

Stereoselective synthesis of coordination compounds

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Abstract

After an introduction, where the general aspects of stereoselective synthesis of coordination species are shortly reviewed, an account of the use of pyridine and bipyridine ligands that are made chiral through incorporation of structural elements taken from terpenes, which

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occur naturally as enantiopure or at least non-racemic compounds, is given. It is shown that this ligand family, which presently comprises about 90 different characterized species, can be used for many different purposes: (i) tetradentate ligands of the so called CHIRAGEN type create a chirality element of well defined configuration in an octahedral complex, where two coordination sites are left for further binding to other didentate ligands. In this way the synthesis of polynuclear coordination species of predetermined stereochemistry becomes feasible. (ii) Didentate chiral thienyl–pyridine ligands yield dinuclear complexes with octahedral coordination sites, where one homochiral configuration is strongly preferred. Through cleavage of the bridge in these dinuclear species, mononuclear complexes with predetermined configuration are accessible. (iii) Tripodal ligands containing chiral structural elements from terpene molecules yield octahedral complexes with predetermined configuration. (iv) Terpyridine-type ligands can be synthesized that form either chiral C_2 -symmetric complexes if the two ligands are identical, or achiral S_4 -symmetric complexes, when two ligands have opposite chirality. (v) The configuration of chiral ‘square–planar’ complexes can be predetermined, using terpene-chiralized pyridine ligands in cyclometallated species. (vi) Terpene–bipyridine ligands can render a large number of d^8 metal complexes chiral. (vii) The use of certain CHIRAGEN-type ligands results in complexes with tetrahedral coordination sites, where the configuration is predetermined. (viii) It is shown that a number of terpene–pyridines and –bipyridines yield a non-racemic alcohol, when used as catalysts in ethylation reactions of a prochiral aldehyde. Enantiomeric excess values of up to 86% are reached. (ix) CHIRAGEN-type ligands can yield with labile coordination centers, either linear or circular helicates with predetermined configuration. In such self assembly reactions, complete chiral recognition was observed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Stereoselective synthesis; CHIRAGEN-type ligands; Chirality

1. Introduction

Stereoselective synthesis, by definition the synthesis of a molecular species that can exist in two or more stereoisomeric forms in a ratio of these isomers, which is different from the statistical one, has been for quite a long time, a neglected subject in coordination chemistry. A particular type of stereoselectivity is the formation of a coordination center representing an element of chirality with preference for one of the two possible configurations. The importance of this type of stereoselectivity seems to have been already clearly recognized by Alfred Werner and his coworker Smirnoff. The latter author describes in a paper published shortly after Werner's death [1], the observation that Pt(IV) complexes are formed in a preferential configuration, when non-racemic chiral ligands are used. Smirnoff says: “...that optically active diamine molecules of one configuration, reach a specific orientation around the platinum atom and form only one of two possible mirror isomeric forms”. The possibility of stereoselective synthesis of coordination species with respect to chirality, has thus been clearly described already 80 years ago. Yet, with some exceptions, the field has not been developed systematically, until recently.

The main emphasis of our research described in this lecture is the development of synthetic methods that allow for the preparation of chiral coordination species

where the chirality element centered at the metal atom is formed in a preferential configuration. This goal is reached through diastereoselectivity, where the source of chirality are molecules from the terpene family that are formed somewhere in a pine tree or another plant in an enantiomerically pure or at least strongly non-racemic form. This corresponds exactly to the systems investigated by Werner and Smirnof. The chirality element formed at the metal center is in most cases a two- or three-bladed helix, for which the chirality descriptors Δ and Λ , respectively are used in accordance to IUPAC recommendations.

The use of terpenes as a source of preferential chirality, represents a favorable basis for potential practical applications, since these natural products are highly abundant and consequently, economically affordable, and the synthetic methods leading to the chiral ligands are relatively simple and efficient.

1.1. Definitions, scope, and early examples

Chirality is defined, as usual in chemistry, in the original sense given by Lord Kelvin. According to Lord Kelvin, an object is chiral, when its mirror image is not superimposable to the object itself. Stereoisomers that are related by not superimposable mirror images are called enantiomers, whereas all other stereoisomers are diastereomers. According to IUPAC recommendations, we designate a reaction as stereoselective, if stereoisomers of the target species are formed in a non-statistical ratio. A reaction is called stereospecific, if there exists a well defined relationship between the stereoisomeric configuration of the educt and of the product.

The family of terpene-pyridines comprises at present, about 90 different characterized species. With many of these ligands, metal complexes can be prepared that show preferential chirality at the metal center through diastereoselectivity. The coordination centers studied comprise a series of octahedral metals (designated in accordance with IUPAC as OC-6), like Ru^{II} , Os^{II} , Rh^{III} , Fe^{II} , Cd^{II} , as well as tetrahedral sites (T-4), like Cu^{I} and Ag^{I} , and finally also the square planar arrangements (SP-4) in Pt^{II} and Pd^{II} . In the latter case, the chirality of the inherently achiral SP-4 geometry is caused by a helical distortion.

