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Review

# Bispyridylamides—coordination chemistry and applications in catalytic reactions

Oscar Belda, Christina Moberg*

*Department of Chemistry, Organic Chemistry, Royal Institute of Technology, SE-10044 Stockholm, Sweden*

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## Abstract

Complexes of bis(2-pyridylamides) with most metal ions have been described. A variety of coordination modes, with the neutral or the deprotonated amide functions binding either via the carbonyl oxygen atom or the amide nitrogen atom have been identified. The modular technique used for the preparation of the compounds permits facile access to ligands with substituted pyridine nuclei and ligands with different backbones. Moreover, symmetric as well as asymmetric compounds, with equal or different pyridine rings and with symmetric

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* Corresponding author. Fax: +46 8 791 2333.
*E-mail address:* kimo@kth.se (C. Moberg).

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or non-symmetric amines, can conveniently be prepared. Chiral derivatives are easily obtained starting from chiral diamines. Several metal complexes have been studied as mimics of biological systems. In recent years a variety of metal complexes have also been employed in catalysis. Oxidations of alkanes and alkenes have been particularly well studied, although modest reactivity has usually been encountered. Other applications include their use as ligands in Lewis acid catalyzed processes. Recently, it was shown that complexes with molybdenum catalyze highly regio- and enantioselective allylic alkylations.

*Keywords:* Bispyridylamide; Metal complex; Coordination; Structure; Catalysis

## 1. Introduction

The coordination chemistry of bispyridylamides with the general structure **L**$H_2$ (Fig. 1) has been intensively studied since the compounds were first prepared by Ojima [1] in 1967.

Metal complexes with a large variety of metal ions, including both hard high-valent and soft low-valent ions and even zerovalent metals, have been prepared. The pyridine nitrogen atoms regularly take part in coordination to the metal ion. The amide groups can be neutral or deprotonated and bispyridylamides can thus serve as neutral, mono- or dianionic ligands. Deprotonated amide groups usually coordinate via the nitrogen atom whereas coordination via oxygen is more frequent for neutral ligands. The anionic ligand is a strong σ-donor capable of stabilizing metal ions in high oxidation states. Complexes with square planar, square pyramidal or octahedral geometry where the compound acts as a planar tetradentate $N_4$ ligand are common, but examples of other geometries with $N_4$-, $N_2O_2$- or NO-coordination exist. In addition to monomeric complexes, dimers, trimers and oligomers with either $N_4$- or $N_2O_2$-coordination, and complexes with different metal to ligand ratios, are known.

Although a large number of metal complexes have been characterized and their electrochemical, spectroscopic and magnetic properties as well as their ligand exchange ability studied, it is only recently that they have found more extensive applications in catalysis. One factor which makes the ligands attractive for catalytic applications is the simplicity whereby the structure of the ligands can be modified by a modular approach. The electronic and steric properties can conveniently be modified by altering the diamine backbone and by the introduction of suitable substituents in the pyridine nuclei. Furthermore, chirality can be introduced by employing chiral, $C_2$-symmetric or asymmetric, diamines, and attachment to solid supports can conveniently be achieved via substituents in the diamine backbone or in the aromatic rings. Together, these possibilities make the ligands attractive for catalytic applications, particularly in asymmetric catalysis.

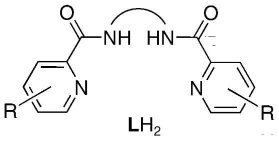


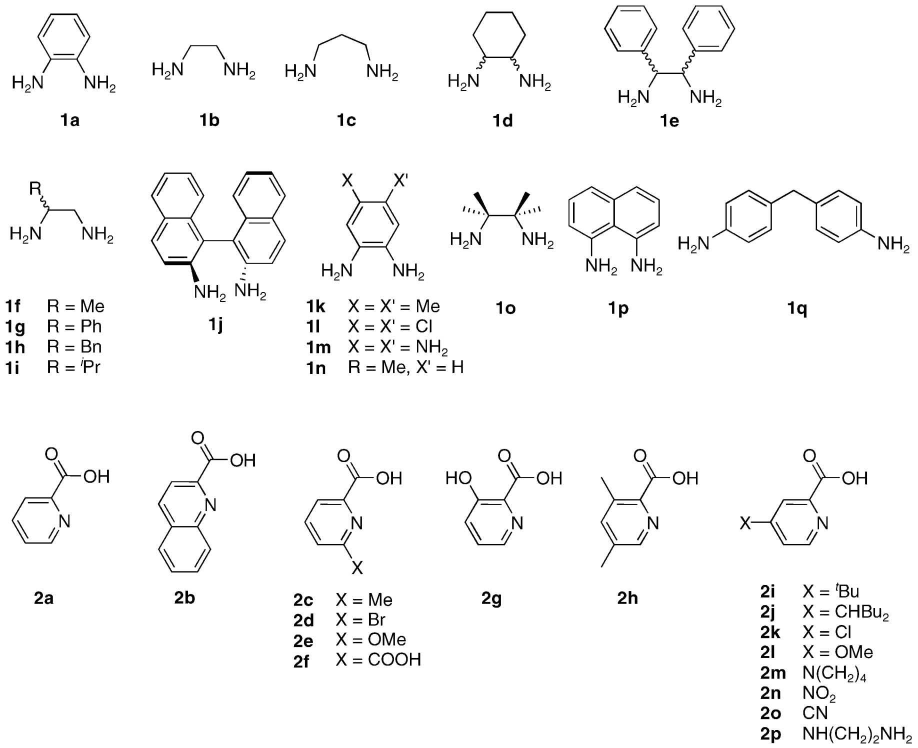
Fig. 1. General structure of bispyridylamides.

The coordination chemistry and catalytic applications of bis(2-pyridylamides) were briefly summarized in 1996 [2]. Applications of bispyridylamides in asymmetric catalysis were also included in a recent review covering chiral tetraaza ligands [3]. The present review covers the synthesis, coordination chemistry and catalytic applications of bis(2-pyridylamides) derived from primary diamines, i.e. ligands which are capable of forming deprotonated metal complexes.

## 2. Ligand synthesis

Bispyridylamides are conveniently prepared by condensation of an appropriate diamine (**1**) and a picolinic acid (**2**) or a picolinic acid derivative (Scheme 1). A number of diamines, including chiral nonracemic diamines, are commercially available. The most commonly used achiral diamines are 1,2-diaminobenzene (**1a**), 1,2-diaminoethane (**1b**) and 1,3-diaminopropane (**1c**). The ligand prepared from **1a** and picolinic acid (**2a**), $\mathbf{L^1}H_2$ (Fig. 2), is by far the most intensively studied bispyridylamide [4]. $C_2$-symmetric (*R**,*R**)-1,2-diaminocyclohexane [5], (*R**,*R**)-1,2-diphenyl-1,2-diaminoethane [6], the former first used as a mixture of isomers but later in enantiomerically pure form [7], and (*R**)-2,2′-diamino-1,1′-binaphthyl [8] are the most frequently used chiral diamines, and amides prepared from the two former amines and picolinic acid, (*R*,*R*)-$\mathbf{L^4}H_2$ and (*S*,*S*)-$\mathbf{L^5}H_2$ (Fig. 2), are the most extensively employed chiral bispyridylamides. Chiral amines devoid of $C_2$ symmetry have also been used [6,9]. Quinoline carboxylic acid (**2b**) and 6-methylpicolinic acid (**2c**) were employed to affect the steric properties of the ligand, preventing planar coordination [10]. A number of 3-, 4- and 6-substituted picolinic acids, such as **2c**–**2p** have been employed in order to affect the steric and/or electronic properties of the ligand. Few substituted picolinic acids are commercially available and therefore they must be prepared from different pyridine derivatives. A compilation of bispyridylamides described in the literature is presented in Scheme 1 and Table 1.

Ojima reported the first synthesis of bispyridylamide ligands **L**$H_2$ by direct amidation of methyl picolinate with 1,2-ethanediamine, 1,3-propanediamine and *rac*-1,2-propanediamine at high temperatures in 1967 [1]. Biniecki and Herold reported in 1972 the synthesis of (*R*,*S*)-$\mathbf{L^5}H_2$ by condensation of *meso*-1,2-diphenyl-1,2-diaminoethane and ethyl picoloyl carbonate [12]. Since then,



Scheme 1. Diamines (**1**) and carboxylic acids (**2**) used for the preparation of bispyridylamides.

more than 50 bis(2-pyridylamide) derivatives have been described.

