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Predetermination of chirality at octahedral centres with tetradentate ligands: prospects for enantioselective catalysis

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Contents

Abstract

Methods for creation of chiral-at-metal architectures, principally at octahedral metal centres using tetradentate ligands are reviewed. Where achiral ligands are employed, one chiral racemic topography may be formed selectively, and complex resolution strategies have been successfully applied to furnish optically pure systems. The use of chiral ligands has allowed the diastereomeric formation of complexes with stereogenic metal centres, and this area is becoming quite well developed. A number of applications to stoichiometric and catalytic syntheses are described. In certain instances, chiral-at-metal systems outperform their traditional chiral

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ligand + metal counterparts as a result of the excellent expression of chirality in the active site(s). Prospects for future developments are indicated.

Keywords: Tetradentate ligands; Predetermination of chirality; Chirality at metal

1. Introduction

1.1. Chirality-at-metal

Coordination complexes may contain an element of chirality by virtue of an enantiomeric arrangement of ligands about the metal [1]. It is well known for example that certain tris(chelate) $[M(AA)_3]^{n+}$ complexes of inert metals may be separated into Δ and Λ enantiomers (Fig. 1). When chiral nonracemic ligands are used, one isomer may be formed preferentially [2,3]. This has been termed predetermination of chirality-at-metal [2,4].

Chiral-at-metal complexes have potential for application to enantioselective catalysis; indeed the well-expressed disymmetry should be strongly communicated to prochiral co-ligands [5]. It remains, however, that in order to produce systems which have significant catalytic activity, free or potentially free coordination sites must exist where the substrate and reagent species may interact in close proximity. The challenge of synthesis of single diastereomeric chiral-at-metal complexes for which this criterion is satisfied places significant demands on coordination chemists in terms of chiral ligand design.

1.2. Ligand design

In order to furnish two mutually *cis* coordination sites in an octahedral mononuclear complex, we are likely to require chiral tetradentate 'spectator' ligands. Linear systems (Fig. 2) provide many attractive avenues for exploration since a large number of such ligand classes are readily assembled, and it is these ligands that will be the subject of this review. Other possibilities such as tripodal and macrocyclic ligands [6,7] are also appealing since they offer relatively rigid and well-defined coordination frameworks, but in general they are more difficult to synthesise, and in the latter case usually lead to *trans* structures which cannot usually be termed chiral-at-metal.

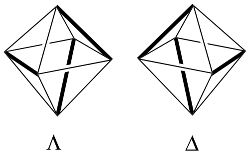

Fig. 1. Chirality descriptors for octahedral tris(chelate) and similar systems.

1.3. Geometrical isomerism

For linear tetradentate ligands in an octahedral coordination environment, three geometrical isomers may be formed (*trans*, *cis*-α and *cis*-β, Fig. 3).

The *trans* structure has C_{2v} symmetry and is therefore not chiral-at-metal. The C_1-symmetric *cis*-β and C_2-symmetric *cis*-α structures have enantiomers with Δ and Λ helicity, and most importantly for the purposes of enantioselective catalysis, *cis* orientated co-ligands, (X, Fig. 3). If the X ligands mutually differ, either as two monodentate ligands or in a bidentate ligand, then further isomers are possible (Fig. 4).

The configuration *cis*-β_1 (Fig. 4) is defined where X^1 has a higher CIP priority than X^2 (e.g. O > N) and is *trans* to the central donor of the tetradentate [8]. If the tetradentate ligand is also unsymmetrical then *cis*-α_1 and *cis*-α_2 configurations are possible. Thus, *cis*-α_1 is defined where X^1 has a higher ranking than X^2 and is *trans* to the higher ranking central donor ($A^1 > A^2$, Fig. 4) of the tetradentate [9]. An example of this can be seen in Fig. 18.

1.4. Scope of review

A variety of linear tetradentate ligands are reported in the literature, but we shall be examining in most detail complexes with amine [10], pyridine [11], amide and Schiff base functionalities. Other types of tetradentate

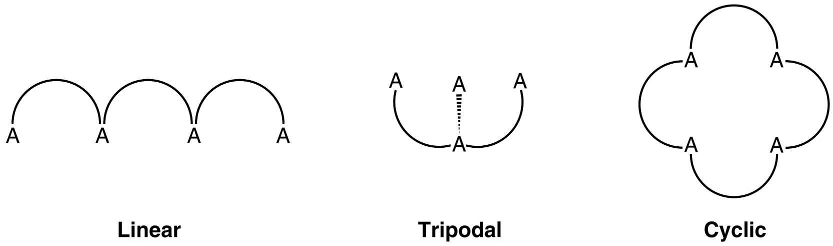

Fig. 2. Classes of potentially tetradentate ligand systems.

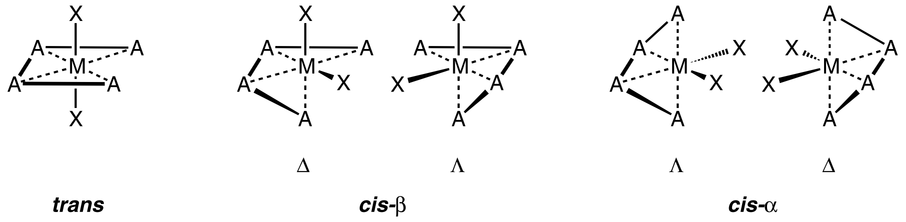

Fig. 3. Octahedral-based geometric isomers for a linear tetradentate ligand.

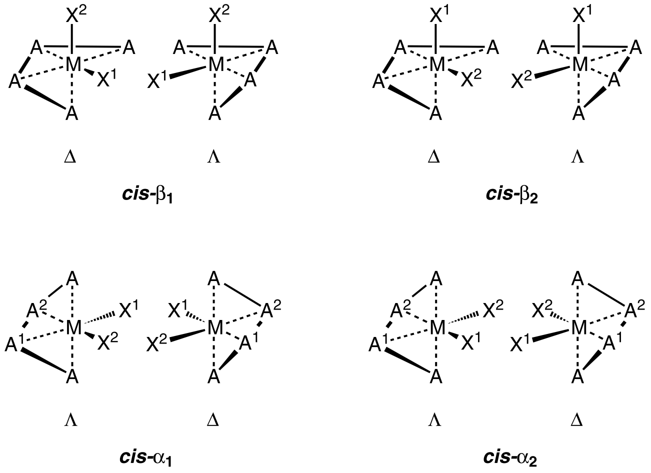

Fig. 4. Sub-classes of the chiral *cis* geometries.

ligand functionalities include amino acids [12,13], phosphines [14–16] and thiols/thioethers [17–20], but these have generally been explored in less detail. Unsymmetrical functionalities have also been reported, e.g. NSNN ligands [21], but this type of ligand may be expected to give a wider variety of diastereoisomers upon coordination, and for this reason are not included here. Finally, we mention only in passing the well-developed work on half-sandwich structures with chiral metal atoms. This topic is reviewed elsewhere [4,22,23].

2. Chiral topographies from achiral ligands

In this section we will examine the 'natural' coordination preferences (*trans*, *cis*-α, or *cis*-β) of various achiral tetradentate ligand groups. This has bearing on the design of chiral ligands with which we might efficiently predetermine chirality-at-metal since, for example, we might reasonably want to concentrate our efforts on ligands which are prone to adopt chiral topographies.

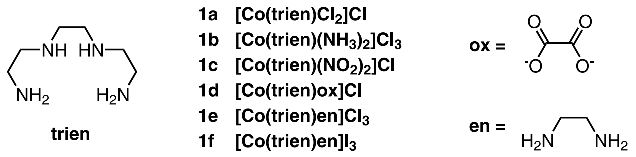

Fig. 5. Basolo's trien complexes of cobalt(III).

In their 1971 review on alkylamino ligands, Legg and co-workers [10] pointed out that the inert nature of cobalt(III) complexes enables isolation and characterisation of the various product isomers. The ability to isolate and study cobalt(III) complexes allows them to be used as a structural model for the ligand systems with more labile metals, which may not be readily isolated, but may have utility in catalysis. For these reasons, structural studies of, in particular, the amino ligand systems have involved mainly cobalt(III).

2.1. Alkylamino ligands

In 1948, Basolo [24] reported the synthesis of several cobalt(III) complexes of **trien** (Fig. 5).

All the complexes were assigned as having *cis* geometries due to their purple colour, as it was known that *trans* complexes of cobalt(III) are green. Basolo recognised the possible existence of the *cis*-α and *cis*-β isomers, but separation of these isomers could not be achieved at the time of the report. For **1d**–**f** the constraints of the bidentate ancillary ligands would require them to occupy mutually *cis* coordination sites, but that **1a**–**c** are also *cis* indicates a strong preference for *cis* geometry coordination with **trien**. The *cis*-α and *cis*-β isomers were subsequently isolated by Sargeson and Searle [25], who along with Bailar and Kyuno, showed that conversion between the two isomers is possible [26,27].

Following many attempts by a number of groups [28–32] a *trans* complex of cobalt(III) **trien** was isolated in 1967 by Sargeson and Searle, *via* conversion of a *cis*-β complex [33]. It was noted that the secondary amine groups of **trien** are stereogenic when coordinated. This has been studied in detail by Sargeson and co-workers [34].

The effect of increasing alkyl chain length between the nitrogen atoms of the ligand was examined using **2,3,2-tet** and **3,2,3-tet** (Fig. 6).

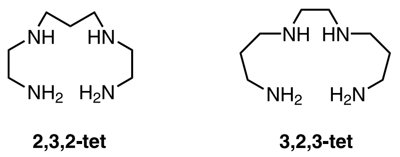

Fig. 6. Longer-chain polyamine ligands.