Stereoselective synthesis, or more precisely diastereoselective synthesis of coordination species, has been almost exclusively restricted to octahedral coordination centers (designated in accordance with IUPAC as OC-6). The first reports were those of Smirnof of 1919, where he used non-racemic propylenediamine (1,2-diamino propane). During the decades since the death of Werner, several reports on diastereoselective synthesis of coordination compounds have appeared in the literature. Yet, no systematic development comparable to organic chemistry has taken place so far. It seems, however, that we are in the beginning of an evolution in this field, which might lead to methods that allow for the complete control of the stereochemical properties of coordination species. The much more varied stereochemical possibilities of the metallic coordination centers as compared to the carbon atom represents a challenge of remarkable complexity. For an overview see a review, summarizing the state of the art in this field [2].

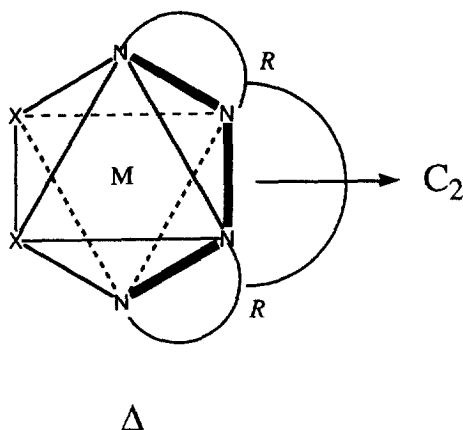


Fig. 1. Schematic representation of a bis-didentate ligand, where the two coordinating units are connected by a bridge that is anchored on chiral centers (*R,R*) therewith predetermining the chirality at the metal center (Δ). The overall symmetry of this coordination unit is C_2 .

2. The terpene–pyridine ligand family and the CHIRAGEN ligands

Our original aim in the field of stereoselective synthesis of a metal complex, was the design and realization of a bis-didentate ligand, where two bipyridine units are connected through a chiral bridge, in a way that one, and only one, configuration of an octahedral complex is formed, where two ligand sites are still accessible for coordination. This is schematically depicted in Fig. 1.

The key to ligands that fulfill the requirements of predetermining the stereochemistry of a complex according to the way shown in Fig. 1, was the development of a synthesis of the so called pinene–bipyridines (Fig. 2).

Both molecules shown in Fig. 2 can be synthesized in a few steps from commercially available compounds in a high yield synthesis [3]. An important property of these molecules is the relatively high acidity of one of the diastereotopic protons of the CH_2 group adjacent to the pyridine ring, which allows for the stereoselective synthesis of a bis-bipyridine ligand according to the schematic representation of Fig. 3.

The bridged, C_2 symmetric ligand is predisposed for coordination to an octahedral center, where the preferential chirality at the metal is determined by the chirality of the pinene groups. Accordingly, these ligands are called CHIRAGENS

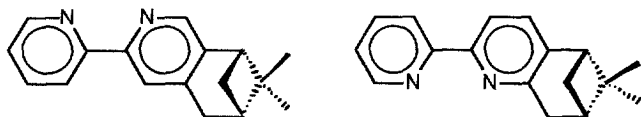


Fig. 2. The key molecules for stereoselective synthesis. 4,5-pinene–bipyridine (left) and 5,6-pinene–bipyridine (right).

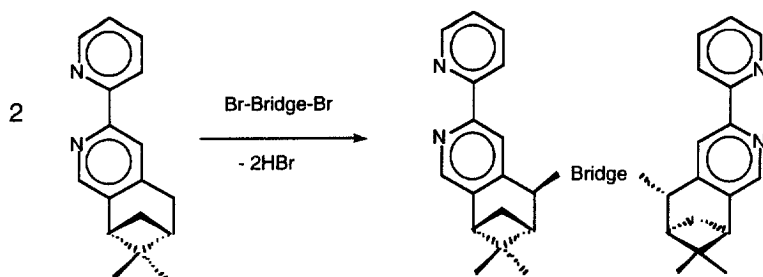


Fig. 3. Stereoselective synthesis of a bis-didentate ligand, CHIRAGEN[bridge] from 4,5-pinene-bipyridine.

(see next section). Since pinene is available from natural products in either of the two enantiomeric forms, the CHIRAGENS are also accessible in both enantiomeric forms.

