Review

Bridging ligands comprising two or more di-2-pyridylmethyl or amine arms: Alternatives to 2,2′-bipyridyl-containing bridging ligands

Christopher J. Sumby *

School of Chemistry & Physics, The University of Adelaide, North Terrace, Adelaide, SA 5005, Australia

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A R T I C L E I N F O

A B S T R A C T

Bridging ligands incorporating 2,2′-bipyridine as a chelating component have been utilised for several decades and are widely employed in coordination chemistry, supramolecular chemistry and materials synthesis. Such ligands form stable 5-membered chelate rings upon coordination to a metal. Two related chelating units, di-2-pyridylamine and di-2-pyridylmethane, which form 6-membered chelate rings when coordinated to a metal, have been studied far less as components of bridging ligands but have recently garnered significant levels of attention. Of around 140 reports on the incorporation of these moieties into bridging ligands some 75% have been published in the last 15 years. This review covers the synthesis of bridging ligands containing di-2-pyridylamine and di-2-pyridylmethane chelating moieties, and a survey of their coordination and supramolecular chemistry. Applications of the resulting systems as structural and functional models of enzyme active sites, and spin-crossover materials, and for investigations into anion–π interactions are covered.

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1. Introduction

Nitrogen-containing heterocycles are one of the most important classes of ligand in coordination chemistry [1–4]. The ability to readily incorporate more than two donor atoms, or two or more aromatic nitrogen-containing heterocycles, into one molecule has provided access to numerous chelating and bridging ligands [1–7]. In the latter case, ligands possessing more than one coordination site can link a number of metal atoms. These bridging ligands have attracted a significant degree of attention in recent years because they enable the formation of multinuclear metallosupramolecular
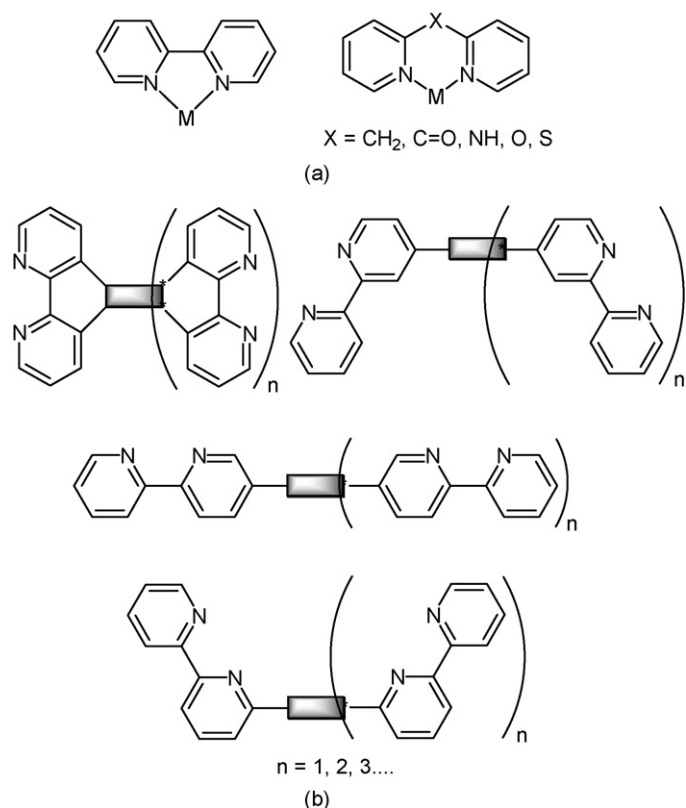
Fig. 1. (a) Examples of ligands able to form five- and six-membered chelate rings and (b) bridging ligands containing two or more 2,2′-bipyridine units.

Fig. 2. A schematic representation of bridging ligands containing two or more di-2-pyridylmethyl or di-2-pyridylamine units.

assemblies [3,8,9] or coordination polymers [10–17] with desirable structures and properties. Within such bridging ligands the additional stabilising effect of chelation to multiple metal atoms can be achieved through incorporation of bidentate donor groups that form either a five- or six-membered chelate ring with each coordinated metal centre (Fig. 1a).

Bridging ligands with the potential to chelate at both metal centres result in complexes with greater stability and potentially enhanced metal–metal interactions. The 2,2′-bipyridyl moiety has been extensively used as a chelating donor site within such bridging ligands due to its robust redox stability and relative ease of functionalisation. This ease of functionalisation allows ligands containing multiple 2,2′-bipyridine units to be synthesised and the interconnection of metal centres to be achieved with well-defined spatial arrangements (Fig. 1b). The synthesis of such ligands and their use in coordination chemistry have been reviewed elsewhere [4].

While bridging ligands that contain donor sets capable of forming five-membered chelate rings, such as those derived from 2,2′-bipyridine (bpy), have been extensively studied over many years [4], related bridging ligands that comprise at least two di-2,2′-pyridylmethyl or amino arms have only recently attracted a significant level of attention. This attention has been directed toward studying metal–metal interactions (e.g. electronic and magnetic), in supramolecular chemistry to study anion–π interactions, as sensors, in new coordination materials, and as structural and functional enzyme active site models. This review article discusses compounds represented by the schematic shown in Fig. 2, where 'X' is either a carbon or nitrogen linker and 'n' is the number of additional di-2-pyridyl arms (n = 1, 2, 3, etc.). This furnishes ditopic, tritopic, tetratopic ligands capable of bridging two, three, four or more metal centres, respectively.

While bridging ligands containing multiple 2,2′-bipyridyl or di-2-pyridyl (either di-2-pyridylamino/methyl) moieties can both
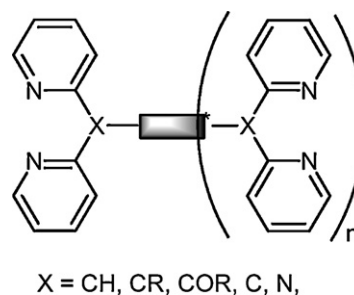
chelate to metal centres, the former achieves this by a five-membered chelate ring and the latter by a six-membered chelate ring (Fig. 3a). Both types of ligand form very stable multinuclear complexes but the differences between the number of atoms in the chelate rings impose some important differences on the two classes of ligand; namely in the synthesis of the ligands and in the properties of the resulting complexes. In the case of the 2,2′-bipyridyl-containing ligands, particularly those with restricted rotation about the biaryl bond, the ligands are planar and more readily able to facilitate metal–metal interactions through the conjugated π-system of the ligand (Fig. 3b). In related di-2-pyridyl-containing bridging ligands the six-membered chelate ring typically adopts a boat conformation which limits ability of the π-system to facilitate metal–metal interactions (Fig 3c and d). There are subtle differences between the conformations of the di-2-pyridyl-containing ligands where X is an sp³ (e.g. CH, CR, COR, Fig. 3c) or sp² centre (e.g. C=, N, Fig. 3d) The non-planarity and flexibility of di-2-pyridyl-containing bridging ligands often ensures they are more soluble than similar 2,2′-bipyridyl-containing ligands. This flexibility can also manifest itself in the ability to display variable coordination behaviour; while the predominant mode of coordination is to chelate a particular metal centre, it is possible for the di-2-pyridyl motif to act as a monodentate donor or to bridge two metal centres (Fig. 3e).

As noted, this review article discusses compounds represented by the schematic shown in Fig. 2, where 'X' is either a carbon or nitrogen linker and 'n' is the number of additional di-2-pyridyl arms (n = 1, 2, 3, 4, etc.). As the functional context of these ligands is rather broad, the focus of the review is predominantly synthetic and those looking for in-depth reviews of the application of such complexes are directed elsewhere. This review outlines the synthesis of bridging ligands containing di-2-pyridylamine and di-2-pyridylmethane chelating moieties, and a survey of their coordination and supramolecular chemistry. Where feasible and timely, the application of the resulting complex species is described to indicate the functional context guiding the design of the ligands discussed. Bridging ligands of the type covered in this review have featured as part of other review articles, on binucleating ligands [18], ligand design [7], starburst complexes [19], cyclometallation [20], spin-crossover systems [21], cross-conjugated organic compounds [22], and anion templated synthesis [23], for example.

2. The synthesis and coordination chemistry of bridging ligands comprising two or more di-2-pyridylmethyl arms

2.1. General synthetic approaches to prepare di-2-pyridylmethane-containing bridging ligands

Di-2-pyridylmethane (dpm) is a relatively easily accessible starting material that has less commonly been incorporated, as a chelating motif, into bridging ligands. Di-2-pyridylmethane can be
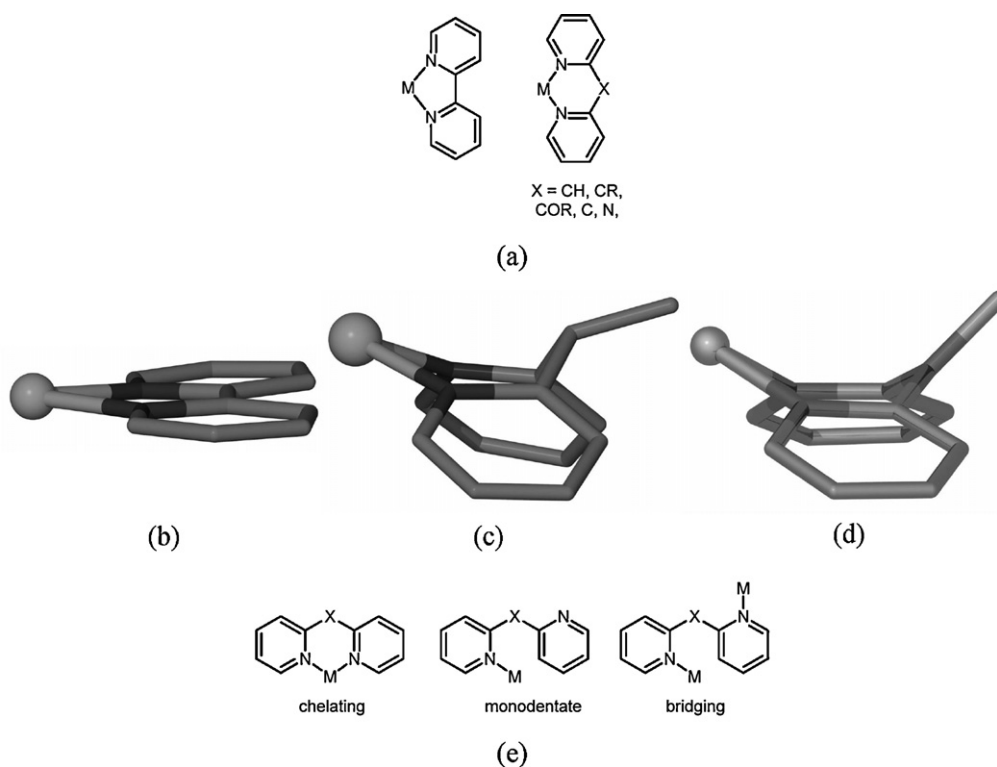
Fig. 3. (a) The five- and six-membered chelate rings observed for biheterocycles and di-2-pyridyl compounds; (b)–(d) representations of the five-membered chelate rings in 2,2-bipyridyl ligands (b) and six-membered chelate rings in di-2-pyridylmethyl (c) and di-2-pyridylamino (d) ligands; and (e) the coordination modes possible for a di-2-pyridylmethyl or di-2-pyridylamino chelating moiety.

prepared from commercially available di-2-pyridylketone (dpk) by a Wolff–Kishner reduction (Eq. (1)) and these two precursors have been commonly used for the synthesis of bridging ligands containing a di-2-pyridyl moiety. Reaction of dpk with hydrazine or aliphatic diamines leads to diimines, while the acidic CH_2 group of dpm can be readily deprotonated and the stable anion employed in synthesis. An alternate approach to prepare such dpm-containing ligands is to utilise 2-lithiopyridine as a nucleophile.

(1)
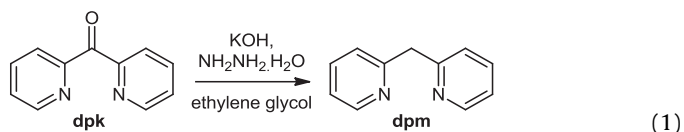
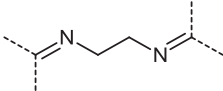### 2.2. Ditopic ligands with aliphatic cores
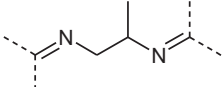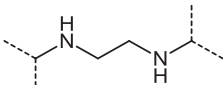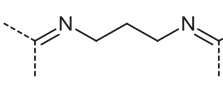
The simplest conceivable bridging ligand in this series (Table 1), tetrakis(2-pyridyl)methane, **1**, was first synthesised by reaction of 2-chloropyridine with the lithium salt of tris-2-pyridylmethane [24]. The reaction required quite severe conditions to achieve reasonable yields of **1**; for example, reaction of 2-chloropyridine and tris-2-pyridylmethyl lithium (5 equiv.) in THF at reflux for 24 h only gave **1** in low yield, whereas in mesitylene at reflux a much improved yield of 52% was obtained. Considerable quantities of unreacted tris(2-pyridyl)methane were recovered. More recently, Abu-Shanab reported that treatment of 2-methylpyridine with excess of lithium diisopropylamide (LDA), at low temperature, followed by 2-bromopyridine, provided **1** as the main product in 60% yield [25]. Only traces of the by-products tri-2-pyridylmethane and dpm were observed. Oda and co-workers reported a 1D coordination polymer with **1** and Ag(I), {[Ag(**1**)]ClO$_4$}$_n$, as well as two discrete Cu(II) complexes, [Cu(**1**)$_2$](ClO$_4$)$_2$ and [Cu(**1**)$_2$](ClO$_4$)$_2$·2(CH$_3$CN), whereby **1** displayed several coordiantion modes [26].

A dinuclear manganese(II) complex of **1** [{Mn(hfa)$_2$}$_2$(**1**)], was also synthesised (where hfa = hexafluoroacetoacetate) [27]. [{Mn(hfa)$_2$}$_2$(**1**)] was characterised by X-ray crystallography and has a dihedral angle of 87.4(2)° between the two chelate rings around the sp^3 carbon atom. Studies of the magnetism revealed a very weak antiferromagnetic interaction between manganese(II) spins. In attempts to study other spiro-compounds involving orthogonally fused π-conjugated moieties for molecular electronic devices, Ishida 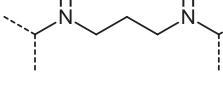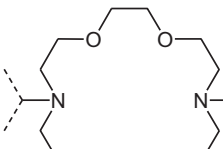et al. targeted the synthesis of a dinuclear copper(II) complex [{Cu(hfa)$_2$}$_2$(**1**)] [28]. Unlike the dimanganese compound also reported by these authors, only mononuclear copper species, [Cu(hfa)$_2$(**1**)] and [Cu(hfa)(**1**)][Cu(hfa)$_3$], were obtained. In these complexes **1** acts as a bi- and tridentate ligand, respectively. The same researchers also reported a dinuclear nickel(II) complex [{Ni(hfa)$_2$}$_2$(**1**)] [29]. An X-ray crystal structure revealed, like the previous reported Mn$_2$ complex, an orthogonal arrangement between the two coordination planes. Ferromagnetic exchange coupling was demonstrated for the complex and a mechanism for ferromagnetic coupling proposed on the basis of the orthogonal dσ-type magnetic orbitals.

Mononuclear Fe(II) and Co(II) metal complexes of **1** have also been synthesised [30]. In the complexes, [M(**1**)$_2$](ClO$_4$)$_2$·CHCl$_3$ (M = Co(II), Fe(II)), **1** acts as a tridentate ligand. [Co(**1**)$_2$](ClO$_4$)$_2$·CHCl$_3$ undergoes a gradual spin-crossover (SCO) to the high-spin state at temperatures above >300 K, while the Fe(II) derivative exhibits no SCO over the range 5–400 K used for the studies.

Separation of the two di-2-pyridylmethane subunits by a carbon–carbon single bond gives 1,1,2,2-tetrakis(2-pyridyl)ethane, **2**. This bridging ligand, was first prepared by Canty and Minchin [34,35] via oxidation of di-2-pyridylmethyl lithium with mercuric iodide in excellent 85% yield (Scheme 1). This transformation could also be carried out by oxidation of di-2-pyridylmethyl lithium with iodine which avoids the formation of metallic mercury [37].

Table 1
Ditopic dpm containing ligands with aliphatic cores.

