Pyridinamides in Asymmetric Catalysis[†]

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Chiral pyridinamides are promising metal complexing ligands for use in asymmetric catalytic reactions. A large variety of complexes with different structure have been prepared and their properties investigated. Metal complexes containing early transition metals in high oxidation states have found use as chiral Lewis acids.

Asymmetric transition metal catalysis is an efficient method to obtain chiral compounds in enantiomerically pure form.[1] The chiral information is transferred to the substrate from chiral ligands bound to the transition metal, and it is therefore not surprising that a multitude of different kinds of ligand have been designed and prepared in recent years.[2] Ligands containing nitrogen as donor atom have proved to be highly useful since such ligands are often efficient in metal catalysis and stable and easy to synthesize.[3] Among nitrogen ligands, pyridine derivatives are particularly attractive for several reasons. Pyridines are stable ligands, as shown by their ability to withstand a variety of oxidative and reductive conditions,[4] and they have electronic properties rendering them suitable for catalytic applications involving transition metal ions.[5] Important pyridine-type ligands are, besides pyridine (1) itself, 2,2'-bipyridine (2), 1,10-phenanthroline (3), and di(2-pyridyl)methane (4).

Pyridine ligands substituted in the 2-position with a variety of chiral substituents containing coordinating heteroatoms capable of forming chelates with metal ions have been prepared and investigated in catalytic applications.[5] Examples of such ligands include pyridyl ethers[6] and alcohols (5),[7] pyridylamines (6),[8] and pyridyloxazolines (7),[9] as well as other derivatives[10] and compounds containing combinations of these groups.[11] Another type of ligand is the pyridinamide group (8), which has been prepared with large structural variations, but with relatively few catalytic applications.

1   2

3   4
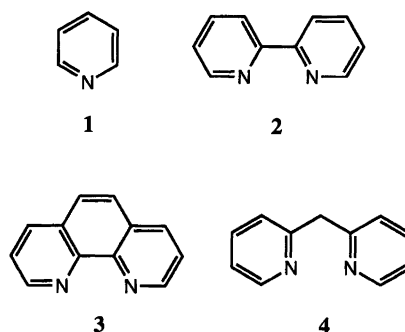
Pyridinamides: topology and structure

A variety of pyridinamides with different topology derived from pyridine, bipyridine, phenanthroline, and dipyridylmethane have been prepared. These include, in addition to simple pyridylamides (8), open (9)[12] and cyclic (10)[13] bisamides of pyridine, dimeric pyridinamides (11),[14] open (12)[9e] and cyclic (13)[15] bisamides of bipyridine, and open (14)[16] and cyclic (15)[17] bisamides of dipyridylmethane. Many of these compounds have been prepared for use in applications other than catalytic synthesis.
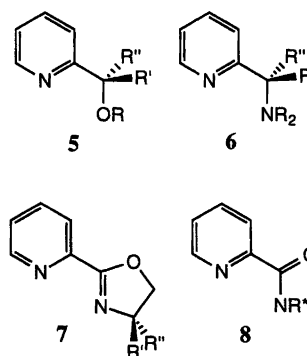
5   6

7   8

In metal complexes with pyridinamides, the properties of the complexes are dependent on the amide group as well as on which type of pyridine derivative that is incorporated into the ligand. Some structural features which are important for the coordinating properties of pyridine-containing ligands will therefore be examined first.

Electronic properties of pyridine ligands

Pyridine ligands are on the borderline between hard and soft Lewis bases.[18] They are soft donors compared with aliphatic amines, which have lower energy HOMOs. In contrast with aliphatic amines, which are pure σ-donors, pyridine ligands may be both σ-donors and π-acceptors. Although pyridine is a weaker donor than aliphatic amines, pyridines give rise to stronger ligand fields than do aliphatic amines.[19]

By comparison of the different types of pyridine ligand, some differences may be observed. All of the ligands have similar σ donating properties. The main difference in energy lies in their aptitude for π-back donation. Bipyridine[20] and phenanthroline, with fully conjugated π-systems, have lower energy LUMOs than pyridine and dipyridylmethane, as demonstrated by simple Hückel calculations (Fig. 1).[21] This implies that the two former are more prone to accept electrons from filled metal d orbitals and thus to stabilize late transition metal ions in low oxidation states. These types of ligand are therefore suited to a variety of catalytic applications involving soft metal ions, such as Cu^I and Pd^{II}. Although a similar situation might be expected in dipyridylmethane,[22] since the pyridine rings in this compound might theoretically be expected to be conjugated to a small extent by hyperconjugation, no or little conjugation occurs between the aromatic rings, and the electronic properties of dipyridylmethane therefore resemble those of pyridine.