Unlike **trien**, which showed a preference for *cis* coordination, these ligands showed a preference for *trans* coordination in cobalt(III) complexes [35–37]. This was attributed to the increased flexibility of **2,3,2-tet** and **3,2,3-tet**, and the configurational influences from forming six-membered chelate rings. Octahedral complexes of nickel displayed similar preferential coordination trends with **trien**, **2,3,2-tet** and **3,2,3-tet** [38].

Yoshikawa and co-workers [39] believed that methylation of the terminal end groups of **trien** and **2,3,2-tet** would considerably affect the stability of possible geometrical isomers of cobalt(III) complexes. They found that in both cases the *trans* isomer was the more stable.

In summary, we can see that **trien** shows a strong preference for *cis*-β coordination, though complexes of *trans* and *cis*-α geometries have been isolated. Increasing the chain lengths between the amine groups renders the ligands more flexible and results in preferentially *trans* coordination with **2,3,2-tet** and **3,2,3-tet**.

2.2. Pyridine ligands

The earliest examples of octahedral complexes with linear tetradentate N_4-ligands were the range of *trans* complexes reported by Morgan and Burstall (Fig. 7) [40].

Notionally replacing the backbone bipyridine unit with alkyl diamines allows for greater ligand flexibility and the possibility of *cis* coordination. Three such achiral ligands are shown in Fig. 8. These are comparable to **trien**, **2,3,2-tet** and **3,2,3-tet**.

Gibson and McKenzie [41] reported that **picen** adopted *cis*-α or *cis*-β geometries upon coordination with cobalt(III), whereas **pictn** showed a preference for *cis*-β geometry only. No evidence of *trans* isomers was observed. Goodwin and Lions [42] synthesised complexes of **picen** and **quinen** with copper and ruthenium and assigned *cis* geometries to these complexes. Coordination with nickel and palladium was also explored in the report.

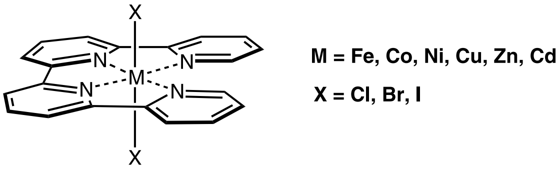

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Fig. 7. Tetrapyridine complexes.

We can see that these more rigid and sterically demanding pyridine ligands show a strong preference for *cis* geometry coordination. Indeed, with flexible diamine backbones no *trans* isomers are detected with cobalt(III). It has been proposed that the steric influences of the pyridine terminal groups disfavours their mutually *cis* coordination in the *trans* configuration, and this effect is increased by substitution of the pyridine rings at the six-position [42].

2.3. Phenolate ligands

2.3.1. Amide backbones

N_2O_2 ligands based on amide backbones were examined during the mid 1980s by Collins [43] (Fig. 9).

They found that an osmium complex of ligand **I** adopted the *trans* geometry, but that there was evidence for the formation of and isomerisation to a *cis*-α complex [44–46]. Ligand decomposition *via* oxidation of the backbone to an ethene unit was precluded by use of the 1,2-phenylene backbone ligand **II**. A mixture of *trans* and *cis*-α complexes were obtained [47–49].

2.3.2. Schiff base backbones

The use of N_2O_2 Schiff bases as tetradentate ligands has been a subject of interest for many years, **acen** and **salen** (Fig. 10) being the most commonly studied core units.

These ligands and their derivatives coordinate predominantly in a planar arrangement to various metal ions giving *trans* geometries in octahedral complexes. The literature abounds with examples of complexes of this type. Interest in *trans* complexes was aroused by Bailes and Calvin [50] in 1947, who showed that cobalt **salen** complexes could act as oxygen carriers and that oxidation of the complexes was reversible. In 1970, Bigotto et al. [51] suggested that the planar coordination of the ligand and the reversible oxidation of the complexes made them suitable models for metal porphyrin systems. Since many oxygen carrying enzymes which occur naturally are based on metal porphyrin systems [52], the cobalt **salen** complexes were examined by various groups [53–57], particularly as models of coenzymes for vitamin B_{12}. The advantage of these

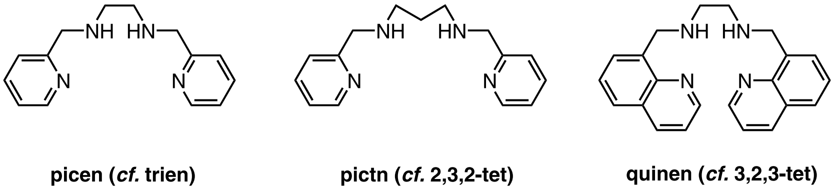
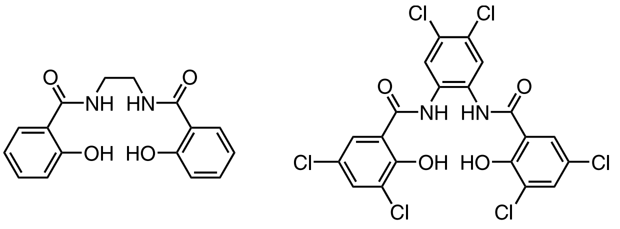
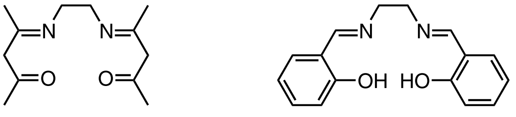


Fig. 8. Dipyridine ligands with alkylamino backbones.



I **II**

Fig. 9. Amido/phenolate ligands.



acen **salen**

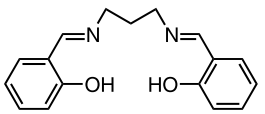
Fig. 10. N_2O_2 Schiff base ligands.

linear Schiff base tetradentate ligands over cyclic tetrapyrrole-type [6,7] ligands arises from the fact they are in the main readily synthesised, readily derivatised *via* introduction of substituents on the phenolic ring and can be made chiral by using chiral diamines as backbone moieties.

It was not until 1968 that a series of **salen** complexes were observed to have the *cis* geometry. These cobalt(III) complexes, synthesised by Poddar and Biswas [58], utilised bidentate β-diketonates as ancillary ligands, which forced the **salen** ligand to adopt a non-*trans* geometry. The *cis*-β geometry of one of these complexes was subsequently confirmed by Calligaris et al. [59,60], who determined the molecular structure by X-ray analysis. The *cis*-β geometry was also identified by McKenzie and co-workers [61], who synthesised a similar complex in the belief that a *trans* structure could exist, with the β-diketonate binding through the α-carbon. However, they found no evidence for this *trans* species and only the *cis*-β isomer was observed. They also determined the X-ray molecular structure and noted that the *cis*-β arrangement caused significant elements of strain within the coordinated **salen** ligand.

Subsequent work by McKenzie and co-workers with **salen** and **salen** derivatives showed that the *cis*-β cobalt(III) β-diketonate complexes could isomerise to the *trans* geometry in donor solvents. The cobalt bound β-diketonate is replaced by two donor solvent ligands (e.g. pyridine or DMSO) to give complexes of the type *trans*-[Co(**salen**)(solvent)$_2$]$^+$[β-diketonate]$^-$ [62].

The **salen** unit has been examined with various metals, and as with cobalt the ligand predominantly forms *trans* complexes. The complex [(**salen′**)Y(OC$_6$H$_3$-2,6-*tert*-butyl) (thf)] (**salen′** = *N*,*N′*-bis{3,5-di-*tert*-butylsalicylidene}ethylenediamine) has been shown to have *cis*-α geometry [63]. Molybdenum(VI) dioxo [64–66], tin(IV) [67,68], iron(III) [69] and chromium(III) [69] complexes of **salen** have been shown to possess *cis*-β geometry.



III

Fig. 11. Salen derivative with propyl backbone chain.

Group 4 metal complexes of tetradentate salicylaldimine ligands had until relatively recently only been formed with *trans* geometry. In 1990, Floriani and co-workers [70] reported seven coordinate **acen** complexes of zirconium and hafnium [M(**acen**)Cl$_2$(thf)] with *pseudo trans* structure. Upon elimination of tetrahydrofuran the *cis*-β structure was observed (Scheme 1). Jordan and co-workers also reported the synthesis of the complex *cis*-β-[Zr(**acen**)Cl$_2$] and showed that alkyl complexes, [Zr(**acen**)R$_2$] (R = CH$_2$CMe$_3$, CH$_2$Ph), adopt the *trans* configuration [71]. Titanium complexes with a **salen** derivative have also recently been shown to adopt the *cis*-β geometry [72].

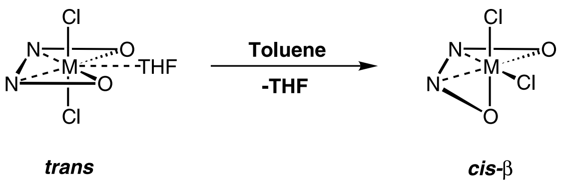
Increasing the backbone chain length to C$_3$ using a 1,3-diaminopropane backbone (**III**, Fig. 11) increased the propensity to form *cis* structures, and while *cis*-β complexes of cobalt(III) and manganese(IV) with **III** have been synthesised [73,74], bidentate ancillary ligands were required.

A *cis*-β vanadium complex with **III** has been described by Leigh and co-workers [75], using monodentate ancillary ligands. They infer that a similar vanadium **salen** complex also has *cis*-β geometry.

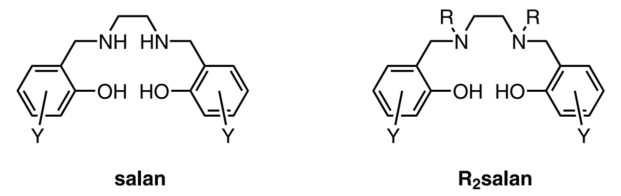
In general **salen**, **acen** and similar ligands preferentially adopt the *trans* configuration in octahedral coordination environments. The formation of *cis* geometry complexes is in the main only afforded by use of bidentate ancillary ligands or molybdenum dioxo fragments, which are known to preferentially generate *cis* complex structures. The *cis* complexes have been observed to contain elements of strain within the coordinated ligand, particularly with **salen** derivatives.