Number	X——☐——X	Reference	Number	X——☐——X	Reference
1		[24–30]	7a		[31–33]
2		[34–37]	7b		[31]
3		[36,38]	8		[31–33]
4		[36,37,39]	9		[31,32]
5		[40]	10		[32]
6		[41]	11		[42]

A dinuclear palladium acetate complex, [{Pd(O₂CCH₃)₂}₂(**2**)] was reported by Canty and Minchin in which **2** bridges two palladium centres by forming the more favourable six-membered, rather than seven-membered, chelate rings [35]. Sumby and Steel also reported dinuclear complexes of **2**, in this case with copper(II) nitrate and zinc(II) nitrate [36]. Additionally, a discrete [Ag₂(**2**)₂]²⁺ complex was observed with silver tetrafluoroborate whereby each molecule of **2** acts as a tridentate bridging ligand

for the 3-coordinate silver atoms [36]. Compound **2** also forms a 1D coordination polymer [Ag(NO₃)(**2**)]ₙ where it acts as a tetradentate bridge [36]. Despite several examples where **2** acts a tetradentate bridging ligand, reaction with [Ru(bpy)₂Cl₂] and [Ru(dmb)₂Cl₂] gave only mononuclear complexes [37]. Oddly, a crystal structure of one of these complexes revealed there was no steric impediment to forming the anticipated dinuclear Ru(bpy)₂ or Ru(dmb)₂ complexes.
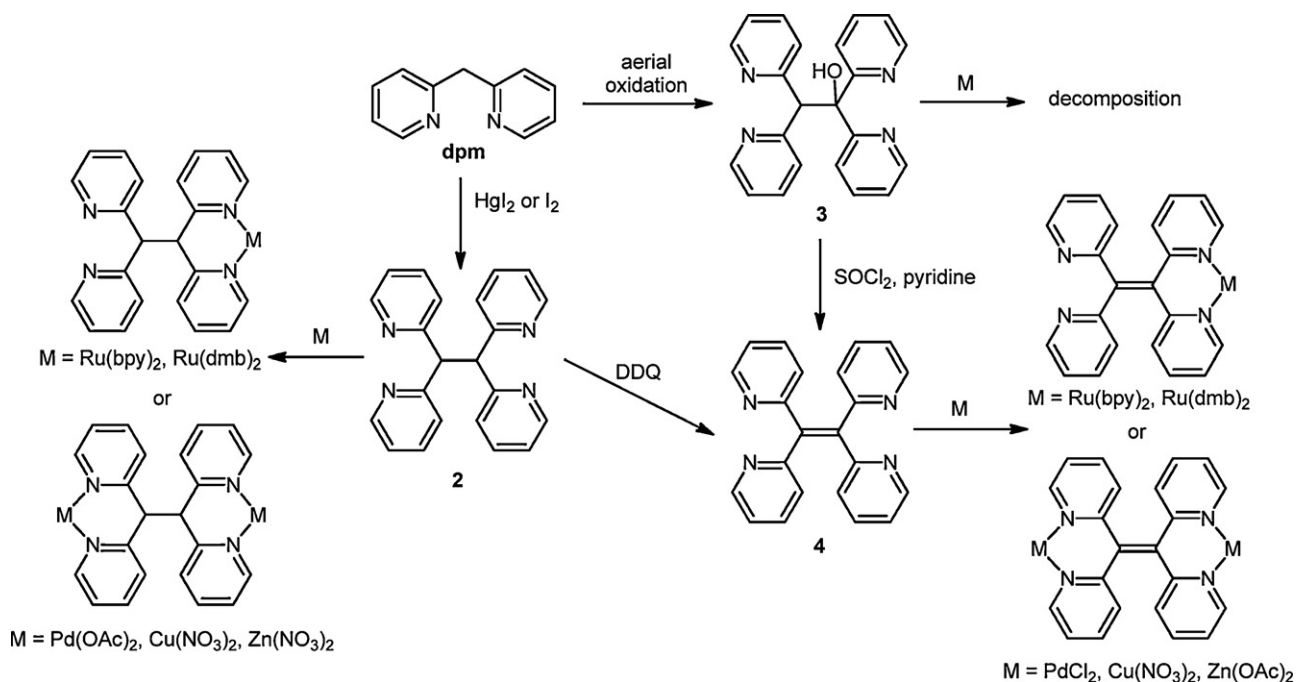
Scheme 1. (after Ref. [36]).
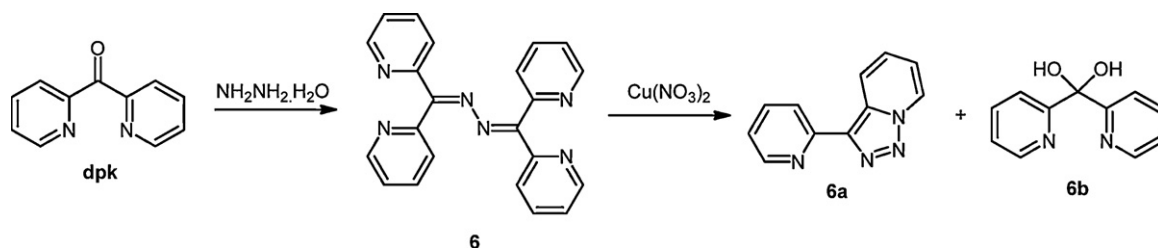
Scheme 2. (after Ref. [41]).

An *in situ* synthesis of 1,1,2,2-tetrakis(2-pyridyl)ethanol, **3** from dpm and dpk was originally reported by Manzur et al. when forming a dinuclear copper complex [Cu$_2$(dpm)$_2$(**4**)(OH)](ClO$_4$)$_3$·2H$_2$O [39]. If the reaction mixture is heated for 60 min, as opposed to the short reaction periods used to give [Cu$_2$(dpm)$_2$(**4**)(OH)](ClO$_4$)$_3$·2H$_2$O, then a mononuclear complex [Cu(dpm)(**3**)](ClO$_4$)$_2$·MeOH is obtained [38]. Ligand **3**, a potential tetra- or pentadentate ligand, was also isolated by Sumby and Steel after aerial oxidation of di-2-pyridylmethane over a period of weeks to months (Scheme 1) [37]. Colourless crystals of **3** form in di-2-pyridylmethane when left to stand, and these can be isolated by dissolving the residual di-2-pyridylmethane in diethyl ether and isolating the solid by filtration. Compound **3** is a useful starting material for the synthesis of 1,1,2,2-tetrakis(2-pyridyl)ethene **4** but a poor ligand; **3** readily undergoes a retro-Knoevenagel reaction to form di-2-pyridylmethane and di-2-pyridylketone in the presence of silver(I), palladium(II) and copper(II) [36].

1,1,2,2-Tetrakis(2-pyridyl)ethene (**4**) was synthesised by DDQ oxidation of **2** in low yield (25%) and then more effectively by room temperature dehydration of **3** with thionyl chloride and pyridine in 81% yield (Scheme 1) [37]. As noted above, Manzur et al. formed a dinuclear copper complex [Cu$_2$(dpm)$_2$(**4**)(OH)][ClO$_4$]$_3$·2H$_2$O from *in situ* synthesis of **4** [39]. In a similar manner to **2**, the unsaturated tetrapyridyl compound readily forms dinuclear complexes with a variety of transition metal precursors, including copper(II) nitrate, palladium(II) chloride and zinc(II) acetate [36]. Despite this however, compound **4** could not be induced to form dinuclear complexes with [Ru(bpy)$_2$Cl$_2$] and [Ru(dmb)$_2$Cl$_2$] even under prolonged heating in ethylene glycol in a microwave on high power [37].

The synthesis of the cumulene (buta-1,2,3-triene) derivative, 1,1,4,4-tetrakis(2-pyridyl)butatriene (**5**) was reported by Newkome [40] over thirty years prior to the synthesis of the related alkene **4**. The starting material for the synthesis of the cumulene, 1,1,4,4-tetrakispyridylbutyne-1,4-diol was didehydroxylated by treatment with P$_2$I$_4$ in pyridine at 0 °C to give the unstable cumulene, **5** (Eq. (2)). While the compound could be carefully purified by chromatography, all attempts to crystallise the compound or evaporate the solution afforded mixtures of decomposition products. As such, no coordination complexes of this compound have been reported:

$$(2)$$
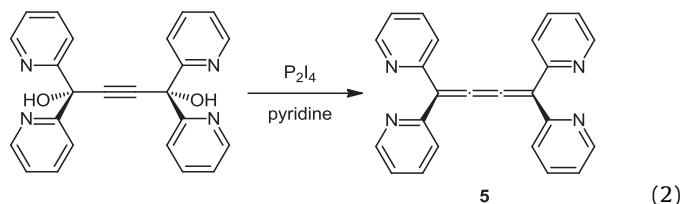
The related tetrapyridyl compound bis(di-2-pyridylketone)azine (**6**), in which a similar distance between the di-2-pyridylmethane subunits is obtained, was synthesised by reaction of commercially available di-2-pyridyl ketone with hydrazine hydrate in 89% yield (Scheme 2) [41]. The coordi-

nation chemistry of **6** was studied with silver nitrate, copper nitrate and palladium chloride, although in the latter two cases only decomposition products or mixtures of products were obtained. Upon reaction with silver nitrate a discrete tetranuclear complex was obtained wherein two molecules of **6** sandwich four silver(I) centres to generate a tetragonal prismatic structure, [Ag$_4$(NO$_3$)$_2$(**6**)$_2$]$^{2+}$. Copper nitrate appears to catalyse the decomposition of the ligand **6** to give individual copper complexes of 3-(2-pyridyl)-triazolo[1,5-a]pyridine (**6a**) and di-2-pyridylmethanediol (**6b**), [Cu(NO$_3$)$_2$(**6a**)$_2$], and [Cu(**6b**)$_2$](NO$_3$)$_2$·H$_2$O, respectively (Scheme 2) [41].

More flexible and larger aliphatic spacers have also been used to connect two di-2-pyridyl subunits. The Schiff base compounds **7a**, **7b** and **9** were prepared by Ortego from di-2-pyridyl ketone and 1,2-diaminoethane, 1,2-diaminopropane, and 1,3-diaminopropane, respectively, using boron trifluoride diethyl etherate as a catalyst [31]. The same workers also reported the secondary amine derivatives **8** and **10** [32], along with three discrete complexes of these ligands [32]. Otego reported that reactions of **8** with CoCl$_2$·6H$_2$O, CoBr$_2$·6H$_2$O and NiBr$_2$·3H$_2$O in THF gave [M(**8**)][MX$_4$] complexes (where, M = Co, Ni, and X = Cl or Br). Ye and Chen have also reported the synthesis of **7a** and **8** [33].

1,10-Diaza-18-crown-6 was used as a linker by Tsukube to separate two di-2-pyridylmethyl substituents in their studies of side arm effects on cation binding, extraction, and transport [42]. Reaction of a mixture of di-2-pyridylmethylbromide and diaza-18-crown-6 in ethanol gave *N,N′*-disubstituted diaza-18-crown-6 derivative, **11** in 80% yield. This compound effectively extracts aqueous solutions of several transition metals into dichloromethane, although no structural information on the nature of the extracting complex was provided.
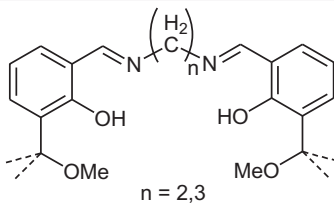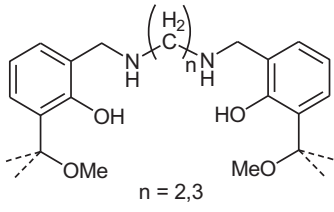
2.3. Ditopic ligands with arene cores

Bosnich reported octadentate ligands **12a**, **12b**, **13a**, and **13b** (Table 2) bearing two terminal di-2-pyridylmethyl substituents as models for the respiratory protein hemerythrin [43]. The dpm substituent was introduced during the synthesis by reaction of 1-dimethoxymethyl-2-methoxymethoxybenzene with dpk, and ultimately, the resulting aldehyde used to form two imine (**12a** and **12b**) and two amine (**13a** and **13b**) derivatives (Scheme 3). The linker in these four ligands provides an additional four donors (Table 2). Bimetallic copper(II) and nickel(II) complexes of some of these ligands were isolated and characterised and crystal structures two of the copper(II) complexes were determined. A monometallic manganese(II) complex of one of these ligands was also isolated, and in solution exposure to dioxygen leads to a manganese(IV) complex.

2.4. Ditopic ligands with heteroarene cores

Heterocycles have also been used as linkers between two di-2-pyridylmethyl substituents (Table 3). Ligands where the substituents are separated by thiophene (**14**), pyridine (**15–18**),

Table 2
Ditopic dpm containing ligands with arene cores.

Number	X—⬚—X	Reference
12a 12b	n = 2,3	[43]
13a 13b	n = 2,3	[43]

pyridazine (**19**), phthalazine (**20**), and pyrimidine (**21**) cores have been prepared. The thiophene derivative was prepared by Kläui as an N_4S ligand to model cyctochrome P450 activity [44]. Compound **14** was synthesised by treating 2,5-thiophenedicarbonyl dichloride with 2-lithiopyridine but could also be prepared in better yields by treatment of 2,5-dilithiothiophene with dpk. An iron(II) complex was prepared and slowly epoxidates alkenes, namely styrene, cyclooctene and 1-octene.

A large amount of activity has focused on pyridine derivatives **15**–**18**. Canty first reported the synthesis of 2,6-bis[1,1-bis(pyridin-2-y1)ethyl]pyridine **15** by a two-step synthetic scheme involving reaction of lithiated dpm with MeI and subsequent reaction of the resulting 1,1-bis(di-2-pyridyl)ethane with 2,6-dichloropyridine in approximately 39% overall yield (Scheme 4) [50]. A mononuclear palladium complex was reported, [Pd(OAc)(**15**)](OAc)·3H₂O whereby the ligand chelates one palladium centre as a tridentate donor.
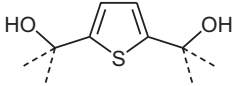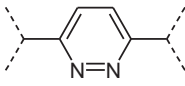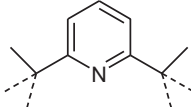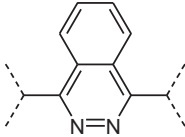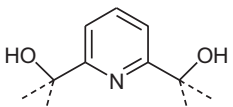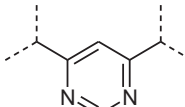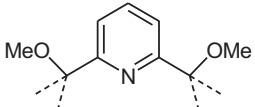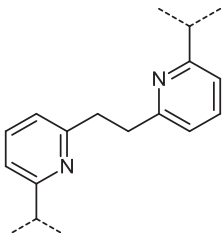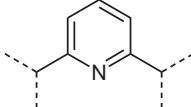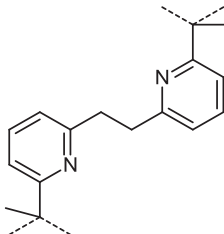
Long and co-workers have studied the magnetic properties of star-like clusters $[\{V(\mathbf{15})\}_4M(CN)_6]^{5+}$ (where M = Cr, Mo) and $[\{Mn(\mathbf{15})\}_4Re(CN)_7]^{4+}$ [51,52]. The pentadentate ligand **15** was used as a capping moiety, chelating the external vanadium and manganese centres to ensure the formation of discrete, star-like clusters that were magnetically isolated. More recently, Long and co-workers reported the related series of pentanuclear clusters with the formulas $[\{M(\mathbf{15})\}_4Re(CN)_7]^{5+}$ (M = Co, Ni, Cu) and $[\{Cu(\mathbf{15})\}_4Re(CN)_7]^{4+}$ [53]. The complexes are electrochemically interesting; the cobalt species undergoes intramolecular Co(II) to Re(IV) charge-transfer upon formation, giving a Co(II)₃Co(III)Re(III) species, and the copper pentanuclear cluster undergoes a rhenium-based one-electron reduction at room temperature [53].

