Available online at www.sciencedirect.com
SCIENCE DIRECT®
Coordination Chemistry Reviews 242 (2003) 33–46
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

1,1′-Binaphthyl-2,2′-diol and 2,2′-diamino-1,1′-binaphthyl: versatile frameworks for chiral ligands in coordination and metallosupramolecular chemistry

Shane G. Telfer[a,*], Reiko Kuroda[a,b]

[a] *JST ERATO Kuroda Chiromorphology Project, Park Building, 4-7-6 Komaba, Meguro-ku, Tokyo 153-0041, Japan*
[b] *Graduate School of Arts and Sciences, University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan*

Received 3 December 2002; accepted 12 February 2003

Contents

Abstract

This review covers the use of chiral 1,1′-binaphthyl-2,2′-diol and 2,2′-diamino-1,1′-binaphthyl frameworks for the construction of ligands for coordination and metallosupramolecular chemistry. The 1,1′-binaphthyl-2,2′-diol unit is readily functionalised with ligating groups at both the diol oxygen atoms and at a variety of positions on the binaphthyl rings. This has allowed the synthesis of a wide range of ligands which, in combination with metal ions, has given rise to an array of chiral coordination compounds and supramolecular complexes. This review details polynuclear complexes prepared in this manner. 2,2′-Diamino-1,1′-binaphthyl has been used as a ligand in a number of complexes. Also, ligating groups have been attached to the 2,2′-diamino-1,1′-binaphthyl framework via its amine nitrogen atoms, usually by formation of a Schiff base. The coordination chemistry of both the parent 2,2′-diamino-1,1′-binaphthyl compound and of its derivatives are covered by this review.

Keywords: Binaphthyl ligands; Chiral metal complexes; Supramolecular chemistry; Asymmetric catalysis; Nitrogen ligands; Oxygen ligands

---

Abbreviations: biphep, 2,2′-bis(diphenylphosphantl)biphenyl; chxn, 1,2-diaminocyclohexane; COD, cycloocta-1,5-diene; CSI-MS, cold-spray ionisation mass spectrometry; dab, 2,3-diaminobutane; dap, 2,3-diaminopropane; dpen, diphenylethylenediamine; dppf, diphenylphosphinoferrocene; dppp, 1,3-diphenylphosphinopropane; GPC, gel permeation chromatography; HEX, 1,5-hexadiene; NBD, bicyclo[2,2,1]hepta-2,5-diene; OTf, trifluoromethanesulfonate; TBDMS, *tert*-butyldimethylsilyl; tmda, N,N,N′,N′-tetramethylethylenediamine.

[*] Corresponding author. Tel./fax: +81-3-5465-0104.

E-mail address: shane.telfer@chiromor2.erato.rcast.u-tokyo.ac.jp (S.G. Telfer).

0010-8545/03/$ - see front matter
doi:10.1016/S0010-8545(03)00026-2

1. Introduction

1,1′-Binaphthyl units functionalised at the 2- and 2′-positions exhibit axial chirality as a result of restricted rotation about the *trans*annular bond [1]. The resulting atropisomers can often be resolved and usually show excellent optical stability. Common examples include the 2,2′-diphenylphosphino (BINAP), 2,2′-diol (BINOL) and 2,2′-diamino (BINAM, [2]) derivatives.

Recent years have seen a considerable upsurge in interest in the chirality of coordination compounds [3–6]. This can be ascribed to a number of factors: (i) the role of chiral metal complexes in asymmetric synthesis; (ii) advances in the field of bioinorganic chemistry; and (iii) the development of metallosupramolecular chemistry. This final factor has been a strong stimulus as polynuclear complexes often have multiple stereogenic centres, the combination of which gives rise to a large number of possible diastereomers.

One method of synthesizing a certain diastereomer of a metal complex is to ‘predetermine’ the chirality at the metal centre(s) by using enantiopure chiral ligands. Many examples of such diastereoselective procedures have appeared in the literature, and ligands derived from readily available chiral building blocks such as amino acids and terpenes have featured prominently [3,6].

Other building blocks which are readily available in an enantiopure form are the above-mentioned 2,2′-functionalised-1,1′-binaphthyls (Fig. 1). These compounds, especially BINAP and BINOL, have received a great deal of attention as chiral ligands for transition metal catalysts. In recent times, they have also found use as chiral building blocks in coordination and metallosupramolecular chemistry. This review aims to highlight the growing role that C_2-symmetric ligands based on BINOL and BINAM frameworks are playing in these fields. The rapid growth in this area is reflected by the fact that the number of references which pertain to coordination chemistry covered by this review which were published in 2002 alone is greater than the total of those published up to (and including) 1999.

The coordination chemistry of *mononuclear* complexes of BINOL and ligands based on the BINOL framework is beyond the scope of this review (mononuclear BINAM complexes are included, however). For lanthanide complexes this chemistry has been well documented elsewhere [7,8], and Pu has reviewed many other BINOL complexes [9].

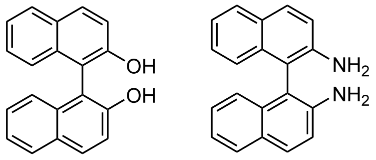


Fig. 1. BINOL and BINAM.

2. An overview of synthetic strategies for the preparation of ligands based on BINOL and BINAM frameworks

A brief overview of useful synthetic methods for the preparation of ligands based on BINOL and BINAM frameworks is presented here. More comprehensive reviews can be found in the literature [9–11]. With respect to BINOL-based ligands, two general approaches exist (Fig. 2) which are dealt with in Sections 2.1 and 2.2, respectively. Section 2.3 outlines methods for the synthesis of BINAM derivatives.

2.1. Construction of the BINOL framework from substituted *β*-naphthol compounds

The most efficient and straightforward method for construction of the BINOL skeleton is the oxidative coupling 2-naphthol by [CuClOH(tmda)] in air [12]. This procedure is also suitable for a wide range of substituted 2-naphthols [13–15].

If achiral 2-naphthols are used, naturally this method leads to a racemic mixture of *R*- and *S*-BINOL products. Efficient resolution of BINOL into its enantiomeric forms has been achieved by co-crystallisation with (8*S*, 9*R*)-(−)-*N*-benzylcinchodinium chloride [16]. An alternative method for the resolution of BINOLs involves the covalent attachment of a chiral moiety to the oxygen atoms. The resulting two diastereomers can often be separated by column chromatography. A wide variety of chiral substituents have been employed for this purpose, most notably camphorsulfonate [17]. A recent publication from Einhorn’s group describes the use of N-protected amino acid esters which give very impressive chromatographic separation factors [18].

In order to avoid laborious resolution procedures, efforts have been directed towards developing methods for the *asymmetric* coupling of 2-naphthols [19]. Recently, excellent results have been reported by Gong and co-workers who employed a dinuclear oxovanadium(IV)

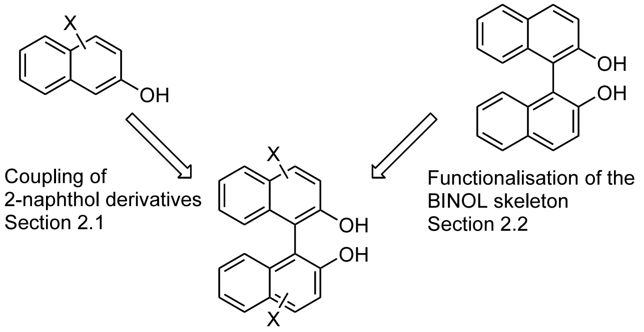


Fig. 2. Two approaches to the synthesis of BINOL derivatives.

catalyst to achieve ee's of up to 97% [20], and also by Nakajima et al. who used a chiral analogue of the above-mentioned [CuClOH(tmda)] catalyst to obtain substituted BINOLs with ee's of up to 78% [21].

2.2. *Functionalisation of BINOL*

Ligands based on the BINOL framework can also be prepared starting from the parent BINOL compound. One of the major advantages of this approach is that both enantiomers of BINOL are commercially available in an enantiopure form. Many synthetic protocols have been devised for derivatisation of the BINOL skeleton, and selective functionalisation of the 3,3′-, 4,4′-, or 6,6′-positions of BINOL is possible [9]. For example, bromination of BINOL by Br_2 gives 6,6′-dibromo-BINOL in quantitative yield, while reaction with $C_2Br_2Cl_4$/BuLi at low temperature gives the 3,3′-dibromo derivative [22,23]. Once the BINOL skeleton is brominated at the desired positions, ligating groups can be introduced directly (e.g. by coupling reactions), or further derivatisation gives access to alternative functional groups (e.g. carboxaldehyde).

Reaction at the BINOL oxygen atoms also provides straightforward access to BINOL derivatives. This synthetic route has been widely exploited as shown by the examples presented in Section 3.