2.3.3. Aminophenolate ligands

The aminophenolate ligands studied here (Fig. 12) are more flexible than the **salen** ligands (Section 2.3.2) of which they may be regarded as imine-reduced versions.



Scheme 1. Formation of *cis*-β-[Ti(acen)Cl$_2$] from *pseudo trans*-[Ti(acen)Cl$_2$(thf)].



salan **R$_2$salan**

Fig. 12. Aminophenolate ligands.

We shall explore how this affects coordination modes to various metals.

The ligand **salan** [76] was shown to coordinate to chromium(III) with *trans* configuration [77], and an iron(III) oxalate complex with **salan** unsurprisingly adopted a *cis*-β structure [78]. However, **salan** and several related derivatives upon coordination to a molybdenum(VI) dioxo fragment gave rise to *cis*-α complexes [79,80]. The *cis*-β structure is observed with corresponding Schiff base complexes.

Alkylation of the secondary amine groups of **salan** gives rise to the ligand set **R$_2$salan**, (Fig. 12). The **R$_2$salan** family of ligands also formed *cis*-α structures in molybdenum(VI) dioxo complexes [80,81] as well as in tungsten(VI) dioxo complexes [80]. A study using various **R$_2$salan** derivatives with cobalt(II) was carried out by Djebbar-Sid et al. [82]. They found that the ligand –OH groups were not deprotonated in the complex and assigned a *trans* configuration. However, copper(II) complexes with similar ligands gave rise to distorted planar structures, the distortion increasing with steric bulk of the ligand amino-R group (Fig. 12) [83,84]. An iron(III) complex with **R$_2$salan** gave a *cis*-β structure when a catecholate ancillary ligand was used, but a five coordinate chloride complex had *pseudo trans* structure [85]. A zirconium complex with a **R$_2$salan** derivative was synthesised by Kol and co-workers [86]. They observed *cis*-α topography with benzyl ancillary ligands and this complex was found to be highly active in tacticity-controlled living polymerisation catalysis of 1-hexene. A titanium complex with a similar ligand was subsequently reported by Walsh and co-workers [87]. They observed *cis*-α geometry with isopropoxide ancillary ligands. Walsh and co-workers also reported a chiral version of **R$_2$salan**, incorporating the (*S*,*S*)-1,2-diaminocyclohexyl backbone. The coordination of this chiral ligand to a titanium diisopropoxide fragment gave rise to both Δ and Λ-*cis*-α complex diastereoisomers which had mutually opposite configurations at the stereogenic NH units.

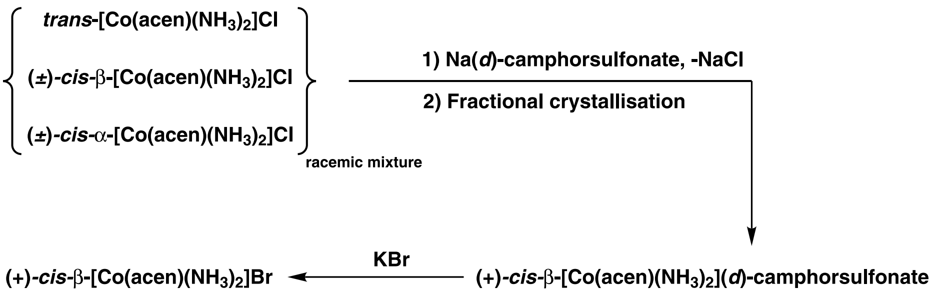
2.4. Resolution strategies

In a landmark paper, Morgan and Smith [88] described the synthesis of the cobalt(III) complex, [Co(**acen**)(NH$_3$)$_2$]$^+$, with a variety of counter-anions. They recognised the possible existence of *trans*, *cis*-β and *cis*-α isomers as well as the enantiomers (Δ and Λ) of the two *cis* structures. They obtained all three geometric isomers, and using the anion (d)-camphorsulphonate were able to resolve the *cis* complexes by fractional crystallisation, which were then transformed to the corresponding *cis*-α or *cis*-β-[Co(**acen**)(NH$_3$)$_2$]$^+$[Br]$^-$ species (Scheme 2). They obtained a very high optical rotation for one complex showing it to be chiral-at-metal and assigned the *cis*-β configuration. They also report sending samples of the complex to an independent observer, without informing them of the nature of the compound. The observer corroborated Morgan and Smiths' results. They also noted that upon keeping, the optically active complexes isomerised to the optically inactive *trans* isomer.

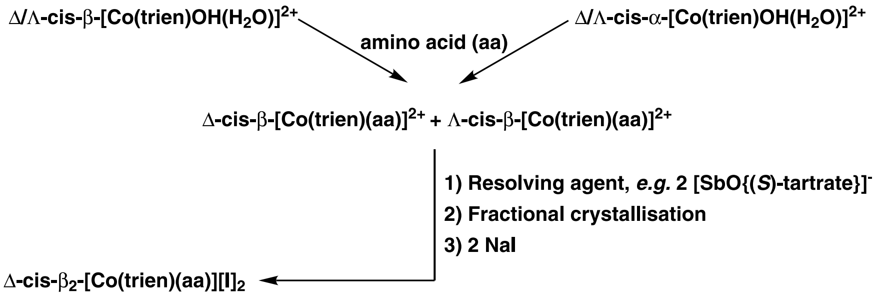
Using chiral nonracemic amino acidate ligands and chiral counter-anions which act as resolving agents, Marzilli and Buckingham [8],and Lin and Douglas [89] achieved resolution of **trien** cobalt(III) complex enantiomers of the *cis*-β topography by fractional crystallisation. Use of *cis*-α complexes to form the amino acid derivatives resulted in isomerisation to the *cis*-β geometry (Scheme 3).

No isomerisation was found to occur after resolution of the **trien** complex enantiomers. This allowed study of asymmetric metal-mediated transformations with these complexes as we shall see in Section 4.

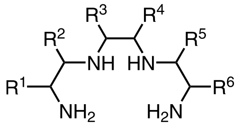
Various chiral counter-ions [90,91] have been used for resolution of complex enantiomers, and isolation may be achieved by fractional crystallisation. Though this technique has been successful, it relies on significantly different solubility properties between the two diastereomeric salts, and the overall yield of the desired



Scheme 2. Resolution of isomeric mixture of [Co(acen)(NH$_3$)$_2$]Cl.



Scheme 3. Resolution of isomers of $[Co(trien)OH(H_2O)]^{2+}$.

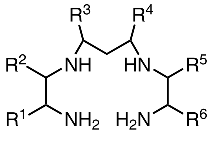


trien

IV	$R^1 = R^6 = Me$	**2,9-dimetrien**
V	$R^2 = R^5 = Me$	**3,8-dimetrien**
VI	$R^3 = Me$	**5-metrien**
VII	$R^3 = R^4 = Me$	**5,6-dimetrien**

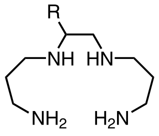
R^n = H unless stated otherwise

Fig. 13. Chiral trien derivatives.



2,3,2 tet

VIII	$R^1 = R^6 = Me$	**2,10-Me$_2$-tet**
IX	$R^2 = R^5 = Me$	**3,9-Me$_2$-tet**
X	$R^3 = Me$	**5-Me-2,3,2-tet**
XI	$R^3 = R^4 = Me$	**5,7-Me$_2$-2,3,2-tet**



3,2,3-tet

XII	R = Me	**5-Me-3,2,3-tet**

R^n = H unless stated otherwise

Fig. 14. Longer-chain tetraamine derivatives.

complex is generally low. Further complications may arise from epimerisation or isomerisation of the isolated enantiomer. Predetermining the chirality-at-metal with chiral nonracemic ligands negates these problems, as we shall see in the following section.

3. Chiral ligands: predetermination of chirality-at-metal

3.1. Alkylamino ligands

The first chiral N_4-ligands to be synthesised utilised methyl substituents at various points on the alkyl chains of **trien**, **2,3,2-tet** and **3,2,3-tet** (Figs. 13 and 14). The chronological order of ligand and complex synthesis is fairly random, so instead we shall examine the effects of substitution starting at the terminal positions of the ligand and working around to backbone substitution.

Complexes of cobalt(III) with **IV** were reported by Asperger and Liu [92] in 1965. All three geometric isomers of [Co{(*S*,*S*)-**IV**}Cl$_2$]Cl were isolated. It was noted that the *cis*-α and *cis*-β isomers formed with high stereoselectivity for Λ and Δ absolute configurations, respectively. Subsequent work by Saburi and Yoshikawa [93] showed that the ligand preferentially adopted Λ-*cis*-α geometry, which was attributed to the more favourable equatorial orientation of the methyl groups upon coordination. Primary amine methylation of **IV** resulted in preferentially *trans* complexes [39].

Sargeson and co-workers [94] found **V** gave almost exclusively *trans* coordination complexes with cobalt(III), however, complexes with *cis* geometries were subsequently isolated by Saburi and Yoshikawa [93].

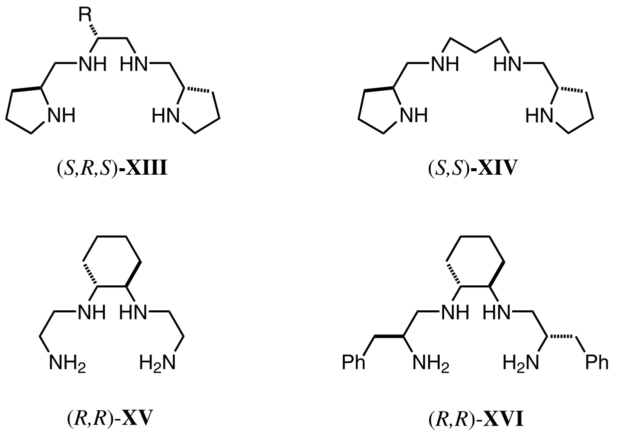
Using **VI**, cobalt(III) dichloride and dinitro complexes of *cis*-β geometry were obtained with high selectivity. The enantiomers, Λ and Δ, were observed using (*R*)-**VI** and (*S*)-**VI**, respectively [95,96]. The C_2-symmetric disubstituted derivative, **VII**, showed similar selectivity upon coordination. This was again attributed to the equatorial preference of the methyl groups. However, these complexes are shown to isomerise to the *trans* geometry [95].