Fig. 1. Relative energies of the highest occupied and lowest unoccupied π orbitals of benzene, pyridine, 2,2′-bipyridine, 1,10-phenanthroline and di(2-pyridyl)methane, (the HOMO–LUMO distance has been compressed).

five-membered chelate rings are favored over six-membered rings for entropy reasons, enthalpy considerations suggest that six-membered chelates are sometimes more stable. It has been found that on going from a small ion to a larger one, the five-membered chelate ring is relatively more stabilized than a six-membered chelate ring.[23] The explanation is thought to lie in differences in steric interactions within chelate rings of different sizes (Fig. 2). This is illustrated by considering the different bite angles of bipyridine and dipyridylmethane, which form five- and six-membered chelates, respectively.

From the considerations of orbital energy levels and chelate ring sizes, it may be concluded that bipyridine or phenanthroline should be chosen for applications involving large metal ions in low oxidation states, whereas dipyridylmethane should find suitable applications in reactions catalyzed by small metal ions in high oxidation states.

The chelate ring size effect

The size of the chelate ring is also an important factor in determining the stability of metal complexes. Although
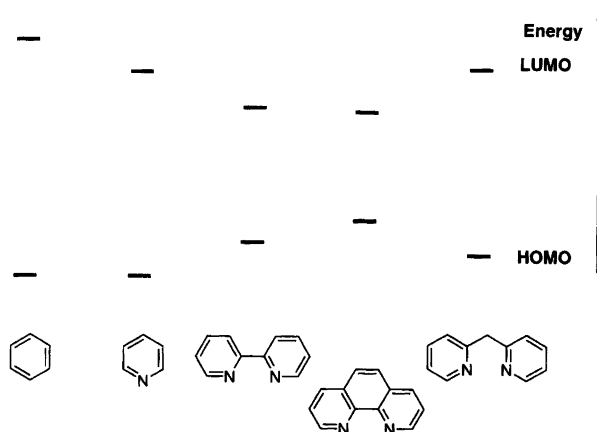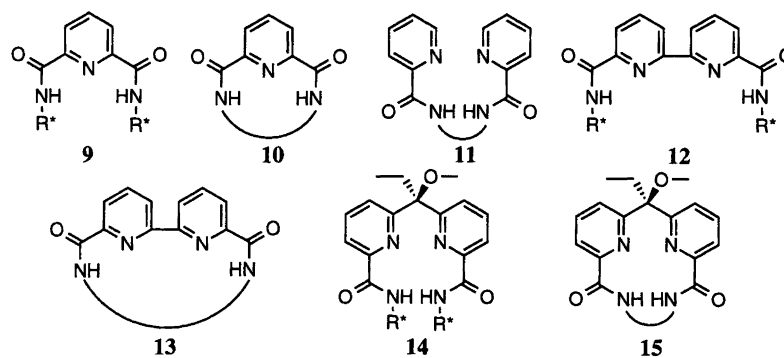
Conformation and stereoelectronic effects