The synthetic principle leading to the pinene-pyridines is very versatile, and therefore an almost unlimited number of such ligands can be produced in either of the two enantiomeric forms. In the authors lab, ca. 90 different ligands of the terpene-pyridine type and of the CHIRAGEN family have been synthesized and characterized [4]. All of these ligands contain at least one pyridine ring. The big advantage of these building blocks compared with 'classical' ones (like enantiomerically pure complexes obtained through resolution of a racemate [5]) is their 'chiral stability'; no racemization occurs, even under harsh conditions.

3. Octahedral complexes with predetermined chirality

3.1. Complexes with CHIRAGEN ligands

The CHIRAGEN ligands behave, indeed, the way they have been designed for. The first complex prepared was the species $\text{Ru}(4,5\text{-CHIRAGEN}[6])(\text{DMbpy})^{2+}$ where DMbpy is 4,4'-dimethylbipyridine [4]. It is a complex where four coordination sites are occupied by the CHIRAGEN molecule in C_2 -symmetric configuration and the remaining two sites in *cis*-position by the additional didentate ligand. A more versatile species was subsequently produced by the use of 4,5-CHIRAGEN[*m*-xyl]. The complex $\text{Ru}(4,5\text{-CHIRAGEN}[m\text{-xyl}])\text{Cl}_2$ [6] can be used as a building block for polynuclear systems, where the stereochemistry is completely defined at each coordination center [7]. As an example, a trinuclear complex $[\{\text{Ru}(4,5\text{-CHIRAGEN}[m\text{-xyl}])\}_3(4,5\text{-CHIRAGEN}[5,5'\text{-M-2,2'bpy}])]^{6+}$ was synthesized. The ligands used in these complexes are shown in Fig. 4.

The ligands described so far, need the use of high dilution techniques for the synthesis of the chirally predetermined building blocks, in order to prevent the formation of polymeric materials. Studies are under way, in order to improve the geometry of the cleft provided by the CHIRAGEN ligand. In addition, 'linear'

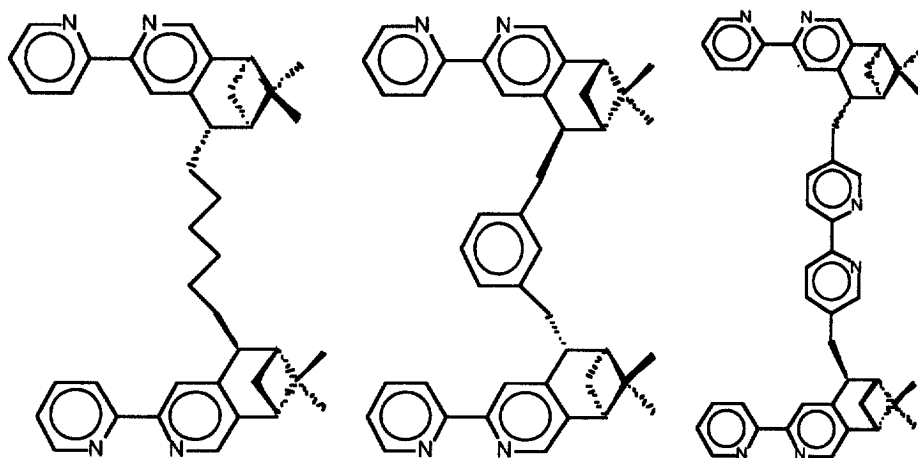


Fig. 4. Three ligands of the CHIRAGEN family. 4,5-CHIRAGEN[6] (left) 4,5-CHIRAGEN[m-xy] (middle) and 4,5-CHIRAGEN[5,5'-M-2,2'bpy] (right).

tetradentate ligands can wrap in three different ways around an octahedral coordination center, as shown in Fig. 5. The C_2 symmetric ligands, in general, induce the C_2 symmetric coordination, and the examples given above all coordinate according to this configuration. However, some ligands of the CHIRAGEN family, may also induce the C_1 symmetric configuration, or even the ' C_{2v} ' arrangement, breaking down the symmetry to C_2 again, through the C_2 symmetry of the ligand.

3.2. Diastereoselectivity with two homochiral didentate ligands

The pinene–pyridine ligands also offer numerous other possibilities for stereoselective synthesis of coordination species. Some time ago, we studied the formation of dinuclear rhodium(III) compounds, where two pyridine derivatives are bound to a rhodium center as cyclometallated ligands. The two rhodium centers are bridged via two chloride ligands (Fig. 6).

The formation of the dinuclear complex with thienylpyridine, an achiral ligand, is in one respect already highly diastereoselective. Caused by a strong *trans*-influ-

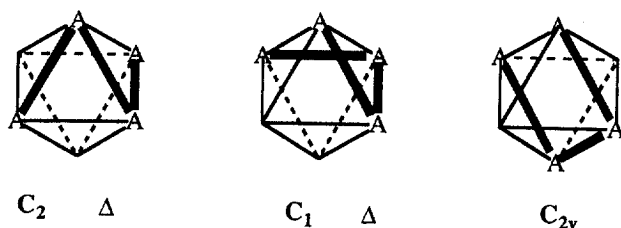


Fig. 5. The three possibilities for linear tetradentate ligands to wrap around an octahedral coordination center.