Among the variety of general coupling reagents that have been used for the reaction between picolinic acid or its derivatives and a diamine, triphenylphosphite has been the most commonly employed. The method was originally used in 1978 by Vagg and coworkers to prepare $\mathbf{L^1}H_2$–$\mathbf{L^4}H_2$ in moderate to excellent yields [4]. Transformation of picolinic acid to the acid chloride by treatment with thionyl chloride or oxalyl chloride is not usually a viable method. Nevertheless, ligands (*R*)-$\mathbf{L^{10}}H_2$ [8], (*S*)-$\mathbf{L^{10}}H_2$ [8], $\mathbf{L^{15}}H_2$ [17], (*R*,*R*)-$\mathbf{L^{27}}H_2$ [19], (*S*,*S*)-$\mathbf{L^{27}}H_2$ [19], $\mathbf{L^{28}}H_2$ [19], (*R*,*R*)-$\mathbf{L^{29}}H_2$ [21], and (*R*,*R*)-$\mathbf{L^{33}}H_2$ [20] were prepared by this procedure in acceptable yields. Another way to activate the carboxylic acid is by reaction with Mukaiyama's reagent (*N*-methyl-2-chloropyridinium iodide). Thus, ligands (*R*,*R*)-$\mathbf{L^{23}}H_2$, (*R*,*R*)-$\mathbf{L^{37}}H_2$, and (*R*,*R*)-$\mathbf{L^{41}}H_2$ were prepared in moderate to good yields but separation from coproducts could be tedious [20]. Activation of the carboxylic acid by using Staab's reagent (*N*,*N*′-carbonyldiimidazole, CDI) has been used more recently to prepare ligands (*R*,*R*)-$\mathbf{L^{25}}H_2$ [21] and (*R*,*R*)-$\mathbf{L^{35}}H_2$ [21], in moderate to excellent yields and this method usually allows for an easier separation from byproducts. By this procedure, $\mathbf{L^4}H_2$ was prepared on a kilo-scale [26].

Aromatic nucleophilic substitution of the bis(4-chloropyridyl)- or bis(6-bromopyridyl)amides (*R*,*R*)-$\mathbf{L^{25}}H_2$ and (*R*,*R*)-$\mathbf{L^{35}}H_2$ has been employed in order to introduce functionality in the 4- and 6-position of the pyridine rings, instead of preparation of the corresponding picolinic acid derivative [21,25]. A number of nucleophiles were used, giving rise to ligands with different electronic and steric properties. These reactions were conveniently performed in a microwave cavity with excess of the nucleophile in 15–20 min, affording the ligands in nearly quantitative yields. Recently, ligands $\mathbf{L^{43}}H_2$ and $\mathbf{L^{44}}H_2$, with 4-cyano-substituted pyridine rings, were prepared by microwave accelerated $NiBr_2$ catalyzed cyanation of the corresponding 4-chloro substituted ligand [24].

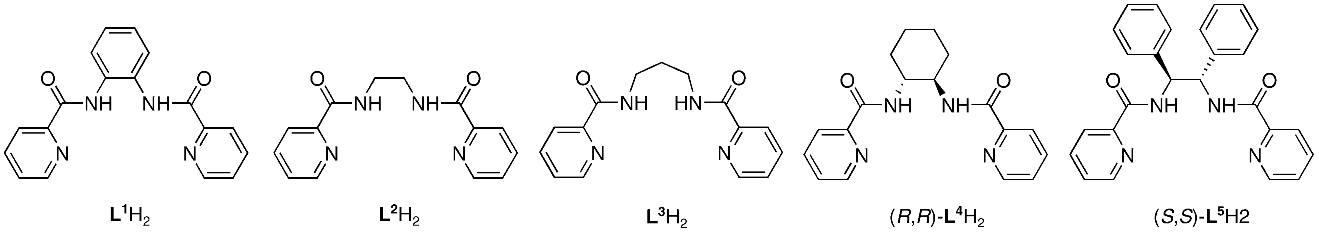
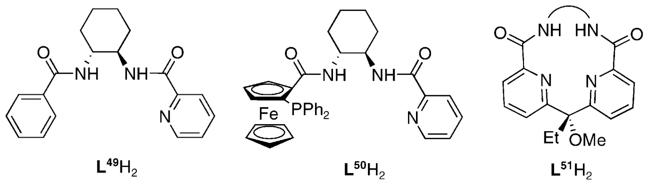


Fig. 2. Most frequently studied bispyridylamides.

Table 1
Bispyridylamides reported in the literature

| Ligand | Diamine | Picolinic acid | Reference |
|---|---|---|---|
| $\mathbf{L}^{1}H_2$ | **1a** | **2a** | [4] |
| $\mathbf{L}^{2}H_2$ | **1b** | **2a** | [1,4] |
| $\mathbf{L}^{3}H_2$ | **1c** | **2a** | [1,4] |
| $\mathbf{L}^{4}H_2$ | **1d** | **2a** | *R*,*S*+*R**,*R**: [4]<br>*R*,*S*: [11]<br>*RS*,*SR*: [5]<br>*R*,*R*: [7] |
| $\mathbf{L}^{5}H_2$ | **1e** | **2a** | *R*,*S*: [12]<br>*S*,*S*: [6] |
| $\mathbf{L}^{6}H_2$ | **1f** | **2a** | *RS*: [1] |
| $\mathbf{L}^{7}H_2$ | **1g** | **2a** | *S*: 6, *R*: [9] |
| $\mathbf{L}^{8}H_2$ | **1h** | **2a** | *S*: [9] |
| $\mathbf{L}^{9}H_2$ | **1i** | **2a** | *S*: [9] |
| $\mathbf{L}^{10}H_2$ | **1j** | **2a** | *R*: [8], *S*: [8] |
| $\mathbf{L}^{11}H_2$ | **1k** | **2a** | [13] |
| $\mathbf{L}^{12}H_2$ | **1l** | **2a** | [14] |
| $\mathbf{L}^{13}H_2$ | **1m** | **2a** | [15] |
| $\mathbf{L}^{14}H_2$ | **1n** | **2a** | [16] |
| $\mathbf{L}^{15}H_2$ | **1o** | **2a** | [17] |
| $\mathbf{L}^{16}H_2$ | **1p** | **2a** | [18] |
| $\mathbf{L}^{17}H_2$ | **1q** | **2a** | [19] |
| $\mathbf{L}^{18}H_2$ | **1b** | **2b** | [10] |
| $\mathbf{L}^{19}H_2$ | **1e** | **2b** | *S*,*S*: [7] |
| $\mathbf{L}^{20}H_2$ | **1j** | **2b** | *R*: [7] |
| $\mathbf{L}^{21}H_2$ | **1a** | **2c** | [10] |
| $\mathbf{L}^{22}H_2$ | **1b** | **2c** | [10] |
| $\mathbf{L}^{23}H_2$ | **1d** | **2c** | *R*,*R*: [20] |
| $\mathbf{L}^{24}H_2$ | **1e** | **2c** | *S*,*S*: [7] |
| $\mathbf{L}^{25}H_2$ | **1d** | **2d** | *R*,*R*: [21] |
| $\mathbf{L}^{26}H_2$ | **1d** | **2e** | *R*,*R*: [21] |
| $\mathbf{L}^{27}H_2$ | **1d** | **2f** | *R*,*R*: [19]<br>*S*,*S*: [19] |
| $\mathbf{L}^{28}H_2$ | **1q** | **2f** | [19] |
| $\mathbf{L}^{29}H_2$ | **1d** | **2g** | *R*,*R*: [21] |
| $\mathbf{L}^{30}H_2$ | **1k** | **2h** | [13] |
| $\mathbf{L}^{31}H_2$ | **1l** | **2i** | *R*,*R*: [22] |
| $\mathbf{L}^{32}H_2$ | **1m** | **2i** | [15] |
| $\mathbf{L}^{33}H_2$ | **1d** | **2i** | [20] |
| $\mathbf{L}^{34}H_2$ | **1k** | **2j** | [23] |
| $\mathbf{L}^{35}H_2$ | **1d** | **2k** | *R*,*R*: [21] |
| $\mathbf{L}^{36}H_2$ | **1e** | **2k** | [24] |
| $\mathbf{L}^{37}H_2$ | **1d** | **2l** | *R*,*R*: [20] |
| $\mathbf{L}^{38}H_2$ | **1e** | **2l** | [24] |
| $\mathbf{L}^{39}H_2$ | **1d** | **2m** | *R*,*R*: [21] |
| $\mathbf{L}^{40}H_2$ | **1e** | **2m** | [24] |
| $\mathbf{L}^{41}H_2$ | **1d** | **2n** | *R*,*R*: [20] |
| $\mathbf{L}^{42}H_2$ | **1e** | **2n** | [24] |
| $\mathbf{L}^{43}H_2$ | **1d** | **2o** | [24] |
| $\mathbf{L}^{44}H_2$ | **1e** | **2o** | [24] |
| $\mathbf{L}^{45}H_2$ | **1d** | **2a + 2k** | *R*,*R*: [25] |
| $\mathbf{L}^{46}H_2$ | **1d** | **2a + 2l** | *R*,*R*: [25] |
| $\mathbf{L}^{47}H_2$ | **1d** | **2a + 2m** | *R*,*R*: [25] |
| $\mathbf{L}^{48}H_2$ | **1d** | **2a + 2p** | *R*,*R*: [25] |

Reaction with a second equivalent of the carboxylic acid derivatives occurs more slowly than the first amide bond formation. This opens up the possibility to form unsymmetrical ligands containing pyridine rings with different substituents, such as $\mathbf{L}^{45}H_2$ [25], as well as various ligands having one pyridine replaced by some other group. For example, replacement of one picolinic acid by a phenyl ring yielded monopyridine ligand $\mathbf{L}^{49}H_2$ [27], and by a (Sp)-2-phosphinoferrocenyl carboxylic acid resulted in diastereomeric P,N-ligands $\mathbf{L}^{50}H_2$ (Fig. 3) [28]. Ligand $\mathbf{L}^{45}H_2$ was subsequently transformed via functional group interconversions to unsymmetrical compounds $\mathbf{L}^{46}H_2$–$\mathbf{L}^{48}H_2$.