In the free ligands bipyridine[24] and dipyridylmethane,[25] the aromatic rings adopt a *transoid* conformation due to
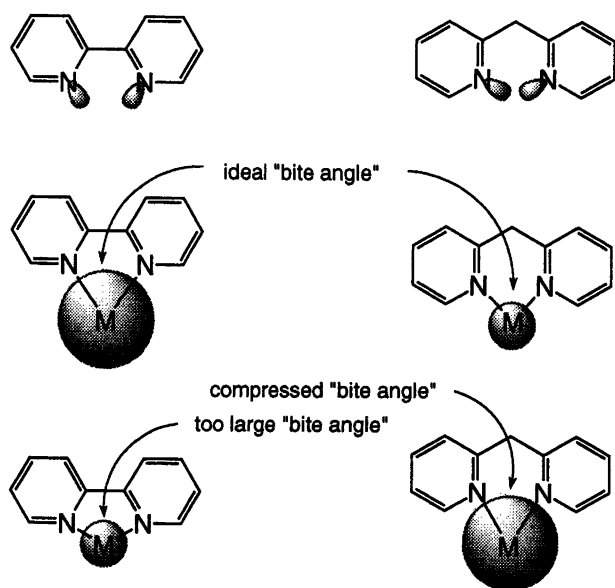
Fig. 2. Small metal ions prefer six-membered chelate rings and large metal ions prefer five-membered chelate rings.

the repulsion between the electron pairs on the nitrogen atoms. Therefore, before coordination, the rings must rearrange into a *cisoid* conformation to allow for chelate formation with the metal ion. In contrast, phenanthroline has as a free ligand a conformation suitable for coordination to a metal ion.

Another factor that is important for the conformation of pyridine derivatives is the presence of a β-heteroatom substituent.[26] In 2-oxymethylpyridines and 2-(fluorom-ethyl)pyridine, orbital interaction between a carbon–nitrogen σ-bond in the ring and the carbon–heteroatom antibonding σ-orbital, and also between the nitrogen lone pair and the same antibonding σ-orbital, stabilizes a planar conformation with the heteroatoms *anti* to one another, the barrier to rotation amounting to 20–25 kJ mol^{-1} (Fig. 3). That this is the only stable conformation has been shown theoretically as well as experimentally.[26] This stereoelectronic effect, as demonstrated for X = OR and F (Fig. 3) but also expected for X = NR$_2$, is therefore an important conformational factor in the free ligands as well as in metal complexes in which the β-heteroatom does not take part in complexation to the metal ion. Illustrative examples of this effect are provided by some di(2-pyridyl)alkoxymethyl derivatives, in which the effect has
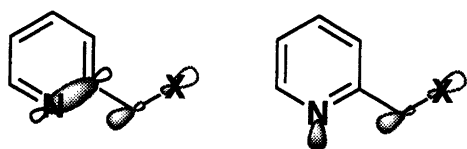

Fig. 3. Orbital interactions involving the C$_2$–N σ-bond and the C–X (X=O or F) antibonding σ-orbital (left) and the nitrogen lone pair and the C–X antibonding σ-orbital (right).

important consequences for the properties of the compounds.[17,27]

Amide coordination

Amides are both weak bases and weak acids. Despite this, coordination by neutral amides to metal ions is often observed, as is deprotonation to form anionic metal binding ligands.[28] Upon coordination, the amide group, which in the non-coordinated state is planar,[29] becomes more or less tetrahedrally distorted.[30] The deprotonation of the amide group is facilitated by chelation to some other coordinating group present in the molecule, and it is also facilitated in cases where a conjugated system results. Coordination via nitrogen (A and B) as well as via oxygen (C and D) is possible. Most commonly, neutral amides coordinate metal ions via the carbonyl oxygen (C), whereas the deprotonated amides coordinate via the amide nitrogen (B), although the other situations have been observed as well. In some cases, the amide group may adopt a *cis* or *trans* conformation, thus further extending the number of possible structures of its metal complex. Deprotonated amides give rise to strong ligand fields[31] which stabilize high oxidation states.[32] As expected, amide complexes have been most extensively studied in connection with ligands derived from naturally occurring amino acids.