2.3. *Synthesis of BINAM derivatives*

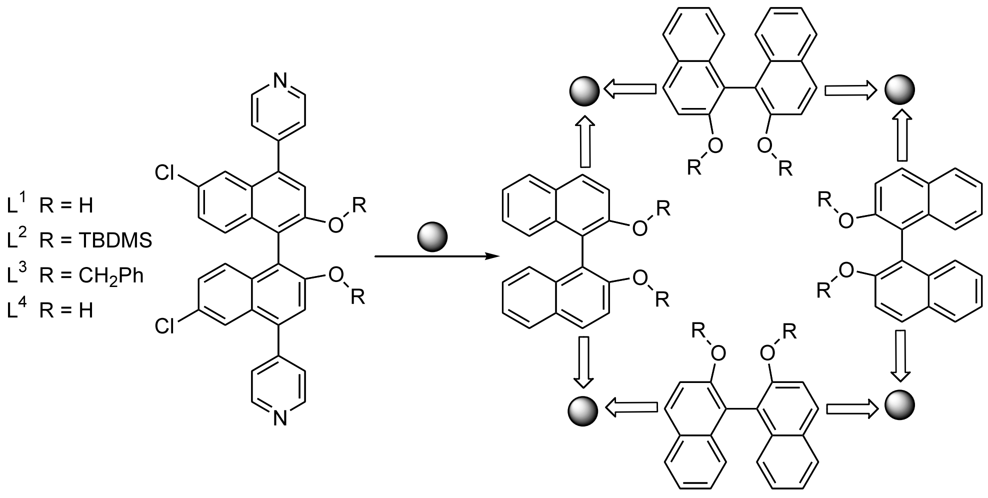
BINAM can be efficiently synthesized in its racemic form by the Cu(II)-catalysed coupling of 2-naphthylamine (Note: 2-naphthylamine is extremely carcinogenic). The same reaction in the presence of (−)-sparteine affords BINAM with an ee of 84% [24,25]. Enantiopure BINAM can be purchased from commercial sources. Synthetic approaches to ligands based on the BINAM scaffold have relied on functionalisation at the nitrogen atoms: there being very few literature reports of BINAM derivatives which are functionalised at any of the aromatic carbons. Most commonly this has involved condensation of the amine groups with an aromatic aldehyde to generate a Schiff-base ligand.

3. Coordination and supramolecular chemistry of derivatives of BINOL

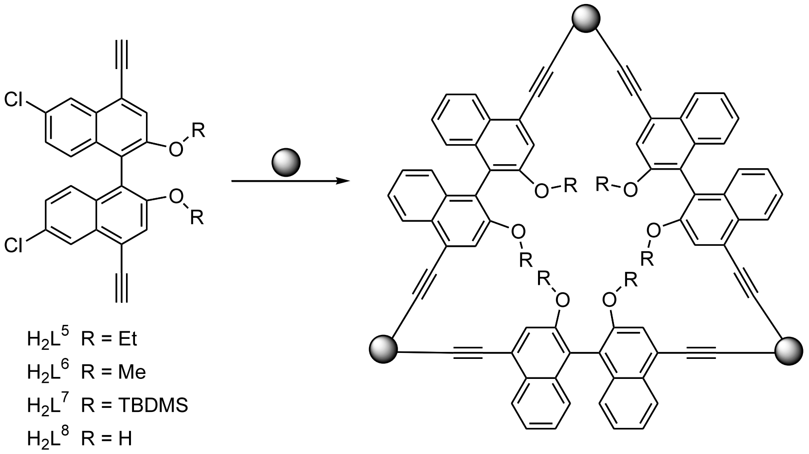
3.1. *Polynuclear complexes of derivatives of BINOL*

Ligands L^1–L^4 were synthesised by Lin et al. from commercially available enantiopure BINOL in good yield [26]. Upon refluxing with $[ReCl(CO)_5]$, the cyclic tetramers $[Re_4Cl_4(L^{1-4})_4(CO)_{12}]$ are formed (Scheme 1), and these were well characterised by NMR, mass spectrometry, UV–vis and CD spectroscopy. $[Re_4Cl_4(L^4)(CO)_{12}]$ was found to be luminescent in solution at room temperature, and the emission was assigned to both ligand-centred and MLCT excited states. This emission is quenched by chiral amino alcohols, probably as a result of their inclusion in the chiral cavity of $[Re_4Cl_4(R\text{-}L^4)_4(CO)_{12}]$ via hydrogen bonding interactions. Interestingly, the rate of quenching of the luminescence signal is highly enantiomer-dependent, thus the tetramer is able to function as an enantioselective sensor for chiral amino alcohols.

A series of molecular triangles was prepared from the enantiopure bis(alkynyl) derivatives H_2L^5–H_2L^8 [27] by reaction with a *cis*-protected Pt(II) centre, $[PtCl_2(PEt_3)_2]$, making use of the facile insertion of Pt(II) into alkyne C–H bonds to drive complex formation (Scheme 2). The organometallic triangles $[Pt_3(L^{5-8})_3(PEt_3)_6]$ were isolated and well characterised by a wide range of methods. Although the combination of 90° metallo-corners with linear linkers may be expected to produce molecular *squares*, the authors



Scheme 1. Schematic of the synthesis of a chiral cyclic tetramer with $ClRe(CO)_3$ corners (represented as grey spheres).

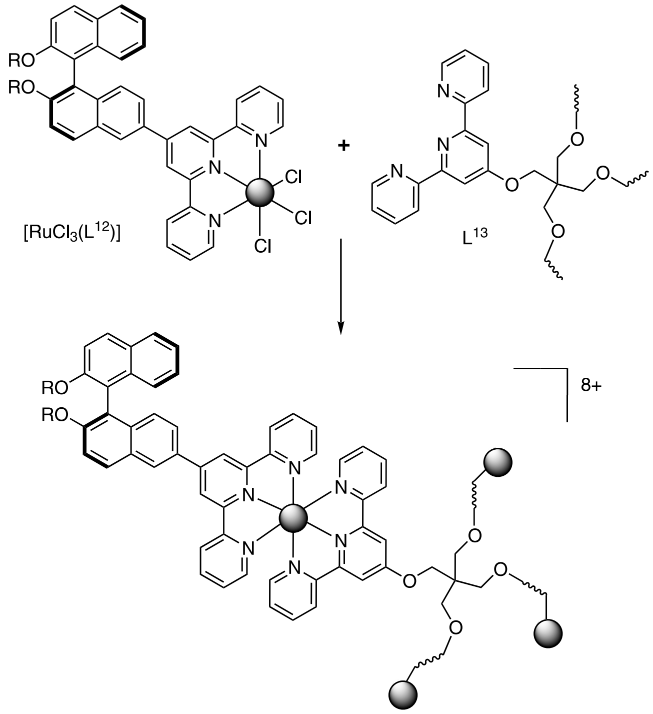


Scheme 2. Schematic of the synthesis of a molecular triangle with $Pt(PEt_3)_2$ corners (represented as grey spheres).

note that the observation of *triangles* in such cases is not without precedent. The free hydroxyl groups of $[Pt_3(L^8)_3(PEt_3)_6]$ enable the trimer itself to act as a ligand and, impressively, its Ti(IV) complex catalyses the addition of diethylzinc to aromatic aldehydes (giving ee's of up to 92% for a range of substrates). The same methodology was employed for the synthesis of the Pt-acetylide metallamacrocycles *cis*-$[Pt_2(PEt_3)_4(L^{9-11})_2]$ (Scheme 3) [28], which again proved to be effective metalloligands for asymmetric catalysis.

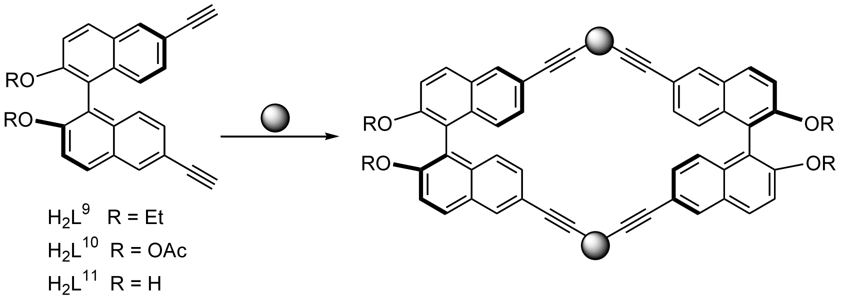
Although the potential for metallosupramolecular complexes to perform useful functions has long been touted, the above complexes represent some of the few examples where real functionality (sensing, catalysis) is observed in practice. These observations seem likely to stimulate further interest in the application of such metallosupramolecular complexes in these and other fields.

A chiral Ru(II) dendrimer has also been prepared by Lin's group [29]. Ligand *R*-L^{12}, prepared from enantiopure BINOL in five steps, was reacted with $RuCl_3$ to yield the complex $[RuCl_3(R\text{-}L^{12})]$ (Scheme 4). This complex was then used to cap the four termini of the tetrakis(terpyridine) ligand L^{13} to generate the tetranuclear dendrimer $[Ru_4(R\text{-}L^{12})_4(L^{13})]^{8+}$.

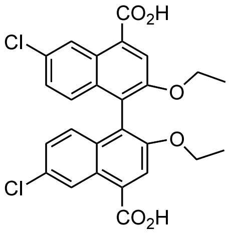


Scheme 4. Schematic of the construction of a tetranuclear metallodendrimer from the combination of ligand L^{12}, a tetrakis(terpyridine) core (L^{13}), and Ru (represented as a sphere).

BINOL derivatives have also found use in lanthanide chemistry, Lin's group having reported the synthesis of racemic H_2L^{14} (Fig. 3) and its reaction with Gd(III) and La(III) salts [30]. The ligand coordinates via its carboxylate groups to give a $[Ln_4(L^{14})_6(H_2O)_{12}]$ cluster which



Scheme 3. Schematic of the synthesis of a chiral metallamacrocycle with $Pt(PEt_3)_2$ linkers (represented as grey spheres).



H_2L^{14}

Fig. 3. The structure of H_2L^{14}.