Studies on cobalt(III) complexes of the more flexible ligand **VIII** (Fig. 14) showed the *trans* geometry to be the most stable isomer [97,98]. Solutions of *cis*-[Co{(*S*,*S*)-**VIII**}Cl$_2$]$^+$ in acidic methanol isomerised to the *trans* geometry. The corresponding ligand, **IX**, was also found to give preferentially *trans* cobalt(III) dichloride complexes [99].

Using **X** [100] and **XII** [101,102] it was again shown that the *trans* geometry was favoured, though *cis*-β products could be obtained using ancillary ligands other than chloride. This was also true for the dimethyl ligand **XI** [103–105].

The ligand **XIII** (Fig. 15) was shown by Jun and Liu [106] to coordinate to cobalt(III) with high stereoselectively. Both pyrrolidine rings were of (*S*) conformation and the (*R*)-methyl and (*S*)-methyl diastereoisomers of the ligand yielded Λ-*cis*-β and Δ-*cis*-β absolute configurations, respectively. The more flexible ligand, **XIV**, was shown to coordinate with a very strong preference for *trans* geometry with monodentate ancillary ligands [107–109].

The ligand **XV** also yielded *cis*-β cobalt(III) complexes highly stereoselectively [95,110]. The Δ and Λ



(*S*,*R*,*S*)-**XIII** (*S*,*S*)-**XIV**

(*R*,*R*)-**XV** (*R*,*R*)-**XVI**

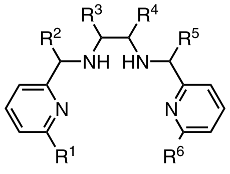
Fig. 15. Trien-like ligands with cyclic stereogenic units.

enantiomers of the complexes were predetermined by the (*R*,*R*) or (*S*,*S*) configuration of the cyclohexyl backbone. Asperger [111] synthesised **XVI** in the hope that it would also coordinate with cobalt(III) stereoselectively. However, *cis*-β and *trans* isomers were observed.

We have thus seen that the use of substituents on **trien** produce chiral derivatives (Figs. 13 and 15), and can strongly influence the preference for *cis* coordination as well as predetermine the formation of a particular chirality-at-cobalt(III). The chiral cyclic groups offer more stereochemical rigidity than their methyl branching counterparts and impose their chirality onto the metal centre to a higher degree. Indeed, the chiral cyclic substituents (pyrrolidyl for ligand **XIII** and cyclohexyl for ligand **XV**, Fig. 15) give rise to essentially complete predetermination of chirality-at-metal irrespective of the ancillary ligands that have so far been explored. Longer-chain tetraamines (Figs. 14 and 15) give *trans* complexes with monodentate co-ligands. This was to be expected given the strong preference of the achiral analogues for the *trans* structure (Section 2.1).

3.2. Pyridine ligands

The pyridine derivatives have fewer positions for substitution of the ligand chains (R^{2-5}, Figs. 16 and 20), as compared to trien-type ligands, but substitution of the pyridine ring ($R^{1,6}$, Figs. 16 and 20) may play a significant role [42].



picen

XVII **$R^2 = R^5 = Me$** **peaen**
XVII **$R^3 = Me$** **picpn**
XIX **$R^3 = R^4 = Me$** **picbn**
XX **$R^3,R^4 = -(CH_2)_4-$** **picchxn**
XXI **$R^3 = R^4 = Ph$** **picstien**

$R^n = H$ unless stated otherwise

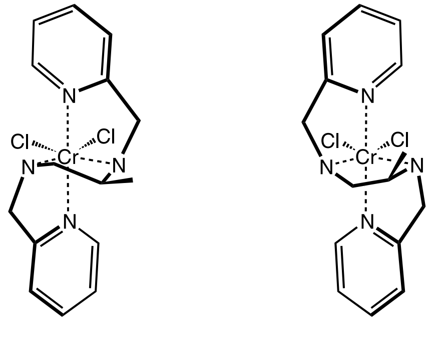
Fig. 16. Chiral dipyridine ligands.

Using **XVII**, cobalt(III) complexes were found to adopt *cis*-α and *cis*-β geometries. Further isomeric complications were caused by the different configurations adopted by the secondary amine groups upon coordination [112,113]. No *trans* isomers were observed.

Bosnich [114] first reported the synthesis of cobalt(III) and chromium(III) complexes of **XVIII**. He assigned the complexes as having the *cis*-α geometry only. In 1972, Cragel and Brubaker [101] further studied the coordination of **XVIII** with cobalt(III) and concluded that the resulting complexes were formed as *cis*-β isomers with high stereoselectivity. They also believed that isomerisation of *cis*-β-[Co(**XVIII**)(ox)]$^+$ to the *cis*-α geometry occurred. Subsequently, strain energy minimisation and conformational analysis of the complexes were carried out by Brubaker and Euler [115], which showed that the *cis*-α geometry was marginally the more stable conformation. The cobalt(III) **XVIII** system was studied again by Yamamoto and Shimura [116] in 1980. They concluded that the initial analysis by Bosnich was correct and that the ligand coordinated highly stereoselectively to yield *cis*-α complexes, and gave the Δ diastereoisomer with (*S*)-**XVIII**. They also isolated complexes of chromium(III) with (*S*)-**XVIII** and found stereoselective coordination of *cis*-α topography [117]. However, Δ and Λ diastereoisomers of *cis*-α-[Cr{(*S*)-**XVIII**}Cl_2]$^+$ were formed, though the Δ diastereoisomer has the greater stability (Fig. 17).

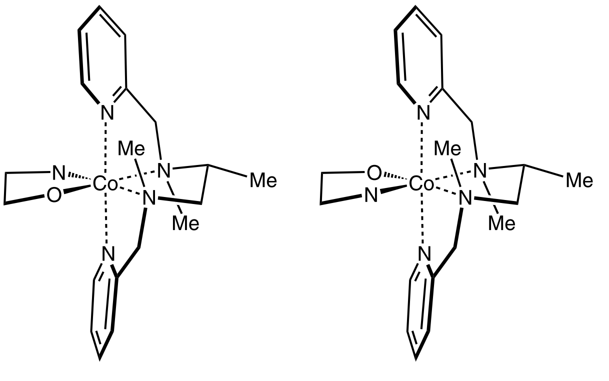
Further complications with this ligand were observed by Vagg and co-workers. They showed the complex Λ-*cis*-α-[Co{(*R*)-**XVIII**)}Cl_2]$^+$ was capable of highly stereoselective isomerisation to Δ-*cis*-β-[Co{(*R*)-**XVIII**)}Cl_2]$^+$ [118]. The effects of the configurations of the coordinated **XVIII** secondary amine groups were also explored using amino acidate ancillary ligands. Four diastereoisomers (Λ-*cis*-α, Δ-*cis*-α, Λ-*cis*-β and Δ-*cis*-β) of the complex were observed, using (*R*)-**XVIII** [119–122].

Methylation of the secondary amine groups of (*R*)-**XVIII** yielded a ligand that coordinated highly stereoselectively to cobalt(III) giving the absolute configura-



Δ-***cis***-α Λ-***cis***-α

Fig. 17. Chiral-at-metal diastereomers of *cis*-α-[Cr{(*S*)-**XVIII**}Cl_2]$^+$; secondary amine hydrogen atoms omitted for clarity.



Δ-***cis***-α_1 Δ-***cis***-α_2

Fig. 18. Chiral-at-metal diastereomers of *cis*-α-[Co{(*R*)-**XVIII**}(amino acidate)]$^{2+}$ resulting from the presence of unsymmetric co-ligature.

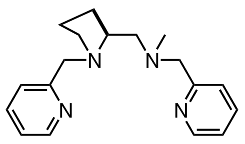


Fig. 19. A dipyridine ligand with chiral pyrrolidine backbone.

tion Δ-*cis*-α [9]. Due to the unsymmetrical nature of the ligand, two isomers (Δ-*cis*-α_1 and Δ-*cis*-α_2) of this configuration were observed using amino acids as ancillary ligands (Fig. 18).

Using a more inflexible ligand that incorporated a pyrrolidine group as part of the secondary amine-backbone chain (Fig. 19) led to *cis*-α_1 complexes as the only isomer [123].

Benzylation of the secondary amines of **XVIII** has been achieved and the coordination of the resultant ligand with a variety of metals has also been explored by Fraser and co-workers [124], with *cis* geometries of the complexes being observed.

Cobalt(III) complexes using **XIX** were synthesised by Bosnich and Kneen [125]. They assigned the complexes as having the *cis*-β geometry only and this was later confirmed by Vagg and co-workers, who showed the (*S*,*S*) and (*R*,*R*) ligand configurations gave Δ and Λ enantiomers, respectively [126]. Thus the ligand was shown to result in essentially complete predetermination of chiral-at-cobalt complexes. Yamamoto and Shimura [127] synthesised chromium(III) complexes using (*S*,*S*)-**XIX** and found the absolute configuration to be Λ-*cis*-α only (within detectable limits).