Another contribution to the study of molecular magnetism by Long and co-workers also employed **15** [54]. In this work they reported a series of mixed-valence complexes of the type $[\{V(II)(\mathbf{15})\}(\mu\text{-}L_{br})\{V(III)(\mathbf{15})\}]^{4+}$ (where L_{br} = imidazolate,
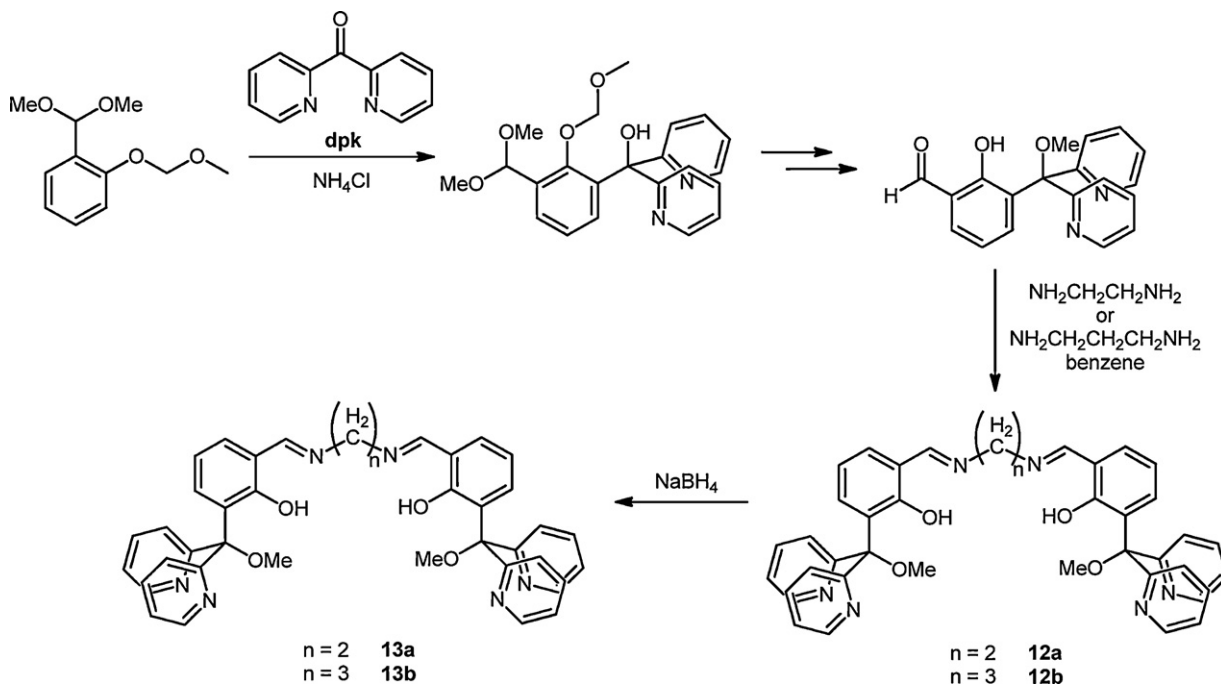
Scheme 3. (after Ref. [43]).

Table 3
Ditopic dpm-containing ligands with heteroarene cores.

Number	X—▭—X	Reference	Number	X—▭—X	Reference
14		[44]	19a 19b		X = dpm [45–48] X = CHpy(6-Mepy) [49]
15		[50–55]	20a 20b		X = dpm [56–60] X = CH(6-Phpy)₂ [59,61]
16		[62–64]	21		[65]
17		[66–72]	22a 22b		X = dpm [73–77] X = CH(6-Mepy)₂ [78]
18		[79]	22c		X = C(6-Mepy)₂ [80]
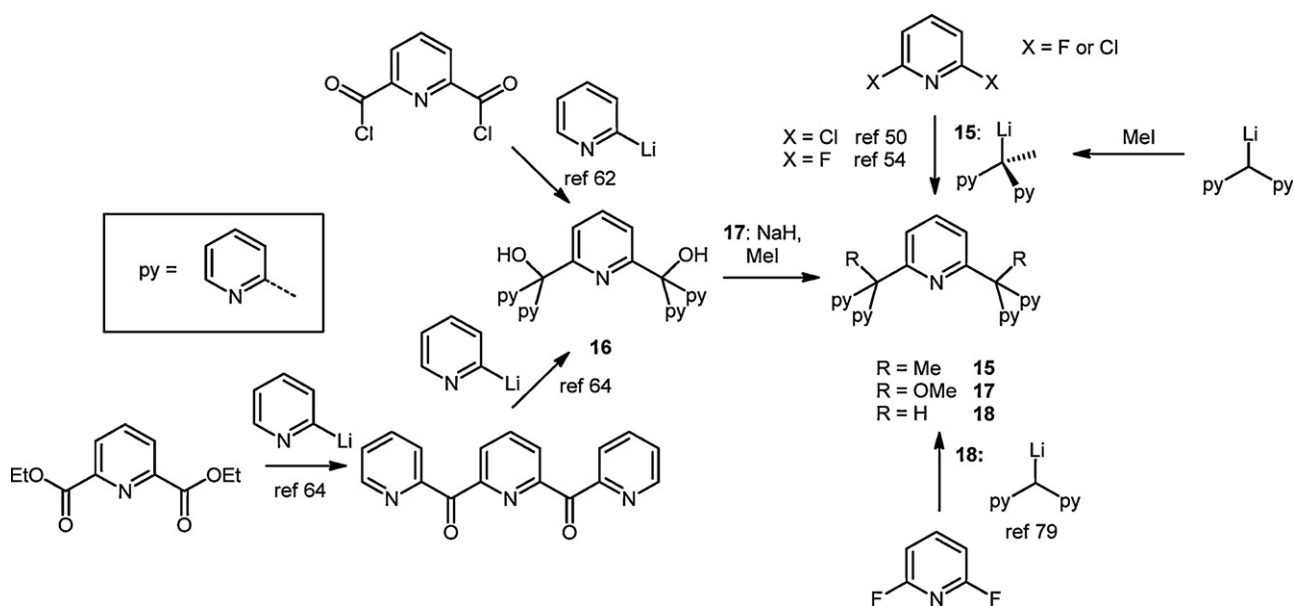
Scheme 4. (after Refs. [50,54,62,64,79]).
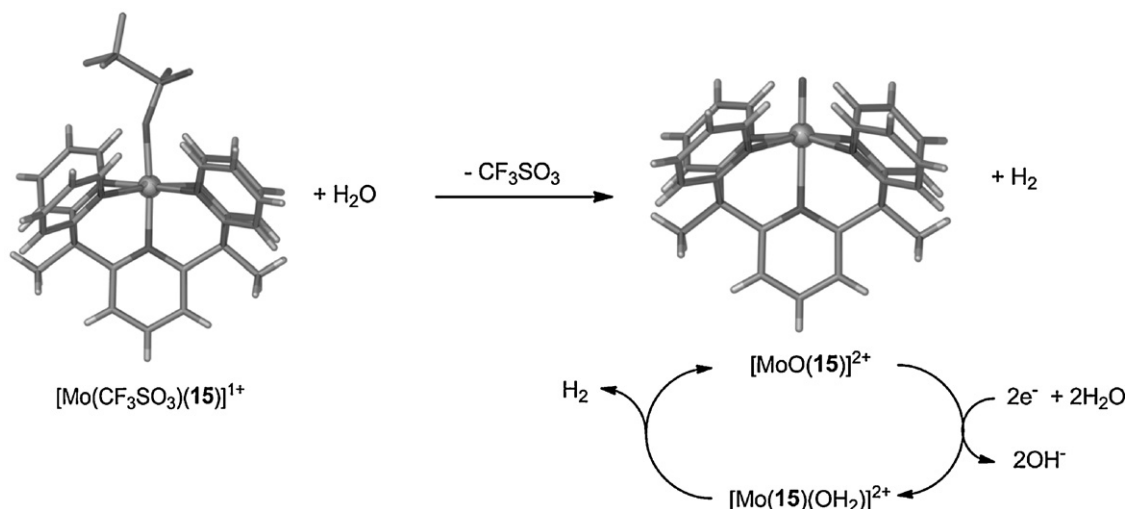
Fig. 4. The use of the pentadentate ligand **15** to form a molybdenum complex [Mo(CF₃SO₃)(**15**)] (CF₃SO₃) that generates hydrogen (after Ref. [55]) and the proposed catalytic cycle used to generate hydrogen.

benzimidazolate, 2-methylimidazolate, 2-chloroimidazolate, 5,6-dimethylbenzimidazolate, or 4,5-diphenylimidazolate). The pentadentate ligand **15** was chosen again as a capping group, because it dictates a rigid octahedral coordination environment about the metal centre, while leaving one site open for the bridging ligand. Based on the report of Dyker and Muth [79], a higher yielding (75% over two steps) and straightforward synthetic route to **15** was developed by Long [54] that gave access to the compound on a multi-gram scale (Scheme 4). The electron delocalization within the complexes was studied by cyclic voltammetry and spectroelectrochemistry.

Very recently, Karunadasa, Chang and Long reported the synthesis of a molybdenum-oxo catalyst that generates hydrogen from water [55]. During the course of investigating the second-row transition-metal chemistry of the pentadentate ligand **15** a [MoI(**15**)]I₂ complex was obtained from reaction of **15** with MoI₂(CO)₃(CH₃CN)₂ (Fig. 4). Water was observed to react with [MoI(**15**)]I₂ to form hydrogen and a molybdenum–oxo complex, [MoO(**15**)]I₂. A cleaner two-electron reaction with water was observed for the Mo(II) compound [Mo(CF₃SO₃)(**15**)](CF₃SO₃), which generates [MoO(**15**)](CF₃SO₃)₂ and hydrogen. The Mo(IV)–oxo complex observed was then tested in an electro-
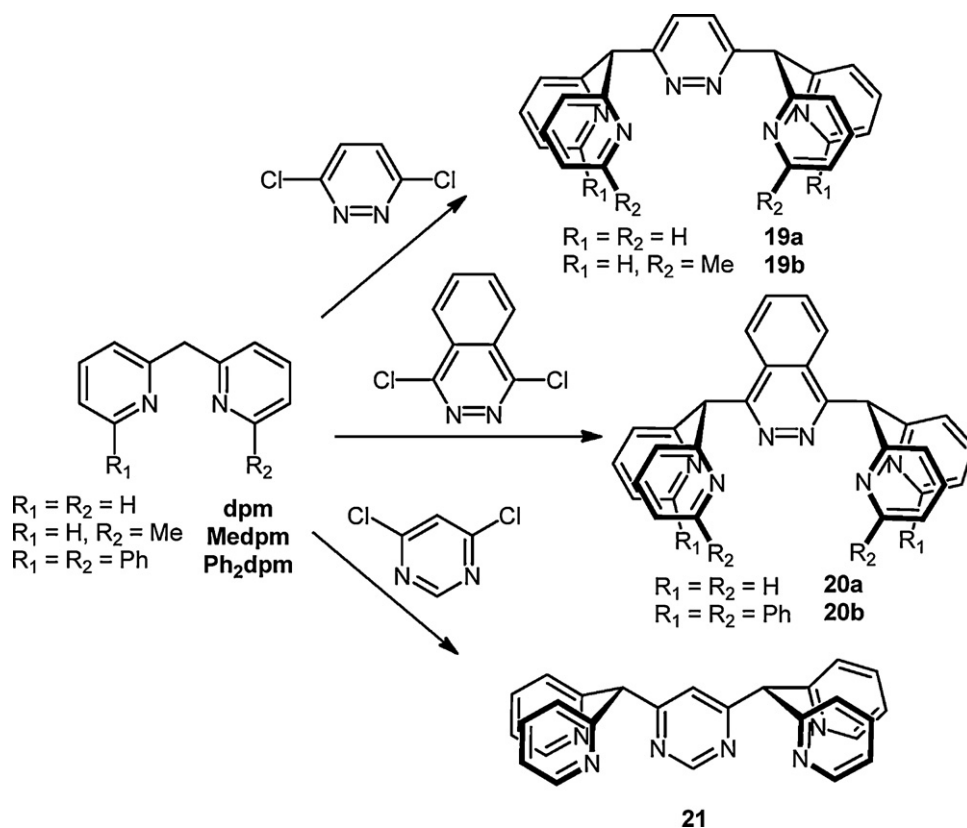
Scheme 5. (after Refs. [45,49,56–58,65]).
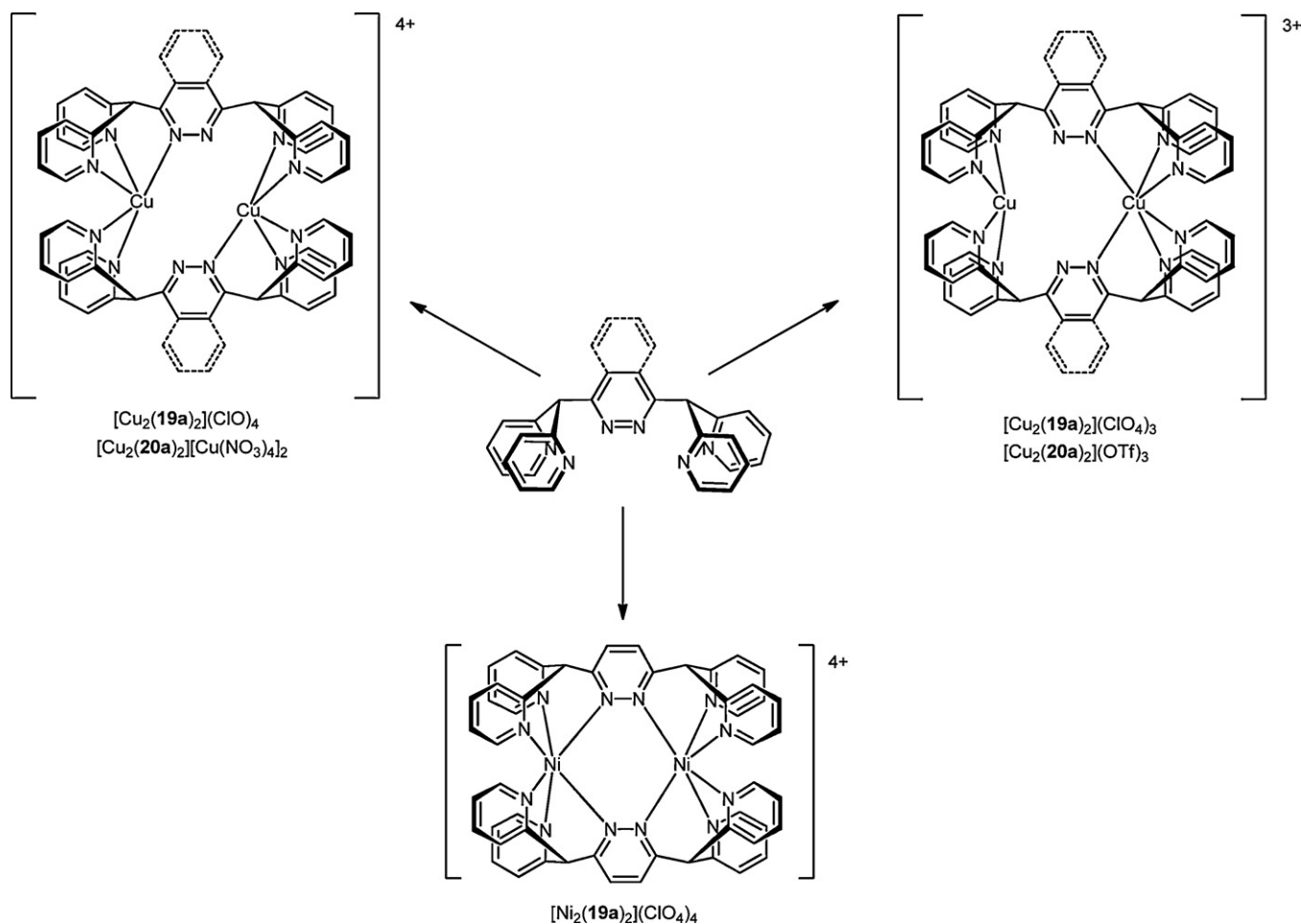
Scheme 6. (after Refs. [45,46,48,59,60]).

chemical cycle for generating hydrogen from water. The turnover frequency increases with overpotential, reaching 1600 moles of H_2 per mole of catalyst per hour, while control experiments performed using Na_2MoO_4 or **15** showed no catalytic activity. Catalyst lifetime was significant and the catalyst was examined in seawater.

Compound **16** was first reported in 2004 when it was synthesised by reaction of 4 equivalents of 2-lithiopyridine with the diacid chloride of 2,6-pyridinedicarboxylic acid (Scheme 4) [62]. Iron(II) complexes of this pentadentate pyridyl ligand were studied as part of a search for new anti-tumour agents by Che [63]. While iron complexes of the related pentadentate ligand 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinapyridine cleave supercoiled plasmid DNA, iron(II) complexes of **16** did not.