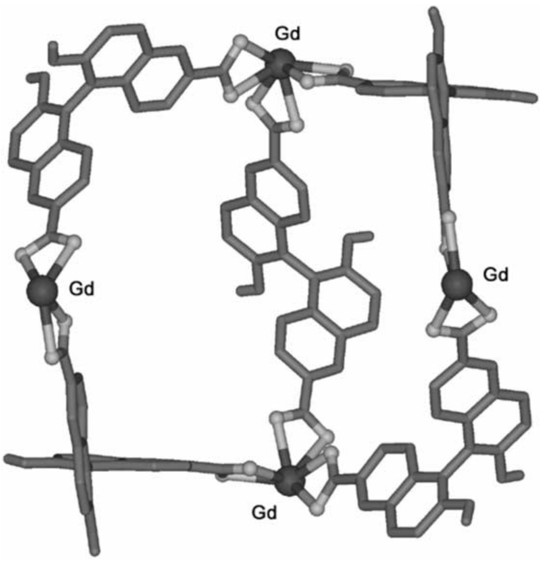


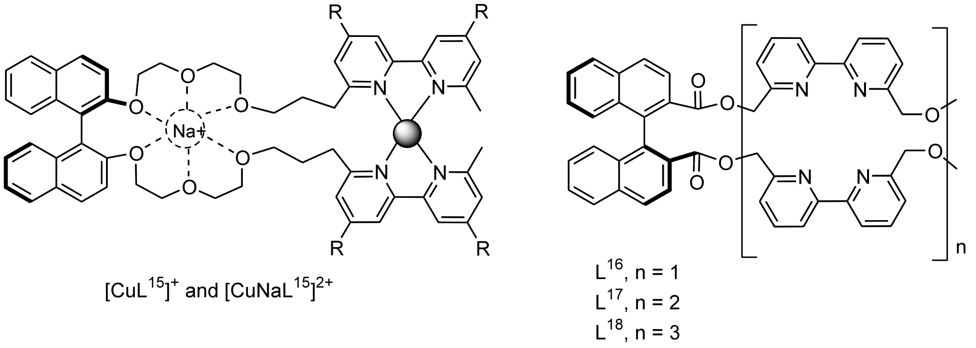
Fig. 4. X-ray crystal structure of the cluster $[Gd_4(L^{14})_6(H_2O)_{12}]$ (H_2O ligands removed for clarity).

was found to have an adamantoid structure by X-ray crystallography (Fig. 4). All the ligands in each cluster are of the same handedness (vide infra for further discussion of this phenomenon). A large number of intercluster hydrogen bonds were detected involving the free hydroxyl groups and the carboxylate oxygen atoms. These bonds connect each cluster to four of its neighbours which, are all of opposite chirality.

Recently, Nabeshima et al. reported the synthesis of the ligand R-L^{15} ($R = p$-$OMeC_6H_4$) in which a bipyridyl chelate is linked to both BINOL oxygens by a polyether chain [31]. Upon reaction with Cu(I), the complex $[Cu(R\text{-}L^{15})]^+$ is formed where the metal ion is coordinated to two bipyridyl units of the same ligand (Fig. 5a). The metal ion thereby becomes a stereogenic centre, hence two diastereomers are possible for the complex. Initially, the transfer of chiral information along the polyether chain from the binaphthyl unit to the metal centre is not very efficient; the two diastereomers of $[Cu(R\text{-}L^{15})]^+$ being formed in a 42:58 ratio. However, the addition of Na^+ cations, which bind to the polyether chains, changes the ratio of diastereomers to 89:11. Consequently a strong signal develops in the visible region of the CD spectrum. This is a very interesting example of a system whereby a chiroptical signal can be 'switched on' by upon the binding of an achiral guest (without the formation of a new stereogenic centre).

Although not strictly a derivative of BINOL, a report from Siegel's group concerning a series of ligands derived from S-1,1′-binaphthyl-2,2′-dicarboxylic acid is worthy of note. Strands containing up to three bipyridyl units were connected via ester linkages to the binaphthyl scaffold to give ligands L^{16}–L^{18} (Fig. 5b) [32]. Upon complexation to Cu(I), a single set of signals was observed in the ^{1}H-NMR spectrum and the signals in the CD spectrum became greatly amplified. This indicates firstly that polypyridyl chain wraps around the Cu(I) centres in a helical fashion, and secondly that this process is highly diastereoselective; the stereochemical information being efficiently transferred along the chain from the binaphthyl unit. Removal of the binaphthyl unit by hydrolysis of the ester moieties was attempted, however this led to decomplexation.

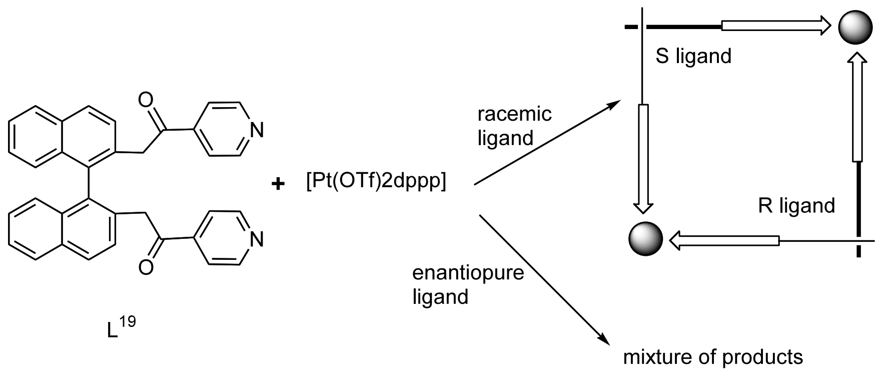
A number of systems have been reported in the literature whereby the reaction of a *racemic* mixture of a chiral ligand with metal ions resulted in a *homochiral* complex i.e. a complex where all the ligands possess the same handedness [33]. This kind of stereospecific association requires that the ligands undergo a self–self recognition process based solely on chirality. On the hand, far fewer systems displaying self-dis-



$[CuL^{15}]^+$ and $[CuNaL^{15}]^{2+}$

L^{16}, n = 1
L^{17}, n = 2
L^{18}, n = 3

Fig. 5. (a) $[CuL^{15}]^+$ and $[CuNaL^{15}]^{2+}$ (left); and (b) ligands L^{16}–L^{18}.



Scheme 5. The self-assembly of L^{19} and $[Ptdppp]^{2+}$ to give a molecular rectangle proceeds only if racemic ligand is used ($[Ptdppp]^{2+}$ corners represented as grey spheres).

crimination—the stereospecific association of ligands of *opposite* handedness to form heterochiral complexes—are known [34]. One example of self-discrimination has been recently noted for Pt(II) complexes of ligand L^{19} [35]. Upon reaction of enantiopure S-L^{19} with $[Pt(OTf)_2(dppp)]$, a complicated ^{1}H-NMR spectrum was observed, indicating that a mixture of products had formed (Scheme 5). However, reaction with *racemic* ligand produced a single set of ^{1}H-NMR resonances assignable to the *heterochiral* complex $[Pt_2(R\text{-}L^{19})(S\text{-}L^{19})(dppp)_2]^{4+}$. This assignment was supported by X-ray crystallography which showed the assembly to adopt a rectangular box-like structure.

A large number of transition metal helicates have been synthesised in recent years [36]. A number of design principles have emerged, foremost amongst which is the requirement that the binding units of each ligand strand are prevented from coordinating to the same metal ion. Often this involves the linking of the binding units by a rigid spacer unit. The BINOL framework appears ideally suited to this task and recently the synthesis of helicates derived from S-L^{20} (Fig. 6) was reported [37]. The utility of the chiral BINOL spacer became even more apparent when it was found that it efficiently 'predetermined' the chirality of the metal centres of the helicates. The solid-state structure of the $[Zn_2(S\text{-}L^{20})_3]^{4+}$ complex was elucidated by X-ray crystallography and the Zn(II) centres were found to adopt the Δ configuration (Fig. 7). This stereoselectivity is maintained in solution, as evidenced by NMR spectroscopy. Double helicates $[M_2(S\text{-}L^{20})_2]^{2+}$ are formed with the 'tetrahedral' metal ions Cu(I) and Ag(I), with NMR again indicating complete stereoselectivity at the metal centres.

Two other 3,3′-disubstituted binaphthol ligands have been reported. Gong and co-workers have found that vanadium complexes of the amino acid derivatives L^{21} function as enantioselective catalysts for the oxidation of 2-naphthols (to produce substituted 2,2′-bi-

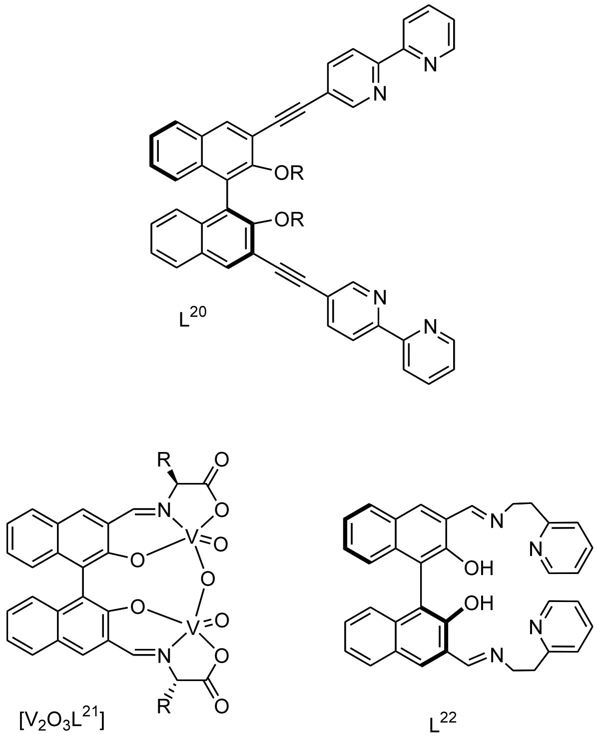


Fig. 6. 3,3′-Disubstituted BINOL ligands.