Similarly, using the diaminocylcohexyl backbone moiety yielded **XX**. The ligand (*R*,*R*)-**XX** was found to coordinate to cobalt(III) with the Λ-*cis*-β configuration. Small amounts of Δ-*cis*-α were observed under certain conditions, but these isomerised to the more stable Λ-*cis*-β configuration [122]. Chromium(III) complexes of (*S*,*S*) and (*R*,*R*)-**XX** have been prepared and were shown to have configurations of Λ-*cis*-α and Δ-*cis*-α, respectively [127,128]. The ligands *N*,*N*′-dimethyl-[(*R*,*R*) and (*S*,*S*)]-**XX** give complete predetermination of chirality-at-cobalt with configurations Λ-*cis*-α and Δ-*cis*-α, respectively [129]. These ligand have also been shown to coordinate to iron(II) giving *cis*-α and *cis*-β geometries [130]. Interconversion of the two iron complex geometries was not observed.

Coordination of (*R*,*R*) and (*S*,*S*)-**XXI** resulted in complete predetermination of chirality-at-metal of configuration Λ-*cis*-β and Δ-*cis*-β, respectively. This was observed for both cobalt(III) and rhodium(III) [131].

According to Suzuki et al. [112], (*R*,*R*)-**XXII** (Fig. 20) gave highly stereoselectively the Δ-*cis*-β-[Co{(*R*,*R*)-**XXII**)}X_2]$^+$ structure, where $X_2 = Cl_2$, $(NO_2)_2$ and oxalate. The configuration of the secondary amines was believed to be (*S*,*S*) and was confirmed by X-ray crystallographic analysis [132]. **XXIII** was synthesised by Vagg and co-workers [133], and contains a rigid cyclic backbone. This was found to coordinate to cobalt(III) with high stereoselectivity for *cis*-β geometry.

Ligand **XXIV** was found to coordinate to cobalt(III) yielding complexes of deprotonated and neutral forms of the ligand. The deprotonated ligand complexes were isolated with greater ease than the neutral ligand complexes, and were found to adopt *cis*-β geometry though both diastereoisomers were observed with the optically pure (*R*)-**XXIV**.

The deprotonated and neutral forms of **XXV** have been coordinated to cobalt(III). However, the experimental assignment of absolute configuration is not given due to difficulties in interpretation of CD spectra [134] (Fig. 20).

We have thus seen that the achiral pyridine ligands have a natural preference for coordination to cobalt(III) with *cis* geometries. Indeed, with flexible diamino alkyl backbones no *trans* isomers are detected. The steric bulk of the terminal pyridine group may aid this preferential coordination. Chiral versions of this ligand type have given rise to essentially complete predetermination of

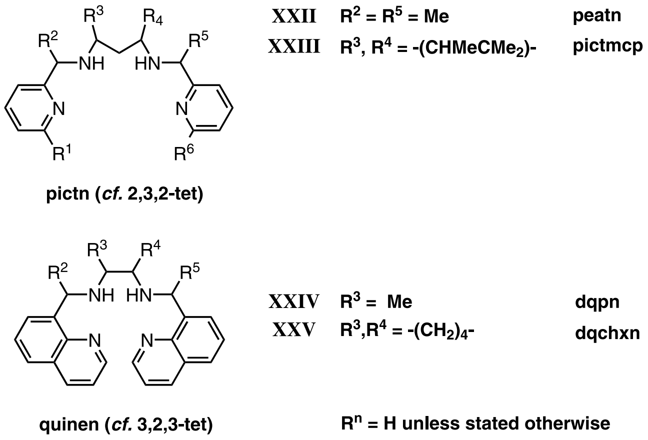


Fig. 20. Longer-chain chiral dipyridine ligands.

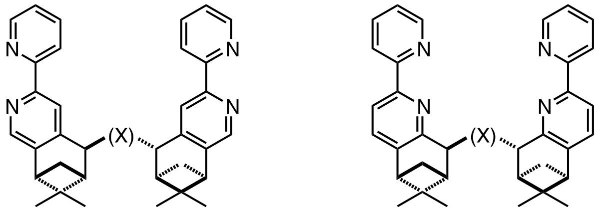


Fig. 21. Examples of pyridine donor chiragens.

chirality-at-metal in several instances, and such examples are more common than for **trien** and related ligands. Problems associated with unsymmetrical ligand substitution patterns are highlighted with ligands **XVIII** and **XXIV**. A greater number of complex diastereoisomers are possible and have been observed. However, further substitution *via* alkylation of amine groups renders certain diastereoisomers more stable, and allows efficient predetermination of chirality-at-metal.

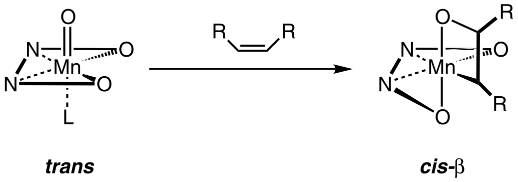
A further class of chiral pyridine ligands form part of the family of chiragens (Fig. 21) developed by von Zelewsky et al. Efficient predetermination of chirality has been achieved with these and related ligands, but since they have been extensively reviewed elsewhere [2,3] we omit them here.

3.3. Chiral N_2O_2 Schiff base ligands

3.3.1. Distorted trans structures

The first optically active manganese(III) complex was synthesised by Boucher and Herrington [135] using a chiral **salen** ligand derived from the 1,2-diaminopropyl backbone. This was shown to have *trans* configuration though the ligand was distorted from the planar arrangement around the metal. This was also observed by Gullotti et al. [136,137] in a study of various iron **salen** derivatives employed as mimics of oxygenase enzymes.

Enantioselective catalysis using chiral nonracemic Schiff base ligands has been vigorously explored in recent years and has been the subject of many papers and reviews [138–143]. The Katsuki and Jacobsen systems for asymmetric epoxidation are based on chiral **salen** ligands coordinated to various metals, and in particular manganese. The exact nature of the catalytic species caused some debate during the mid 1990s, as two mechanisms were postulated. One mechanism proposed by Norrby et al. [144] and Katsuki and co-workers [145] suggested that the manganese **salen** complex, which has the *trans* structure in the resting state, adopts a *cis*-β configuration during the catalytic cycle (Scheme 4). The alkene reacts with the metal bound oxygen to generate a bidentate ligand, which as we saw in Section 2.3.2, can generate *cis*-β structures for **salen** cobalt(III), iron(III) and chromium(III) complexes. The metallacycle fragment ring closes to generate the epoxide.



Scheme 4. Disymmetric conversion *trans* to *cis*-β.

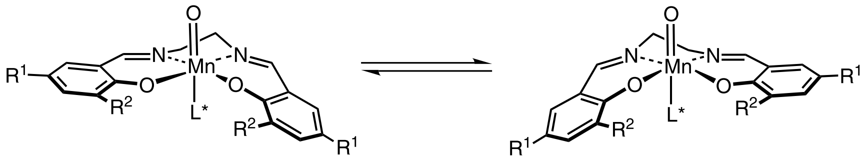
In this mechanism the potential for predetermination of chirality-at-metal might be described as being latent in the *trans* complex, but activated upon formation of the metallacycle to give one enantiomer (Δ or Λ) of the *cis*-β structure. In any event it is now accepted that the tetradentate ligand remains *trans* throughout the catalytic cycle [146,147]. Nevertheless, Katsuki and co-workers [148,149] showed that deviation from planar coordination of the Schiff base gives rise to the stereoselectivities observed from the epoxidation catalysis. An achiral salen-type ligand was shown to give good enantiomeric excess for epoxidation catalysis, by virtue of using a chiral ancillary ligand (L*, Scheme 5), which favoured one conformer over the other (Scheme 5).

Using chiral salen-type ligands, the complexes may adopt *trans* configurations, but deviation from planar coordination is exacerbated by the use of chiral backbones and sterically demanding phenolic substituents. This gives rise to a preference for one conformer (Scheme 5), generating a well-defined chiral coordination sphere around the metal. Catalysis occurs on the same face of the complex, with the non-planar coordination and steric influences from ligand substituents directing the approach of incoming substrates [147]. The directionally limited approach of the incoming substrates gives rise to the excellent stereoselectivities observed, but only by virtue of highly sterically demanding ligand substituents.

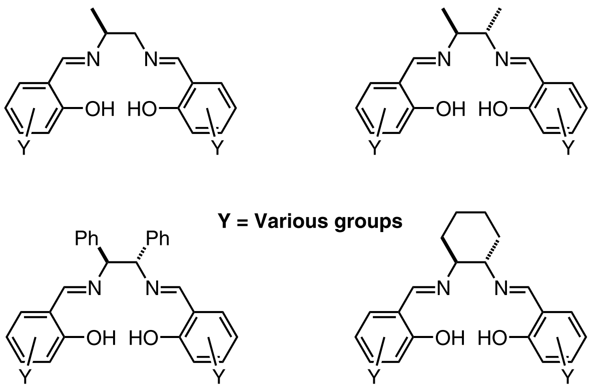
3.3.2. Schiff base N_2O_2 complexes with cis geometry

Chiral diamines have been used to synthesise chiral salen-type ligands (Fig. 22) and for the most part these adopt the *trans* geometry. As we have just seen the *trans* complexes have found utility in enantioselective catalysis and have been well studied.

Cobalt(III) complexes of **salen** and related ligands have been extensively studied by Fujii et al. They reported a large number of amino acidate complexes and showed that epimerisation of the complex diastereoisomers could occur. Chiral recognition and optical resolution of amino acids was also explored. In all cases the amino acidate complexes posses *cis*-β geometry [150–156]. One such suitably derivatised complex was copolymerised with styrene and divinylbenzene. This created a chiral cavity with active sites for preferential coordination of (*R*)-phenylalanine from a racemic mixture of (*R*,*S*)-phenylalanine [157].

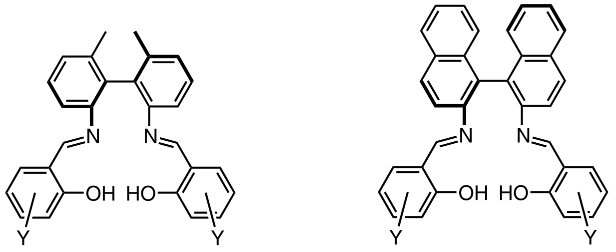


Scheme 5. Disymmetric conformational changes.