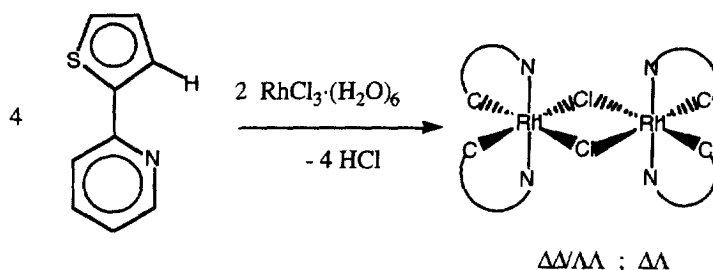


Fig. 6. Formation of a dinuclear cyclometallated complex from thienylpyridine and Rh^{III} .

ence, only the N/N-*trans*, C/C-*cis* isomer is formed. But the reaction is, of course, not at all enantioselective. The two enantiomers $\Delta\Delta$ and $\Lambda\Lambda$ and the mesoform $\Delta\Lambda$ are produced in the statistical ratio of 1:1:2 [8]. If the same reaction is carried out with 4,5-(*R,R*)-pinene-thienylpyridine, the three diastereomers are formed in a ratio of 9:1:0 (Fig. 7). The two diastereomers $\Delta\Delta$ and $\Lambda\Lambda$ can be separated by chromatographic methods.

Cleavage of the dinuclear complex by didentate ligands is a stereospecific reaction, i.e. the configuration at the metal is completely preserved. In this way, a large number of rhodium^{III} complexes of the type $\text{Rh}(4,5\text{-pinene-thienylpyridine})_2(\text{AA}')$, where AA' represents a symmetrical, or an unsymmetrical ligand, can be prepared in either the Δ - or the Λ -configuration at the metal center, without the necessity of ever resolving a racemate. Cleavage with racemates of chiral didentate ligands like 1,2-diaminocyclohexane proceed slightly stereoselectively. Higher stereoselectivities in the cleavage reactions are observed with ligands that create new centers of chirality upon complexation, e.g. like N-methyl ethylenediamine, or N,N'-dimethylethylenediamine.

3.3. Chiral tripod ligands for octahedral coordination

The pinene-bipyridines can be used to construct chiral tripod ligands in a similar way as the CHIRAGEN-family. With $\omega\omega'\omega''$ -tribromo-mesitylene, the tripodal

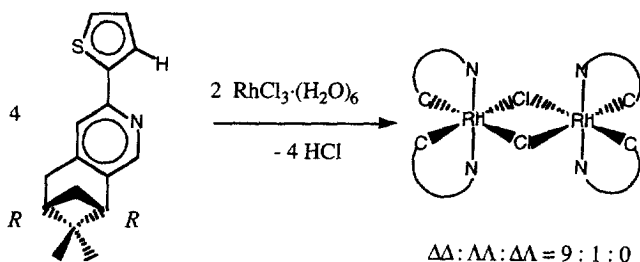


Fig. 7. The highly diastereoselective formation of a dinuclear, cyclometallated complex.

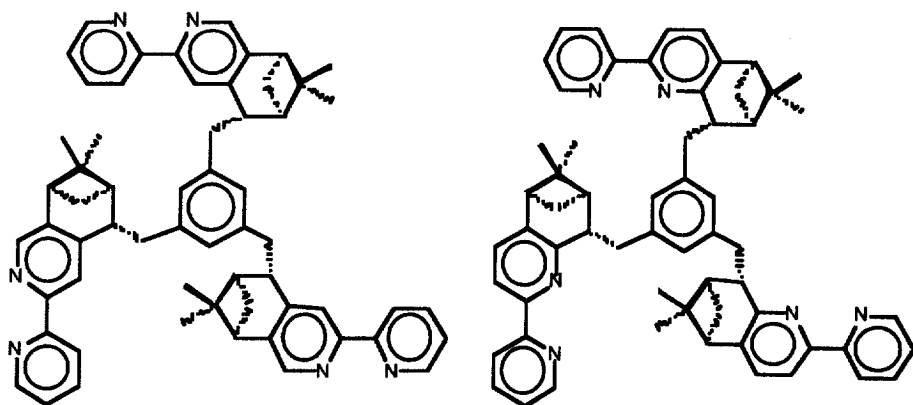


Fig. 8. Tripodal ligands derived from 4,5-pinene-bipyridine and from 5,6-pinene-bipyridine.

ligands shown in Fig. 8 are obtained. These ligands can either form trinuclear species with building blocks of the $M(\text{CHIRAGEN})$ -type, or mononuclear, half-cage complexes, where the bipyridine units coordinate to one center. The resulting complexes of C_3 symmetry are configurationally completely predetermined.