$\mathbf{L}^{49}H_2$ $\mathbf{L}^{50}H_2$ $\mathbf{L}^{51}H_2$

Fig. 3. Non-symmetric and cyclic pyridylamides.

Two examples of bispyridylamides grafted to polymers have been described, by attachment to the solid support either via the diamine part of the molecule or via the pyridine ring. Thus, a 4-substituted diaminobenzene attached to a Tentagel resin was employed as a starting diamine [29]. Attachment of a ligand with a 4-aminopyridine group to a carboxylic acid substituted Tentagel resin in the presence of DCC also afforded a heterogeneous ligand [25].

Macrocyclic ligands with the general structure $\mathbf{L}^{51}H_2$ were obtained from 1,1-bis(2-pyridyl)-1-methoxypropane and 1,2-diaminobenzene (**1a**), 1,2-diaminoethane (**1b**), 1,3-diaminopropane (**1c**), (*R*,*S*)-1,2-diaminocyclohexane ((*R*,*S*)-**1d**), (*R*,*R*)-1,2-diaminocyclohexane ((*R*,*R*)-**1d**), and 1,8-diaminonaphtalene (**1p**) (Fig. 3) [30–32].

## 3. Coordination chemistry

Complexes with a 1:1 metal:ligand ratio where the ligand acts as a planar $N_4$-donor are formed with a variety of metal salts, resulting in complexes with square planar, square pyramidal, or octahedral geometry (I–III, Fig. 4). Tetrahedral $N_4$-coordination (IV) has also been observed in a few cases. In addition, a variety of dimeric (V–VII) and oligomeric (VIII) $N_2O_2$-complexes exist. Complexes with a 2:3 metal:ligand ratio with $N_2O_2$ or $N_4$ coordination (IX, X) and 2:1 complexes with NONO-coordination (XI) have also been characterized. Finally, in a few complexes only one pyridylamide moiety or only the pyridine nitrogen atoms take part in coordination to the metal ion.

The amide hydrogen atoms become labile when the ligand undergoes complexation, which often results in the formation of a mono- or a dianionic ligand. Whether base is required or not for deprotonation to occur depends on the metal ion and the counter ion as well as on the reaction conditions. Hydrogen bonding to the acidic hydrogen atom, with the electron rich metal center serving as the hydrogen bond acceptor [33], may increase the tendency for deprotonation. This type of interaction was indeed suggested to be responsible for the facile deprotonation of a Pt(II) amide complex [34].

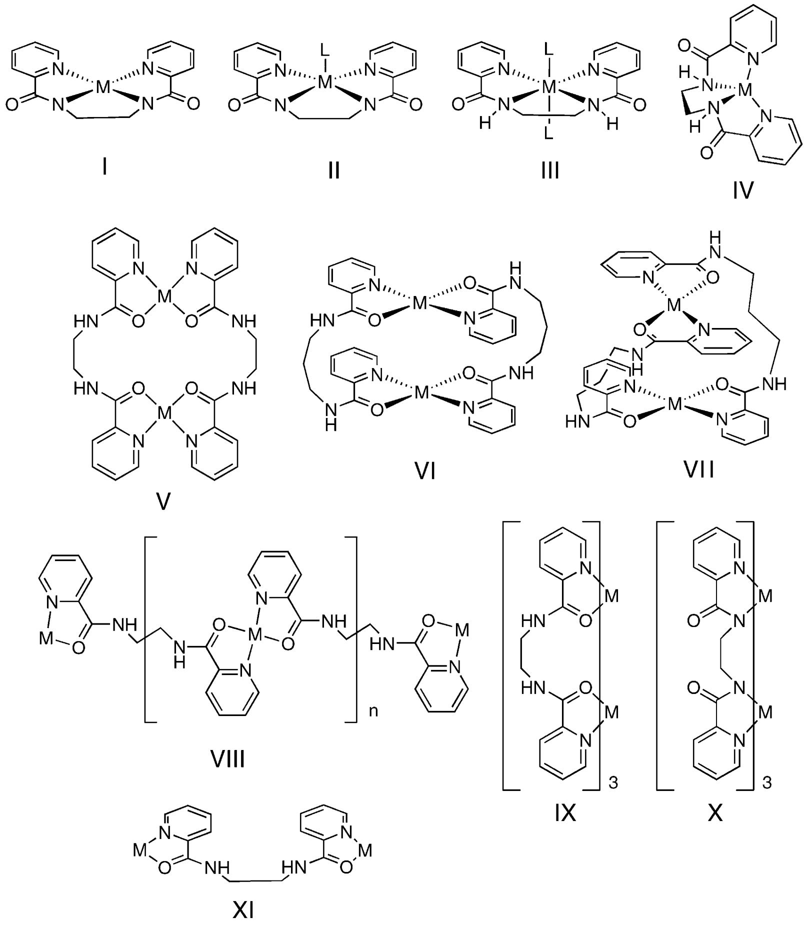


Fig. 4. General structures of metal complexes with bispyridylamides.

The deprotonated amide nitrogen atom is a strong field ligand favoring N-coordination of the planar tetradentate ligand, although rare examples of coordination via the oxygen atom of the deprotonated amide group, and deviation from planarity, have been encountered [35]. As a rule, the neutral amide binds via oxygen, but N-coordinated neutral amides have been observed [36].

Early studies on the coordination chemistry of bispyridylamides were reported by Ojima [1] and later by Chapman and Vagg [36]. A series of complexes with *N*,*N*′-bis(2′-pyridinecarboxamide)-1,2-benzene (**L$^1$**H$_2$) were among those first studied. Since then, complexes with most metal ions in different oxidation states have been described.

### 3.1. Copper

Studies of Cu(II) complexes were first reported by Ojima [1]. A brown deprotonated 1:1 complex was obtained by mixing $Cu(OAc)_2$ with **L$^1$**H$_2$ in ethanol. Exchanging the acetate for $CuCl_2$ afforded instead a green 1:1 high spin octahedral complex containing the neutral ligand [36]. The latter complex lost HCl at 160 °C, probably yielding the deprotonated square pyramidal complex. From **L$^2$**H$_2$, exhibiting a lower degree of electronic delocalization than **L$^1$**H$_2$ in the deprotonated form, a deprotonated complex was obtained by treatment of the metal salt with the ligand in the presence of NaOH [37]. A crystal structure determination of the deprotonated complex with **L$^2$**H$_2$ showed a five-coordinated Cu(II) with the ligand binding in a planar $N_4$ tetradentate fashion and with an apical water molecule [38]. The same type of coordination was observed in **L$^1$**H$_2$ (II, Fig. 4) [39]. Attempts to replace the axially coordinated water by pyridine were unsuccessful [36]. The Cu(II) complex of deprotonated **L$^3$**H$_2$ was found to crystallize in two forms, one exhibiting higher thermodynamic stability [40], the other being kinetically favored [41]. From the same ligand a violet 1:1 complex was formed at high pH, whereas at low pH a complex was obtained which was suggested to be a dimer [42]. This was later confirmed by an X-ray structure determination, which showed an anti-form (VII, Fig. 4) of the complex [43,44]. Dimeric complexes were also obtained from the homologues with two (**L$^2$**H$_2$) or four methylene group in the diamine part of the ligand [45]. Although the dimeric complexes exhibited steric strain, stabilization was provided by intramolecular π-stacking of the pyridine nuclei and by hydrophobic interactions. Dimers stabilized by the same type of interactions

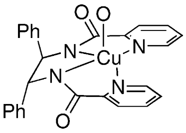


Fig. 5. Cu(II) complex of (*S*,*S*)-**L⁵**$H_2$ [6].