To avoid the extensive chromatography previously required for the purification of **16**, Goldsmith and Stack developed an alternative two-step synthesis (Scheme 4) through 2,6-bis(2-pyridyl ketone)pyridine [64]. The intermediate could be purified by recrystallisation to allow the large-scale synthesis of without the need for chromatography. A lipoxygenase mimic [Fe(II)(**16**)(CH_3CN)](CF_3SO_3)$_2$ was prepared and oxidation to [Fe(III)(OH)(**16**)](CF_3SO_3)$_2$ was proposed to proceed through a green iron(IV) oxo-species [64].

Compound **17** is one of the most extensively studied ligands in this series. The pentadentate ligand forms stable complexes with a variety of metal ions [66,67]. This ligand is particularly capable of stabilising Fe(II) and Mn(II) centres [68], thus modelling intermediates in the oxygenation cycle with lipoxygenase [69,70] and allowing the development of novel biomimetic catalysts. Stack used a mononuclear manganese(III) hydrox-

ide complex of **17** to demonstrate C–H activation as part of studies into manganese–lipoxygenase mimics [71]. Che and co-workers prepared cyclic [Ag$_2$(**17**)$_2$]$^{2+}$ and also [Ag$_2$(**16**)$_2$]$^{2+}$ metallacycles and studied the dissociation to mononuclear complexes [Ag(**17**)(solvent)]$^+$ and [Ag(**16**)(solvent)]$^+$ in acetonitrile or methanol solutions [72].

In 2004, as part of a study of the synthesis of oligopyridine compounds using fluoropyridine derivatives as the electrophiles, Dyker and Muth reported the synthesis of compound **18** (Scheme 4) [79]. Compound **18** was prepared from di-2-pyridylmethyl lithium and 2,6-difluoropyridine in an extremely good 96% yield. No complexes of this particular compound have yet been reported.

A series of hexadentate ligands have also been extensively studied. Hexadentate ligands in this theme can be formed by incorporation of a diazene core into the bridging ligand motif; in this series pyridazine (**19a** and **19b**), phthalazine (**20a** and **20b**) and pyrimidine (**21**) have been investigated (Scheme 5). Ligands based on a pyridazine core were first reported in 1993 and 1997, namely compounds **19a** and **19b**, from reaction of 3,6-dichloropyridazine with di-(2-pyridyl)methyllithium or (6-methyl-2-pyridyl)(2-pyridyl)methyllithium, respectively [45,49]. Manzur and co-workers studied the magnetism of binuclear copper(II) complexes with **19b**, which present six-membered chelate rings around the metal centres; in these complexes the copper centres are bridged by both the diazine ligand and hydroxide, leading to quite short metal–metal distances [49]. In an earlier report, copper(II) chloride and bromide complexes were described in which two chloride or two bromide anions bridge the copper centres supported by coordination to **19a** [45]. The authors concluded that **19a**
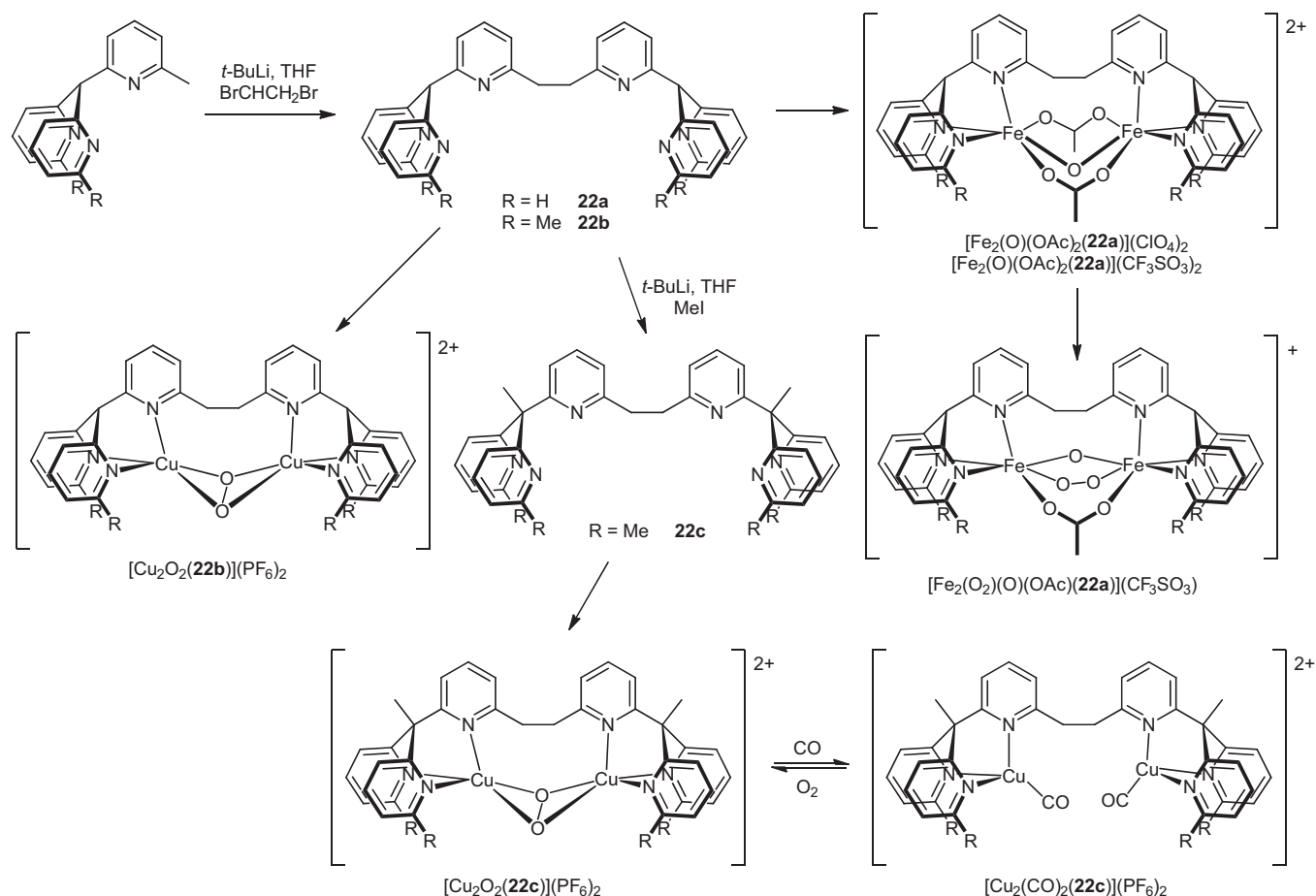
Scheme 7. (after Refs. [73–78,80]).

is not a particularly efficient bridge for facilitating magnetic interaction through the N–N diazine bridge, when it acts as a hexadentate ligand generating octahedral species and that the efficiency is even lower when the ligand is pentadentate and does not bond through both N–N atoms. A related dinuclear copper(I) complex was also reported by the same researchers but not structurally characterised [47]. This was reported to undergo facile oxidation in air.

Manzur and co-workers also reported a dinuclear copper complex $[Cu_2(19a)_2](ClO_4)_3$ containing the 3,6-bis(di-2-pyridylmethyl)pyridazine, **19a** (Scheme 6) [46]. The compound consists of a mixed-valence copper(I)–copper(II) entity with localised valences, co-ordinated to two bridging ligand molecules. The geometry around the copper(I) centre is distorted tetrahedral, while that of the copper(II) centre is tetragonally distorted octahedral [46]. Steel and Sumby reported structurally related dinuclear copper(II) and nickel(II) complexes [48]. In $[Cu_2(19a)_2](ClO_4)_4$, a complex that was first reported by Manzur et al. [45], the two copper centres are square pyramidal, while the two nickel centres in $[Ni_2(19a)_2](ClO_4)_4$ are octahedral (Scheme 6) [48]. To form this latter complex a significant distortion of the coordination about the bridging pyridazine centre is required. These three complexes represent a series of closely related dinuclear helicates. $[Cu_2(19a)_2](ClO_4)_3$ is a heterotopic homostranded dinuclear helicate with tripodal coordination of at least one metal centre, while $[Cu_2(19a)_2](ClO_4)_4$ and $[Ni_2(19a)_2](ClO_4)_4$ are homotopic homostranded dinuclear helicates. In the latter compound, there is tripodal coordination by both strands to the two octahedral metal centres.

The closely related phthalazine ligand has also been extensively studied, mainly as a model for the enzyme urease [56–58]. Barrios

and Lippard reported the synthesis of this compound from 1,4-dichlorophthalazine and di-2-pyridylmethyl lithium in 81% yield (Scheme 5). Using this ligand, a series of dinuclear nickel complexes, $[Ni_2(20a)(H_2O)_4](OTs)_4$, $[Ni_2(OH)(20a)(H_2O)_3](OTs)_3$, and $[Ni_2(OH)_2(20a)(H_2O)]_2(OTs)_4$ (where OTs is p-toluenesulfonate), were prepared as models for urease. $[Ni_2(OH)(20a)(H_2O)_3](OTs)_3$ carries out the stoichiometric hydrolysis of picolinamide in ethanol, which mimics the hydrolysis of urea by the metalloenzyme urease. The same complex is also able to decompose alkyl-substituted urea derivatives upon heating [57]. The same researchers also established that the phthalazine-based ligand system is a useful framework for the syntheses of dinuclear metal complexes, namely manganese, iron, copper, and zinc complexes, to model the structural and functional aspects of metalloenzymes [58].

Lippard and co-workers also investigated a family of dinuclear copper complexes containing the phthalazine ligand **20a** which were all prepared from the copper(I) species $[Cu_2(20a)(CH_3CN)_2](OTf)_2$ [59]. When $[Cu_2(20a)(CH_3CN)_2](OTf)_2$ was treated with sodium acetate, a class I mixed-valence compound $[Cu_2(20a)_2](OTf)_3$, was obtained by disproportionation of Cu(I). This compound has a very similar structure and properties to the pyridazine ligand containing complex $[Cu_2(19a)_2](ClO_4)_3$ previously reported by Manzur (Scheme 6) [46]. $[Cu_2(20a)_2](OTf)_3$ has the same tetrahedral copper(I) and tetragonally distorted copper(II) geometries and exhibits a reversible redox wave at −452 mV versus Cp_2Fe^+/Cp_2Fe. Two dicopper(II) complexes of **20a** were prepared by oxidation. $[Cu_2(\mu\text{-}OH)(20a)(CH_3CN)_2](OTf)_3$ was prepared by oxidation of $[Cu_2(20a)(CH_3CN)_2](OTf)_2$ with AgOTf, while exposure of $[Cu_2(20a)(CH_3CN)_2](OTf)_2$ to oxygen afforded $[Cu_2(\mu\text{-}OH)_2(20a)]_2(OTs)_4$. A dicopper(I) complex,

[Cu$_2$(**20a**)(2-vinylpyridine)](OTf)$_2$ was also prepared with **20a** as a bridging ligand, whereby 2-vinylpyridine bridges the two Cu(I) centres by using both its pyridine nitrogen and the olefin as donor functionalities.

Lippard and co-workers also studied the affect additional steric bulk around the pyridine donors has on the resulting complexes [59,61]. The ligand 1,4-bis[bis(6-phenyl-2-pyridyl)methyl]-phthalazine (**20b**) forms the sterically hindered compounds [Cu$_2$(**20b**)(CH$_3$CN)$_2$](OTf)$_2$ and [Cu$_2$(OAc)(**20b**)](OTf), where the four phenyl rings form a hydrophobic pocket that houses the acetonitrile and acetate ligands. The hydrophobic binding pocket drastically improves the stability of the dicopper(I) centres [59]. Related investigations of diiron complexes of **20b** revealed that the steric bulk of the phenyl substituents generates a hydrophobic pocket for small molecule binding and block dimerisation of the complex species [61]. Four carboxylate-bridged compounds [Fe$_2$(μ-O$_2$CR)$_2$(**20b**)](OTf)$_2$ (where R = CH$_3$; C$_2$H$_5$; CH$_2$Ph; C(CH$_3$)$_3$), and the phosphodiester bridged species [Fe$_2$(μ-O$_2$P(OPh)$_2$)$_2$(**20b**)](OTf)$_2$ were reported by Lippard and co-workers as small molecule models of the catalytic sites in non-heme carboxylate-bridged diiron enzymes.
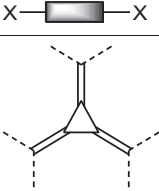
More recently, Steel and Sumby reported three discrete copper(II) complexes of **20a** with Cu$_2$L, Cu$_3$L and Cu$_2$L$_2$ compositions [60]. The latter compound, [Cu$_2$(**20a**)$_2$][Cu(NO$_3$)$_4$]$_2$·4CH$_3$CN is a homotopic homostranded dinuclear helicate, analogous to those obtained for the structurally similar ligand **19a** and the mixed-valance species reported by Lippard (Scheme 6) [59]. An interesting structural relationship involving [Cu$_2$(**20a**)$_2$](OTf)$_3$ and [Cu$_2$(**20a**)$_2$][Cu(NO$_3$)$_4$]$_2$ exists, where one electron reduction of [Cu$_2$(**20a**)$_2$]$^{4+}$ to [Cu$_2$(**20a**)$_2$]$^{3+}$ appears to induce a switching process wherein one of the central phthalazine rings is transferred from one metal to the other. As noted [60], this represents a redox-driven molecular movement and this behaviour is also observed for complexes of the pyridazine-derived ligand (Scheme 6) [45,46,48].

In a similar method to that used for the syntheses of **19a** and **20a**, compound **21** was synthesised in a one-pot reaction from easily obtained starting materials, namely di-2-pyridylmethane and 4,6-diiodopyrimidine, which provided **21** in 48% yield (Scheme 5) [65]. Reactions of **21** with nickel(II) perchlorate and ammonium thiocyanate gave a discrete M$_2$L complex, [{Ni(NCS)$_2$(DMSO)}$_2$(**21**)], with tridentate facial coordination of the octahedral metal centres. This was significantly different to the equivalent reaction of the dpa analogue of **21** with nickel(II) perchlorate and ammonium thiocyanate whereby the triaryl-nitrogen linker adopts a trigonal planar geometry and prevents tridentate facial coordination of the octahedral metal centres [65].

A dinucleating hexapyridine ligand, 1,2-bis[2-(bis(2-pyridyl)methyl)-6-pyridyl]ethane (**22a**), was prepared in two steps (Scheme 7) by reaction of a carbanion of 2,6-lutidine with two equivalents of 2-bromopyridine to give 2-(bis(2-pyridyl)methyl)-6-methylpyridine, which was then converted to **22a** quantitatively by treatment with *tert*-butyllithium and 1,2-dibromoethane [74]. Kodera et al. reported a (μ-oxo)bis(μ-acetato)diiron(III) complex of [Fe$_2$(O)(OAc)$_2$(**22a**)](ClO$_4$)$_2$ whereby the diiron(III) core structure seems to be stabilized by encapsulation of the ligand [74]. The diiron(III) complex efficiently catalyses the oxygenation of cyclohexane, methylcyclohexane and adamantane in the presence of *m*-chloroperbenzoic acid [73]. Subsequently, Kodera also reported the synthesis of a thermally stable (μ-acetato)(μ-oxo)(μ-1,2-peroxo)diiron(III) complex, [Fe$_2$(O$_2$)(O)(OAc)(**22a**)](CF$_3$SO$_3$) and studied its activation for the oxygenation of hydrocarbons [77].

A closely related ligand, 1,2-bis[2-(bis(6-methyl-2-pyridyl)methyl)-6-pyridyl]ethane (**22b**), which like **22a** has two sterically hindered tripyridylmethane units connected by an ethylene spacer, was prepared by treating tris(6-methyl-2-pyridyl)methane with *tert*-butyllithium and 1,2-dibromoethane

Table 4
Tritopic dpm-containing ligands.