The steric constraints increase markedly going from the derivative of the 4,5-pinene-bipyridine to the tripodal ligand derived from the 5,6-pinene-bipyridine.

3.4. Chiralized terpyridine ligands

The often investigated terpy complexes of octahedral coordination centers are in most cases achiral species. The octahedral $M(\text{terpy})_2$ unit has D_{2d} symmetry and it is often used with the intention of avoiding the complications of stereoisomerism due to chirality. Various terpyridine derivatives have been synthesized, and again both enantiomers of a given ligand are easily accessible (Fig. 9).

The synthesis of the ligand shown in Fig. 9 and of similar species is described in Ref. [9]. One enantiomer of a ligand $L = \text{bis-pinene-terpyridine}$ yields with an octahedral coordination center, a C_2 -symmetric complex ML_2 . All symmetry elements of D_{2d} in $M(\text{terpy})_2$ are broken, except the C_2 -axis. If the two enantiomeric ligands $(+)L$ and $(-)L$ are coordinated to one metal center, an S_4 -symmetric complex $M[(+)L][(-)L]$ is obtained [9].

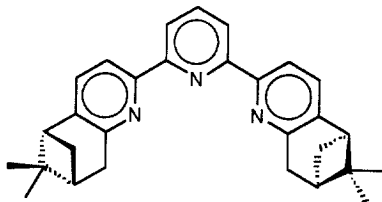


Fig. 9. One representative of a chiralized terpyridine.

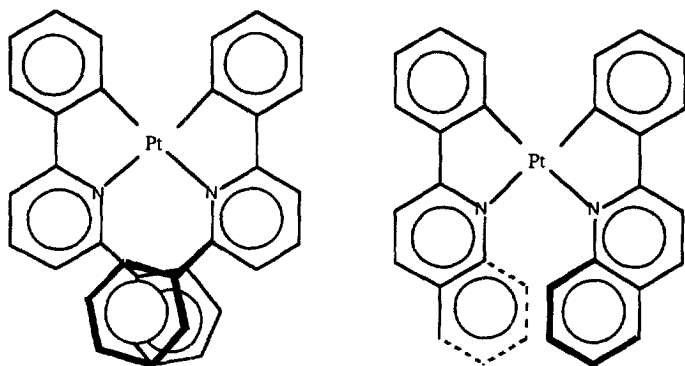


Fig. 10. Two cases of SP-4 Pt^{II} complexes where ligand/ligand interactions result in a chiral distortion of the complexes.

4. Complexes with coordination number four

4.1. Chiral square planar complexes with predetermined configuration and their oxidative addition products

Square-planar complexes (accordingly to IUPAC recommendations designated as SP-4) are in most cases achiral species. Recently, some bis-cyclometallated Pt^{II} compounds were described where a strong distortion from planarity leads to a helical arrangement of two didentate ligands (Fig. 10) [10].

The very strong *trans*-influence of the C-donor leads to a *cis*-arrangement that results in a helical distortion from the planar coordination geometry. The two chelating ligands form a two bladed helix in these species. With non-chiral ligands, racemic products are obtained that are difficult to resolve. The availability of chiral derivatives of these ligands prompted us to repeat the synthesis of such bis-didentate complexes with enantiopure terpene-pyridine molecules. The ligands shown in Fig. 11 were used to prepare cyclometallated complexes.

The 2-(2'-thienyl)-[5,6]-terpene-pyridines form helically distorted SP-4 complexes of predetermined chirality, whereas the 4,5-annellated ligands give dynamic mixtures of Δ - and Λ -chirality, respectively [11]. One example is given in Fig. 12, where a stereo pair representation of a complex of this type with the atomic positions determined by X-ray diffraction is shown [12].

Complexes of this type undergo oxidative addition reactions, either under thermal or under photochemical conditions. Thereby the SP-4 Pt^{II} complex is transformed into an OC-6 Pt^{IV} compound. It has been observed in several cases, e.g. with CH_2Cl_2 as the added molecule, that the two monodentate ligands formed, in this case Cl^- and CH_2Cl^- , respectively, occupy *cis*-positions. The absolute configuration at the metal center, predisposed in the SP-4 complex is completely preserved in the oxidative addition reaction, yielding an OC-6 complex stereospecifically. Using the terpene-pyridine ligands, Pt^{II} and Pt^{IV} complexes are accessible in stereoselective processes.

4.2. Pt^{II} complexes with chiral bipyridine and terpyridine ligands

With many of the chiral bipyridine and terpyridine ligands, Pt^{II} and presumably also Pd^{II} complexes can be formed. The resulting species, so far mainly $Pt(\text{pinene-bipyridine})Cl_2$, show interesting structural features (Fig. 13) as molecules, and also varied properties concerning packing in the crystal structures [13].