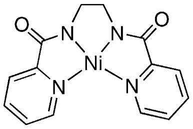


Fig. 6. Square planar coordination of Ni(II) complex [55].

were also obtained from quinoline analogues [46], whereas from racemic **$L^2$**$H_2$ an open chain dimer was obtained [45]. The violet complexes obtained from *trans*- [47] and *cis*[11]-**$L^4$**$H_2$ exhibited typical square pyramidal structures. Another crystalline form of the complex with the deprotonated trans ligand, with a different hydrogen bonding pattern and with a different crystal packing, was also obtained [48]. From **$L^{16}$**$H_2$ Cu(II) complexes with both the deprotonated [18] and the non-deprotonated [49] ligand were obtained. With the sterically hindered ligand **$L^{21}$**$H_2$ a significant tetragonal distortion was observed [50]. Electrochemical oxidation of Cu(II) complexes of **$L^1$**$H_2$ and **$L^{14}$**$H_2$ showed quasi-reversible oxidation and reduction waves assigned to Cu(III) and Cu(I) species, respectively [16]. Replacing the tetradentate ligand with two bidentate pyridylamides resulted in positive shift of the potentials [51]. Chiral enantiopure Cu(II) complexes were prepared from (*S*,*S*)-**$L^5$**$H_2$ (Fig. 5) and (*S*)-**$L^7$**$H_2$ [6]. Pseudo-axial orientation of the phenyl rings was observed in the crystals of the two complexes.

### 3.2. Silver, zinc, cadmium

A white Ag(I) complex with neutral **$L^1$**$H_2$, thought to coordinate only via the pyridine nitrogen atoms, was among the first pyridylamide complexes studied [36]. In the same study, a monomeric Zn(II) complex with deprotonated ligand and a dimer with the neutral ligand were isolated. A coordination polymer was obtained from **$L^2$**$H_2$ and $AgClO_4$ [52]. The X-ray structure showed quasi-linear chains and trans bis-bidentate bridging coordination to the metal involving the pyridine nitrogen atoms and the carbonyl oxygen atoms (type VIII, Fig. 4). In contrast, the isomer *N*,*N*′-bis(3-pyridinecarboxamide)-1,2-ethane (**$L^2$**$H_2$) formed infinite chains with two-coordinated silver ions joined by the pyridine nitrogen atoms. The amide groups did not take part in coordination to the metal atom, thus allowing the polymer chains to aggregate via amide hydrogen bonds to form corrugated sheets in the solid state. The polymer crystallized in two polymorphs with different supramolecular structures. Complexes with different supramolecular arrangements were also obtained with $Zn^{2+}$ and $Cd^{2+}$.

### 3.3. Gold

Reaction of $K[AuCl_4]$ with **$L^{10}$**$H_2$ gave a gold(III) complex in which only one pyridine-2-carboxamide unit took part in coordination to the metal [53]. The complex was found to display room temperature photoluminescence.

### 3.4. Nickel

Ni(II) was early shown to give square planar complexes with deprotonated bispyridylamide ligands [1]. Attempts to produce a pyridine adduct of **$L^1$**Ni resulted in the original complex being recrystallized, demonstrating the stability of the square planar coordination [36]. This mode of coordination was verified by X-ray structure analyses of complexes with **$L^1$**$H_2$ [54], **$L^2$**$H_2$ (Fig. 6) [55], and **$L^3$**$H_2$ [56], racemic **$L^4$**$H_2$ [57]. **$L^3$**Ni was later shown to crystallize in another form with similar coordination [58]. $^1$H NMR spectroscopy indicated analogous coordination for complexes with chiral ligands (*S*,*S*)-**$L^5$**$H_2$ and (*S*)-**$L^7$**$H_2$; in both complexes the phenyl groups occupied pseudo-axial positions [6]. The Ni(II) complexes with cyclic ligands **$L^{51}$**$H_2$ prepared from diamines **1a** and **1b** exhibited analogous coordination behaviour [32]. From **$L^{16}$**$H_2$ Ni(II) complexes with both the deprotonated [18] and the non-deprotonated [49] ligand were obtained. The complex formed from **$L^{21}$**$H_2$, having 2-methyl-substituted pyridine rings, exhibited severe distortion from planarity, with a tetrahedral twist at the nickel atom and non-planar amide groups [54].

Due to the involvement of Ni(I) in catalytic reactions and in enzymatic processes, studies of monovalent nickel complexes are considered to be of interest. Treatment of **$L^1$**Ni in DMF with sodium amalgam resulted in reduction at the metal center and formation of a Ni(I) complex, accompanied by a color change of the solution from orange to deep purple [59]. The complex was characterized by EPR and electronic spectroscopy. It was suggested that the complex could serve as a model for $F_{430}$, a cofactor for metal–coenzyme M reductase.

### 3.5. Palladium, platinum

Pd(II) complexes with deprotonated ligands were formed even in acidic solution [36]. The complex with **$L^3$**$H_2$, shown by crystal structure determination to exhibit square planar coordination, was not protonated even at pH 0.5 [58]. However, with the sterically hindered **$L^{22}$**$H_2$ a square planar $PdCl_2$ complex with only the pyridine nitrogen atoms taking part in coordination in a trans fashion was obtained [10]. The deprotonated complexes adopted square planar geometries, although an additional coordinating molecule (water) may occupy a fifth site [36]. With **$L^{16}$**$H_2$ a deprotonated square planar complex was obtained with Pd(II), whereas Pt(II) initially afforded a complex with the neutral ligand coordinating via the pyridine nitrogen atoms only; the latter complex slowly afforded the deprotonated square planar complex [60].

The structures of Pd(II) complexes with chiral (*S,S*)-$\mathbf{L^5}H_2$ and (*S*)-$\mathbf{L^7}H_2$ were analogous to those of the Ni(II) complexes [6]. $^{195}$Pt–$^1$H couplings to the 6-pyridyl protons were observed in Pt complexes of the ligands [4,37].

### 3.6. Cobalt

From Co(II) complexes with neutral as well as deprotonated $\mathbf{L^1}H_2$ have been prepared [36]. The former were assumed to be polymers exhibiting $N_2O_2$-coordination. Reaction of the hydrate of $\mathbf{L^1}$Co with additional ligand, in the presence of triethylamine and air, yielded a Co(III) complex containing one bisdeprotonated and one monodeprotonated ligand [35]. The metal ion was shown by X-ray crystallography to bind to a deprotonated amide group via oxygen. Oxidation with *t*-BuOOH of the complex containing the deprotonated ligand in the presence of 4-methylpyridine gave an alkylperoxy complex [61]. When the analogous complex with pyridine as apical ligand was stored in chloroform, the peroxy ligand was exchanged for chloride via an unknown mechanism [62]. Reaction with sodium azide, sodium cyanide and pyridine/$LiClO_4$ gave Na[$\mathbf{L^1}$Co$(N_3)_2$], Na[$\mathbf{L^1}$Co$(CN)_2$] and [$\mathbf{L^1}$Co$(py)_2$]$ClO_4$, respectively, whereas reduction followed by oxidative addition of alkyl halides afforded Co(III) alkyl complexes [63]. The X-ray crystal structure of the cyanide complex was determined later and shown to have the expected octahedral geometry [64]. From 3,3-dimethylallyl bromide the homoallylic complex was unexpectedly obtained. The X-ray crystal structure of this complex and the ethyl analogue showed a distorted octahedral geometry with one axial position occupied by a water molecule. Cyclic voltammetry data suggested one-electron oxidation to be mainly ligand-centered. In agreement with these results, ligand-centered one-electron oxidation was also found in Na[$\mathbf{L^{12}}$Co(III)$(CN)_2$] [65]. From $\mathbf{L^2}H_2$ and Co(II) acetate a $D_3$-symmetric bimetallic complex with bridging ligands, $\mathbf{L^2}_3Co_2$ (type X, Fig. 4), as determined by X-ray crystallography, was obtained [66]. Each cobalt ion had octahedral geometry. Treatment of $\mathbf{L^1}H_2$ or $\mathbf{L^{12}}H_2$ with $Co(OAc)_2$ in DMF, MeCN or methanol, yielded Co(III) complexes with the dianionic bispyridylamide ligands, whereas use of $CoCl_2$ or $CoClO_4$ as the metal source required the addition of base for deprotonation to occur [67]. Oxidation to Co(III) was probably achieved by atmospheric oxygen. Ligand exchange provided complexes with $Cl^-$, $N_3{}^-$, $SCN^-$, $NO_2{}^-$ or $AcO^-$ as axial ligands. Electrochemical studies revealed irreversible reduction to Co(II), and a quasi-reversible Co(II)–Co(I) couple, except for the complex having $SCN^-$ as axial ligands, where both couples were irreversible. Stronger field axial ligands shifted the potential to more negative values.