Metal complexes

Complexes of tetradentate pyridine derivatives 11 with metal ions such as Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Pd^{II}, Pt^{II}, Cu^{II}, Ag^{I} and Zn^{II} have been particularly well studied.[33] Examples exist of at least coordination modes A, B and C, as evidenced by a large number of X-ray structural determinations, even though coordination by the neutral ligand via nitrogen, as in A, is energetically unfavorable.[34] When complexing Ni^{II}, Pd^{II} and Cu^{II}, the amide hydrogens become extremely labile, in particular when proton loss results in an extended conjugated system. Deprotonated complexes are often obtained even in the absence of base, and in the case of Pd^{II}, even under acidic conditions.[33] Deprotonated complexes are usually obtained when metal acetates are used as complex precursors. They are typically low-spin compounds with square planar geometry[35] [or square pyramidal with a water molecule in the apical position, as found for Cu^{II} complexes[36]] with the four nitrogen atoms coordinated to the metal ion (I or II), even if coordination via oxygen is also a possibility.[33] Complexes with the neutral ligand are obtained when metal chlorides are used in place of metal acetates. The neutral ligands may either coordinate via the four nitrogen atoms in a high-spin octahedral (III) or a tetrahedral (IV) arrangement, or, which is usually more favorable, via the pyridine nitrogen atoms and the carbonyl oxygen atoms. This results in dimeric complexes
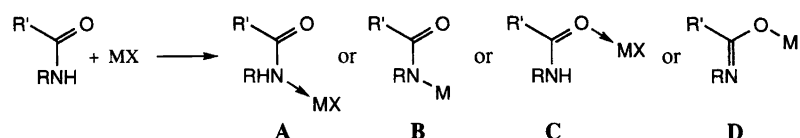
with *cis*-N₂O₂ (**V**) or, provided this is sterically possible, *trans*-N₂O₂-coordination (**VI** or **VII**),[37] or in oligomeric or polymeric (thought to be *trans*-N₂O₂) structures (**VIII**). In addition, 2:3 metal–ligand complexes of some M^{II} ions have been isolated as perchlorate salts, in which each metal atom exhibits N₃O₃ coordination (**IX**).[38] A 2:3 Co^{III} complex containing three deprotonated ligands was reported to have octahedral N₆ coordination around the metal ions and D_3 symmetry (**X**).[39] An Os^{III} complex was shown to have a structure resembling **II** with L = PPh₃, although with a chloride ion present to complete an octahedral configuration.[40]

A few other complexes, most of which contain high-

valent, early transition metal ions, have been studied in connection with catalytic applications, see below. Since these complexes have been analyzed only spectroscopically, details of their structures are therefore unknown. It may be assumed that these structures resemble **I–X**, but several other possibilities exist.