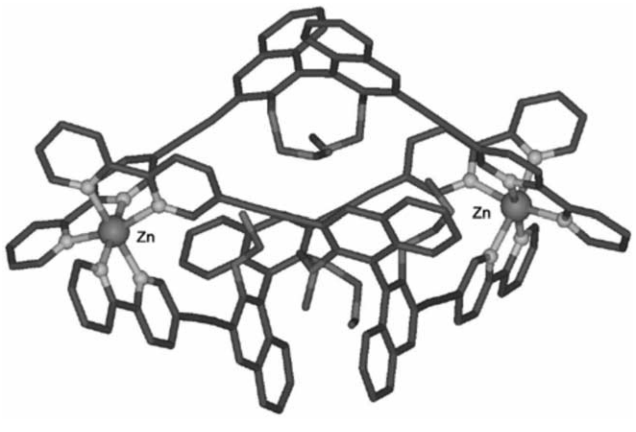


Fig. 7. X-ray crystal structure showing the non-hydrogen atoms of the complex cation Δ,Δ-$[Zn_2(S\text{-}L^{20})_3]^{4+}$.

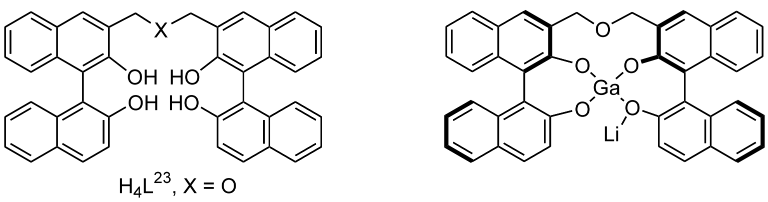


Fig. 8. The general structure of linked BINOL ligands (left), and the complex [GaLi(R,R-L^{23}].

naphthols). The catalysts were assigned the [$V_2O_3L^{21}$] structure presented in Fig. 6, however this assignment must be regarded as provisional as it is supported only by mass spectrometry and IR spectroscopy [38]. L^{22} (Fig. 6) was prepared by the condensation of 2-(2-pyridyl)ethylamine with S-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxaldehyde [39]. A green precipitate was obtained in high yield upon reaction with $Cu(OAc)_2$, and ES-MS and elemental analysis indicated that it was a complex with the stoichiometry [Cu_2-L^{22}]$(OAc)_2$, though no attempts to further characterise this product were reported.

Shibasaki's group have prepared a number of 'linked BINOL' ligands which feature two BINOL units connected via their 3-positions by an alkyl, ether, or sulfide bridge (Fig. 8) [40]. A number of complexes of L^{23} have been reported, including the heterobimetallic complex [GaLi(R,R-L^{23})] which was characterised by X-ray crystallography [41]. As envisioned by the authors, the ligand coordinates to the Ga(III) centre in a bisbidentate fashion, providing an environment at the metal centre similar to other catalytically active binaphthoxide complexes. The complex [GaLi(R,R-L^{23})] functions effectively as a catalyst for the asymmetric ring-opening of *meso*-epoxides with 4-methoxyphenol [40]. The heterobimetallic complex [La(ZnEt)(R,R-L^{23})] was found to catalyse Michael addition reactions, giving excellent ee's [42].

Upon reaction of ligand S,S-H_4L^{23} with Et_2Zn, an effective catalyst for Michael addition and Aldol reactions is formed [43]. Initially, this catalyst was tentatively proposed to be [Zn_2(S,S-L^{23})]. However, a very recent X-ray crystallographic study demonstrated that the complex [Zn_3(S,S-L^{23})$_2$] (Fig. 9) is the actual product [44], and ^{1}H-NMR and CSI-MS indicated that this complex is also present in solution. Detailed mechanistic studies, however, suggest that the catalytic picture is rather more complicated and that an ill-defined oligomeric Zn-rich species such as [Zn_7(S,S-L^{23})$_3$] or [Zn_4(S,S-L^{23})$_3$] is the catalytically active species.

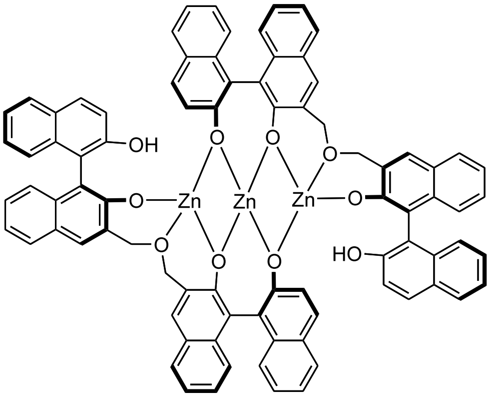
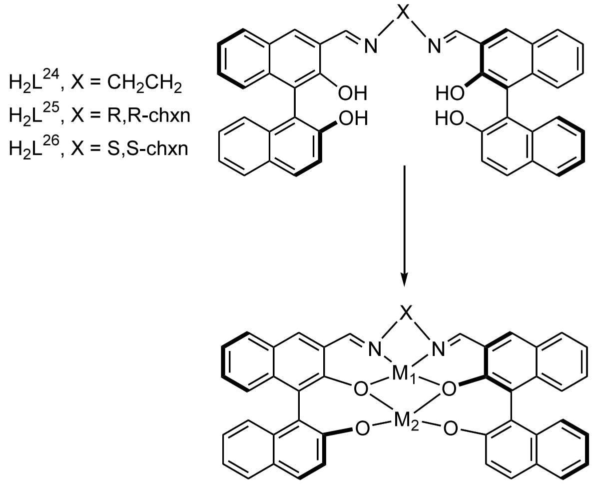


Fig. 9. The reaction of S,S-H_4L^{23} with $ZnEt_2$ affords complex [Zn_3(S,S-HL^{23})$_2$]. Each Zn(II) is also coordinated by a THF molecule (omitted).

DiMauro and Kozlowski have recently described the synthesis and coordination chemistry of a series of similar ligands S,S-H_4L^{24}-S,S-H_4L^{26} (Scheme 6) [45]. Reaction with $M(OAc)_2$ salts (M = Ni(II), Cu(II), Pd(II)) affords the corresponding [M_1(S,S-H_2L^{24-26})] complexes where the ligand coordinates to the metal ion in a tetradentate fashion via both imine nitrogens and the proximate oxygen donors. The similarity to salen-type complexes was reinforced by the X-ray crystal structure of [Ni(S,S-H_2L^{24})] which shows the Ni(II) centre to adopt a square planar geometry. A range of heterobimetallic complexes was generated by the addition of NaO^{t}Bu, LiO^{t}Bu, KO^{t}Bu, or Cs_2CO_3, where the second metal ions (M_2) are coordinated by the deprotonated ancillary naphthol groups. These bimetallic complexes proved to be effective catalysts for the Michael addition reaction of benzyl malonate to cyclohexanone, giving ee's of up to 90%.



Scheme 6. The synthesis of heterobimetallic complexes of ligands L^{24}–L^{26}.

3.2. Metal-organic coordination polymers based on derivatives of BINOL

Motivated by potential applications in enantioselective sensing and separations, a number of research groups have employed ligands derived from BINOL for the synthesis of homochiral metal-organic coordination polymers.

Enantiopure H_2R- and H_2S-L^{14} were reacted with M(II) metal salts (M = Mn(II), Co(II)), in a pyridine/DMF/methanol/water solvent mixture [46]. Crystals formed from the reaction mixture, and X-ray crystallography showed the coordination environment of the metal centres to be as shown in Fig. 10. Each dinuclear core is linked to four others by coordination of the *exo*-carboxylate group. A rhombohedral 2-D grid structure is thereby created. Chiral cavities are formed within these grids, however, these are not aligned into channels in the third dimension.

Enantiopure H_2L^{14} was also reacted with a range of lanthanides salts to produce a series of homochiral coordination networks [47]. In this instance, a very unusual six-connected topology was observed with two independent hexagonal grids identified. A narrow channel lined by the ligand ethoxy groups and chlorine atoms is formed in the crystal.

The bisphosphonate ligand R-H_4L^{27} (Fig. 11), prepared from R-BINOL in four steps, was employed as a chiral building block for the synthesis of homochiral metal-organic networks with $MnCO_3$, $CoCO_3$, $2NiCO_3 \cdot 3Ni(OH)_2$, CuO, and $Zn(ClO_4)_2$ [48]. X-ray crystallography revealed that the ligands coordinate via their deprotonated phosphonate groups with solvent molecules completing the coordination spheres in some instances. As the phosphonate groups of each ligand are unable to bind to the same metal centre, it was noted that the ligands often form bridges between two metal centres. This bridging mode was responsible for the formation of infinite chains within many of the crystal structures, and was assisted by hydrogen-bonding motifs in the building up of networked 2- and 3-D structures. In terms of potential applications as porous solids, the Mn(II) and Co(II) networks are most interesting as they display rather open framework structures.

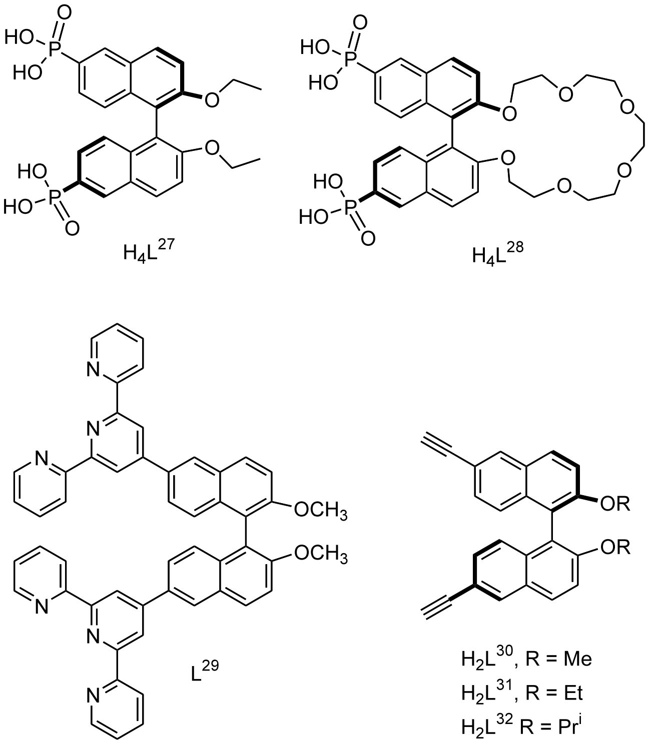


Fig. 11. Chiral BINOL-derived ligands employed for the construction of metal-organic coordination polymers.