Aerobic oxidation of $\mathbf{L^1}$Co $H_2O$ in the presence of amines afforded Co(III) complexes with two amine ligands in trans axial positions, as shown by X-ray crystallography [68]. The oxidation was accompanied by a color change from red–brown to green.

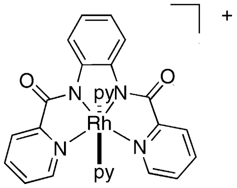


Fig. 7. Octahedral Rh(III) complex [14].

Studies of Co(III) alkyl complexes are of interest as models for the $B_{12}$ coenzymes. Co(III) alkyl complexes of $L^1$ were prepared by oxidative addition of alkyl halides to Na[$\mathbf{L^1}$Co] [69]. Complexes with axially situated phosphines and pyridine were obtained by addition of ligand. Oxidation, either electrochemically or chemically, was believed to result in a Co(IV) compound; an absorption in the 600–800 nm region was assigned to an amide-to-Co(IV) charge transfer transition. Cyclic voltamograms showed reversible Co(III)/Co(IV) couples and irreversible reduction waves. Solutions of the Co(IV) alkyl complexes were found to be stable for 12 h in the dark, but decomposed within a few minutes in the presence of light. Both reaction of the Co(IV) species with pyridine and oxidation of the Co(III) pyridine complex resulted in Co–C bond cleavage. The Co–C stretching frequency in the Co(III) methyl complex was determined by FT-Raman spectroscopy and found to be in the same range as that of methyl-$B_{12}$ compounds. Oxidation to Co(IV) resulted in lowering of the Co–C stretching frequency, which is consistent with the observed lability of that bond in the oxidized complexes.

### 3.7. Rhodium, iridium

Investigations of $B_{12}$ mimics have been extended to bispyridylamide complexes of other metals than cobalt. Refluxing $RhCl_3$ and $\mathbf{L^1}H_2$, $\mathbf{L^2}H_2$ or $\mathbf{L^{12}}H_2$ afforded **L**Rh(III)Cl complexes, which served as starting material for the preparation of complexes with e.g. pyridine and $PPh_3$ as axial ligands; the structure of the $\mathbf{L^1}$Rh$(py)_2$ cation was determined by X-ray crystallography (Fig. 7) [14]. A range of analogous Rh(III) complexes containing neutral or deprotonated $\mathbf{L^{16}}H_2$ were prepared [70]. The neutral amide served as a bisbidentate ligand in oligomeric or polymeric complexes with octahedral geometry, whereas the deprotonated complexes, with chloride, cyanide and pyridine ligands, were found to be octahedral monomers. Photolysis of the $\mathbf{L^{11}}$ complex with an axial methyl group yielded a dimeric Rh(II) complex [23]. This dimer reacted slowly with hydrogen in a reversible process to produce a monomeric rhodium hydride, with carbon monoxide to form a metalloketone complex, and with ethylene to yield an ethylene-bridged complex. A Rh formyl complex was obtained by reaction of the monomeric hydride with CO. Rh(III) alkyl complexes were obtained by reduction to Rh(I) followed by oxidative addition. Complexes with $\mathbf{L^1}H_2$ and $\mathbf{L^{12}}H_2$ displayed reversible one-electron oxidation couples, whereas complexes with $\mathbf{L^2}H_2$ were oxidized irreversibly [14]. To further elucidate the factors governing the alkyl-metal bond strength, methyl–Rh and methyl–Ir complexes of $\mathbf{L^1}H_2$ with a variety of axial ligands were studied by FT-Raman spectroscopy [71]. The influence of the nature of the axial ligand in square planar $N_4$ complexes on the metal–alkyl bond dissociation energy, was studied. A variety of complexes containing a pyridine or phosphine ligand trans to the methyl group, as verified by X-ray crystallography, were prepared. The complexes were stable in the solid state as well as in solution. Phosphines, exhibiting stronger trans influence than pyridine ligands, resulted in longer Ir–carbon bonds for complexes with the former type of ligands. The metal–carbon force constant was shown to decrease in the order Ir > Rh > Co and to be insensitive to coordination of nitrogen ligands. In the pyridine complexes metal–carbon stretching frequencies were therefore not influenced by substituents in the heterocyclic ring.

### 3.8. Iron

$FeCl_2$ coordinates to the neutral ligand $\mathbf{L^1}H_2$, probably via the carbonyl oxygen atoms, forming a polymeric structure (type VIII, Fig. 4), whereas the Fe(II) perchlorate reacts to give a 2:3 metal:ligand complex (type IX), probably with $N_3O_3$ coordination [37]. A series of low spin Fe(III) complexes of $\mathbf{L^{12}}H_2$ having tributylphosphine, imidazole, methylimidazole, and *tert*-butylpyridine as axial ligands were prepared [72]. The complexes displayed reversible one-electron oxidation and reduction couples. Fe(III) complexes with a variety of axial ligands were prepared from $\mathbf{L^1}H_2$ and $\mathbf{L^{12}}H_2$ [73]. The spin state was regulated by manipulation of the axial ligands. Low spin complexes displayed a reversible Fe(III)–Fe(II) reduction, whereas that process was irreversible for high spin complexes. Complexes containing $\mathbf{L^1}H_2$ and having pyridine or cyanide as axial ligands were low spin, whereas the others were high spin complexes. $FeCl_3{\cdot}6H_2O$ formed a dark green complex with deprotonated ligand in the presence of NaOH [65]. Treatment of $(NEt_4)[\mathbf{L^{12}}FeCl_2]$ [73] with $AgClO_4$ gave high spin $\mathbf{L^{12}}FeCl{\cdot}H_2O$, which underwent displacement of water by DMF upon crystallization from DMF [74]. Reaction of this complex with $Bu_4NOH$ yielded a μ-oxo-bridged dimer. Low spin Fe(III) perchlorate complexes with axial pyridine ligands were also prepared [73]. To increase the solubility a hexamethyl-substituted complex was prepared [13]. Addition of cyanide [13] or azide [65,73] to this type of complex afforded anionic green complexes with two axial cyanide (low spin complex) or azide (high spin complex) ligands, isolated as their sodium or tetrabutyl ammonium salts. The one- and two-electron oxidation products of the dicyano complex contained low spin ferric ions and oxidized ligand, and, whereas N-bridged dimeric photolysis products were shown to contain low spin Fe(IV) ions [65]. The dinucleating ligand $\mathbf{L^{52}}H_4$ yielded dinuclear Fe(III) complexes with the fully deprotonated ligand (Fig. 8) [15]. The crystal structures of $(NHEt_3)[\mathbf{L^{11}}FeCl_2]$ [75] and $(NEt_4)[\mathbf{L^{12}}FeCl_2]$ [76] were recently determined. A complex analogous to $(NEt_4)[\mathbf{L^{12}}FeCl_2]$ was prepared by simultaneous ligand and metal oxidation. Thus, reaction of a ligand prepared from **2a** and 3,4-diaminopyridine with $FeCl_2{\cdot}4H_2O$ under aerobic conditions afforded a dark brown high spin complex having octahedral geometry around Fe(III) with two axial chloride ligands [77].

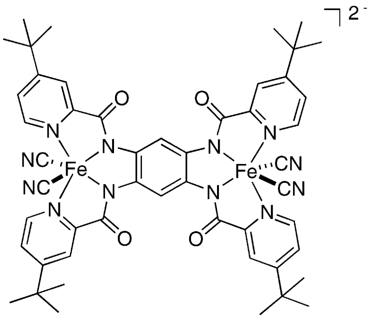


Fig. 8. Dinuclear Fe(III) complex made from $\mathbf{L^{52}}H_4$ [15].

### 3.9. Ruthenium, osmium

Reaction of $K_2[OsO_2(OH)_4]$ with $\mathbf{L^1}H_2$ in methanol in the presence of HCl afforded *trans*-$[(\mathbf{L^1}H_2)OsO_2]Cl_2$ [78]. Deprotonation of the ligand was achieved by treatment of the complex with base, affording *trans*-$[\mathbf{L^1}OsO_2]$, whereas reaction with triphenylphosphine resulted in reduction to *trans*-$[\mathbf{L^1}Os(IV)(OR)_2]$ in the presence of an alcohol ROH and *trans*-$[\mathbf{L^1}Os(III)(PPh_3)Cl]$ in non-alcoholic medium [79]. The latter complex was characterized by X-ray crystallography [78]. A chiral octahedral Os(VI) complex containing $\mathbf{L^{10}}$ was also prepared [8].