In macrocyclic amides **15**, prepared from either 1,2-diamines or 1,3-diamines, coordination via the carbonyl oxygen is prevented for steric reasons. Coordination in these systems usually occurs via deprotonation to yield complexes with structures similar to those of the open ligands,[17,41] but occasionally non-deprotonated complexes seem to form.[42]
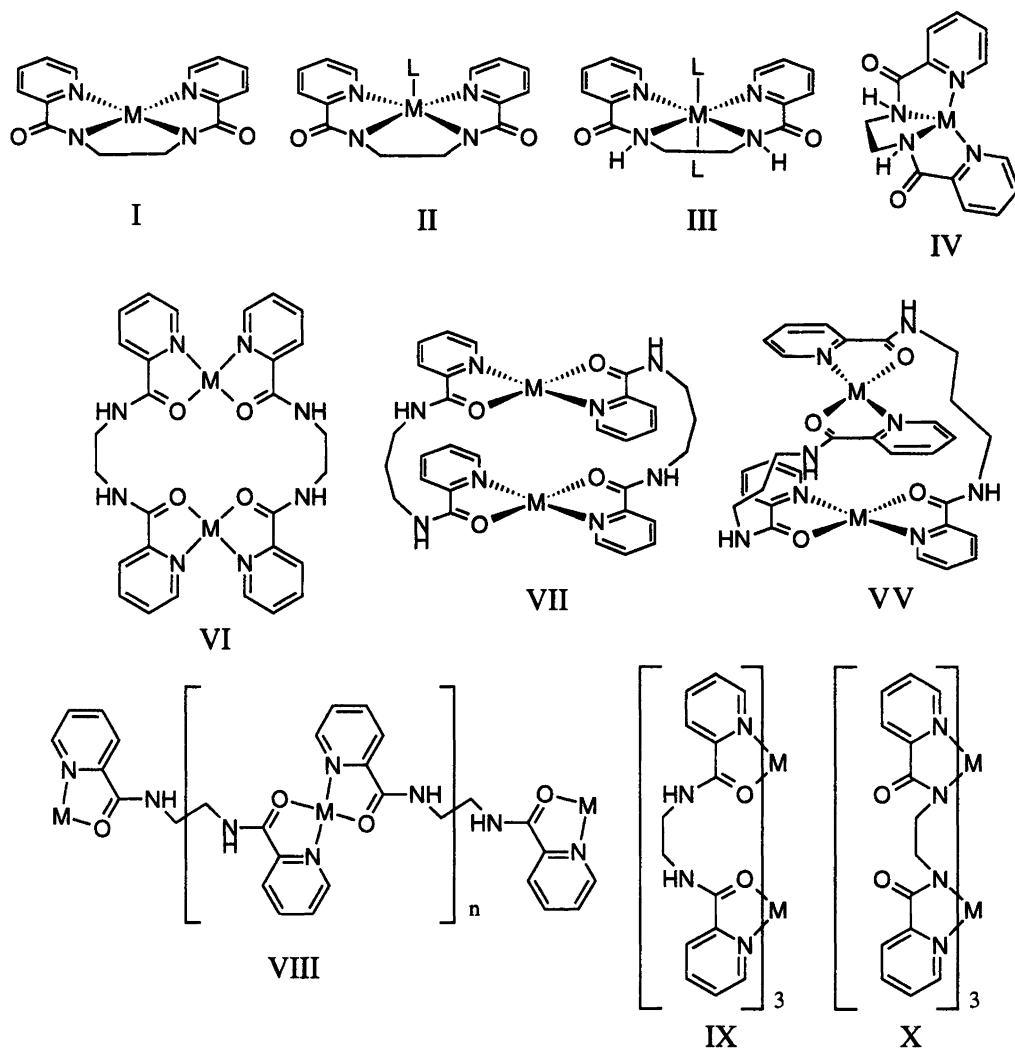
Chiral pyridinamides

Pyridinamides are obtained by condensation of a suitable pyridinecarboxylic acid derivative and the appropriate amine or diamine. Since several enantiopure amines and diamines are commercially available or easily prepared, various chiral pyridinamides are easily accessible. C_2-symmetric chiral ligands 11 have thus been obtained using C_2-symmetric diamines. The first enantiomerically pure dipyridylamide complexes to be more thoroughly investigated were obtained from (S,S)-1,2-diphenyl-1,2-diaminoethane.[43] What is particularly interesting about the structure of the copper complex obtained from the deprotonated ligand is that both phenyl groups assume axial positions, which is an uncommon situation, and that the water molecule normally occupying the apical position is replaced by a carbonyl oxygen atom from a neighbouring molecule. This suggests that this and similar complexes might be promising candidates for catalytic asymmetric applications. Slight variations in the structure may cause conformational change, as demonstrated by the copper(II) complex of the monophenyl analogue, in which a water molecule occupies the apical position, and the substituent, a quasi-equatorial position. A crystal structure determination of the Ni^{II} and Pd^{II} complexes of this ligand, however, showed the phenyl groups to be in the axial positions.[43]

Analogous ligands derived from enantiopure (R)- and (S)-2,2′-diamino-1,1′-binaphthyl[44] and (R,R)-1,2-diaminocyclohexane[16] have also been described. The crystal structures of an Os^{VI} oxo complex of the former ligand[44] and Cu^{II}[36b] and Ni^{II}[35] complexes of the latter in racemic form have been determined. No exceptional features were observed. In addition, some more sterically hindered derivatives containing quinoline or 2-methylpyridine rings in place of pyridine have been tested in catalytic applications.[16]

Among the chiral macrocyclic bipyridinamides reported, one of the few of interest in connection with catalysis is a macrocycle incorporating two amino acid residues.[15b] Chiral macrocyclic ligands containing dipyridylmethane residues with 2-alkoxymethyl substituents were shown to have a bowl-shaped conformation, originating from the stereoelectronic effect discussed above,[17] possibly indicating a potential application of the pure ligands as chiral host molecules rather than their use in metal catalysis, since coordination to metal ions tends to flatten the structure.[41]

Catalytic applications

Catalytic applications in which successful results may be expected when pyridinamides, at least those based on pyridine and dipyridylmethane, are used as ligands for the catalytically active metal centers, are primarily those utilizing early transition metal ions in high oxidation states. It is therefore not surprising that the reactions catalyzed by metal complexes of pyridinamides that have been studied so far are of two major types, namely oxidative processes and Lewis acid catalyzed processes. Ligands incorporating bipyridine and phenantroline are of potentially wider use, owing to their ability also to stabilize soft metal ions.