The crown ether/phosphonate ligand R-H_4L^{28} (Fig. 11) was reacted with lanthanide ions (Nd(III) and Sm(III)) to produce homochiral solids [49]. As often observed for L^{27}, the phosphonate groups of each ligand bind to different metal centres to create a 2-D coordination network. The crown ether groups lie sandwiched between these layers along with free R-H_4L^{28}. The structure of these solids is rather compact which has thus far prevented their application in chiral separations.

Kimura et al. synthesised the 6,6′-terpyridyl appended binaphthols R- and S-L^{29} (Fig. 11) via a Krohnke methodology [50]. The ligand was designed so that the divergent orientation of the two chelate vectors would encourage the ligand to coordinate to two metal centres in a bridging fashion, thereby forming a single-stranded

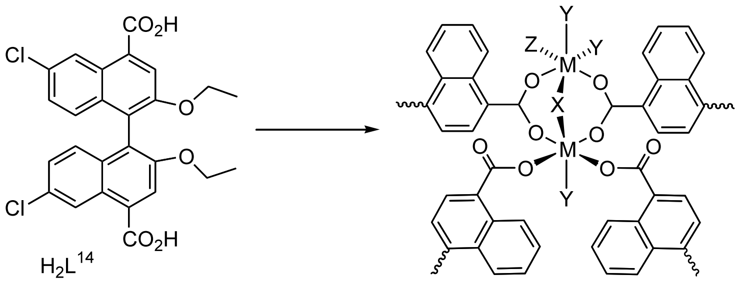


Fig. 10. The coordination environment of the Mn(II) and Co(II) centres in coordination polymer networks with L^{14} (X, H_2O; Y, pyridine; Z, DMF).

coordination polymer. Indeed, upon reaction with Fe(II), UV–vis and CD spectral changes consistent with the formation of a chiral [Fe(II)(terpy)$_2$]-type complex were noted. The polymeric nature of the $[Fe_n(L^{29})_n]^{2n+}$ product was established by GPC which indicated that the average coordination polymer comprises around 50 repeat units.

The 6,6′-acetylene functionalised ligands R-H_2L^{30}–R-H_2L^{32} (Fig. 11) lead to metallopolymers with molecular weights in the range 5–100 kDa upon reaction with *trans*-[M(PEt)$_3$Cl$_2$] (M = Pt(II), Pd(II)) [51]. These ligands are very similar to those subsequently employed by Lin for the synthesis of metallamacrocycles $[Pt_2(PEt_3)_4(L^{9-11})_2]$ discussed above. The crucial difference lies with the stereochemistry of the metal centre: *cis*-protected M(II) centres lead to discrete dinuclear complexes whilst *trans*-protected centres yield polymeric products.

4. Coordination and supramolecular chemistry of BINAM and its derivatives

4.1. Coordination chemistry of BINAM

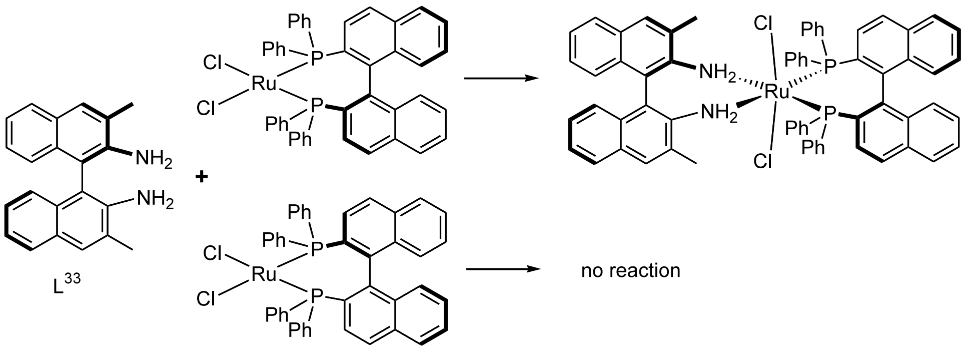
The majority of early literature reports concerning the coordination chemistry of the free BINAM ligand are notable for their poor characterisation of the obtained products. Whilst it is a reasonable assumption that BINAM should act as a bidentate ligand, it was not before 1999 that, on the basis of experimental data, this could be stated with certainty! Somewhat surprisingly, there have not been any reports of complexes containing more than one BINAM ligand.

The first paper concerning a metal complex of BINAM appeared in 1985 [52], detailing the reaction of R-BINAM with K_2PtCl_4 to yield [PtCl$_2$(R-BINAM)]. The [PtCl$_2$(R-BINAM)] complex was characterised by elemental analysis, UV and CD spectroscopy, and was subsequently reacted with a racemic mixture of R,R/S,S-chxn. The complex $[Pt(R,R\text{-chxn})(R\text{-BINAM})]^{2+}$ crystallised from the reaction mixture in 27% yield. From this observation, the authors concluded that coordination of the chxn [PtCl$_2$(R-BINAM)] ligand is stereoselective, generating *exclusively* $[Pt(R,R\text{-chxn})(R\text{-BINAM})]^{2+}$. However, this conclusion seems to have little validity as no attempt was made to characterise the reaction products which remained in solution. A further report from this group describes the preparation and CD spectra of a series of [Pt(R-BINAM)X$_2$] and [Pt(R-BINAM)X$_2$] complexes ($X = H_2O$, X_2 = dab, dap) and contains a useful discussion of the CD spectra of these complexes [53].

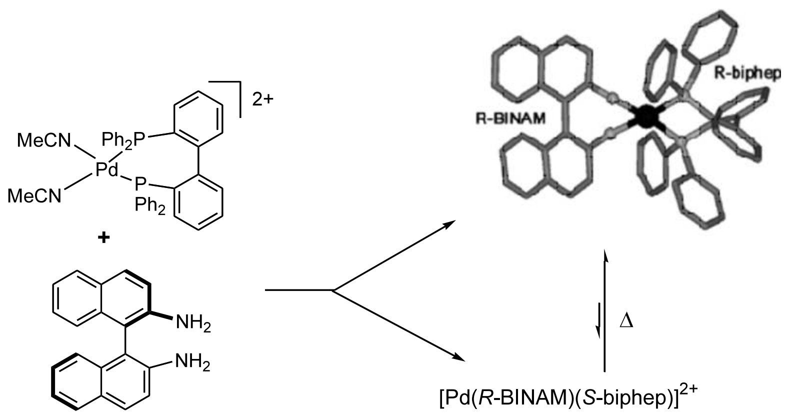
The photochemistry of the complex [PtCl$_2$(BINAM)] (characterised only by elemental analysis and UV spectroscopy) has been investigated and it was found that, unlike free BINAM, it is not emissive [54]. Steady state photolysis of this complex in the UV or visible wavelength regions leads to expulsion of the BINAM ligand.

[Cr(CO)$_4$(BINAM)] was isolated as an air-sensitive solid from the reaction of R-BINAM with [Cr(CO)$_4$(norbornadiene)] [55], and was well characterised by a variety of methods. Reaction of BINAM with a Ti(IV)-alkoxide precursor gave [TiCl$_2$ (O-2,6-Me$_2$-C$_6$H$_3$)$_2$(BINAM)], which was characterised by ^{1}H-NMR. Binding was found to be rather weak compared with other diamine ligands [56].

Mikami's group have investigated the reaction of R-3,3′-dimethyl-BINAM (R-L^{33}) with two equivalents of racemic [RuCl$_2$(BINAP)] [57]. The outcome is very interesting: the sole product is [RuCl$_2$(R-L^{33})(R-BINAP)]. This implies that R-L^{33} is unreactive towards [RuCl$_2$(S-BINAP)], and coordinates stereospecifically to [RuCl$_2$(R-BINAP)] (Scheme 7). This observation was rationalised by noting that the [RuCl$_2$(R-L^{33})(S-BINAP)] diastereomer would incur sever steric strain. [RuCl$_2$(R-L^{33})(R-BINAP)] was characterised in the solid state by X-ray crystallography. Although this complex is itself a rather poor catalyst for the asymmetric hydrogenation of ketones, it was used in conjunction with [RuCl$_2$(R,R-dpen)(S-BINAP)] as part of an 'asymmetric activation' strategy [58].



Scheme 7. R-L^{33} reacts with [RuCl$_2$(R-BINAP)] though not with [RuCl$_2$(S-BINAP)].



Scheme 8. Control of the axial chirality of the coordinated biphep ligand by R-BINAM in complexes [Pd(R-BINAM)(biphep)]$^{2+}$. The structure of the [Pd(R-BINAM)(biphep)]$^{2+}$ cation is shown (hydrogen atoms omitted).