XXVI

Fig. 22. Chiral nonracemic salen derivatives.



XXVII **XXVIII**

Fig. 23. Salicylaldimine ligands based on atropisomeric diaminobiaryls.

The use of biaryl diamine backbone groups in tetradentate ligands was explored by Lions et al. in 1957 [158] and 1960 [42]. They showed that these ligands were capable of coordination in a non-planar fashion with practically no ligand strain, and synthesised an octahedral ruthenium(II) complex which they assigned as having *cis*-α geometry. Holm and co-workers [159] subsequently studied biaryl tetradentate salicylaldimine ligands (Fig. 23) in tetrahedral coordination complexes. It was shown that the configuration of *psuedo* tetrahedral chiral-at-nickel(II) complexes was predetermined by the ligand and that no epimerisation occurred in solution.

In 1996, work from our laboratory appeared on complexes of zirconium incorporating a derivative of ligand **XXVII** (Y = 3,5-di-*tert*-butyl) [160]. These were the first examples of tetradentate salicylaldimine complexes with *cis*-α geometry. Subsequent work showed that this ligand type gives essentially complete predetermination of chirality-at-zirconium, quite independent of the auxiliary ligands [161]. The ligand arrangement also survived chemical reduction to give the *cis*-α amido/alkoxido complex (Scheme 6).

Rare Schiff base complexes of niobium [162] incorporating this ligand class also gave *cis*-α structures, while in the case of ruthenium, *cis*-β complexes were observed exclusively (Fig. 24) [163].

For titanium [164], high stereoselectivity for the *cis*-α structure was observed, with the exception of the halides such as [Ti(**XXVII**)Cl_2] for which, inexplicably, mixtures of *cis*-α and *cis*-β complexes were observed (Fig. 25). In no instance has interconversion between isomeric forms been detected.

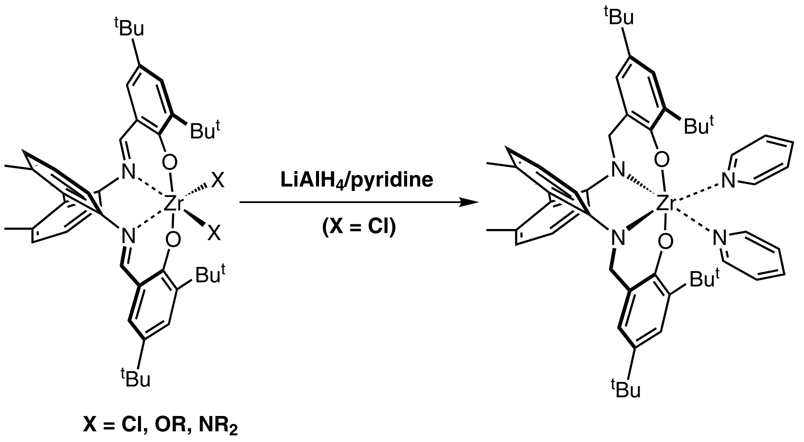
Using the binaphthyl ligand **XXVIII**, Che and co-workers showed that complexes of manganese(III) and iron(III) could adopt *cis*-β geometry, though a bidentate ancillary ligand was used [165]. A ruthenium(II) complex was observed to have *cis*-β geometry in the presence of monodentate ancillary ligands [166]. Evans et al. have also reported a *cis*-β structure for an octahedral aluminium complex with this ligand type [167].

As with the parent **salen**, the chiral tetradentate salen-type ligands preferentially adopt the *trans* configuration. Generation of *cis* geometry complexes is in the main only afforded by use of fragments which are known to preferentially generate *cis* complex structures. Elements of strain within the coordinated ligand for these *cis* complexes have been observed. However, by using biaryl backbones such as in **XXVII**, highly efficient predetermination of chiral-at-metal *cis* geometries can be achieved in most cases.

4. Stereoselective transformations

4.1. Enantioselective epimerisation

Buckingham et al. [90] reported the epimerisation under basic conditions of *N*-methyl-(*S*)-alanine in the complex Δ-*cis*-β_2-[Co(**trien**){*N*-Me-(*S*)-ala}]$^{2+}$ (Scheme 7). The α-proton of the chelated amino acidate moieties in the chiral complex ions undergo proton exchange in basic aqueous solution, giving rise to a diastereomeric mixture after the establishment of equilibrium. The orientation of the [Co(**trien**)] unit, which was retained throughout, fixes the absolute configuration of the



Scheme 6. *cis*-α Zirconium complexes based on XXVII.

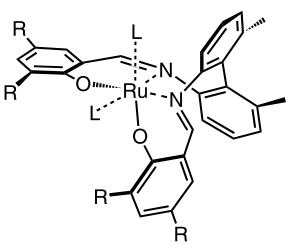
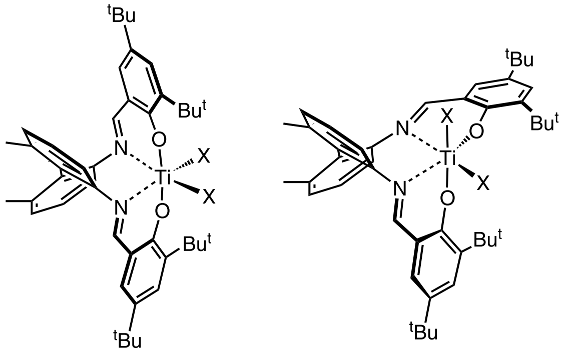


Fig. 24. *cis*-β Ruthenium complexes based on XXVII.



cis-α-[Ti(XXVII)X_2] *cis*-β-[Ti(XXVII)X_2]

Fig. 25. Detected isomers of chiral-at-metal titanium Schiff base complexes.

Table 1
Enantioselective *N*-methylalanine epimerisation at chiral-at-metal cobalt

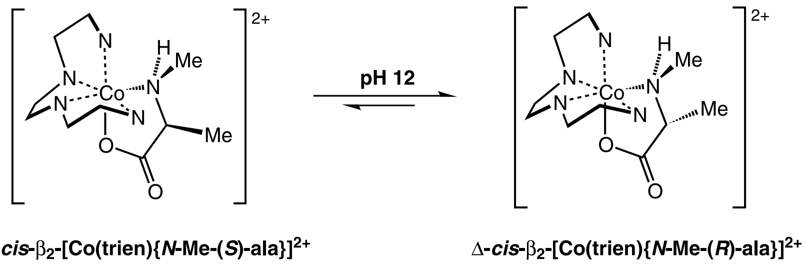
Entry	N_4	(*S*)/(*R*) of amino acid	
		ala	*N*-Methyl ala
1	**(en)**$_2$	50/50	80/20
2	**trien**	–	60/40
3	(*S*,*S*)-**V**	50/50	85/15
4	(*R*)-**VI**	–	76/24
5	(*S*,*S*)-**VIII**	66/34	90/10
6	(*S*,*S*)-**IX**	61/39	87/13
7	(*R*,*R*)-**XV**	–	88/12

amino acidate-NHMe group as shown in Scheme 7. The consequent steric compression with the α-methyl group causes this diastereoisomer to be less stable than the Δ-*cis*-β_2-[Co(**trien**){*N*-Me-(*R*)-ala}]$^{2+}$ diastereoisomer.

Further complications arise from the formation of two diastereoisomers of Δ-*cis*-β_2-[Co(**trien**)(N-Me-(*S*)-ala)]$^{2+}$ caused by different configurations of the secondary amine groups of the coordinated **trien** ligand.

The metal-mediated epimerisation of various amino acids and *N*-methyl amino acids has been explored. Comparison of results [168,169] between the epimerisation of alanine and *N*-methyl alanine using cobalt(III) complexes can be seen in Table 1.

trien-NH bonds ommitted for clarity



Δ-*cis*-β_2-[Co(trien){*N*-Me-(*S*)-ala}]$^{2+}$ Δ-*cis*-β_2-[Co(trien){*N*-Me-(*R*)-ala}]$^{2+}$

Scheme 7. Epimerisation of coordinated alanine.

Table 2
Enantioselective amino acid epimerisation at chiral-at-metal cobalt

Entry	N_4	(*S*)/(*R*) of amino acid						
		ala	asn	asp	glu	leu	phe	val
1	**(en)**$_2$	50/50	–	40/60	46/54	–	54/46	37/63
2	(*S*,*S*)-**V**	50/50	–	–	–	–	–	34/66
3	(*S*,*S*)-**VIII**	66/34	80/20	84/16	68/32	65/35	61/39	47/53
4	(*S*,*S*)-**IX**	61/39	87/13	91/9	–	–	64/36	30/70
5	(*S*,*S*)-**XIV**	17/83	–	–	–	–	–	–

For ethylenediamine (**en**) and **trien** complexes (entries 1 and 2, Table 1), resolution of the complex enantiomers is required before conducting the epimerisation experiments (Section 2.4). Complexes with the chiral ligands (entries 3–7, Table 1) were obtained highly stereoselectively, even when generated from *trans* cobalt(III) dichloride complexes for entries 3, 5 and 6. This highlights the latent predetermination of chirality (*c.f.* Section 3.3.1) imposed by these chiral nonracemic ligands.

Comparison of results between the epimerisation of various amino acids using Λ-*cis*-β_2-$[Co(N_4)(aa)]^{2+}$ complexes can be seen in Table 2 [99,168–171].

4.2. Enantioselective amino acid synthesis

Synthesis of amino acids *via* metal-assisted decarboxylation of aminomalonic acid derivatives under acidic conditions (Scheme 8) was first proposed by Asperger and Liu [172], and subsequently improved upon by Job and Bruice [173].