Ruthenium complexes with the metal in different oxidation states have been characterized. By reaction of $\mathbf{L^1}H_2$ with ruthenium trichloride a dinuclear Ru(III) complex was obtained [80]. A Ru(III) complex with a structure analogous to that of *trans*-$[\mathbf{L^1}Os(III)(PPh_3)Cl]$ could be isolated by using $\mathbf{L^{31}}H_2$, as ligand [22]. Os(VI) and Ru(VI) nitrido complexes with neutral bidentate N,O-ligands were produced from $(NBu_4)[M(VI)NCl_4]$ (M = Os, Ru) and $\mathbf{L^{15}}H_2$ (Fig. 9) [17]. The complexes had octahedral coordination, with the carbonyl oxygen atom of the ligand situated trans to the $N^{3-}$ ligand. From two equivalents of $Ru(dmso)_4Cl_2$ and $\mathbf{L^1}H_2$, $\mathbf{L^2}H_2$, or $\mathbf{L^3}H_2$, binuclear complexes with the ligand serving as two bidentate N,O-donors and with octahedral Ru(II) having the chloride ions in trans position were obtained [81].

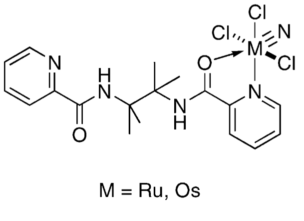


Fig. 9. Nitrido-Ru(VI) and Os(VI) complexes [17].

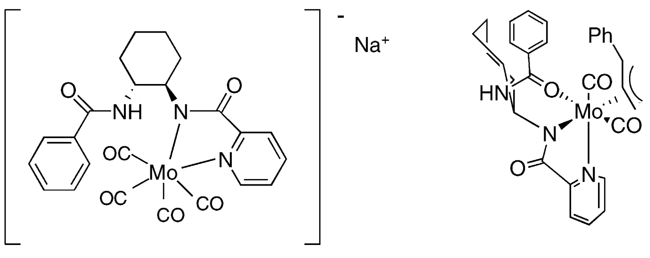
### *3.10. Manganese*

The role of manganese in biological systems has stimulated studies of the properties of Mn complexes with synthetic ligands exhibiting properties mimicking those of the naturally occurring systems. This has resulted in numerous studies of the redox behaviour of manganese complexes of bispyridylamide ligands.

A Mn(II) complex with neutral $\mathbf{L^{16}}\mathrm{H_2}$ was isolated [49]. Refluxing $\mathrm{Mn(OAc)_3}$ and $\mathbf{L^{1}}\mathrm{H_2}$ or $\mathbf{L^{12}}\mathrm{H_2}$ in methanol containing LiCl or $\mathrm{LiN_3}$ resulted in deprotonation of the ligand and formation of **L**Mn(III) Cl and $\mathbf{L}\mathrm{Mn(III)N_3}$, respectively [82]. Spectroscopic studies of the complexes with $\mathbf{L^{1}}\mathrm{H_2}$ suggested five-coordinated square pyramidal geometries with the ligand functioning as a dianionic $\mathrm{N_4}$ ligand and the fifth coordination site occupied by the anion [83]. Electron transfer studies showed that the complexes displayed a Mn(III)–Mn(II) couple as well as a Mn(IV)–Mn(III) couple, the latter indicating the versatility of this type of complexes for oxidative processes. $\mathbf{L^{1}}\mathrm{MnCl{\cdot}H_2O}$, characterized by X-ray crystallography, was shown to serve as a superoxide dismutase mimic, with an activity similar to that of a Mn(III) salen complex [84].

### *3.11. Chromium*

Due to its interest as a porphyrin model, $\mathbf{L^{1}}$Cr(V)N was prepared by photolysis of the Cr(III) azide complex [85]. Deprotonation of the ligand occurred when treating $\mathbf{L^{1}}\mathrm{H_2}$ and $\mathbf{L^{12}}\mathrm{H_2}$ with $\mathrm{CrCl_3}$, resulting in highly coloured, air stable, high spin $\mathbf{L}\mathrm{CrCl{\cdot}H_2O}$ complexes [86]. The water molecule could be replaced by neutral as well as anionic ligands and the chloride anion could be replaced after treatment of the complex with hydroxide or $\mathrm{Ag^+}$, the latter procedure yielding $\mathbf{L}\mathrm{CrB_2}$ complexes with B equal to pyridine, 4-*tert*-butylpyridine or tributylphosphine. The complexes exhibited reversible oxidation and reduction couples with potentials highly dependent on the nature of the axial ligand. The oxidation was assumed to be largely ligand centered. An X-ray structure investigation of reddish orange $\mathbf{L^{1}}$Cr(V)N showed a distorted square pyramidal geometry around the metal [87], which was situated 0.508 Å above the plane of the four nitrogen atoms of the amide ligand [85]. ESR and UV–vis data for the complex have been reported [88]. From ESR parameters moderate covalency in the in-plane bonds was concluded [89]. Powder pattern ESR spectra of $\mathbf{L^{1}}\mathrm{Cr(III)(N_3)_2}$ and $\mathbf{L^{1}}\mathrm{Cr(III)Cl(H_2O)}$, precursors to $\mathbf{L^{1}}$Cr(V)N, indicated that the quartet states were characterized by large fine-structure parameters compared with microwave transition energy [90]. From a computational study using the B3LYP hybrid HF/DFT method of $\mathbf{L^{1}}$Cr(V)N and $\mathbf{L^{1}}$Cr(V)(N-*t*-Bu)Cl, with geometries taken from X-ray diffraction data, it was concluded that the Cr–N bond displayed essentially a triple bond character, with one σ and two π bonds [91].



**3** **4**

Fig. 10. Intermediates in Mo-catalyzed allylation reference [93].

### *3.12. Molybdenum*

A bimetallic complex was obtained from reaction of two equivalents of $\mathrm{[MoCl(\eta^3\text{-}C_3H_3)(CO)_2(NCMe)_2]}$ with (*R*,*R*)-$\mathbf{L^{4}}\mathrm{H_2}$ (type XI, Fig. 4) [92]. The red crystals obtained were analyzed by X-ray crystallography. Octahedral coordination, with each molybdenum atom coordinating to a pyridine nitrogen atom and a carbonyl oxygen atom of the ligand, one allyl and two carbonyl groups, was observed.

In connection to mechanistic studies of molybdenum catalyzed allylic alkylations, a series of Mo complexes with the unsymmetrical ligand $\mathbf{L^{49}}\mathrm{H_2}$, having one pyridine ring replaced by a phenyl ring, were identified. Reaction of cinnamyl carbonate with two equivalents of $\mathbf{L^{49}}\mathrm{H_2Mo(CO)_4}$ (**3**), obtained from $\mathbf{L^{49}}\mathrm{H_2}$ and $\mathrm{Mo(CO)_4}$(norbornadiene), gave free ligand, $\mathrm{Mo(CO)_6}$ and a Mo(II) allyl complex, $(\mathbf{L^{49}}\mathrm{H})\mathrm{Mo(\eta^3\text{-}C_3H_3)(CO)_2}$, which was isolated and its structure elucidated by X-ray crystallography (Fig. 10) [93]. The ligand coordinated via the nitrogen atom of the pyridine ring, the deprotonated adjacent amide nitrogen atom and the carbonyl oxygen atom of the other amide, which remained protonated. One CO ligand was situated trans to the pyridine nitrogen while the other CO was trans to the carbonyl oxygen, and the allyl group was situated trans to the deprotonated amide nitrogen. In the catalytic cycle, this complex was suggested to lead to anionic Mo(0) complex **3**, coordinating via the deprotonated amide nitrogen atom. The structures of **3** and **4** (Fig. 10) illustrated the preference of the neutral amide group to coordinate via the oxygen atom and the deprotonated amide to coordinate via the nitrogen atom.

