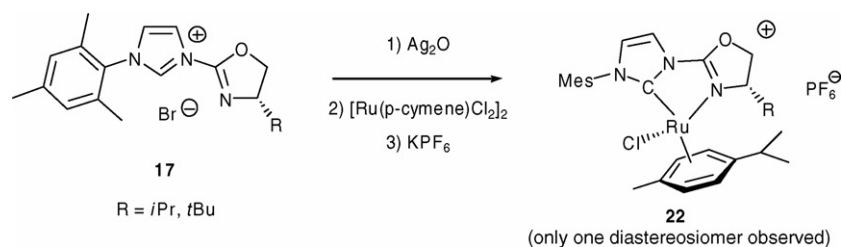
Scheme 8. Synthesis of ligand precursor **17** and complexation with rhodium(I) **18**.Fig. 3. Enantioselectivity data for the hydrosilylation of acetophenone with diphenylsilane with a catalyst loading of 1.0 mol% of complex **19** in the presence of AgBF_4 .

THF (Scheme 8) [29]. *N*-heterocyclic carbene rhodium complexes **18** could be obtained by reaction of the imidazolium salt **17** with $[\{\text{Rh}(\mu\text{-O}^t\text{Bu})(\text{nbd})\}_2]$ generated in situ [30].

This direct condensation of an oxazoline and an imidazole to give the respective imidazolium salts provides a straightforward and modular route to the development of a new family of stereodirecting ligands. Based on this strategy, a highly stereo-

selective Rh^{I} catalyst for the asymmetric hydrosilylation of ketones was developed [31]. An initial screening of catalyst structures, the results of which are displayed in Fig. 3, identified complex **19** (Fig. 4) as the most selective catalyst.

Fig. 4. Molecular structure of the hydrosilylation catalyst **19**.Scheme 9. Synthesis of the copper(I) complex **21** from imidazolium **20**.

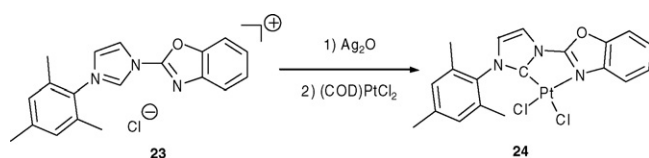
Scheme 10. Synthesis of the chiral ruthenium complexes **22**.

Whereas, for example, the asymmetric hydrosilylation of 2-naphthyl methyl ketone with complex **19** was carried out with 99% yield and 91% ee, the enantioselectivities for most aryl alkyl ketones were found to be slightly below those of the most efficient phosphane-based systems. However, catalyst **19** was found to be exceptionally selective in the hydrosilylation of unsymmetrical dialkyl ketones (Table 3) which are “difficult” substrates [32]. The selectivity for the reduction of prochiral dialkyl ketones is comparable or even superior to the best previously reported for prochiral nonaromatic ketones. Whereas cyclopropyl methyl ketone was hydrosilylated with an enantioselectivity of 81% ee, the increase of the steric demand of one of the alkyl groups led to improved ee's, reaching 95% ee in the case of *tert*-butyl methyl ketone. Linear chain *n*-alkyl methyl ketones, which are particularly challenging substrates, were reduced with good asymmetric induction, such as in the case of 2-octanone (79% ee) and even 2-butanone (65% ee).

The coordination chemistry of the imidazolium **17** has also been investigated with copper(I) [33]. For example, reaction of achiral imidazolium **20** with KO*t*Bu and CuBr.SMe₂ gave the corresponding carbene copper(I) complex **21** which is monomeric in solution but dimerize in solid state (Scheme 9). Following the same procedure, a coordination polymer in the solid state was obtained upon reaction of the chiral ligand **17** (Ar = mesityl, R = *i*Pr) with a copper(I) compound.