Number	X━▭━X	Reference
23		[37,81–83]

[78]. A Cu$_2$O$_2$ complex of **22b**, [Cu$_2$O$_2$(**22b**)](PF$_6$)$_2$, was prepared either by reaction of di-μ-hydroxodicopper(II) complex [Cu$_2$(OH)$_2$(**22b**)](PF$_6$)$_2$ with H$_2$O$_2$ or by O$_2$ addition to dicopper(I) complex [Cu$_2$(MeCN)$_2$(**22b**)](PF$_6$)$_2$. [Cu$_2$O$_2$(**22b**)](PF$_6$)$_2$ was reported to be one of the most stable μ-η^2:η^2-Cu$_2$O$_2$ model complexes isolated with physicochemical properties similar to oxyhemocyanin. The ethylene spacer and the linking of the tris(6-methyl-2-pyridyl)methane tridentate moieties was reported to be particularly important in stabilising this complex. The room-temperature-stable Cu$_2$O$_2$ complex required heating at 80 °C in solution to achieve release of O$_2$ [78] and thus Kodera and colleagues targeted the synthesis of a tense form of oxyhemocyanin (low O$_2$ affinity), which releases O$_2$ more easily [80]. To achieve this a new, more sterically hindered, hexapyridine ligand, **22c**, having bridgehead methyl groups, was prepared (Scheme 7). In μ-η^2:η^2-Cu$_2$O$_2$ complexes of **22c**, Kodera and co-workers reported that the bridgehead methyl groups facilitate the release of O$_2$ and result in an almost reversible CO/O$_2$ binding cycle, simply by exchanging the gas phase between O$_2$ and CO.

2.5. Tritopic ligands

The only tritopic ligand in this series (Table 4) is hexa(2-pyridyl)[3]-radialene, **23**, which was first reported independently by Sumby and Steel [81], and Oda et al. [82]. Compound **23** was prepared by treating tetrachlorocyclopropene with six equivalents of di-2-pyridylmethyl lithium (Scheme 8). The three-fold double bladed propeller conformation of the compound means the three di-2-pyridylmethyl substituents are less than ideally positioned to chelate three different metal centres. Nonetheless, a range of complexes have been prepared in which **23** acts as a tetradentate, pentadentate or hexadentate ligand.

This last mode of coordination was observed when **23** was reacted with silver tetrafluoroborate. This reaction resulted in the formation of a crystalline product that has the constitution [Ag$_6$F(**23**)$_2$](BF$_4$)$_5$·11H$_2$O by X-ray crystallography, in which an M$_6$FL$_2$ cage is formed by self assembly of two molecules of **23**, acting in a hexapodal hexadentate mode, and six silver atoms around a central μ_3-fluorido anion (Scheme 8) [81]. The other modes of coordination were observed when **23** was reacted with either silver nitrate or silver hexafluorophosphate. In both cases these reactions gave one-dimensional coordination polymers in which molecules of **23** acted as tetradentate or pentadentate bridges [83].

Dinuclear bis(2,2′-bipyridyl)ruthenium(II) complexes, where **23** acts as a tetradentate ligand, were prepared by a microwave assisted reaction [37]. The two resulting diastereoisomers, $\Delta\Lambda/\Lambda\Delta$ and $\Delta\Delta/\Lambda\Lambda$ (rac), were separated and characterised by ^{1}H NMR spectroscopy, mass spectrometry and cyclic voltammetry. The two isomers were confirmed to be locked in C$_1$ and C$_2$ point-group symmetry, respectively, and in the former case, represents a rare case where a $\Delta\Lambda/\Lambda\Delta$-dinuclear complex of an achiral symmetrical bridging ligand is not a meso isomer. The locked, out-of-plane conformation of the bridging ligand and the cross-conjugated nature of the central [3]-radialene core also appear to preclude the interaction of the ruthenium centres through the bridging ligand. Electrochemical studies on the isomers of [{Ru(bpy)$_2$}$_2$(**23**)](PF$_6$)$_4$
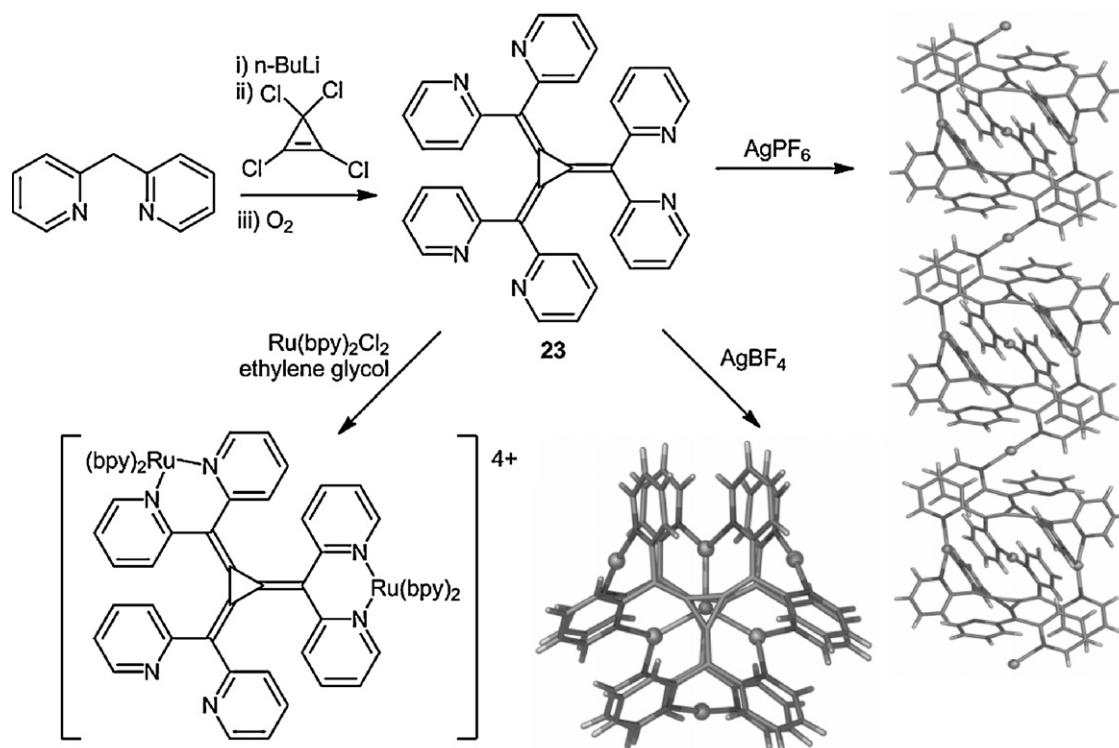
Scheme 8. (after Refs. [37,81–83]).

revealed that each dinuclear complex underwent simultaneous two electron oxidation events consistent with no interactions between the metal centres.

3. The synthesis and coordination chemistry of bridging ligands comprising two or more di-2-pyridylamine arms
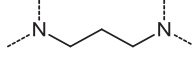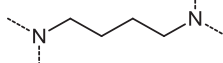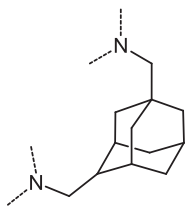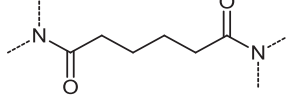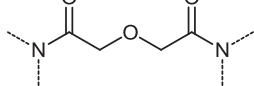
3.1. General synthetic approaches to prepare di-2-pyridylamine-containing bridging ligands

Unlike dpm, which has to be synthesised from commercially available dpk, dpa is a commercially available starting material. As a consequence, the coordination chemistry of this compound as a chelating ligand, and its inclusion into bridging ligands of the type described here, has been more extensively studied. Furthermore, the Buchwald–Hartwig amination strategy [84,85] allows rapid and high yielding synthesis of ligands containing a dpa moiety. Thus, two major strategies are employed for the synthesis of dpa containing bridging ligands (Scheme 9). The first utilises addition of dpa to aryl halides using Ullmann chemistry or nucleophilic substitution reactions on alkyl halides (route A), as typified by the synthesis of **25**, while the second uses Buchwald–Hartwig amination conditions (route B) to synthesise the dpa moiety from alkyl or aryl amines and halopyridines (Scheme 10). This latter route is typified by the synthesis of **24**.

3.2. Ditopic ligands with aliphatic cores

Potential ligands possessing two di-2-pyridylamine subunits separated by aliphatic spacers have been reported (Table 5). Com-

Table 5
Ditopic dpa-containing ligands with aliphatic cores.

Number	X——[ ]——X	Reference
24		[86]
25		[87]
26		[88]
27		[89,90]
28		[91]
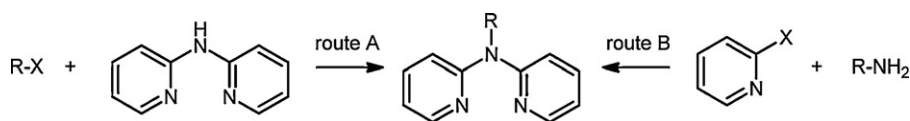
Scheme 9.

pound **24**, containing a propyl spacer, was first reported by Wagaw and Buchwald as a demonstration of their palladium-catalysed methodology for the formation of aminopyridine derivatives (Scheme 10) [86]. The tetrapyridyl derivative was prepared in 70% yield by treating 1,3-diaminopropane with four equivalents of 2-bromopyridine. No complexes have been reported for this compound. *N,N'*-1,4-Bis(di-2-pyridylamino)butane **25**, was prepared by Krebs et al. in their studies of multinuclear platinum complexes for bifunctional DNA binding [87]. In the alternative approach to this class of ligand, reaction of di-2-pyridylamine with 1,4-diiodobutane gave compound **25** in 61% yield (Scheme 10). This new liga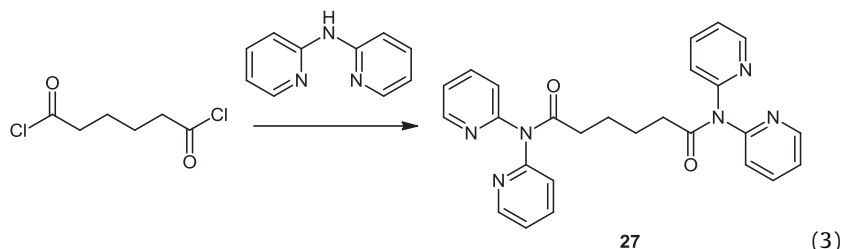nd was then reacted with two equivalents of $K_2[PdCl_4]$ and $K_2[PtCl_4]$ to give $[\{PdCl_2\}_2(\mathbf{25})]$ and $[\{PtCl_2\}_2(\mathbf{25})]$, respectively. The two complexes are isomorphous and were characterised by single crystal X-ray crystallography, with the two metal centres chelating to the di-2-pyridylamino subunits. An adamantanyl-linked dpa containing ligand, **26** was also prepared by Pd-catalysed arylation with 2-bromopyridine but no coordination chemistry has been reported [88].

Tertiary amide derivatives containing two di-2-pyridylamino chelating groups have also been studied in respect of their coordination chemistry [89] and for preparing delivery agents which can carry the {Ru(NO)} chromophore ("caged NO") as potential therapeutics for vasodilation and photodynamic therapy of tumours [90]. *N,N,N',N'*-Tetrakis(2-pyridyl)adipamide, **27**, was prepared by treating the potassium salt of di-2-pyridylamine with adipoyl chloride in dry dimethoxyethane (Eq. (3)) [89]. A binuclear complex was prepared using a 2:1 ratio of [Ru(hedta)(H₂O)] (where hedta = hydroxyethyl ethylenediamine triacetic acid) to the ligand **27** to give $\{[Ru(hedta)]_2(\mathbf{27})\}_2$. The electrochemistry of the binuclear complex was compared to the parent di-2-pyridylamine complex, whereby the RuII/III oxidation wave for $\{[Ru(hedta)]_2(\mathbf{27})\}_2$ is more positive than the parent complex

[Ru(hedta)(dpaH)] by 0.15 V. This indicates that **27** is a better π-acceptor and a poorer π-donor than dpaH alone, as anticipated on the basis of the withdrawing effect of the carbonyl group in the ligand. An additional dinuclear ruthenium complex, $\{[Ru(NO)Cl]_2(\mathbf{27})\}$, was prepared as a potential DNA groove-spanning species [90]. Vögtle and co-workers have reported the synthesis of a related diamide ligand *N,N,N',N'*-tetra(2-pyridyl)-2,2'-oxybis(acetamide), **28**, with only a thallium complex reported in the original work [91].

(3)

3.3. Ditopic ligands with arene cores

One of the most extensively studied di-2-pyridylamine containing ligands, *N,N,N',N'*-tetrakis(2-pyridyl)-1,4-phenylenediamine, **29** (Table 6), was first reported by Wang et al. [92] in their studies of luminescent lanthanide complexes. Compound **29** and its biphenyl derivative *N,N,N',N'*-tetrakis(2-pyridyl)biphenyl-4,4'-diamine, **30**, were prepared under Ullmann coupling conditions from 2,2'-dipyridylamine and 1,4-dibromobenzene or 4,4'-dibromobiphenyl [92]. The two ligands luminesce in the blue region of the visible spectrum. A dinuclear praseodymium complex of **29**, $[\{Pr(hfa)_3\}_2(\mathbf{29})]$ (where hfa is hexafluoroacetoacetate), was prepared in good 70% yield (Scheme 11). The structure of $[\{Pr(hfa)_3\}_2(\mathbf{29})]$ was determined by X-ray crystallography to reveal the two 9-coordinate praseodymium are in an anti arrangement. This contrasts with the dinuclear europium complex, $[\{Eu(hfa)_3\}_2(\mathbf{30})]$, whereby the two metal centres are in a syn arrangement. $[\{Eu(hfa)_3\}_2(\mathbf{30})]$ has a sharp emission band at 613 nm, a weak and broad emission band at 420–500 nm (from **30**).

Following on from this work, other groups have extended this series of ligands [95,97]. Steel and Sumby synthesised the *meta* derivative of **29**, 1,3-bis(di-2-pyridylamino)benzene (**31a**) as well as three naphthalene derivatives, **32–34** [95]. These were prepared as described for **29** under Ullmann coupling conditions or by a palladium-catalysed Buchwald–Hartwig amination (routes A and
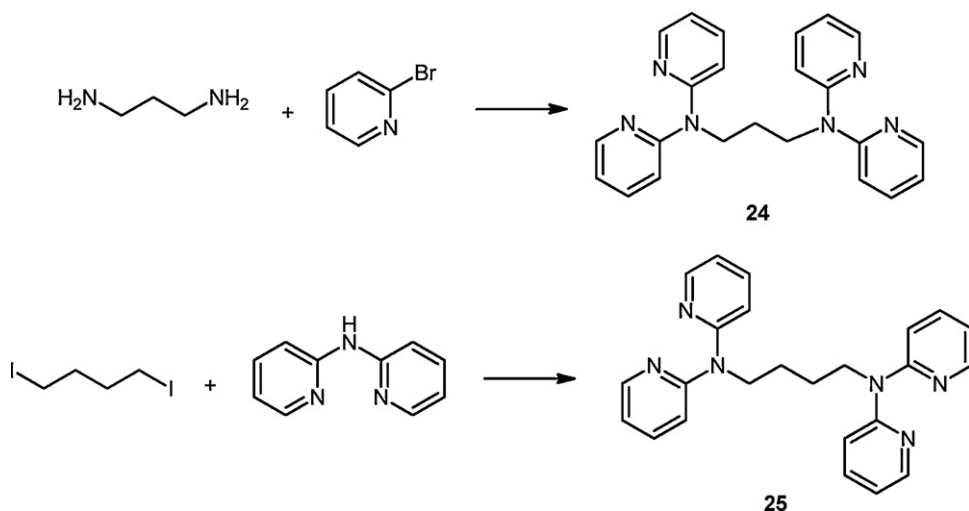
Scheme 10. (after Refs. [86,87]).

Table 6
Ditopic dpa-containing ligands with arene cores.

Number	X—☐—X	Reference	Number	X—☐—X	Reference
29		[92–97]	**36**		[98,99]
30		[92,96]	**37**		[98,99]
31a		R = H [96] [95]	**38**		[98,99]
31b		R = Br [100]			
32		[95,96]	**39**		[101]
33		[95,96]	**40**		[100]
34		[95,96]	**41**		[100]
35		[93]			

B, respectively). This second approach, which provided for *in situ* synthesis of the di-2-pyridylamine subunits, provided a new route to this type of di-2-pyridylamine-based ligand. Dinuclear copper(II) and palladium(II) complexes were prepared with all the new ligands (**31a**–**34**) and compound **29** [95]. A crystal structure of one of the ligands demonstrated that the di-2-pyridylamine subunits are orthogonal to the planar central core of such compounds, akin to the work of Wang with lanthanide complexes [92], and that this conformation is observed in two of the copper(II) complexes

of these ligands that were characterised by X-ray crystallography.