The prochiral aminomalonic acids are desymmetrised on coordination to the (N_4)cobalt(III) fragment. The results for the subsequent decarboxylation reaction are shown in Table 3.

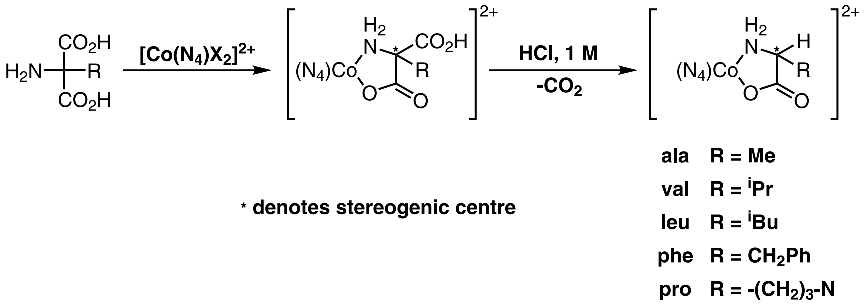
For entries 1 [174] and 2 [173] (Table 3), the amino acids were not isolated, and enantiomeric ratios were calculated for the corresponding amino acidate complexes. The reaction was shown to proceed through inversion of configuration of the coordinated 2-aminomalonic acid derivatives upon decarboxylation. Bruice and co-workers [174] determined the molecular structure of a cobalt(III) malonate complex by X-ray analysis and reasoned that the stereoselectivity of the decarboxylation was due to the predetermined chiral-at-metal geometry of the complex. Diastereomeric hydrogen bonding and steric interactions were present between the N_4-ligand and the 2-aminomalonic acidate. Entries 3–8 (Table 3) were carried out by Yoshikawa and co-workers [175,176] with isolation of the amino acids. Entry 9 (Table 3) was carried out by Liu and co-workers [177,178], who claimed that the decarboxylation step occurs with >95% stereoselectivity, but racemisation occurred during amino acid isolation.

Despite the very strong preference for *cis* geometry coordination in almost all cases with pyridine ligands (Figs. 16 and 20), there are limited reports of metal-mediated transformations using the corresponding complexes. However, a similar study of stereoselective synthesis of amino acids has been undertaken using two N_4-pyridine cobalt(III) complexes. The 2-aminomalonic acid derivatives used by Vagg and co-workers [179,180] can be seen in Scheme 9, and the results are summarised in Table 4.

Metal-mediated reductive cyclisation of 5-amino-2-oxopentanoic acid to yield proline (Scheme 10) has also been examined by Vagg and co-workers [181].

Highly stereoselective generation of the complex Λ-*cis*-β_2-[Co{(*R*,*R*)-**XX**}(5-amino-2-oxopentanoate)]$^{2+}$, followed by cyclisation and reduction of coordinated 5-amino-2-oxopentanoate led to an enantiomeric ratio (*S*)-pro:(*R*)-pro of 16:84.

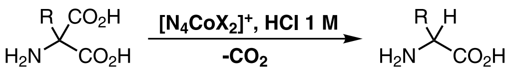
In the search for prochiral synthons that can be catalytically transformed to generate chiral nonracemic



Scheme 8. Enantioselective decarboxylation of aminomalonic acid derivatives.

Table 3
Enantioselective decarboxylation of aminomalonic acid derivatives

Entry	N_4	(*S*)/(*R*) of amino acid				
		ala	val	leu	phe	pro
		65/35	36/64	–	–	–
2	(*S*,*S*)-diisopropyl-**IV**	69/31	–	–	–	–
3	(*S*,*S*)-**V**	56/44	22/78	–	–	–
4	(*R*,*R*)-**XI**	66/34	–	–	–	–
5	*N*,$^1N^4$-dimethyl-(*R*,*R*)-**XI**	17/83	–	–	–	–
6	(*S*,*S*)-**VIII**	54/46	16/84	39/61	41/59	–
7	(*S*,*S*)-**IX**	55/45	9/91	23/77	–	–
8	(*S*,*S*)-**XIV**	14/86	2/98	–	–	–
9	(*S*,*R*,*S*)-**XIII**	40/60	–	–	–	38/62



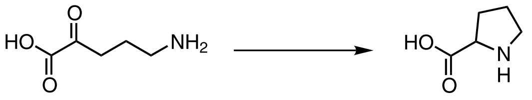
Scheme 9. Enantioselective decarboxylation mediated by chelate dipyridine complexes of cobalt.

Table 4
Enantiomeric ratios obtained from Scheme 9 using $[Co(\{R,R\}\text{-}\mathbf{XX})X_2]^+$

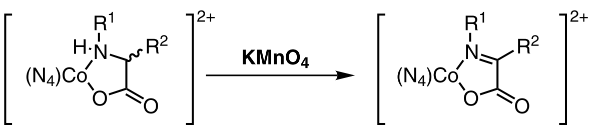
Amino acid	er [a] (*S*)/(*R*)
$R = CH_3$	11/89
$R = CH_3$	7/93 [b]
$R = CH_2CH_3$	16/84
$R = CH_2CH_2CH_3$	30/70
$R = CH_2(CH_2)_2CH_3$	68/32
$R = CH_2Ph$	76/24
$R = CH_2(4\text{-}Bu^t\text{-}C_6H_4)$	65/35
$R = CH_2$(1-Napthyl)	78/22

[a] Enantiomeric ratio.
[b] Using (*R*,*R*)-**XXI**.

amino acids, attention was turned to imino acidato complexes. It is known that coordinated amine ligands can undergo dehydrogenation to give imine functionalities, and a similar dehydrogenation process was explored for amino acid complexes of cobalt(III) (Scheme 11) [182].



Scheme 10. Reductive cyclisation of 5-amino-2-oxopentanoic acid.



Scheme 11. Oxidation of *N*-alkyl amino acidate ligands (N_4 = 2,3,2-tet, (*S*,*S*)-**VIII**).

The dehydrogenation of coordinated amino acidate to imino acidate complexes results in the loss of the stereogenic centre at the α-carbon. However, nucleophilic attack at the imine carbon will regenerate the stereogenic centre, and choice of nucleophile allows for synthesis of non-natural amino acid derivatives [183]. In the same report, the potential of this system has been realised, using chirally resolved bis(1,2-diaminoethane) cobalt(III) complexes. A 1:1 mixture of diastereoisomers was observed for the amino acidate complexes formed from nucleophilic addition. However, the reduced solubility of one diastereoisomer led to its preferential crystallisation, and this was accompanied by isomerisation of the remaining diastereoisomer in solution at equilibrium. This process resulted in isolation of an enantiopure amino acidate complex in good yield (74%). There have been no reports of transformations of this type with complexes containing chiral tetradentate ligands.

Williams and co-workers [184] explored the coordination of 1,2,3-triaminopropane (**tap**), to yield the complex Λ-*cis*-β-$[Co\{(R,R)\text{-}\mathbf{XX}\}(tap)]^{3+}$. They likened 1,2,3-triaminopropane to the 2-aminomalonic acid derivatives (Fig. 26), which have found application in the synthesis of amino acids (*vide supra*). It was hoped that this complex would have application in the transformation of 1,2,3-triaminopropane to chiral vicinal diamines, which are important moieties for the generation of chiral compounds, e.g. chiral tetradentate ligands. However, two different coordination modes were observed for the **tap** ligand and no catalytic application has been reported.

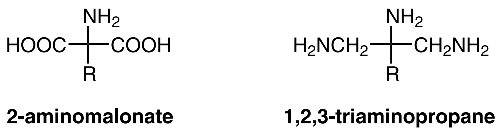
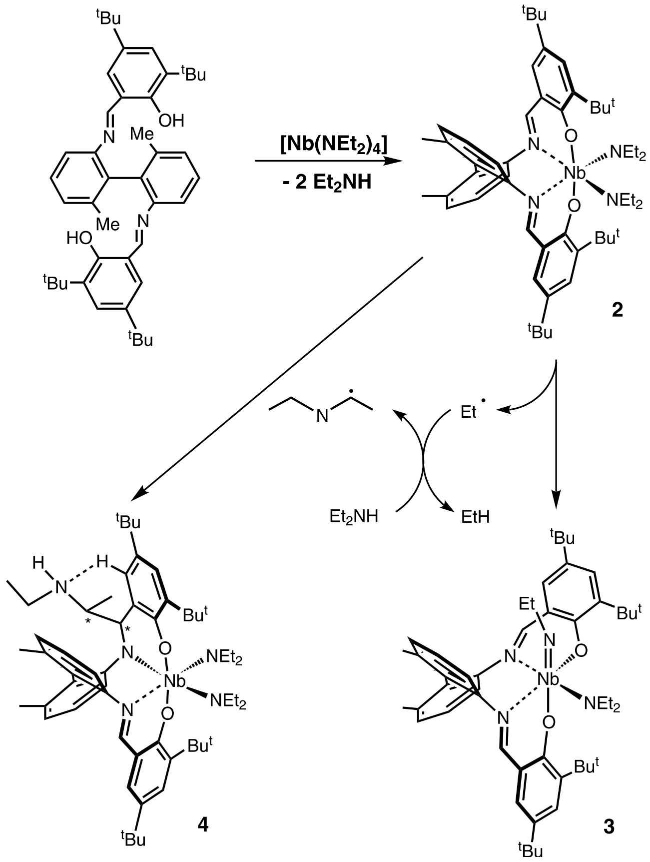


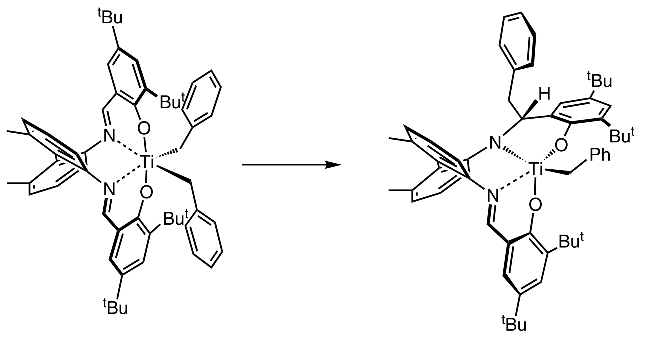
Fig. 26. Prochiral substrates; 2-aminomalonic acid and 1,2,3-triaminopropane.