Upon bidentate coordination to a metal centre, the biphep ligand is rendered atropisomeric. Consequently, two diastereomers are possible for the complex [Pd(biphep)(R-BINAM)]$^{2+}$ which was synthesized by Mikami's group [59]. At elevated temperatures, where the two atropisomeric forms of biphep are able to interconvert, the [Pd(R-biphep)(R-BINAM)]$^{2+}$ diastereomer is formed exclusively (Scheme 8). Thus, the chirality of the R-BINAM ligand controls the axial chirality of the biphep ligand. This complex was characterised by X-ray crystallography—the first such characterisation of a complex of BINAM. The [Pd(R-biphep)(R-BINAM)]$^{2+}$ complex was employed as an activated asymmetric catalyst for hetero Diels–Alder reactions, achieving higher yields and enantioselectivities than the non-activated [Pd(R-biphep)(CH_3CN)$_2$]$^{2+}$ catalyst [60].

In related work, Mikami's group also reported that R-BINAM and R-L^{33} can control the axial chirality of the chirally dynamic dppf ligand in complexes of the type [M(dppf)(R-BINAM)] and [M(dppf)(R-L^{33})]$^{2+}$ (M = Ni(II), Pd(II), Pt(II)) [61]. The thermodynamically most stable diastereomer has the dppf ligand in the P configuration. The Ni(II) complexes were found to be particularly effective asymmetric catalysts for the C–C bond forming reaction between alkenes and ethyl glyoxylate.

4.2. Mononuclear complexes of derivatives of BINAM

The N-methylated derivatives of BINAM, L^{34} and L^{35} (Fig. 12), have been synthesized and along with BINAM, were reacted with [MCl(diene)] (M = Rh(I), Ir(I); diene = COD, NBD, HEX). These reactions afforded complexes [M(diene)(BINAM)]$^{+}$ and [M(diene)(L^{34})]$^{+}$ [62]. However, L^{35} failed to coordinate to the metal centre, the authors attributing this to ligand rigidity imposed by the NMe$_2$ groups.

Schiff base derivatives of BINAM of the general type L^{36} have found wide application in coordination chemistry. These complexes and their application to asymmetric catalysis are the subject of another review in this issue by Che and Huang [63].

Salicaldimine ligands have also been employed in the realm of biomimetic chemistry; a series of Cu complexes of S-H$_2$L^{37} and S-H$_2$L^{38} were investigated by Wang et al. as models of the enzyme galactose oxidase [64]. The ligands were carefully designed; the binaphthyl backbone ensures non-square-planar geometry at the metal centre, and the substituents on the phenyl ring serve to stabilise the phenoxyl radical generated by one electron oxidation of the complex. Despite being only very approximate *structural* models of the enzyme, the complexes are remarkable *functional* models, catalysing the oxidation of benzylic and allylic alcohols to aldehydes with O$_2$ under mild conditions.

The Schiff base-phosphine ligand L^{39} is readily prepared from BINAM and 2-diphenylphosphinoben-

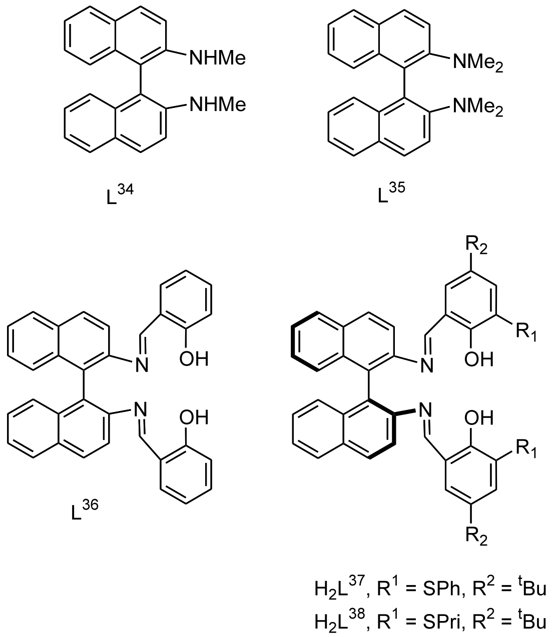
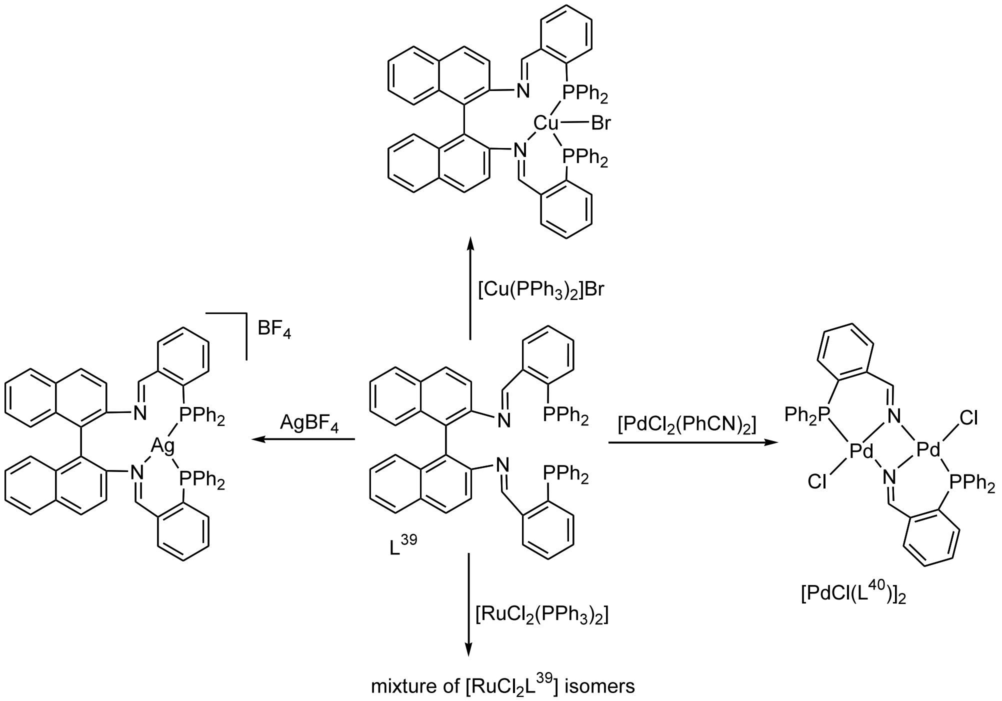


Fig. 12.



Scheme 9. Summary of the coordination chemistry of ligand L^{39}.

zaldehyde. Its coordination behaviour is summarised in Scheme 9. Upon reaction with $[Cu(Ph_3P)_2Br]$, *rac*-L^{39} forms the complex $[CuBrL^{39}]$ [65]. X-ray crystallography demonstrated that the ligand coordinates via both phosphorous donors but via only one of the imino nitrogens. The bromide anion completes the Cu(I) coordination sphere to give a distorted tetrahedral geometry. ^{1}H-NMR spectroscopy in solution showed that the coordinated and uncoordinated imino groups are in rapid exchange even at low temperature. L^{39} behaves in a similar tridentate fashion when reacted with $AgBF_4$ [66]. X-ray crystallography showed that the Ag(I) centre adopts a distorted trigonal planar geometry in the solid state, with the long Ag-imino bond length indicative of a very weak interaction. This interaction persists in solution although, in contrast to the Cu(I) complex, the bound and unbound imino groups exchange slowly if at all.

Upon reaction with $[PdCl_2(PhCN)_2]$ at room temperature, ligand L^{39} was found to eliminate the binaphthylene backbone to give the neutral dimer $[PdClL^{40}]_2$ [67]. This behaviour is in sharp contrast to its biphenyl analogue which forms a square planar $[PdL]^{2+}$ complex under the same reaction conditions [68].

Reaction of $[RuCl_2(PPh)_3]$ with ligand *S*-L^{39} gave $[RuCl_2L^{39}]$ where the ligand coordinates in a tetradentate fashion [69]. Several geometrical isomers are possible for this complex, and it was found that ratio of *cis* and *trans* isomers was dependent on the reaction conditions. When the ligand is wrapped in a *cis* fashion, the Ru(II) centre becomes stereogenic. However, the reaction was not particularly stereoselective, giving a Δ-(cis-β) : Λ-(cis-β) ratio of 5 : 4.

Reetz et al. reported that the reaction of *R*-BINAM with Ph_3PBr_2 yields the diiminophosphorane ligand *R*-L^{41} (Fig. 13). The ligand was reacted with CuOTf, and though the resulting complex was not characterised, it was found to be a useful catalyst for the asymmetric cyclopropanation of styrene by ethyl diazoacetate [70]. Presumably the ligand forms a 1:1 complex with Cu(I), coordinating via both nitrogen centres, as noted for complexes of a related ligand with Rh(I) and Co(II). Reetz's group also investigated ligands *S*-L^{42}–*S*-L^{45} and found that their Pd complexes were active catalysts for allylic substitution reactions and for copolymerisation of *p*-*tert*-butylstyrene with carbon monoxide [71]. Again the complexes were not isolated or characterised though the ligand presumably acts as a bidentate ligand coordinating through both nitrogen atoms.

The Schiff-base ligand H_2L^{46} (Fig. 13) has been prepared and its coordination chemistry with Cu(II) investigated. Based on analogies to similar ligands, L^{46} was assumed to coordinate in a bis(bidentate) fashion via its imine nitrogen and thiolate sulphur donors [72]. The solid-state structures of complexes of similar ligands suggest that the Cu(II) may have a distorted tetrahedral geometry [73].

The Ir(I) and Rh(I) complexes of L^{47}, though not well characterised, were found to be useful catalysts for the asymmetric hydrogenation of ketones, whilst the trimethylsilylcyanation of benzaldehyde was catalysed by its Ti(IV) derivative [74,75].