Epoxidation of olefins. A variety of metal complexes of ligand 11 derived from o-phenylenediamine (or isomers) catalyze the epoxidation of alkenes using iodosylbenzene as the oxidant, to afford epoxides [eqn (1)]. An Os^{III}

$$R\diagup\hspace{-0.3em}=\hspace{-0.3em}\diagdown R' \xrightarrow[\text{Catalyst}]{\text{[O]}} \quad \triangle \quad + \quad \triangle \qquad (1)$$
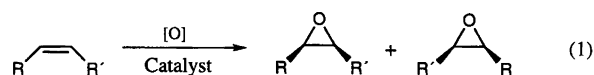
triphenylphosphine complex was shown to oxidize cyclohexene, although in mere 3.6% yield,[40] and, in somewhat higher yield, norbornene.[45] Styrene and stilbenes underwent extensive cleavage under the conditions employed. A comparison with the analogous osmium–salen complex revealed that the two ligands in this case had similar properties, affording essentially identical product mixtures.[45] Higher yields and in many cases acceptable chemoselectivity were observed using Mn^{III}[46,47] and Cr^{III} complexes.[47] Binuclear Ru^{III} complexes were used for the oxidation of a variety of alkenes, but yields were low.[48] Ni^{II} and Fe^{III} complexes of the macrocyclic ligand 15, prepared from racemic $trans$-1,2-diaminocyclohexane, catalyzed the oxidation of alkenes to epoxides by iodosylbenzene or hypochlorite.[49] In a preliminary study using the Ni^{II} complex of the enantiopure ligand, no asymmetric induction was observed, which might be due to a radical pathway for this reaction.[49]

The data presently available do not allow a comparison of the efficiency of the different types of ligand 11 and 15. It is surprising, however, to note that no attempts to achieve asymmetric oxidation using chiral enantiomerically pure complexes have been reported. It is not clear whether this is due to unpublished unsuccessful attempts, or to the unwillingness to undertake such investigations considering the excellent performance demonstrated by salen-type ligands.[50]

An Fe^{III} complex of an enantiopure bipyridinamide ligand of type 13 with bridging amino acid residues, was reported to catalyze the epoxidation of some olefins. No asymmetric induction was observed, though.[15b] In contrast, moderate enantioselectivity was achieved using Fe^{III} complexes of amides derived from 6-substituted picolinic acids and histidine derivatives.[51] Oxidation of (Z)-β-methylstyrene using hydrogen peroxide thus afforded the cis-epoxide with 57% ee, whereas oxidation using iodosylbenzene resulted primarily in cleavage of the substrate to yield benzaldehyde. These complexes were also capable of activating molecular oxygen.[51]

Epoxidation of olefins was also achieved using an Mn^{II} complex of a ligand of type 9 containing coordinating substituents [R = 2-(4-imidazolyl)ethyl], and with iodo-

sylbenzene as the oxidant.[12] With Fe^{II} and Co^{II} complexes of the same ligand, the desired epoxides were obtained, usually along with some byproducts.[52] The efficiency of the system was increased by the addition of 4-ethoxycarbonyl-3-methyl-2-cyclohexenone, the role of which remains unclear.[53]

Oxidation of phenols. The same kinds of ligand also catalyze the oxygenation of phenols to yield quinones, another type of oxidative process.[54] In this case, a Co^{II} complex of a ligand with the 2-imidazolyl groups replaced by 2-pyridyl groups exhibited highest reactivity in a process using oxygen as the oxidant. The activation of molecular oxygen was also achieved using the Co^{II} complex of the phenylenediamine ligand 11, as demonstrated by the oxygenation of phenols.[55]