The reaction of imidazolium **17** (R = *i*Pr or *t*Bu) with Ag₂O and subsequent transmetalation with [Ru(para-cymene)Cl₂]₂ gave the corresponding ruthenium complex **22** after anion exchange (Scheme 10) [34]. The syntheses were found to be highly diastereoselective, since only one diastereoisomer could be observed. These compounds have been tested in transfer hydrogenation of ketones with moderate activity even after in situ abstraction of the chloride. Fairly high activity in Diels-Alder reactions were observed, however, essentially no enantioselectivity was observed.

A different type of bidentate nitrogen-donor carbene ligand, closely related to these oxazolyl-carbene ligands, has been described (Scheme 11). The relatively labile oxazoline ring has

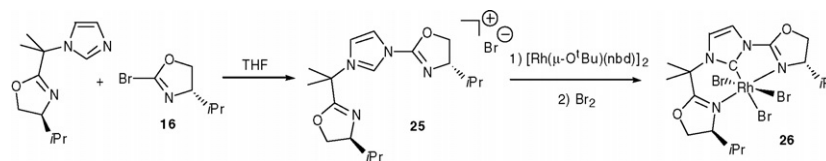
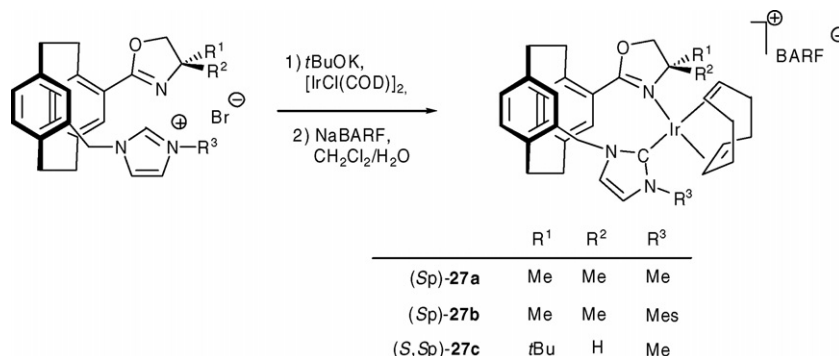
Scheme 11. Synthesis of the platinum(II) complex **24** that contains an oxazolyl carbene ligand.

been replaced by the achiral and more robust benzoxazol unit to give the imidazolium salt **23**. Coordination chemistry of the oxazolyl carbene ligand **23** with silver, palladium, rhodium and platinum has been investigated. Platinum complex **24** was found to be active in the hydrosilylation of alkenes with a reasonable

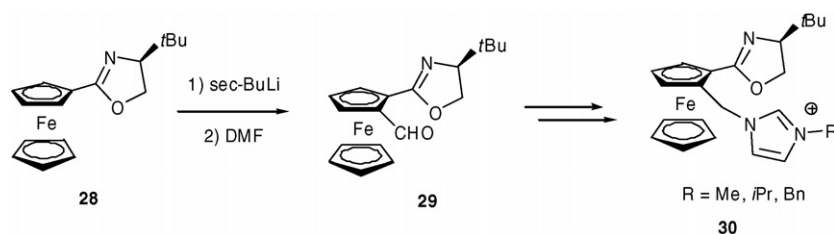
Table 3
Asymmetric hydrosilylation of ketones with catalyst **19**

$\text{R}-\text{C}(=\text{O})-\text{Me} + \text{Ph}_2\text{SiH}_2 \xrightarrow[\text{CH}_2\text{Cl}_2 (2 \text{ M}), -60^\circ\text{C}, 10 \text{ h.}]{\text{19 (1.0 mol\%)} \quad \text{AgBF}_4 (1.2 \text{ mol\%})} \xrightarrow[\text{K}_2\text{CO}_3]{\text{MeOH}} \text{R}-\text{CH}(\text{OH})-\text{Me}$			
Entry	Ketone	ee (%)	Yield (%)
1		81	63 ^a
2		88	53 ^a
3		89	98
4		95	70 ^a
5		77	97
6		79	95
7		74	88 ^b
8		65	n.d. ^b

^a Moderate yield due to the volatility of the product.^b Reaction carried out at -40°C .