Platinum complexes of this type, and the corresponding palladium compounds, are of interest as potential enantioselective catalysts, as chiral drugs, and as chiral intercalating agents, e.g. with DNA.

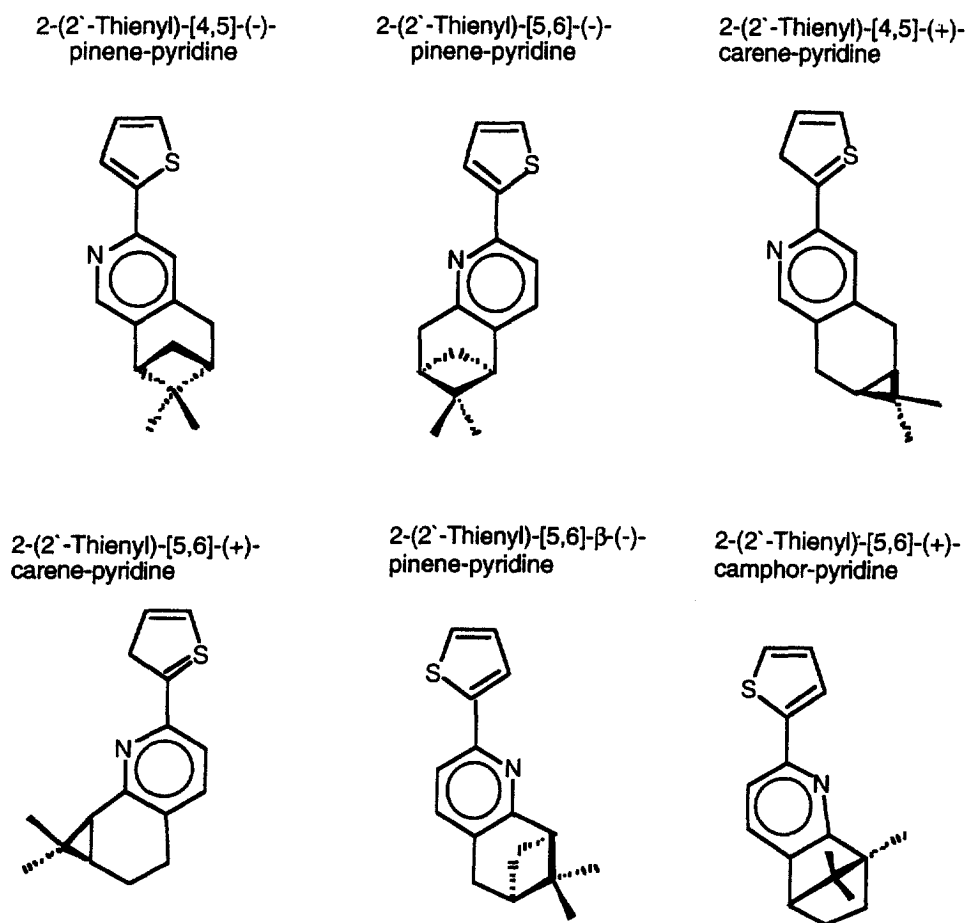


Fig. 11. Thienyl-pyridine ligands that form bis-cyclometallated square planar compounds with Pt^{II} .

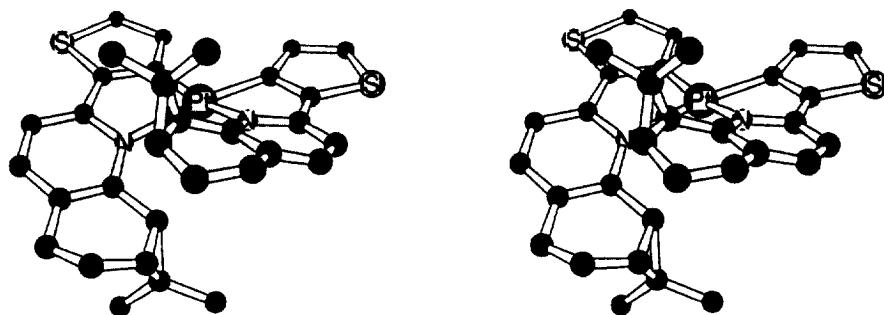


Fig. 12. Stereoview of a the chiral SP-4 complex $\Delta\text{-Pt}\{2\text{-(2'-thienyl)[H}^+\text{]}\text{-[5,6]-(+)-carene-pyridine}\}_2$ according to an X-ray analysis.