### *3.13. Vanadium*

The important but yet not fully understood role of vanadium in biological systems has stimulated studies of the coordination chemistry of simple artificial systems. Vanadium has been shown to be able to bind to $\mathbf{L^{1}}\mathrm{H_2}$ ligands in their neutral, monoanionic and bisanionic forms. Orange $\mathbf{L^{1}}$V(IV)O, obtained from $\mathbf{L^{1}}\mathrm{H_2}$ and $\mathrm{V(O)(O\text{-}\mathit{i}\text{-}Pr)_3}$, was studied as a model of vanadyl-albumin and vanadyl-bleomycin [94]. Electron paramagnetic resonance spectroscopy supported the presence of deprotonated amide ligands in the biomolecules. Under different conditions, V(IV) complexes exhibiting different

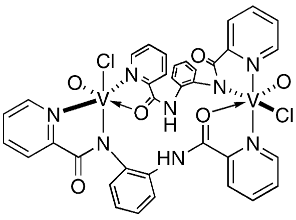


Fig. 11. Dimeric V(IV) complex [95].

types of coordination were obtained. Aerobic oxidation of brick-red $(NHEt_3)[\mathbf{L^1}V(III)Cl_3]$, prepared from $VCl_3$, $\mathbf{L^1}H_2$ and $Et_3N$ and shown by X-ray crystallography to have octahedral coordination at V, afforded a dimeric V(IV) complex (Fig. 11) [95]. Each V had a distorted octahedral environment composed of two pyridine nitrogen atoms, one deprotonated amide nitrogen atom, one amide oxygen (from a neutral amide moiety), one oxygen atom, and one chlorine atom. Replacing $Et_3N$ in the preparation of the V(III) complex by $NH_3$ resulted unexpectedly in formation of $(\mathbf{L^1}H)_3V$, a rare example of coordination of deprotonated amide via the oxygen atom [96]. Other types of dimers, with V(IV) complexed to two neutral carbonyl oxygen atoms, two pyridine nitrogen atoms, one oxygen and one chlorine atom, were obtained from $VOCl_3$ and $\mathbf{L^1}H_2$ or $\mathbf{L^4}H_2$ (without specified absolute configuration) [97].

### 3.14. *Titanium, zirconium*

(*R*,*R*)-$\mathbf{L^5}H_2$ and Zr(O-*t*-Bu)$_4$ yielded a $C_2$-symmetric complex with the doubly deprotonated ligand, as determined by X-ray crystallography [98]. By $^1H$ NMR spectroscopy it was shown that a complex with a monoanionic ligand was an intermediate in the reaction [4]. No complexes with titanium have been isolated and characterized, but such complexes have been shown by NMR spectroscopy to serve as intermediates in catalytic reactions [98].

### 3.15. *The lanthanides*

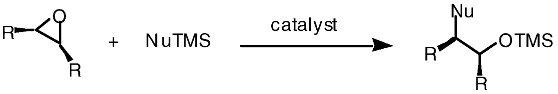
A series of crystalline and air stable lanthanide complexes $(\mathbf{L^{16}}H_2)LnBr_3$, $(\mathbf{L^{16}}H_2)_2LnBr_3$, $(\mathbf{L^{16}}H_2)Ln(NO_3)_3$ and $(\mathbf{L^{16}}H_2)_2Ln(ClO_4)_3$ with dimeric or oligomeric structures were prepared [99]; the analogous chlorides were also reported in a preliminary study [100]. From available spectroscopic data it was concluded that the complexes containing two ligand molecules had coordination number eight, with each ligand coordinating in a bisbidentate bridging *NONO* fashion. The 2:3 complexes were suggested to exist in dimeric form and complexes with one ligand to form oligomeric or polymeric structures. Self assembly of $\mathbf{L^{27}}H_2$ and $\mathbf{L^{28}}H_2$, with two 2,6-pyridinecarboxylic acid units linked by (*R*,*R*)-1,2-diaminocyclohexane and 4,4′-diaminodiphenylmethane units, respectively, and lanthanide ions ($Eu^{3+}$ and $Nd^{3+}$) was studied [19]. Triple helicates with the Ln(III) ions were believed to form, although ultimate structural proof by X-ray crystallography was lacking. Diastereomerically pure helicates were obtained from the chiral ligand. The ΔΔ isomer of the $\mathbf{L^{27}}_3Eu_2$ complex was more stable by 18 kcal/mol than the ΛΛ isomer. From the achiral ligand, racemates were formed.

## 4. Applications in metal-catalyzed reactions

The deprotonated amide is a strong σ-donor capable of stabilizing early as well as late metal ions in high oxidation states, making high-valent metal complexes of the ligands suitable as Lewis acid catalysts. This property, together with the resistance of the ligand to oxidation has also stimulated studies of oxidative processes. At the same time, complexes with low-valent metals have been characterized, and such complexes form part of a number of catalytic cycles. Of special synthetic interest are Mo-calalyzed allylic alkylations, which occur with high regio- and enantioselectivity. Since the pyridine nitrogen resembles the imidazole nitrogen, metal complexes of bispyridylamides have been employed as models for metalloenzymes.

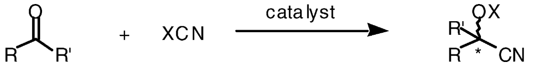
### 4.1. *Ring-opening of epoxides*

The ring opening of *meso* epoxides with nucleophiles is an important synthetic reaction since it gives compounds incorporating two new stereogenic centers (Eq. (1)). Despite the numerous studies of bispyridylamide metal complexes, the first use of a chiral bispyridylamide as ligand in a metal catalyzed asymmetric process was not reported until 1995 when a series of chiral bispyridylamides were evaluated as ligands in the Lewis acid mediated ring opening of cyclohexene oxide [7]. Ligand (*S*,*S*)-$\mathbf{L^5}H_2$ together with $Zr(O^tBu)_4$ proved to be the best catalytic system for the reaction, giving the product in 48% ee. Interestingly, the rate of reaction and the enantiomeric excess were increased, the latter to 71%, upon addition of 0.01 equivalent of diethylamine. The catalytic reaction involved a dimeric Zr complex, as shown by $^1H$ NMR spectroscopy by the formation of two diastereomeric complexes when racemic ligand was employed. (*R*,*R*)-$\mathbf{L^4}H_2$ proved to be less efficient in the chirality transfer for this reaction.

 (1)

### 4.2. *Cyanide addition to aldehydes*

The preparation of enantioenriched cyanohydrins has been a topic of major interest in the field of asymmetric synthesis (Eq. (2)) [101]. The reaction is known to proceed both in the presence of a Lewis acid and a Lewis base. Lewis acid catalyzed cyanation reactions have frequently been performed using trimethylsilyl cyanide (TMSCN). Metal complexes, with different Lewis acidity, containing bispydidylamide units were screened in the cyanation of benzaldehyde with TMSCN [98]. The results were strongly dependent on the quality of the TMSCN used. The product was obtained with a maximum of 70% ee in 90% yield using a catalyst derived from $\mathrm{Ti(O^{\mathit{i}}Pr)_4}$ and (*R*,*R*)-$\mathbf{L^{5}}\mathrm{H_2}$. The enantiomeric excess was found to increase with time. Use of a complex derived from $\mathrm{Zr(O^{\mathit{t}}Bu)_4}$ and (*R*,*R*)-$\mathbf{L^{5}}\mathrm{H_2}$ afforded the product with merely 26% ee. However, the addition of one equivalent of water with respect to the catalyst afforded a catalyst with enhanced reactivity and selectivity, yielding the product with 56% ee. Substituted benzaldehydes as well as aliphatic aldehydes also afforded products with moderate enantioselectivity.



(2)

### 4.3. Aziridinations

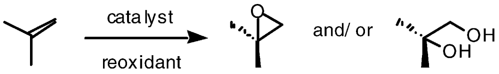
$\mathbf{L^{31}}\mathrm{Ru(III)PPh_3Cl}$ was shown to catalyze the aziridination of styrene using $\mathrm{PhI{=}NO_2SC_6H_4Me}$-*p*, albeit in low yield [22]. A cationic complex obtained by treating an equimolar mixture of $[\mathrm{MoCl(\eta^3\text{-}C_3H_3)(CO)_2(NCMe)_2}]$ and ligand (*R*,*R*)-$\mathbf{L^{4}}\mathrm{H_2}$ with AgCl was found to catalyze the formation of a mixture of aziridine and enamines from *N*-benzylideneaniline and ethyl diazoacetate in the presence of 2,6-di-*t*-butylpyridine. The catalyst failed to induce asymmetry, however [92].

### 4.4. Cyclopropanations

$\mathbf{L^{31}}\mathrm{Ru(III)PPh_3Cl}$ was shown to catalyze the cyclopropanation of styrene by ethyl diazoacetate in high yield and with high *trans*:*cis* ratio (6:1) [22].