Lewis acid catalyzed ring opening of epoxides. Another catalytic application of this type of ligand is the ring opening of *meso* epoxides [eqn (2)]; this reaction being cata-

$$(2)$$
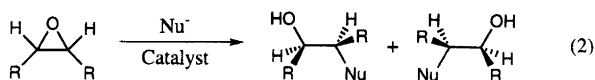
lyzed by Lewis acids.[56] Best results (71% ee) were observed using Zr^{IV} tetra-*tert*-butoxide together with the amide 11 derived from the (*S,S*)-1,2-diphenyl-1,2-diaminoethane (16) and trace amounts of diethylamine as the catalyst, and with trimethylsilyl azide as the nucleophile, yielding synthetically important amino alcohol derivatives.[16]

16   17
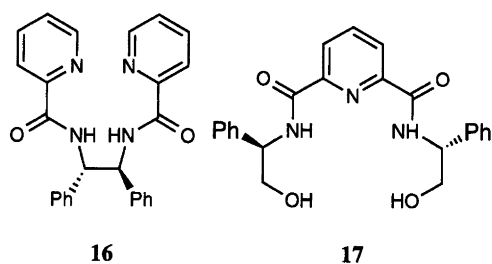
The secondary amine promotes the formation of a Zr^{IV} complex with a structure similar to I, but with two additional *tert*-butoxide ligands. This complex was found to be catalytically inactive, however. The catalytically active mixture consisted of what was believed to be two dimeric complexes present in equal amounts, the catalytic activity increasing with the amount of these complexes. The interpretation that the complexes were dimers, probably with bridging azides, was supported by the appearance of a new set of signals originating from the heterochiral, (*R,R*)(*S,S*), diastereomers in the ^1H NMR spectrum of the mixture when the racemic ligand was use in place of the enantiopure ligand.

Inferior results were obtained using macrocyclic

ligands 15 derived from the same diamine, compounds such as 11 prepared from other optically active C_2-symmetric diamines, and ligands whereby the pyridine rings were replaced by quinoline or 2-methylpyridine rings.[16] Such sterically hindered ligands have previously been shown to have different complexing properties, since, in order to coordinate in a tetradentate fashion, the ligands have to be distorted.[57] In some cases, complexation does not even occur.[57] Quite low selectivity (18% ee) was observed when a Ti^{IV} complex of a pyridine bisamide containing coordinating hydroxy groups (17) was used as the catalyst for the reaction.

It is uncertain, though, whether the optimal conditions for the reaction really are those using the Zr^{IV} complex of ligand 16. A variety of other metal ions are probably also able to catalyze the same reaction. In addition, it would be interesting to investigate other substrates and other nucleophiles and to modify further the structure of the ligand.

Other Lewis acid catalyzed processes. The addition of trimethylsilyl cyanide to benzaldehyde[58] affording, after hydrolysis, cyanohydrins, is another process which may be catalyzed by transition metal Lewis acids. It is of synthetic interest, since the products are useful as starting materials for a variety of products.[59] Moderate enantioselectivity was observed in a preliminary study when the Zr^{IV} complex of 16 was used as the catalyst in the reaction.[60] Further possible applications of this type of ligand, consist of other Lewis acid catalyzed processes, such as Diels–Alder cyclizations[61] and the addition of carbon nucleophiles to carbonyl compounds.[62]

Conclusions

The ligands presented here are promising for use in enantioselective synthesis. The procedure for their preparation, consisting of the reaction of a pyridine derivative with an optically active enantiopure amine, allows for large structural variations. This enables convenient tuning of their reactivity, thus resembling the large structural variations that have been accomplished with salen-type ligands. Sterically hindered ligands are thus easily obtained using either a substituted primary amine or a substituted pyridine derivative, which are also ligands containing additional stereogenic centers or additional coordinating groups. For rational design of such modified ligands, more structural information concerning the conformation and the coordination around the metal ion is required. As yet, complexes with very few metal ions have been investigated in only a small number of catalytic applications.

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