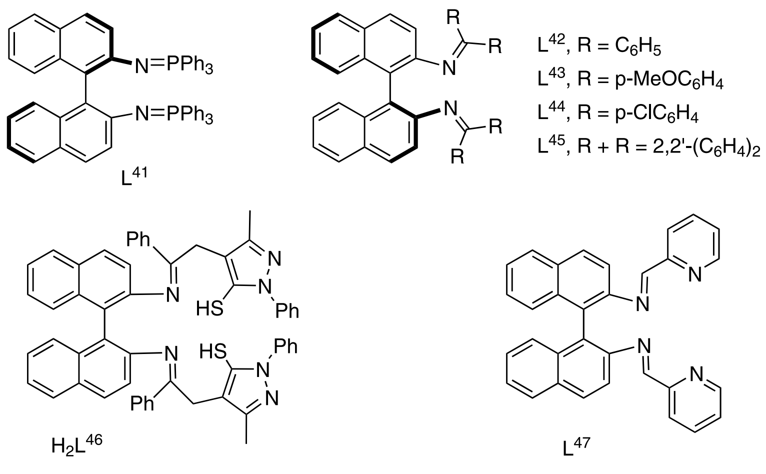


Fig. 13.

4.3. Polynuclear complexes of derivatives of BINAM

The dinuclear Cu(II) macrocyclic complex $[Cu_2L^{49}]^{2+}$ was reported recently by Panther et al. [76]. The macrocycle is constructed via a two-step template methodology, with double condensation of $[CuL^{48}]$ with *S*-BINAM giving the final product in high yield (Scheme 10). The complex was characterised in the solid state by X-ray crystallography.

Recently, Hannon's group employed ligand L^{47} for the diastereoselective synthesis of dinuclear double helicates $[M_2(L^{47})_2]^{2+}$ (M = Cu(I), Ag(I)) [77]. The solid state structures of $[Ag_2(R\text{-}L^{47})_2]^{2+}$ and of $[Ag_2(S\text{-}L^{47})_2]^{2+}$ were elucidated by X-ray crystallography. Significant pyridyl–naphthalene π-stacking was observed, and the geometry at the Ag(I) centres was found to be intermediate between tetrahedral and square planar (Fig. 14). The stereochemistry of the helicates was dependent on the chirality of the ligand, with R-L^{47} leading to a *P* helicate. The stereochemical integrity of the complex was maintained in solution as shown by NMR, ES-MS, and CD spectroscopy.

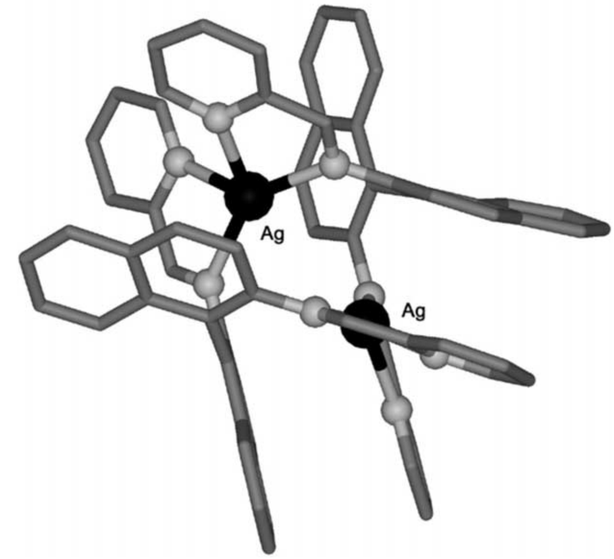
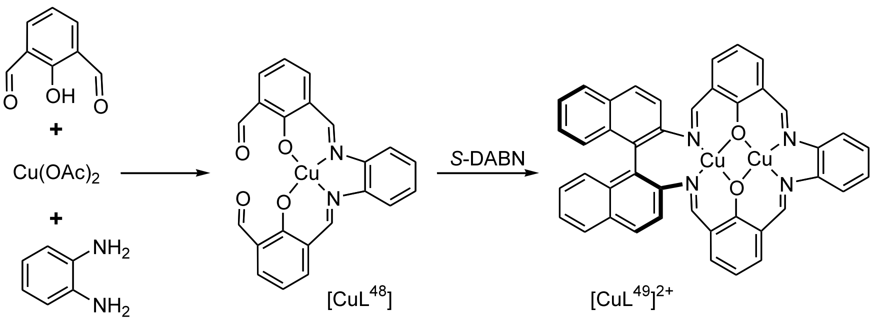


Fig. 14. X-ray crystal structure of the P-$[Ag_2(R\text{-}L^{47})_2]^{2+}$ cation emphasising the distortion from tetrahedral geometry at the Ag(I) centres. Hydrogen atoms omitted.

Why does the coordination behaviour of L^{47} contrast strikingly with its salicaldimine analogues L^{36} which form only mononuclear complexes? In order to shed some light on this question we have recently launched a research project focussing on the synthesis and coordination chemistry of ligands based on the BINAM framework [78]. Initially, we have set out to investigate the complexation behaviour of some close analogues of L^{47}: the novel ligands R-L^{50} and R-L^{51} (Fig. 15). With



Scheme 10. The Cu(II)-templated construction of a dinuclear macrocyclic complex.

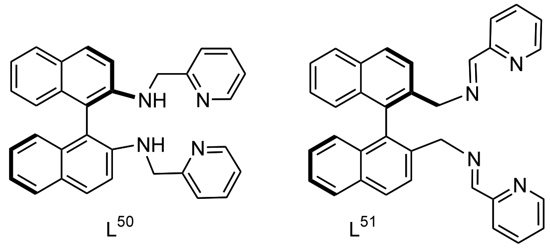


Fig. 15.

respect to the solid state behaviour of their Ag(I) complexes, preliminary results indicate that $[Ag(R\text{-}L^{51})]^+$ and $[Ag_2(R\text{-}L^{51})_2]^{2+}$ co-crystallise. In solution, however, only complex $[Ag(R\text{-}L^{51})]^+$ can be detected. $[Ag(R\text{-}L^{50})]^+$ is observed in solution with no trace of any polynuclear species. It is plausible that the extra flexibility of L^{50} and L^{51} (as compared to L^{47}) enables them to form mononuclear complexes in solution, and that energetically favourable π–π stacking effects encourage the formation of $[Ag_2(R\text{-}L^{51})_2]^{2+}$ in the solid state.

5. Summary

The construction of chiral coordination compounds from ligands based on BINOL and BINAM frameworks is a rapidly growing field. The versatility of this approach for the construction of polynuclear coordination compounds of derivatives of BINOL is highlighted by Fig. 16. Moreover, this figure underscores one of the most promising aspects of this chemistry: the ability to *rationally* design chiral polynuclear complexes. Ligands can be designed by the judicious placement of donor groups which have a suitable ligand binding vector at an appropriate position on the binaphthyl skeleton. In combination with metal ions which have a particular stereochemical preference, the desired complex often readily self-assembles. Furthermore, the chiral information contained in the binaphthyl unit is often efficiently transferred to any new stereogenic metal centres. Recent developments regarding *functional* aspects of these complexes, such as the ability to act as catalysts and sensors, are particularly exciting.

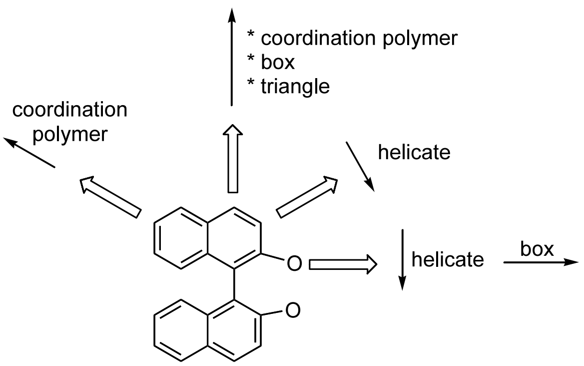


Fig. 16. The formation of various metallosupramolecular arrays from ligands derived from BINOL. The thick arrows represent the point of attachment of the ligating group, and the thin arrows describe the binding vector of the ligand.

BINAM has been employed as a ligand for a relatively small number of complexes though a number of interesting advances regarding the synthesis of complexes of derivatives of BINAM have been made recently. There are, however, many more reports pertaining to derivatives of BINOL and this inequality is likely to persist given the wide range of synthetic routes which give access to these compounds, and the extreme toxicity of 2-naphthylamine (which serves a synthetic precursor to BINAM).

Acknowledgements

We gratefully acknowledge the groups of Professor M. Shibasaki for providing us with some of their unpublished results, and of Professor C.-M. Che for an outline of their manuscript. We thank Dr M. Seki of Tanabe Seiyaku, Japan, for a generous gift of 1,1′-binaphthyl-2,2′-dicarboxylic acid. The Japan Society for the Promotion of Science (JSPS) is thanked for the provision of a post-doctoral fellowship to SGT.

References

[1] E.L. Eliel, S.H. Wilen, L.N. Mander, Stereochemistry of Organic Compounds, John Wiley & Sons, New York, 1994.
[2] There are two common abbreviations for 2,2′-diamino-1,1-binapthyl in the literature: BINAM and DABN. We prefer the latter given its resemblance to the familiar BINAP and BINOL.
[3] U. Knof, A. Von Zelewsky, Angew. Chem. Int. Ed. 38 (1999) 303.
[4] C. Provent, A.F. Williams, in: J.P. Sauvage (Ed.), Transition Metals in Supramolecular Chemistry, John Wiley and Sons, 1999, p. 135.
[5] A. Von Zelewsky, Stereochemistry of Coordination Compounds, Wiley, Chichester, 1996.
[6] A. Von Zelewsky, O. Mamula, J. Chem. Soc. Dalton Trans. (2000) 219.
[7] H.C. Aspinall, Chem. Rev. 102 (2002) 1807.
[8] H.C. Aspinall, N. Greeves, J. Organomet. Chem. 647 (2002) 151.
[9] L. Pu, Chem. Rev. 98 (1998) 2405.
[10] G. Bringmann, R. Walter, R. Weirich, Angew. Chem. Int. Ed. 29 (1990) 977.
[11] J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359.
[12] M. Noji, M. Nakajima, K. Koga, Tetrahedron Lett. 35 (1994) 7983.
[13] H.-F. Chow, M.-K. Ng, Tetrahedron: Asymmetry 7 (1996) 2251.
[14] Z.-Q. Xin, C.-S. Da, S.-L. Dong, D.-X. Liu, J. Wei, R. Wang, Tetrahedron: Asymmetry 13 (2002) 1937.
[15] C.W. Lim, S.-G. Lee, Tetrahedron 56 (2000) 5131.
[16] Q.-S. Hu, D. Vitharana, L. Pu, Tetrahedron: Asymmetry 6 (1995) 2123.
[17] See Ref. [18] for a list of examples.