### 4.5. Oxidations

The analogy of the bispyridineamide system to porphyrins has stimulated studies of oxidative reactions employing metal complexes of the ligand as catalysts (Eq. (3)). The deprotonated ligand is resistant towards oxidation which, together with the ability of the deprotonated amide to stabilize metal ions in high oxidation states, render the metal complexes suitable as catalysts for oxidation reactions [102]. The dioxo Os(VI) complex with $\mathbf{L^{1}}\mathrm{H_2}$ was employed for the oxidation of cyclohexene [78]. Under stoichiometric conditions no attack on the double bond occurred, cyclohexenol being formed as the main product. Under catalytic conditions, with PhIO as oxidant, small amounts of cyclohexene oxide were produced, although low turnover numbers were observed. The analogous Mn(III) complexes with $\mathbf{L^{1}}\mathrm{H_2}$ and $\mathbf{L^{12}}\mathrm{H_2}$ were found to be somewhat more efficient catalysts for the epoxidation of cyclohexene, styrene and norbornene to their oxides, the highest turnover number, 49, and yield, 58%, being observed in the oxidation of styrene [82]. Six-coordinated Cr(III) complexes with $\mathbf{L^{1}}\mathrm{H_2}$ exhibited lower reactivity, probably due to the lack of an available coordination site for the oxidant [86]. An $\mathbf{L^{1}}$Co(II) alkylperoxy complex catalyzed the oxidation of cyclohexane by *t*-BuOOH to a mixture of cyclohexanol, cyclohexanone and *tert*-butylperoxycyclohexane [61]. Fe(II) complexes of $\mathbf{L^{1}}\mathrm{H_2}$, $\mathbf{L^{2}}\mathrm{H_2}$, $\mathbf{L^{3}}\mathrm{H_2}$, $\mathbf{L^{4}}\mathrm{H_2}$ and $\mathbf{L^{6}}\mathrm{H_2}$ encapsulated in zeolite Y were employed for partial oxidations of cyclohexane using hydrogen peroxide as oxidant, yielding mixtures of cyclohexanol, cyclohexanone and cyclohexylhydroperoxide [103]. Attempts to achieve epoxidation of cyclohexene with hydrogen peroxide using a Fe(II) complex of $\mathbf{L^{1}}\mathrm{H_2}$ failed [104]. With Mn(III) complexes of $\mathbf{L^{2}}\mathrm{H_2}$ and $\mathbf{L^{3}}\mathrm{H_2}$ trapped in zeolites, the epoxidation of olefins using hydrogen peroxide was accompanied by less allylic oxidation than the homogenous systems [105]. As part of a study combining ligand design and parallel screening, a Mn(III) complex of tentagel-supported $\mathbf{L^{1}}\mathrm{H_2}$, grafted via the aromatic ring in the amino part of the ligand, was studied as catalyst for the epoxidation of styrene with PhIO [29]. This complex exhibited lower reactivity than an analogous complex having the picolinic acid moieties replaced by ethylenediame tetraacetic acid; with 5 mol% of the Mn(III) complex of the latter ligand 98% epoxide was obtained within 2 min, as compared to 4 h for that containing polymeric $\mathbf{L^{1}}\mathrm{H_2}$. In C–H bond oxidation, the complex derived from EDTA also provided a more reactive catalyst, but the complex with $\mathbf{L^{1}}\mathrm{H_2}$ resulted anyhow in higher yield of product, due to its considerably higher stability. Olefin oxidation with PhIO as the stoichiometric reagent was also achieved with $\mathrm{(Et_3NH)}[\mathbf{L^{1}}\mathrm{Fe(III)Cl_2}]$, although yields were low [106]. The mechanism was suggested to involve electrophilic attack of I(III) on the olefin [107]. Yields obtained using the triflate in place of the chloride were somewhat higher [106]. No metal–oxo intermediate was detected in the reaction. $\mathbf{L^{31}}\mathrm{Ru(III)PPh_3Cl}$ was shown to catalyze the epoxidation of olefins by PhIO but did not, in contrast to analogous Mn complexes, catalyze alkane hydroxylation [22]. The binuclear Ru(II) complexes with $\mathbf{L^{1}}\mathrm{H_2}$, $\mathbf{L^{2}}\mathrm{H_2}$ and $\mathbf{L^{3}}\mathrm{H_2}$ were also employed as catalysts for the epoxidation of olefins using PhIO and the results compared with those obtained using other pyridineamides [108]. Poor catalytic activity was observed.



(3)

$\mathbf{L^{12}}$MnOAc was employed for the hydroxylation of alkanes using PhIO as oxidant to yield mixtures of alcohols and ketones in low to moderate yields [86]. Oxygen activation was achieved with the Co(II) amide $N_4$ chelate of doubly deprotonated $\mathbf{L^{1}}\mathrm{H_2}$, allowing the oxidation of phenols to benzoquinones [109].

The efficiency and selectivity of the $\mathbf{L}^1$Mn(II) system was increased by covalent attachment of the substrate to the benzene ring via a tether (Fig. 12) [110]. This system allowed an otherwise unreactive cyclohexylmethanol to be oxidized by PhIO.

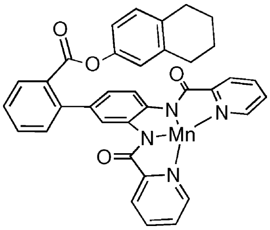
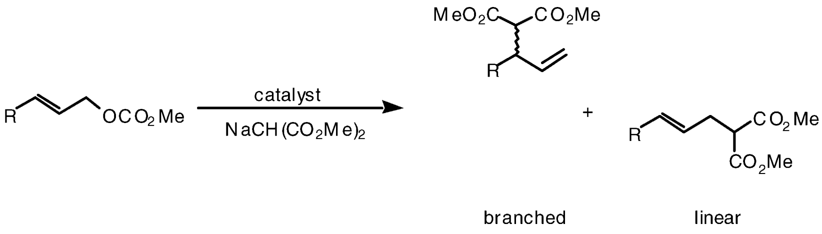


Fig. 12. Mn(II) complex with pendant substrate [110].

### 4.6. Mo-catalyzed allylations [111]

In 1998 Trost and Hachiya reported that a complex made from bispyridylamide $(R,R)$-$\mathbf{L^4}\mathrm{H_2}$ and $\mathrm{Mo(EtCN)_3(CO)_3}$ catalyzed the nucleophilic substitution of cinnamyl carbonate with sodium dimethylmalonate, giving the product in high yield and with excellent regio- and enantioselectivity (49:1 branched to linear ratio and 99% ee, Eq. (4)) [112]. The resulting catalyst exhibited high temperature stability since the reaction could be performed in refluxing THF without deactivation of the catalyst and little loss in regio- and enantioselectivity. Large substrate generality was displayed by the catalyst as well. Di- and polyenyl carbonates were alkylated regioselectively at the non-benzylic position [113]. The same catalyst was recently employed for the regio- and enantioselective addition of oxalactimes to a variety of substrates [114]. The catalyst precursor could be formed from $(R,R)$-$\mathbf{L^4}\mathrm{H_2}$ and a more convenient Mo source, $\mathrm{Mo(CO)_6}$, by microwave heating [115] or by conventional heating [116]. If the catalytic reaction was run under microwave heating, the reaction time could be reduced from hours to minutes, whereas conventional heating required 4 h for formation of a metal ligand complex. The microwave procedure allowed the reaction to be run under air while affording the product with excellent regio- and enantioselectivity (19:1 branched to linear ratio and 98% ee). By introducing different substituents in the pyridine ring of the ligand, the regio- and enantioselectivity of the reaction could be fine tuned [20]. In general, π-donor groups in the 4-position of the pyridine rings afforded the product with higher branched to linear ratio. Having substituents in the 6-position was detrimental for both reactivity and selectivity probably due to steric congestion around the metal center. The reaction could also be performed with $(R,R)$-$\mathbf{L^{48}}\mathrm{H_2}$ attached to a Tentagel resin and the product obtained by simple filtration, exhibited 35:1 branched to linear ratio and 97% ee although reaction times were longer (30 min compared to 5 min using $(R,R)$-$\mathbf{L^4}\mathrm{H_2}$) [25]. Reuse of the ligand was possible without any significant change in the outcome of the reaction.



(4)

### 4.7. Miscellaneous

$\mathbf{L^3}$Ni and *rac*-$\mathbf{L^6}$Ni were shown to serve as catalysts for the cross-coupling of an aryl Grignard reagent with aryl halides [117]. Cobalt and iridium catalyzed hydrogenation with molecular hydrogen and cobalt, rhodium and iridium catalyzed hydrogen transfer with isopropanol as hydrogen source using $(S,S)$-$\mathbf{L^5}\mathrm{H_2}$ as ligand resulted in low conversions and poor enantioselectivites [118].

## 5. Conclusions

The coordination chemistry of bispyridylamides is extremely rich. Examples of coordination via the pyridine nitrogen atoms, the carbonyl oxygen atoms and the amide nitrogen atoms of the ligand in a non-, mono-, or bisdeprotonated form are known. Metal complexes of the ligands have been extensively used to mimic the properties of biologically active systems. For catalytic applications chiral derivatives are particularly interesting, and recently highly enantioselective processes have been described. The convenient structural variation of the compounds by a modular approach gives access to ligands with varied structures having different electronic and steric properties, thus enabling fine tuning of the catalyst. Further applications of bispyridylamides as ligands in asymmetric catalysis are expected to be found due to the ability of the compounds to form complexes with metal ions in different oxidation states.

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