Scheme 12. Stereoselective ligand transformations at niobium(IV) Schiff base complexes.

4.3. Stereoselective ligand transformations

The *cis*-α niobium(IV) complex, **2** (Scheme 12) containing a biaryl Schiff base ligand of the type **XXVII** (Fig. 23) was found to undergo two mechanistically linked oxidation processes, both related to the instability of the ligands [162]. Spontaneous loss of an ethyl radical from a diethylamino unit led to formation of a *cis*-β imido complex, **3** (Scheme 12) as a single diastereomer. Most surprisingly however was the subsequent addition of a resultant diethylamine-2-yl radical at a coordinated imine unit in a highly diastereoselective manner (**4**, Scheme 12). Molecular structures of both products were determined.



Scheme 13. Highly diastereoselective intramolecular imine alkylation.

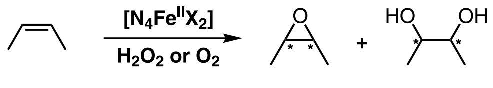
The titanium benzyl complex *cis*-α-[Ti(**XXVII**)(CH_2Ph)$_2$] (Fig. 25) was found to undergo spontaneous and highly diastereoselective 1,2-migratory insertion at a coordinated imine group (Scheme 13) to give a five-coordinate monoalkyl species [164]. In subsequent work on the related zirconium complexes, this intramolecular mechanism was thoroughly characterised and in some instances the reaction was prevented by sterically blocking approach of the alkyl group to the electrophilic carbon centre [185].

4.4. Catalysis with predetermined chiral-at-metal complexes

More recently, olefin epoxidation and *cis*-dihydroxylation (Scheme 14) has been reported using iron(II) complexes of *N*,*N*-dimethyl-**picen** (Fig. 8) and *N*,*N*-dimethyl-**XX**. Steric influences from *ortho* substituents on the pyridine rings have been observed, and good enantiomeric and diastereomeric excesses achieved [186–188]. Both *cis*-α and *cis*-β configurations of these iron(II) complexes have been isolated (vide supra), and a topographical effect on catalysis has been reported [130].

The enantioselective trimethylsilylcyanation of aldehydes has been described by North and Belekon. They found that titanium(IV) dichloride complexes of **XXVI** adopted the *trans* geometry. However, further experiments revealed that the precatalyst was a dimeric titanium oxo complex, [Ti(**XXVI**)O]$_2$, with both titanium centres adopting Δ-*cis*-β geometry using (*R*,*R*)-1,2-diaminocyclohexane. With racemic **XXVI** they obtained homochiral dinuclear complexes only [189]. Subsequent analysis indicated that the reactive species is a dinuclear oxo-bridging complex in which both titanium centres have *cis*-β geometry (Fig. 27) [190]. A vanadium(IV) oxo complex with **XXVI** has also been shown to catalyse the cyanation of aldehydes and a similar catalytic species is implicated in the reaction. Enantiomeric excess of up to 95% has been achieved [191,192].

The *cis*-β ruthenium(II) Schiff base complex containing a ligand of the type **XXVII** (Scheme 15) gave extremely high diastereoselectivity (≤99:1) and enantioselectivity (≤98%) in catalytic alkene cyclopropanation [163]. The origins of this selectivity arise in the chiral-at-metal nature of the catalyst. On reaction of the precatalyst with the carbene source (ethyl diazoacetate), a bidentate carbenoid structure is formed (according to



*denotes chiral centre

Scheme 14. Catalytic olefin epoxidation and *cis*-hydroxylation.

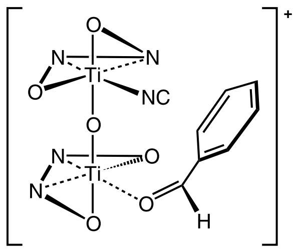
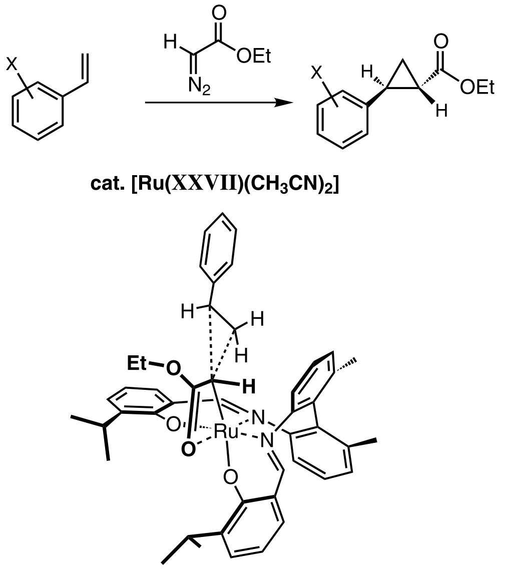
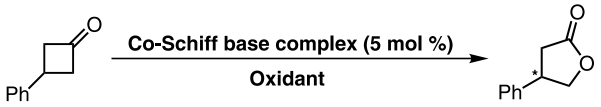


Fig. 27. Oxo-bridged dinuclear titanium complex with *cis*-β geometry at the metal centres.



Scheme 15. Highly enantioselective and diastereoselective alkene cyclopropanation catalysed by a chiral-at-ruthenium complex; the proposed stereochemistry-forming step is shown.



Scheme 16. Baeyer–Villiger oxidation.

DFT calculations) which is exceptionally well oriented to approach of the alkene nucleophile.

Katsuki has recently shown [193,194] that *cis*-β complexes of cobalt(III) incorporating ligands of type **XXVIII** (Fig. 23) give good enantioselectivity in the Baeyer–Villiger oxidation shown (Scheme 16). The similar *trans* complex of **XXVI** (Fig. 22) shows no enantioselectivity.

We have thus seen that chiral-at-metal complexes of achiral ligands are capable of mediating asymmetric transformations. Also, ligands such as **VIII** and **IX**, which generate *trans* complexes may display a *latent* predetermination of chirality-at-metal which is developed upon coordination of chiral or prochiral substrates. The amino acid epimerisation (Tables 1 and 2) and synthesis (Table 3) results indicate that chirality-at-metal per se may not be sufficient to give highly stereoselective metal-mediated transformations. The chirality must be strongly expressed in the active sites through e.g. ligand–substrate steric interactions or hydrogen bonding. This can perhaps be seen with alanine epimerisation (Table 2), where the highest stereoselectivity is obtained with ligand (*S*,*S*)-**XIV**. For amino acid synthesis using **trien** and related ligands (Table 3), the greatest stereoselectivities were achieved with N^1,N^4 -dimethyl-(*R*,*R*)-**XI** and (*S*,*S*)-**XIV**. These ligands have the greatest steric bulk at the terminal groups and strongly communicate the chirality-at-metal to the active sites.

Higher enantioselectivity with pyridine ligand complexes is observed for metal-mediated synthesis of alanine and phenylalanine (Table 4) than with the trien-type complexes (Table 3). The increased enantioselectivities may be attributed to the increased steric bulk at the terminal positions of these ligands. Stereoselective epoxidation and *cis*-hydroxylation catalysis has also been achieved using iron(II) complexes with pyridine ligands (Scheme 14).

The ligands based on **XXVII** developed in our laboratory and elsewhere give extremely efficient predetermination of chirality-at-metal. Metal-mediated transformations with zirconium, titanium and niobium (Schemes 12 and 13) essentially form a single pair of diastereoisomers when racemic ligands are used. The well-expressed chirality-at-metal is transferred to reagent and substrate at the active sites leading to catalysts (Scheme 15) which outperform analogous *trans* systems [195].

5. Conclusions and prospects

Certain tetradentate ligand sets described in this review show a preference at octahedral metal centres for one of the chiral *cis* structures, and this has been exploited through the use of chiral versions of the ligands in the creation of chiral-at-metal complexes. Taking into account both the stereoselectivity of complex formation and the efficiency of subsequent metal-mediated organic transformations, it appears to us that of the classical amino ligands, the pyridine-based systems with stereogenic 'backbones' (Section 3.2) offer the most promise. However, in order for them to be attractive to organic chemists the systems must be rendered catalytic, or perhaps applied to transformations which are more readily catalysed.

The Schiff base ligands (Section 3.3) are for the most part highly selective for *trans* complex configuration in octahedral, square planar or square pyramidal coordination environments. These or other ligands may however display *latent* chirality-at-metal (Sections 3.3.1 and 4.1). By using biaryl backbones such as in **XXVII**, highly efficient predetermination of chiral-at-metal is readily achieved, and this plays a major part in the subsequent stoichiometric and catalytic transformations.

We note that chiral-at-metal complexes may play a role in catalytic reactions outside the scope of this review [5]. Noyori, for example, has shown that transfer hydrogenation by kinetically labile [Ru(η^6-arene)(chiral-diamine)Cl] occurs via diastereomerically-pure chiral-at-metal intermediates, and that this plays an important role in enantioselection [22].

We feel that the application of the chiral-at-metal concept to enantioselective catalysis may have distinct advantages over the traditional approach of chiral ligand + metal, since with appropriate ligand design the chirality of the system should be well-expressed in the active sites. Some instances where chiral-at-metal catalysts outperform traditional systems have been described here. In the future we envisage that the design of chiral-at-metal catalysts incorporating early transition and lanthanide metals will be a fruitful area of study, since the creation of well-defined coordination spheres for these metals has otherwise been extremely difficult to achieve [196,197].

Acknowledgements

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