4.3. Tetrahedral complexes with predetermined chirality

It is a matter of definition, when a distorted SP-4 complex of the type described in Section 4.1 could be designated as a tetrahedral (T-4, according to IUPAC) species. A T-4 complex, with two didentate chelates can, on the other hand, distort towards an SP-4 geometry, becoming therewith, a chiral species. In limiting cases, it is reasonable to classify a coordination center either as distorted SP-4 or T-4, with reference to the genealogical geometry for the metal. According to this, distorted Pt^{II} and Pd^{II} complexes would always be designated as SP-4, whereas a distorted tetracoordinated Ag^{I} complex will be classified as T-4. An example for a chirally predetermined complex of the latter type is given by the species $[\text{Ag}(5,6\text{-CHIRAGEN[0]})]^+$, shown in Fig. 14.

The planes of the isolated pyridine of the two ligands form a dihedral angle of 28° , those carrying the pinene groups form one of 46° , and finally the pinene-rings themselves are twisted by 48° with respect to each other. This is a very strong deviation from the 90° angle in an ideally tetrahedral complex. Other T-4 coordination centers of predetermined chirality will be described in Section 6 of this report.

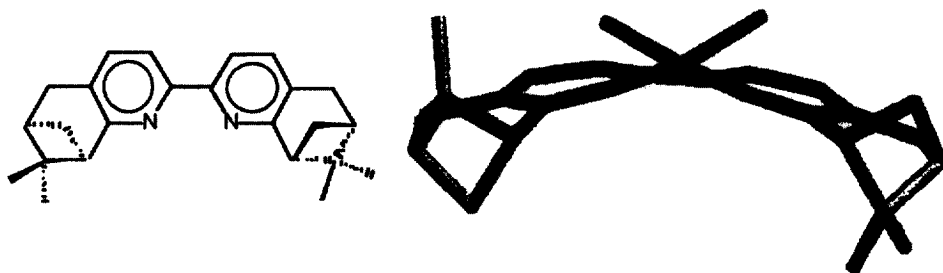
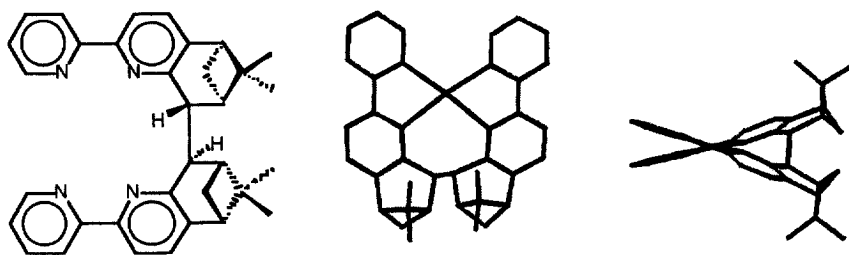
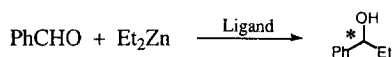


Fig. 13. The ligand bis-5,6-a-pinene-bipyridine and its platinum complex PtLCl_2 . The crystallographic symmetry is C_1 .

Fig. 14. The ligand 5,6-CHIRAGEN[0] and its Ag^+ complex.

5. Chiral pyridine and bipyridine ligands in enantioselective catalysis

Since the terpene-chiralized pyridine and bipyridine ligands often induce one preferred chiral configuration at a metallic coordination center, we have tested some of these molecules in homogeneous catalytic reactions. The standard reaction used for these investigations is the ethylation of the prochiral benzaldehyde, with formation of a chiral secondary alcohol.



The set of ligands shown in Fig. 15 were used as catalysts.

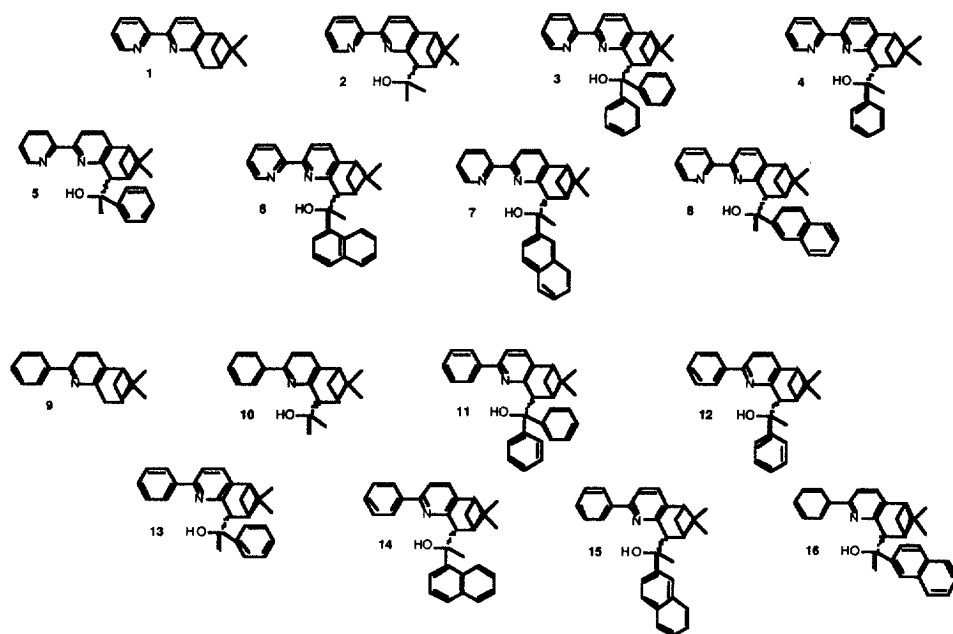


Fig. 15. Catalysts tested for the ethylation reaction.