Scheme 12. Synthesis of the bis(oxazoline)carbene ligand **25** and a rhodium(III) complex **26**.

Scheme 13. Oxazoline-NHC ligands, bridge by a paracyclophane unit and their iridium complexes.



Scheme 14. Oxazoline-NHC ligand bridge by a planar chiral ferrocene.

activity and a good selectivity, favouring the formation of the linear product [35].

The combination of the Herrmann's carbene ligand **10** and the Gade's NHC family **17** resulted in a new chiral *N*-heterocyclic carbene **25** (Scheme 12) [36]. The coupling strategy allows the free combination of oxazoline substituents in a highly modular way. The tridentate ligand has been coordinated to Pd(II) and Rh(III) and established that this ligand is topologically related to the bis(oxazoline)pyridine *pybox*, with an overall reduced symmetry (loss of the *C*₂-axis) [37]. For example, in the molecular structure of rhodium complex **26**, which has been determined by X-ray diffraction, the three heterocycles of the ligand are coordinated meridionally to the rhodium center, rendering the ligand skeleton almost planar.

Bidentate oxazoline-imidazolyliene ligands, in which both units are linked by a chiral paracyclophane, have been studied in Bolm's group [38]. In this case, the planar chirality of the pseudo-*ortho*-paracyclophane is combined with the central chirality of an oxazoline (Scheme 13). Compounds **27** were tested in the asymmetric hydrogenation of olefins displaying moderate selectivity (ee's of up to 46% for dimethylitaconate in the presence of **27b**).

Yet another combination of a molecular fragment possessing planar chirality (ferrocene) and an oxazoline ring has been investigated in a similar context (Scheme 14) [39]. The use of a chiral

oxazolinylferrocene **28** allows an *ortho*-functionalization with sec-butyl lithium. Trapping with DMF afforded the aldehyde **29** which was converted into imidazolium **30** in three reaction steps. Complexation with rhodium(I) was investigated and application of the resulting compounds in hydrosilylation of acetophenone was investigated. All complexes were active giving the secondary alcohol in high yield but with very low enantioselectivity (<6% ee). This is one of many examples in the literature in which the combination of several elements of chirality does not necessarily lead to improved selectivity.

Inspired by the chiral phosphine/oxazoline ligands developed by Helmchen and Pfaltz [40], Crudden and collaborators,

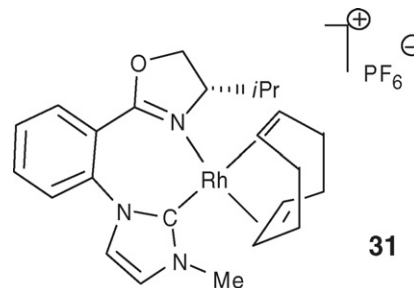


Fig. 5. Molecular structure of an oxazoline-carbene based hydrosilylation catalyst developed by Crudden et al.

have prepared a chiral NHC-oxazoline possessing a rigid backbone (Fig. 5) [41]. The rhodium complex **31** has been used in the catalytic hydroboration of olefins and the hydrosilylation of prochiral ketones with enantiomeric excesses which did not exceed 10%.

4. Conclusions

In the first section of this overview, we have seen that efficient oxazoline-based monodentate NHCs have been reported for organocatalysis. For these monodentate carbenes a well-defined chiral molecular shape – aided by rigid (cross-linked) structural units – appears to be the prerequisite for high stereoselectivity, as has been previously observed for other ligands used in asymmetric catalysis.

The kinetic robustness of the NHC ligand coordinated to a late transition metal makes it an excellent “anchor” function for a stereodirecting ancillary ligand. Such an anchor unit may then readily be combined with the established “privileged” chiral ligating units. In the second section, we have seen that oxazoline-NHC bidentate systems can lead to highly efficient catalysts in particular for the hydrogenation of olefins and the hydrosilylation of ketones. The oxazoline is an effective building block for the introduction of the chirality into the stereodirecting ligand, providing a well-defined chiral environment close to the carbene center.

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