In a series of 1D coordination polymers were obtained when ligands **29** and **31a**–**34** were reacted with silver(I) salts, AgX (where X = NO_3^-, BF_4^-, PF_6^-) [95]. The ligands bridge either two silver centres, in a hypodentate mode where only one donor from each di-2-pyridylamine arm is involved in coordination (i.e. a monodentate mode, Fig. 3e), or four silver atoms (i.e. a bridging mode, Fig. 3e) in preference to a chelating mode of coordination. This generated a
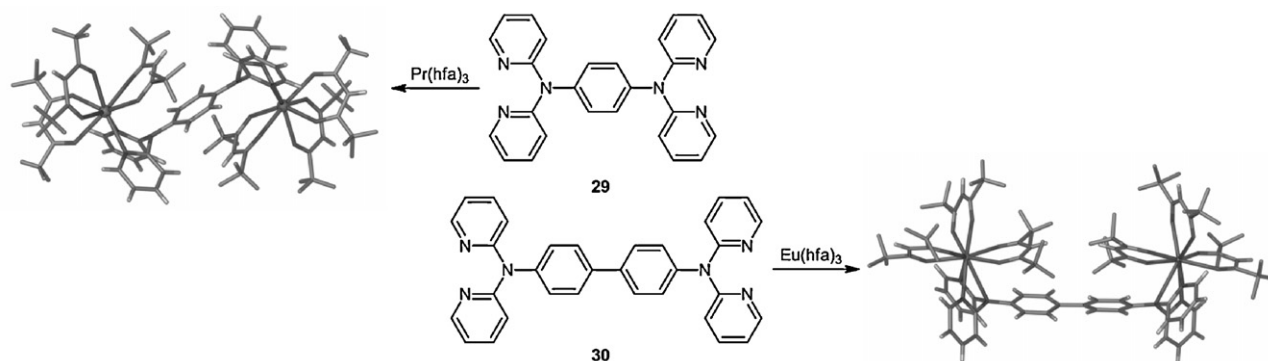
Scheme 11. (after Ref. [92]).

12-membered dimetallocycle connecting unit as a common motif within these 1D coordination polymers. Weaker secondary interactions, such as Ag···π-bonding, plays a role in determining the overall arrangement of the resulting structures [95].

Ward and Barigelletti reported a series of mononuclear rhenium(I) complexes with a di-2-pyridylamine containing ligands [93]. Two particular ligands studied are pertinent to this review but all complexes in the paper have the di-2-pyridylamine-containing ligand chelating to the octahedral rhenium(I) carbonyl chloride species. The luminescence properties of the two ligands, **29** and **35** were reported, with emission at 452 and 405 nm, respectively. This contrasts with the starting amine, di-2-pyridylamine, which is not luminescent. Ward and Barigelletti report complexes of these two ligands with {Re(CO)₃Cl} units and describe visible luminescence for [Re(CO)₃Cl(**29**)] originating from a metal-to-ligand charge-transfer excited state.

Jimenez-Aparicio and Lahiri report the synthesis of a paramagnetic diruthenium(III) complex [{Ru(acac)₂}₂(**29**)](ClO₄)₂, by reaction of binucleating bridging ligand, **29** with the monomeric metal precursor unit [Ru(acac)₂(CH₃CN)₂] in ethanol under aerobic conditions [94]. The corresponding reaction of **29** with the metal fragment [Ru(bpy)₂(EtOH)₂]²⁺ resulted in the diruthenium(II) complex [{Ru(bpy)₂}₂(**29**)](ClO₄)₄ [94]. Variable-temperature magnetic studies revealed that the ruthenium(III) centres in [{Ru(acac)₂}₂(**29**)](ClO₄)₂ are very weakly antiferromagnetically coupled, having $J = -0.45$ and $-0.63\,cm^{-1}$, respectively. The g value calculated using the van Vleck equation turned out to be 2.4, as expected for paramagnetic Ru(III) complexes. Both

complexes display closely spaced Ru(III)/Ru(II) couples with 110, and 80 mV separations in potentials between the successive couples, respectively, implying weak intermetallic electrochemical coupling in their mixed-valence states. Such weak interactions are consistent with the orthogonal arrangement of the dpa arms relative to the central arene core. The bipyridine derivative [{Ru(bpy)₂}₂(**29**)](ClO₄)₄ exhibits a strong luminescence [quantum yield = 0.18] at 600 nm in EtOH/MeOH (4:1) glass at 77 K.

Continuing the study of ruthenium complexes, Steel and Sumby reported mono- and dinuclear ruthenium(II) complexes of six of these bridging ligands, namely **29**, **30**, **31a**, **32**, **33**, and **34** [96]. The ruthenium complexes described in their work were prepared by reaction of the ligand with either [Ru(bpy)₂Cl₂] or [Ru(dmb)₂Cl₂] at reflux in 3:1 ethanol–water for a period of between 48 and 96 h. Ligands **29**, **30**, **31a** and **34** all yielded dinuclear complexes with both ruthenium precursors. Ligands **32** and **33** both readily yielded mononuclear complexes that were characterised by NMR spectroscopy and mass spectrometry. In the case of reaction of [Ru(bpy)₂Cl₂] and **33**, additional reaction time provided a mixture of mono- and dinuclear complexes that were separated by column chromatography.

Upon complexation the ligands cannot undergo two irreversible oxidations of the triarylamine moiety, although oxidation of one triarylamine is a consideration for the mononuclear complexes with a noncoordinated di-2-pyridylamine subunit. In all the dinuclear complexes the oxidation waves are reversible, indicating these redox processes are metal-based, whereas the amine oxidation waves observed in the free ligand are not. All mononuclear
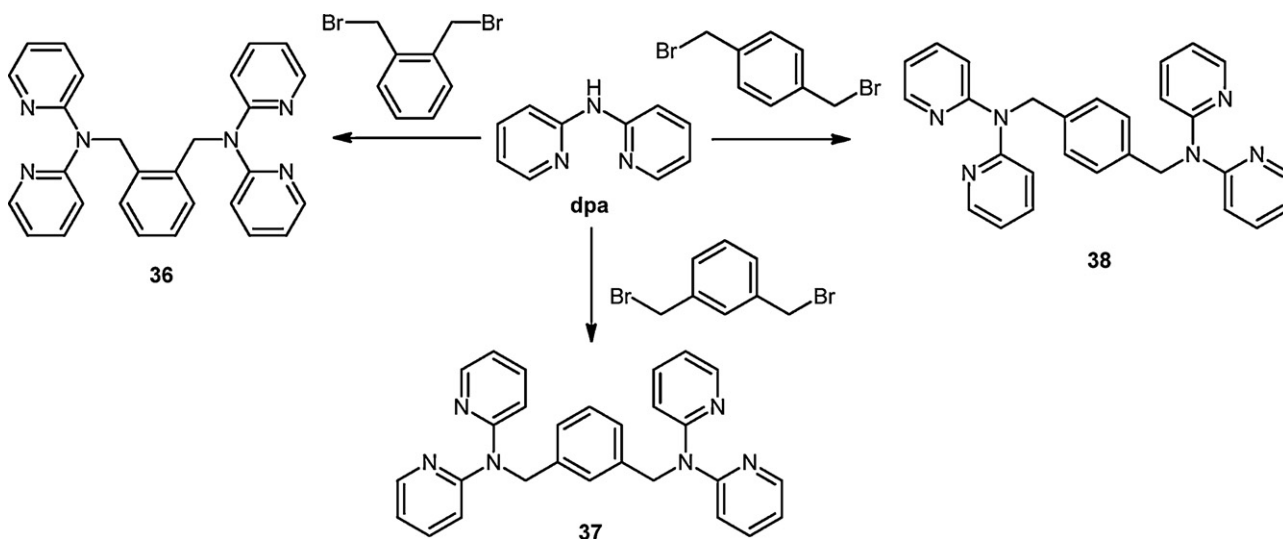
Scheme 12. (after Ref. [99]).
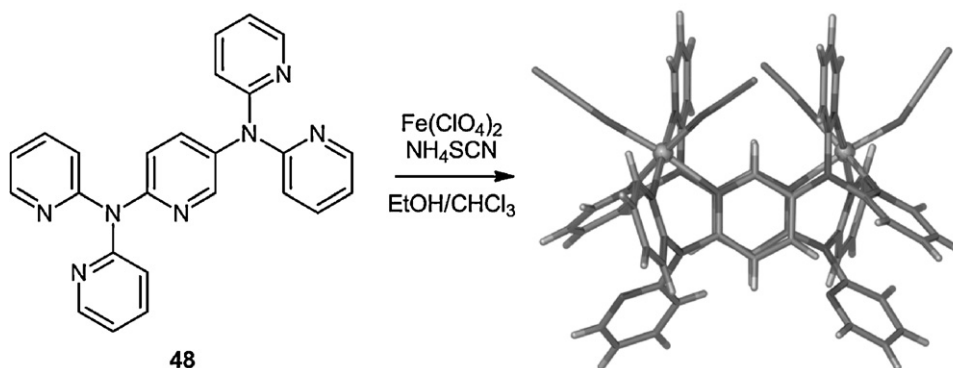
Scheme 13. (after Ref. [107]).

ruthenium(II) complexes have broad absorption maxima at ca. 430 nm, with a shoulder at ca. 457 nm; the MLCT transitions into the orbitals of the ligand are at a higher energy than for [Ru(bpy)$_3$]$^{2+}$ (452 nm), while the shoulder was proposed to correspond to MLCT into the bpy ligands. The cyclic voltammograms for the mononuclear complexes all have four one-electron redox processes. The redox potentials reveal that the ruthenium centre of the complexes are both easier to oxidise and more difficult to reduce than [Ru(bpy)$_3$]$^{2+}$ or [Ru(dmb)$_3$]$^{2+}$.

The dinuclear ruthenium complexes all exhibit broad visible absorption maxima at ca. 442 nm which was assigned to a MLCT, as is the case for [Ru(bpy)$_3$]$^{2+}$. This indicates that the HOMO–LUMO energy gap in these complexes is comparable to [Ru(bpy)$_3$]$^{2+}$, but because of the more electron rich nature of the ligands, slightly larger than that of [Ru(bpy)$_3$]$^{2+}$. It was postulated that the sp^2 character of the tertiary amine in the bridging ligands would aid metal–metal interaction in dinuclear complexes of these ligands. Cyclic voltammetry reveals that complexes [{Ru(bpy)$_2$}$_2$(**29**)] and [{Ru(bpy)$_2$}$_2$(**30**)] undergo four redox processes (two partially overlapped). The oxidation wave appears to be comprised of two redox events occurring ca. 60 mV apart, with ligands **29** and **31a** facilitating weak metal–metal interactions consistent with the conformation of the ligand having the chelating dpa arms orthogonal to the central arene. This is comparable to the separation observed

previously for [{Ru(bpy)$_2$}$_2$(**29**)](ClO$_4$)$_4$ by Jimenez-Aparicio and Lahiri [94]. metal–metal interactions were not reported for the dinuclear complexes of **30** and **34**.

Syntheses of 1,2-bis(di-2-pyridylaminomethyl)benzene **36**, 1,3-bis(di-2-pyridylaminomethyl)benzene **37**, and 1,4-bis(di-2-pyridylaminomethyl)benzene **38**, were reported by Antonioli et al. [99], from reaction of 2,2′-dipyridylamine with o-, m-, and p-bis(bromomethyl)benzenes (Scheme 12). The single-crystal X-ray structures of **36**, **37**, and **38** revealed that the o- and p-derivatives tended to favour more open arrangements conducive to bridging metal ions, while the m-isomer had a pocket between the two 2,2′-dipyridylamine substituents that may bind a single metal or allow the ligand to bridge two metal centres. It was reported that reaction of salts of the type AgX (where X = NO$_3^-$, PF$_6^-$, ClO$_4^-$, or BF$_4^-$) with the above ligands led to the isolation of thirteen Ag(I) complexes, nine of which were characterised by X-ray diffraction [99]. The inherent flexibility of the ligands resulted in the adoption of a range of coordination arrangements in these complex but the overall ligand shape in these structures was very similar to the non-coordinated compound. In the case of silver complexes of **36** the ligands bridge between two silver centres, giving a Ag$_2$L$_2$ metallo-macrocyle in three cases. Both mononuclear and polymeric complexes were obtained for **37**, which adopts a very similar arrangement in both cases. Compound **38** forms a
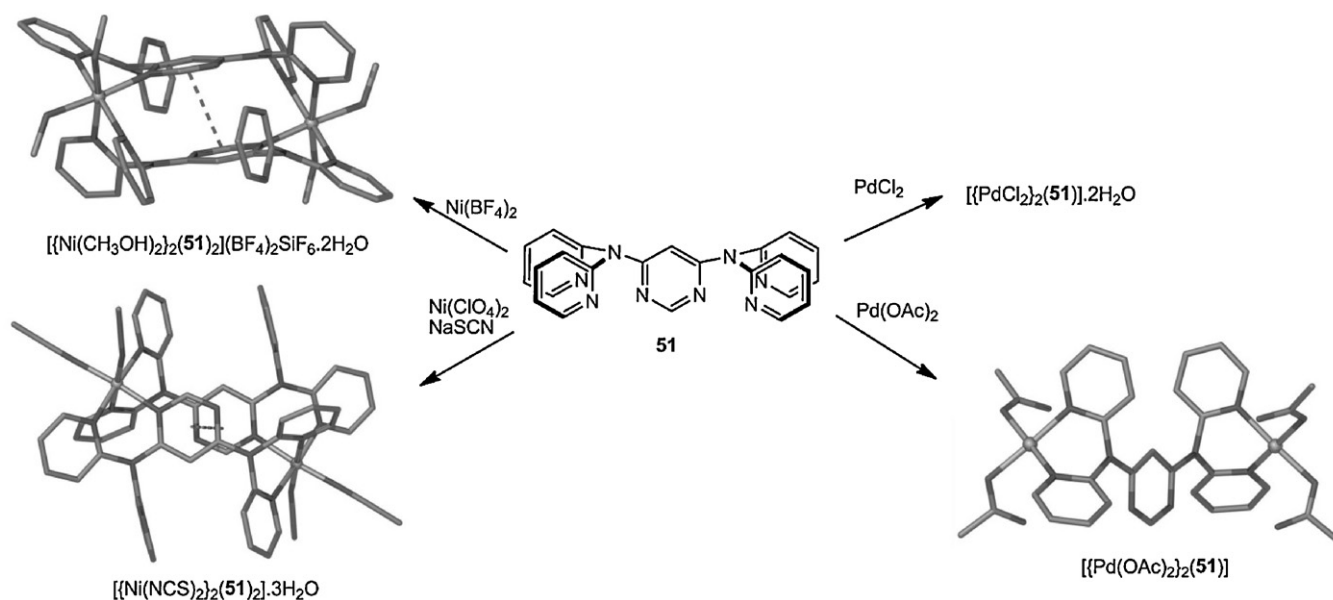
Scheme 14. (after Ref. [65]).

relatively unusual helical $[Ag_3(\mathbf{38})_2]$ species with the largest M–M separation. Ag–π interactions involving the non-coordinated pyridine rings appear to be important in supporting the formation of these complexes.

A series of liquid–liquid (H_2O/CHCl$_3$) extraction experiments of Ag(I) with varying concentrations of **36**–**38** in the organic phase were described, with the counterion in the aqueous phase being respectively picrate, perchlorate and nitrate. In general, extraction efficiencies for a given ionophore followed the Hofmeister order for the anion of picrate > perchlorate > nitrate; in each case **36** and **37** act as the better extractants of the three xylene derivatives investigated. Sole selectivity for Ag(I) was demonstrated for **36** and **37** in competitive seven-metal bulk membrane transport experiments (H_2O/CHCl$_3$/H_2O) employing the above ligands as the ionophore in the organic phase and equimolar concentrations of Co(II), Ni(II), Zn(II), Cu(II), Cd(II), Pb(II) and Ag(I) in the aqueous source phase.

Antonioli et al. have also reported copper(II) complexes of **36**–**38**, namely: $[\{Cu(NO_3)_2\}_2(\mathbf{36})]$, $[\{Cu(NO_3)_2\}_2(\mathbf{37})(CH_3OH)_2]$ and $[\{Cu(NO_3)_2\}_2(\mathbf{38})(CH_3OH)_2]$; and complexation of palladium(II) with **36**–**38** gave $[\{PdCl_2\}_2(\mathbf{36})]$, $[\{Pd(OAc)_2\}_2(\mathbf{36})]$, $[\{PdCl_2\}_2(\mathbf{37})]$, $[\{PdCl_2\}_2(\mathbf{38})]$ and $[\{Pd(OAc)_2\}_2(\mathbf{38})]\cdot CH_2Cl_2$ [98]. Once again, the inherent flexibility of the respective ligands has resulted in the adoption of a diverse range of coordination geometries and lattice arrangements. In all cases the expected dinuclear complexes were obtained but these vary in the nature of the M–M separations due to the different spatial arrangements of the chelating ligands. Liquid–liquid (H_2O/CHCl$_3$) extraction experiments involving copper(II) and a range of di-2-pyridylamine containing ligands, including **37**, show that the degree of extraction depends markedly on the number of dpa-subunits (and concomitant lipophilicity) of the ligand employed [98].