Table 1
Enantioselective addition of diethyl zinc to benzaldehyde

Ligand	Reaction time (h)	Yield (%)	ee (%)	Configuration
2	1	100	73	R
3	1	100	79	R
4	1	100	78	R
5	1	100	52	R
6	1	99	86	R
7	1	100	82	R
8	1	99	47	R
10	8	91	42	S
11	6	90	68	R
12	8	91	45	R
13	8	60	18	R
14	24	91	64	R
15	24	95	46	R
16	24	85	15	R

Table 1 gives a summary of the results. For details, see Ref. [14].

The best results have so far been obtained with the bipyridine ligand 6, where the product could be obtained in almost quantitative yield with an enantiomeric excess of up to 86%. In view of the large number of molecules available, a further screening program for optimization of the catalytic efficiency seems to be necessary.

6. Self assembly of helicates

Recently, self assembly of helicates has become a matter of increased interest, in the context of the formation of supramolecular structures with well defined functionalities. Since helicates are intrinsically chiral objects, it was indicated to test the chiralized bipyridine ligands in view of their ability to form helicates with predetermined chiral configuration.

The 4,5-CHIRAGEN ligands, e.g. 4,5-CHIRAGEN[*m*-xyl], form with labile OC-6 centers dinuclear 2:3 helicates M_2L_3 [15]. As can be shown by CD-spectroscopy, the configuration of the helicate is predetermined by the chiral pinene group of the CHIRAGEN ligand.

An impressive self assembly occurs when 5,6-CHIRAGEN[*p*-xyl] is reacted with labile T-4 centers like Cu^I or Ag^I [16]. A 1:1 complex formation with an oligomerization degree *n* is observed, where CD-spectroscopy indicates the presence of distorted T-4 centers of a given configuration. From 1H NMR-spectroscopy, a highly symmetric arrangement can be deduced. X-ray structure analysis finally revealed a hexameric circular structure with a C_6 symmetry axis (Fig. 16) [16].

An interesting aspect of this assembly is its perfect chiral self recognition. If a racemic mixture (artificial racemate) of the ligand is used instead of the enantiopure form, no mixture of the two enantiomers occurs within one helicate. Such a

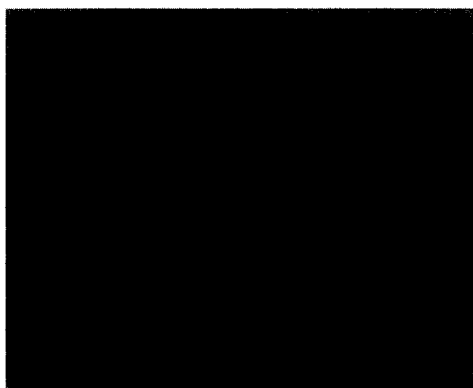
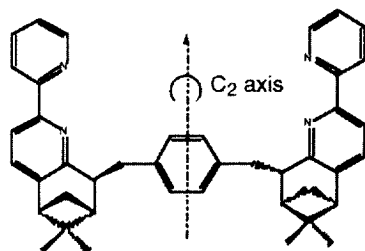


Fig. 16. Self assembled hexanuclear helicate from the ligand 5,6-CHIRAGEN[*p*-xyl] (left) and Cu^I or Ag^I.

racemate yields quantitatively a racemate of the hexanuclear helicates (*P* and *M*), indicating that the coordination of the first CHIRAGEN ligand to one coordination center selects quantitatively homochiral molecules. This phenomenon gives rise to strong nonlinearities in the CD-spectra, if mixtures of the two enantiomeric forms of the ligands are used in various non-racemic ratios.

7. Conclusions and outlook

The incorporation of a chiral structural element derived from naturally occurring substances into a well known coordinating molecule like pyridine, opens up the way for a vast number of new experiments, where all the features of chirality can be exploited in a relatively simple way. Due to the extremely rich stereochemistry of coordination centers of the metallic elements, new possibilities take shape for applications in numerous fields like supramolecular chemistry, enantioselective catalysis, molecular devices etc. These developments give stereochemical considerations a renewed actuality, more than 100 years after Alfred Werner had introduced its basis in a highly imaginative way.

Acknowledgements

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