[18] B.M. Panchal, C. Einhorn, J. Einhorn, Tetrahedron Lett. 43 (2002) 9245.

[19] M. Putala, Enantiomer 4 (1999) 243.

[20] Z. Luo, Q. Liu, L. Gong, X. Cui, A. Mi, Y. Jiang, Angew. Chem. Int. Ed. 41 (2002) 4532.

[21] M. Nakajima, I. Miyoshi, K. Kanayama, S.-I. Hashimoto, M. Noji, K. Koga, J. Org. Chem. 64 (1999) 2264.

[22] H.-J. Deussen, E. Hendrickx, C. Boutton, D. Krog, K. Clays, K. Bechgaard, A. Persoons, T. Bjornholm, J. Am. Chem. Soc. 118 (1996) 6841.

[23] J.M. Chong, L. Shen, N.J. Taylor, J. Am. Chem. Soc. 122 (2000) 1822.

[24] M. Smrcina, M. Lorenc, V. Hanus, P. Kocovsky, Synlett (1991) 231.

[25] M. Smrcina, M. Lorenc, V. Hanus, P. Sedmera, P. Kocovsky, J. Org. Chem. (1992) 1917.

[26] S.J. Lee, W. Lin, J. Am. Chem. Soc. 124 (2002) 4554.

[27] S.J. Lee, A. Hu, W. Lin, J. Am. Chem. Soc. 124 (2002) 12948.

[28] H. Jiang, A. Hu, W. Lin, Chem. Commun. (2003) 96.

[29] H. Jiang, S.J. Lee, W. Lin, J. Chem. Soc. Dalton Trans. (2002) 3429.

[30] Y. Cui, H.L. Ngo, W. Lin, Inorg. Chem. 41 (2002) 5940.

[31] T. Nabeshima, A. Hashiguchi, T. Saiki, S. Akine, Angew. Chem. Int. Ed. 41 (2002) 481.

[32] R. Annunziata, M. Benaglia, M. Cinquini, F. Cozzi, C.R. Woods, J.S. Siegel, Eur. J. Org. Chem. (2001) 173.

[33] For example, see: (a) S.G. Telfer, A.F. Williams, G. Bernardinelli, Chem. Commun. (2001) 1498;
(b) M.A. Masood, E.J. Enemark, T.D.P. Stack, Angew. Chem. Int. Ed. 37 (1998) 928;
(c) D.L. Caulder, K.N. Raymond, Angew. Chem. Int. Ed. 36 (1997) 1440.

[34] For example, see: (a) X.-G. Zhou, J.-S. Huang, Z.-Y. Zhou, K.-K. Cheung, C.-M. Che, Inorg. Chim. Acta 331 (2002) 194;
(b) C. Mazet, L.H. Gade, Chem. Eur. J. 8 (2002) 4308.

[35] T.W. Kim, M.S. Lah, J.-I. Hong, Chem. Commun. (2001) 743.

[36] C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. 97 (1997) 1181.

[37] A. Lutzen, M. Hapke, J. Griep-Raming, D. Haase, W. Saak, Angew. Chem. Int. Ed. 41 (2002) 2086.

[38] Z. Luo, Q. Liu, L. Gong, X. Cui, A. Mi, Y. Jiang, Chem. Commun. (2002) 915.

[39] A. Raffaelli, F. Minutolo, B.L. Feringa, P. Salvadori, Inorg. Chim. Acta 275–276 (1998) 462.

[40] S. Matsunaga, T. Ohshima, M. Shibasaki, Adv. Synth. Cat. 344 (2002) 3.

[41] T. Arai, Y. Yamada, N. Yamamoto, H. Sasai, M. Shibasaki, Chem. Eur. J. 2 (1996) 1368.

[42] S. Matsunaga, T. Ohshima, M. Shibasaki, Tetrahedron Lett. 41 (2000) 8473.

[43] N. Kumagai, S. Matsunaga, M. Shibasaki, Org. Lett. 3 (2001) 4251.

[44] N. Kumagai, S. Matsunaga, T. Kinoshita, S. Harada, S. Okada, S. Sakamoto, K. Yamaguchi, M. Shibasaki, J. Am. Chem. Soc., 125 (2003) 2169.

[45] E.F. DiMauro, M.C. Kozlowski, Organometallics 21 (2002) 1454.

[46] Y. Cui, O.R. Evans, H.L. Ngo, P.S. White, W. Lin, Angew. Chem. Int. Ed. 41 (2002) 1159.

[47] Y. Cui, H.L. Ngo, P.S. White, W. Lin, Chem. Commun. (2002) 1666.

[48] O.R. Evans, D.R. Manke, W. Lin, Chem. Mater. 14 (2002) 3866.

[49] H.L. Ngo, W. Lin, J. Am. Chem. Soc. 124 (2002) 14298.

[50] M. Kimura, M. Sano, T. Muto, K. Hanabusa, H. Shirai, N. Kobayashi, Macromolecules 32 (1999) 7951.

[51] K. Onitsuka, Y. Harada, F. Takei, S. Takahashi, Chem. Commun. (1998) 643.

[52] M.-J. Jun, C.F. Liu, Bull. Korean Chem. Soc. 6 (1985) 173.

[53] M.-J. Jun, C.F. Liu, Bull. Korean Chem. Soc. 6 (1985) 214.

[54] H. Kunkley, A. Vogler, J. Photochem. Photobiol., A 114 (1998) 193.

[55] M. Strotmann, H. Butenschon, Eur. J. Org. Chem. (2000) 2273.

[56] A.O. Larsen, P.S. White, M.R. Gagne, Inorg. Chem. 38 (1999) 4824.

[57] K. Mikami, T. Korenaga, T. Ohkuma, R. Noyori, Angew. Chem. Int. Ed. 39 (2000) 3707.

[58] A chiral activator selectively activates one enantiomer of a racemic catalyst to attain higher enantioselectivity than that achieved with the enantiopure catalyst. See K. Mikami, M. Terada, T. Korenaga, Y. Matsumoto, M. Ueki, R. Angelaud, Angew. Chem. Int. Ed. 39 (2000) 3532.

[59] K. Mikami, K. Aikawa, Y. Yusa, Org. Lett. 4 (2002) 95.

[60] K. Mikami, K. Aikawa, Y. Yusa, M. Hatano, Org. Lett. 4 (2002) 91.

[61] K. Mikami, K. Aikawa, Org. Lett. 4 (2002) 99.

[62] P. Pertici, F. D'Arata, C. Rosini, J. Organomet. Chem. 515 (1996) 163.

[63] C.-M. Che, J.-S. Huang, this issue of Coord. Chem. Rev.

[64] Y. Wang, J.L. DuBois, B. Hedman, K.O. Hodgson, T.D.P. Stack, Science 279 (1998) 537.

[65] W.-K. Wong, J.-X. Gao, W.-T. Wong, C.-M. Che, Polyhedron 12 (1993) 2063.

[66] W.-K. Wong, J.-X. Gao, W.-T. Wong, W.C. Cheng, C.-M. Che, J. Organomet. Chem. 471 (1994) 277.

[67] W.-K. Wong, L.-L. Zhang, Y. Chen, W.-Y. Wong, W.-T. Wong, F. Xue, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (2000) 1397.

[68] A.G.J. Ligtenbarg, E.K. van der Beuken, A. Meetsma, N. Veldman, W.J.J. Smeets, A.L. Spek, B.L. Feringa, J. Chem. Soc. Dalton Trans. (1998) 263.

[69] R.M. Stoop, S. Bachmann, M. Valentini, A. Mezzeti, Organometallics 19 (2000) 4117.

[70] M.T. Reetz, E. Bohres, R. Goddard, Chem. Commun. (1998) 935.

[71] M.T. Reetz, G. Haderlein, K. Angermund, J. Am. Chem. Soc. 122 (2000) 996.

[72] S. Knoblauch, R. Benedix, M. Ecke, T. Gelbrich, J. Sieler, F. Somoza, H. Hennig, Eur. J. Inorg. Chem. 8 (1999) 1393.

[73] S. Knoblauch, F. Hartl, D.J. Stufkens, H. Hennig, Eur. J. Inorg. Chem. (1999) 303.

[74] G.F. Zi, C.L. Yin, Chin. Chem. Lett. 8 (1997) 1013.

[75] G.F. Zi, C.L. Yin, J. Mol. Cat. A 132 (1998) L1.

[76] T. Panther, U. Baumann, U. Behrens, Z. Anorg. Allg. Chem. 627 (2001) 238.

[77] J. Hamblin, L.J. Childs, N.W. Alcock, M.J. Hannon, J. Chem. Soc. Dalton Trans. (2002) 164.

[78] S.G. Telfer, R. Kuroda, T. Sato manuscript in preparation.