N,N′-Bis(2,2′-dipyridyl)isophthaloylamide, **39**, which is very close in structure to **37**, was reported by Guo and co-workers [101]. The amide links contributes to reducing the flexibility of the ligand compared to **37**. Compound **39** has a more open arrangement in the solid-state and due to the strong steric repulsion of four pyridine rings, the two amide N–C=O groups are not co-planar with the phenyl ring. Unlike **37** however, **39** is not stable in the presence of copper(II), and decomposes by hydrolysis to give a copper(II) complex of di-2-pyridylamine, $[Cu(dpa)_2](ClO_4)_2$ [101].

Using **31b** as an intermediate, Wang and co-workers have prepared a series of three-coordinate organoboron derivatives for possible application in organic light emitting diodes (OLEDs) [100]. Two of these compounds, **40** and **41** contain the two di-2-pyridylamine moieties and can potentially bridge two metal centres in a tetradentate mode with chelation of each centre. No complexes of these compounds were reported.

3.4. Ditopic ligands with heteroarene cores

In addition to phenyl (**39**–**35**) and xylenyl spacers (**36**–**38**), a significant number of heteroaromatic spacers have been incorporated (Table 7). Liu et al. reported the formation of a luminescent bridging ligand 3,6-bis(di-2-dipyridylamino)-9-phenyl-carbazole **42** by a modified Ullmann coupling procedure [102]. Single-crystal X-ray diffraction analyses revealed that **42** is a bent tetrapyridyl ligand with a 103° angle between the two dipyridylamine arms. Upon reaction with silver(I) nitrate a novel channel-cupped shape 1D polymer, $\{[Ag(NO_3)(\mathbf{42})](CH_3CN)\}_n$, was obtained. Weak intermolecular forces result in a 3D network solid that is stable to solvent removal until about 220 °C, at which time the material decomposes.

In the area of organic light emitting device (OLED) development, Hirsch and Gerbier reported studies into mono- and bis-silole derivatives [103,120,121]. Their approach was to prepare derivatives functionalised with dipyridylamine, as a hole-transporting group, on the silole ring. This entailed the synthesis of a number of derivatives, namely **43**–**46**. These compounds were prepared by copper-catalysed Ullmann reactions between various aryl spacers and di-2-pyridylamine followed by Suzuki coupling to the mono- and bis-silole cores. No coordination compounds were reported as the focus was on OLED materials.

Xie and Liu have reported the synthesis of the bridging ligand *N,N,N′,N′*-tetrakis(2-pyridyl)-2,6-pyridinediamine, **47**, from 2,6-dibromopyridine and di-2-pyridylamine under modified Ullmann conditions [104]. Compound **47** displays blue-purple luminescence. The coordination chemistry of this ligand was investigated with a series of Zn(II), Cd(II), and Hg(II) salts resulting in the formation of four new complexes, namely $[\{ZnCl_2\}_2(\mathbf{47})]$, $[\{HgCl_2\}_2(\mathbf{47})]$, $[\{HgBr_2\}_2(\mathbf{47})]$, and $[\{HgI_2\}_2(\mathbf{47})]$, whereby each ligand is coordinated to two metal ions, forming dinuclear complexes—a common mode for such ligands. The central pyridine donor is not involved in coordination and the tertiary amine nitrogen is close to trigonal planar and directs the di-2-pyridylamino arms away from a tripodal arrangement. These complexes are further connected to form 1D chains via weak intermolecular M···X interactions. 1D coordination polymer structures with a pseudo helical motif were obtained for three other complexes $\{[Cd_2(\mu\text{-Cl})_2(\mathbf{47})]Cl_2\cdot H_2O\}_n$ and $\{[Cd_2(\mu\text{-Br})_2(\mathbf{47})]Br_2\cdot H_2O\}_n$ by the formation of Cd–halide–Cd bridges. A related 1D coordination polymer with a zigzag motif, $\{[Cd_2(\mu\text{-I})(\mu\cdots I)(\mathbf{47})]I_2\}_n$ forms a zigzag 1D motif with two kinds of Cd–I–Cd bridges. It was observed that in all cases these 1D polymers are further connected by face-to-face π-stacking interactions, affording 2D networks. Solid-state luminescence was observed for all complexes with the emission maxima in the range of 440–520 nm [104].

Lui and co-workers also reported two further Cd(II) coordination polymers incorporating **47** by varying the solvent used in the reaction [105]. When DMF was used as the solvent a 1D pseudo-helical structure, $[Cd_2(\mu\text{-SCN})_2(SCN)_2(\mathbf{47})(DMF)_2]_n$, was obtained. When the same reaction was undertaken in methanol the unsolvated compound $[Cd_2(\mu\text{-SCN})_4(\mathbf{47})]_n$ was obtained with a 2D coordination polymeric structure. Like previous complexes obtained with **47**, and in contrast to compounds **15**–**18** (which have carbon linker atoms), the tertiary amines are planar and the central pyridine donor not involved in coordination. Both coordination polymers emit blue light.

As part of their on-going studies of spin-crossover compounds, Kepert and Murray synthesised **48**, an isomer of **47**, from 2,5-dibromopyridine and di-2-pyridylamine using established methods [106]. This was complexed with iron(II) to give a dinuclear iron(II) complex, $[Fe_2(NCS)_4(\mathbf{48})_2]\cdot 4CH_2Cl_2$, which was characterised by single-crystal X-ray diffraction. $[Fe_2(NCS)_4(\mathbf{48})_2]\cdot 4CH_2Cl_2$ undergoes a two-step full spin crossover, with spin states HS–HS, HS–LS and LS–LS (HS: high spin and LS: low spin) for the two iron(II) centres at the three plateau temperatures. The partially desolvated material $[Fe_2(NCS)_4(\mathbf{48})_2]\cdot CH_2Cl_2$ undergoes a one-step transition with an increased transition temperature with respect to the as synthesised material. This can be resolved to give complete conversion back to the original two-step crossover material. The completely de-solvated material remains high spin over all temperatures and cannot be resolved.

In a more recent report [107], Amoore et al. investigated the effect of changing the type and degree of solvation in the SCO $[Fe_2(NCS)_4(\mathbf{48})_2]$ system previously studied (Scheme 13). This revealed that either a one- or two-step spin transition can be specifically targeted. For example, the chloroform clathrate $[Fe_2(NCS)_4(\mathbf{48})_2]\cdot 4CHCl_3$ undergoes a relatively abrupt one-step SCO, in which the two equivalent FeII sites within the dinuclear molecule crossover simultaneously. Partial desolvation to form $[Fe_2(NCS)_4(\mathbf{48})_2]\cdot 3CHCl_3$ and $[Fe_2(NCS)_4(\mathbf{48})_2]\cdot CHCl_3$ leads to a process attributable to the overlap of two SCO steps in each case. These materials can be resolved to produce the original one-step

Table 7
Ditopic dpa-containing ligands with heteroarene cores.
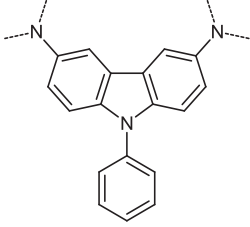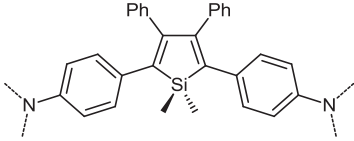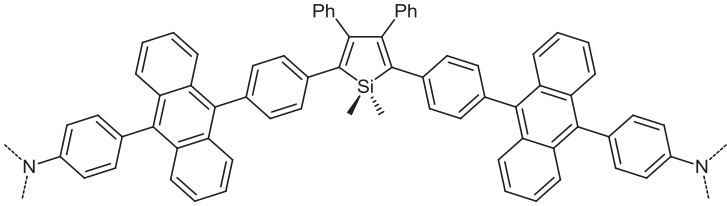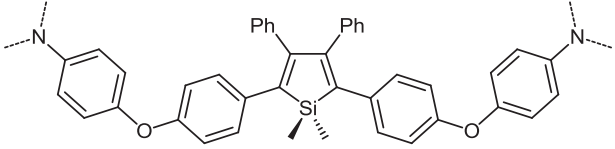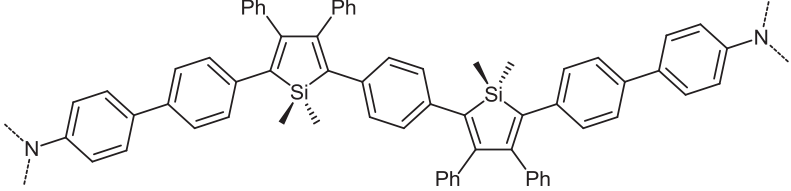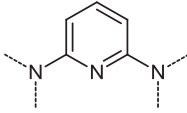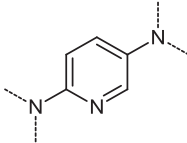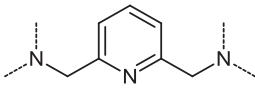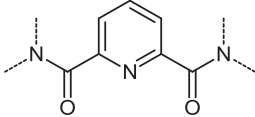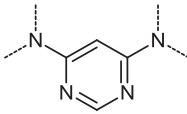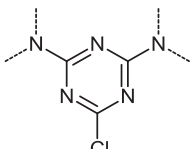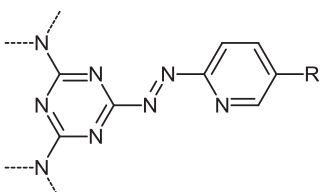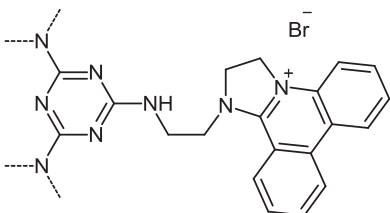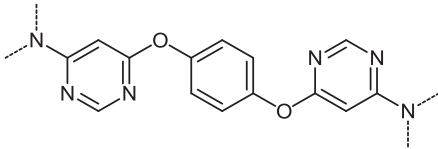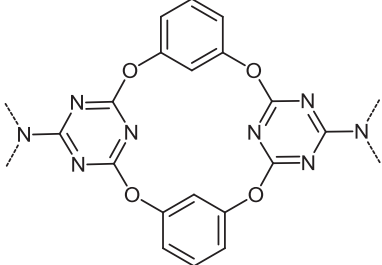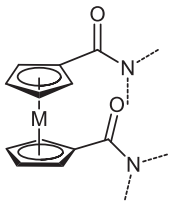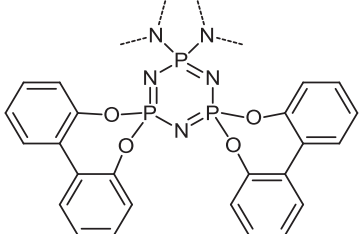
Number	X—▭—X	Reference
42		[102]
43		[103]
44		[103]
45		[103]
46		[103]
47		[104,105]
48		[106,107]
49		[108]
50		[91]
51		[65,109]

Table 7 (*Continued*)

Number	X—▭—X	Reference
52		[110–112]
53a		R = H, Cl [113]
53b		
54a		[114]
55		[115]
56		[116]
57a		M = Fe [117]
57b		M = Co [118]
58		[119]

SCO, or with dichloromethane to produce a two-step SCO reminiscent of that seen for [Fe$_2$(NCS)$_4$(**48**)$_2$]·4CH$_2$Cl$_2$ [106].

A more flexible analogue of **47** has been studied by Glöe and Lindoy [108]. A 2:1 reaction of di-2-pyridylamine with 2,6-bis(chloromethyl)pyridine under basic conditions yielded **49** in a very low 8% yield. Upon reaction with silver(I) nitrate a molecu-

lar ladder motif that consists of pairs of cationic [Ag$_2$(**49**)MeCN]$^{2+}$ units bridged by a previously unobserved [Ag$_2$(NO$_3$)$_6$]$^{4-}$ anion is obtained. The silver anions act as T-shaped connectors that form the rungs and the cationic disilver complexes [Ag$_2$(**49**)MeCN]$^{2+}$ form the sides of the ladder and connect the rungs [108]. An amide analogue of **49**, *N,N′*-2,6-bis(2,2′-dipyridyl)pyridylamide **50** has been

prepared by Vögtle but no complexes have been reported [91]. This is probably because the compound is readily hydrolysed in solution in the presence of metal ions.

The incorporation of pyrimidine as a core in such ligands has been reported independently by Sumby et al. [65], and Murray and co-workers [109], in the form of 4,6-bis(di-2-pyridylamino)pyrimidine, **51**. This was obtained by Ullmann coupling of 4,6-diiodopyrimidine and di-2-pyridylamine in around 30% yield. Sumby et al. reported the synthesis of a number of dinuclear complexes of **51** (Scheme 14), namely [{Ni(CH$_3$OH)$_2$}$_2$(**51**)$_2$](BF$_4$)$_2$SiF$_6$, [{Ni(NCS)$_2$}$_2$(**51**)$_2$], [{PdCl$_2$}$_2$(**51**)]·2H$_2$O, and [{Pd(OAc)$_2$}$_2$(**51**)] [65]. These revealed the ligand could act to bridge two metals as a bis-bidentate bridge, incorporating two coordination modes; one where only the four pyridine nitrogens are involved and a second where chelation to one metal occurs through a pyrimidine and pyridine nitrogen and the other metal is bound at the other di-2-pyridylamino group.

Iron(II) spin crossover materials of **51**, namely [Fe(NCS)$_2$(**51**)]$_n$ and [Fe(NCSe)$_2$(**51**)]$_n$, were reported by Murray et al. [109]. Two polymorphs of the formula [Fe(NCS)$_2$(**51**)] were characterised, which differ magnetically in that phase one undergoes a full two-step spin crossover (at 135 and 90 K) whereas phase two remains high spin over all temperatures. This is correlated with the presence of π-stacking interactions in phase one that are absent in phase two. The isostructural selenocyanate analogue of phase 2 undergoes a full two-step spin crossover (at 200 and 125 K).

Triazine core derivatives have been much studied in coordination chemistry, where typically three di-2-pyridylamino arms have been appended. Some work on compounds containing two arms has been reported, as the synthesis of these ligands from 2,4,6-trichloro-1,3,5-triazene **52** can be controlled by varying the reaction temperature and stoichiometry. This differential reactivity was first exploited by Gamez [110], who prepared 2-chloro[4,6-(di-2-pyridylamino)]-{1,3,5}triazine in 69% yield. This compound was also used to prepare a number of other triazene derived bridging ligands that are discussed below.

Murray et al. reported the synthesis of four isostructural one-dimensional iron(II) coordination polymers incorporating **52** that display solvate-dependent spin-crossover [111]. The polymeric material {[Fe(NCS)$_2$(**52**)](guest)}$_n$, gives three crystallographically distinct phases; including two polymorphs of {[Fe(NCS)$_2$(**52**)]2(CH$_3$OH)}$_n$, and {[Fe(NCS)$_2$(**52**)]½(CHCl$_3$)·(H$_2$O)}$_n$. Each phase shows very different magnetic behaviour; both methanol solvates remain high spin over all temperatures, while {[Fe(NCS)$_2$(**52**)]½(CHCl$_3$)·(H$_2$O)}$_n$ undergoes a "half" spin crossover between 225 and 125 K. By comparison, the selenocyanate complex {[Fe(NCSe)$_2$(**52**)]2(CH$_3$OH)}$_n$

gives a full one-step spin crossover with a $T_{1/2}$ of 200 K. X-ray crystallographic analysis of {[Fe(NCS)$_2$(**52**)]½(CHCl$_3$)·(H$_2$O)}$_n$ below the transition temperature reveals alternating, crystallographically distinct, HS and LS iron(II) centres along the polymers, and structural analysis of {[Fe(NCSe)$_2$(**52**)]2(CH$_3$OH)}$_n$ below the transition temperature reveals all LS iron(II) centres.

In addition to forming 1D coordination polymers, **52** forms dinuclear complexes, [{FeCl(X)}$_2$(**52**)$_2$](Y)$_2$·n(solvent), where X = H$_2$O or CH$_3$CN, Y = ClO$_4^-$, BF$_4^-$, and a cobalt(II) analogue, [{CoCl(H$_2$O)}$_2$(**52**)$_2$](BF$_4$)$_2$·n(solvent) [111]. In all cases the triazene nitrogen atoms are not donors and the ligand acts as a tetradentate bridge.

Pandey et al. described the synthesis of ruthenium, rhodium and iridium complexes of **52** [112]. Dinuclear compounds [{(η^6-arene)RuCl}$_2$(**52**)](X)$_2$ (where X = BF$_4$ or PF$_6$) and [{(η^5-Cp*)MCl}$_2$(**52**)]Cl$_2$ (M = Rh, Ir) were prepared and characterised by elemental analyses, ^{1}H and ^{13}C NMR spectroscopy, electronic absorption and emission spectroscopy and electrochemical studies. The structures of the dinuclear complexes [{(η^6-C$_{10}$H$_{14}$)RuCl}$_2$(**52**)](PF$_6$)$_2$ and [{(η^5-Cp*)RhCl}$_2$(**52**)]Cl$_2$·6H$_2$O were described in which the [{(η^6-C$_{10}$H$_{14}$)RuCl}] units in [{(η^6-C$_{10}$H$_{14}$)RuCl}$_2$(**52**)](PF$_6$)$_2$ are anti, while {(η^5-Cp*)RhCl}- in the rhodium compound [{(η^5-Cp*)RhCl}$_2$(**52**)]Cl$_2$·6H$_2$O are syn with respect to triazine ring. No evidence for metal–metal communication was observed in these complexes.

Aromí and Gamez have utilised a triazine derivative, 2,4-(di-2-pyridylamino)-6-(2-pyridylhydrazino)-1,3,5-triazine **53a** to form a mixed-valence Cu(II)/Cu(I) complex [113]. When **53a** was reacted with copper(II) chloride in methanol a mixed-valent Cu(II)$_4$Cu(I) compound, [Cu$_5$(**53b**)(**53b^R**)Cl$_8$] (where ^{R} indicates a radical) was obtained in which the ligand has been monochlorinated and the hydrazino moiety oxidised (Fig. 5). Within the complex, one of the modified ligands, 2,4-bis(di-2-pyridylamino)-6-(2-(5-chloropyridyl)azo)-1,3,5-triazine **53b** is present as its radical anion (**53b^R**), which was demonstrated by a N–N bond length of about 1.33 Å. This corresponds well to that observed for a one-electron reduced azo group. The copper(I) centre is the only tetracoordinated metal site within the structure. The electronic nature of this compound was also corroborated by X-ray absorption spectroscopy, electron paramagnetic resonance, and magnetic susceptibility measurements [113].

Cronin and co-workers also utilised the versatile, "modular" reactivity of 2,4,6-trichloro-1,3,5-triazine to incorporate a dihydroimidazophenanthridinium (DIP) heterocyclic cation into a multinuclear ligand [114]. These studies were carried out to identify species that act as potential multivalent DNA binding agents. Compound **54a** was prepared from reaction of **52** with

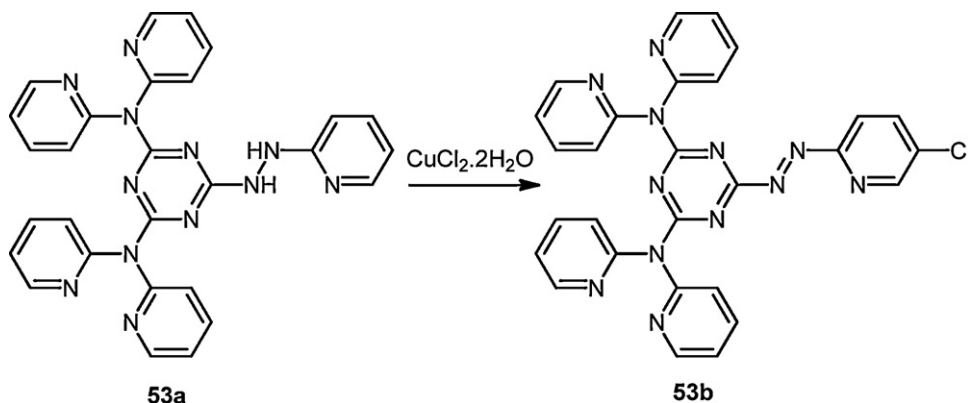**Fig. 5.** The copper chloride catalysed conversion of **53a** to the oxidised and mono-chlorinated form. In the mixed-valence Cu(II)$_4$Cu(I) compound, [Cu$_5$(**53b**)(**53b^R**)Cl$_8$], one ligand is present as its radical anion (after Ref. [113]).
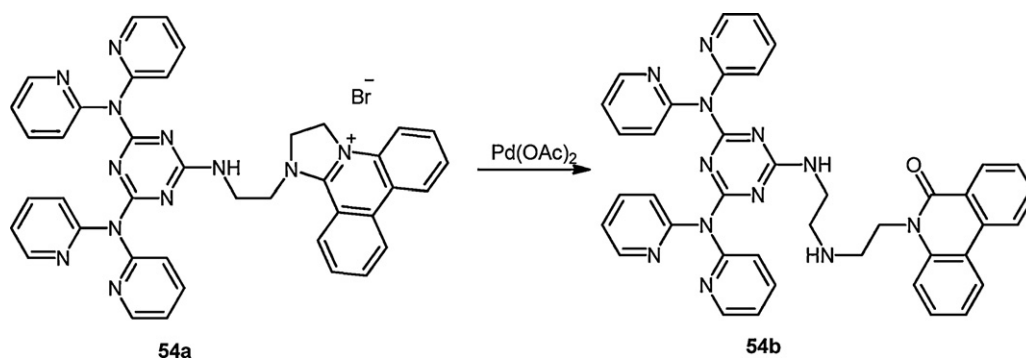
Fig. 6. Hydrolysis of **54a** under the reaction conditions used by Cronin et al. [114].

ethylenediaminedihydroimidazophenanthridinium in good yield. Reaction of palladium(II) acetate with **54a** (2:1 stoichiometry) in dichloromethane provided light-yellow, needle-shaped single crystals of a complex, [Pd$_5$(OAc)$_8$(**54b**)$_2$]Br$_2$, whose crystal structure revealed that the initial compound had been hydrolyzed upon coordination to give a new ligand, **54b** (Fig. 6).

A so-called 'extended-reach' ligand 1,4-bis(6-[di-2-pyridylamino]-4-pyrimidyloxy)benzene (**55**) was synthesised by Steel and Sumby from 4-chloro-6-(di-2-pyridylamino)pyrimidine and hydroquinone in 59% yield [115]. Compound **55** was used to prepare copper(II) and nickel(II) complexes whereby an X-ray crystal structure determination of [Cu$_2$(**55**)$_2$(CH$_3$OH)$_2$](BF$_4$)$_2$(SiF$_6$) revealed that the copper complex is an M$_2$L$_2$ metallomacrocycle with an unusual rectangular shape. This complex is stabilised over its considerable 2 nm length by intramolecular π-stacking.

Heteroatom-bridged calix[2]arene[2]triazenes functionalised on the upper rim with di-2-pyridylamine groups have been prepared by Wang [116]. It was reported that nucleophilic substitution onto the triazene ring to give **56** was accomplished in excellent yield by refluxing a slight excess of the appropriate calix[2]arene[2]triazene with 2.2 equivalents of di-2-pyridylamine and DIPEA in acetone. This compound binds copper to form 1:1 complexes in solution; presumably rotation about the oxygen–carbon bonds of the calix[2]arene[2]triazene allows both di-2-pyridylamino substituents to coordinate the one metal centre.

Organometallic bridging compounds were reported by Braga [117] and Concepción Gimeno [118] who studied bis{[di-2-pyridylamino]carbonyl}-cobaltocenium and ferrocene ligands, respectively. These were prepared by treating the diacid chloride of cobatacenium and ferrocene with di-2-pyridylamine to give **57a** and **57b**, respectively. The coordination chemistry of **57b** has been explored in great detail with Cu(I), Ag(I), and Au(I) precursors and displays a number of coordination modes that are dependent on the metal, stoichiometry, anions, and co-ligands [118]. For instance, with Ag(OTf) and [Ag(OTf)(PPh$_3$)] three different coordination modes are observed; 2 equivalents of Ag(OTf) gave a [Ag$_2$(OTf)$_2$(**57b**)] complex where each silver is coordinated by one pyridyl nitrogen from each arm of the ligand, while a 2:1 [Ag(OTf)(PPh$_3$)] to **57b** mixture gave a dinuclear complex where each silver was coordinated to the two donors from within one di-2-pyridylamine group. Mononuclear complexes could also be obtained with [Ag(OTf)(PPh$_3$)] and [Cu(NCMe)$_4$]PF$_6$ where **57b** is hypodentate in the silver case and acts as a tetradentate ligand for Cu(I). Tetranuclear complexes were obtained for two Au(I) complexes. No coordination chemistry has been reported for the cobaltocenium system **57a**, which is positively charged and thus, anticipated to lead to highly cationic complexes [117].

Harmjanz and co-workers [119] have studied a series of cyclotriphosphazene-based ligand systems, one of which incorporates two di-2-pyridylamine chelating motifs, as

models for coordination by structurally and electronically related high molecular weight polyphosphazenes. 2,2-Bis(di-2-pyridylamino)-4,4,6,6-bis[spiro-(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene **58** was prepared by synthesising the bis-protected precursor 2,2-dichloro-4,4,6,6-bis[spiro-(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene followed by nucleophilic addition of two equivalents of di-2-pyridylamine to the 2-position of cyclotriphosphazene ring. No metal complexes of this presumably quite sterically congested ligand have been reported.

3.5. Tritopic ligands

A series of tritopic ligands based on a benzene scaffold have been prepared (Table 8), with the compound 1,3,5-tris(di-2-pyridylamino)benzene **59** having attracted significant attention since it was first reported by Wang et al. [122]. Like other related compounds, **59** was prepared from 1,3,5-tribromobenzene and di-2-pyridylamine via copper-mediated Ullmann condensations in good yield. Like the other derivatives reported in the original paper, **59** emits blue light both in solution and in the solid-state [122]. A palladium-catalysed arylation has also been utilised for the synthesis of **59** [97].

Steel and Sumby reported the first example of a three-fold cyclometallated benzene derivative with **59** [123]. Compound **59** readily undergoes reaction with palladium acetate or chloride to produce the triply cyclopalladated product [(PdCl)$_3$(**59**)], which was characterised in solution and by X-ray crystallography [123]. Wang and co-workers further investigated the formation of [(PdCl)$_3$(**59**)] and potential precursor complexes and intermediates (Fig. 7) [124]. They investigated the reactions of Pd(II) ions with **59** in 1:1 and 3:1 stoichiometric ratios. Four new palladium complexes were isolated and characterised, including chelate compounds [PdCl$_2$(**59**)], [(PdCl$_2$)$_3$(**59**)], and [(Pd(OAc)$_2$)$_3$(**59**)], and a cyclometalated compound [Pd(OAc)(**59**)]. In the three chelate complexes the Pd(II) ions are chelated by two pyridyl groups from the same di-2-pyridylamine group, although the complexes all have quite distinct ligand conformations and overall structures. Extensive NMR studies of the formation of [Pd(OAc)(**59**)] and related derivatives allowed Wang and co-workers to postulate two mechanisms for the formation of the cyclometallated product. The first mechanism implicated a coordinated acetate group being involved in abstracting the hydrogen from the benzene ring to form the cyclometallated product which rearranged to give the *NCN* pincer species. The second proposes that an intermediate in the 'walking' of the PdX$_2$ unit around the ring, whereby the metal is coordinated by pyridyl donors from two arms of the ligand, is the precursor that is then cyclometallated [124].

More recently, Wang and co-workers reported Cu(I) and Ag(I) complexes of **59** that were investigated by X-ray diffrac-

Table 8

Tritopic dpa-containing ligands with arene and heteroarene cores.
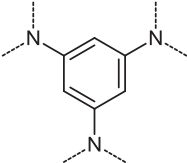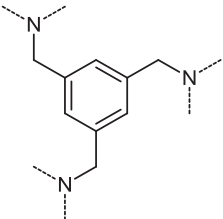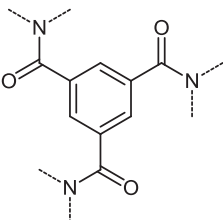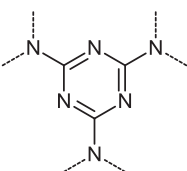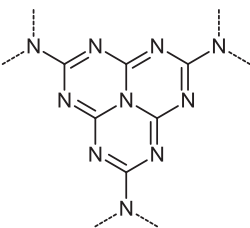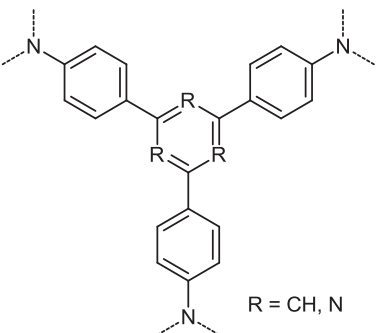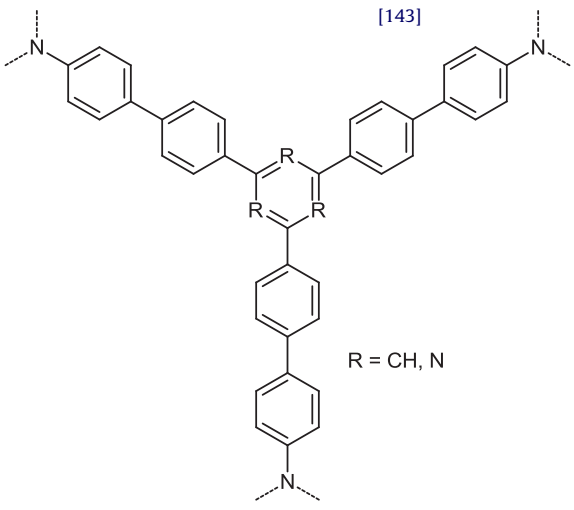
Number	X—▭—X	Reference
59		[97,122–124]
60		[98,99,125,126]
61		[127]
62		[110–112,122,124,128–141]
63		[142]
64a		[122,141,143]
64b	R = CH, N	

Table 8 (*Continued*)

Number	X——☐——X	Reference
65a **65b**		[143]

R = CH, N

tion, NMR and fluorescence spectroscopic analyses [129]. [Cu(PPh$_3$)(59)]BF$_4$ and [(AgNO$_3$)$_4$(59)] were isolated from the reaction of [Cu(PPh$_3$)$_2$(CH$_3$CN)$_2$]BF$_4$ and AgNO$_3$ with 59. The mononuclear Cu(I) complex is discrete, while the Ag(I) complex is polymeric with four crystallographically independent silver cations coordinated by 59 in a range of coordination modes. This resulted in a 2D polymeric structure. Wang et al. noted that differences between the formation of discrete and polymeric structures can in part be attributed to the presence of the phosphine ligand in the copper complexes that saturates the coordination sphere of Cu(I), thus preventing the formation of polymeric species, and also that the steric bulk of the PPh$_3$ ligand limits the number of Cu(I) ions that can access the same molecule of 59 [129].

Guo et al. reported the synthesis of the hexadentate ligand, 1,3,5-tris(di-2-pyridylaminomethyl)benzene 60, in a similar manner to other aminomethylbenzene derivatives, from 1,3,5-tris(bromomethyl)benzene and di-2-pyridylamine in 1:3 molar ratio [125]. It was observed in the solid-state that the three dipyridylamine groups of 60 are almost perpendicular to the central mesityl core, with two of the groups much closer together. Trinuclear Pt(II) complexes [(PtCl$_2$)$_3$(60)] and [{Pt(CBDCA)}$_3$(60)] (where CBDCA = cyclobutane dicarboxylic acid) were prepared, as was a mononuclear complex, [Pt(CBDCA)(60)] supporting the proposal of the Guo group that controlled formation of mono-, di-, and trinuclear complexes with 60 is possible. [{Pt(CBDCA)}$_3$(60)] and [Pt(CBDCA)(60)] are able to bind to calf thymus DNA.

Guo et al. also reported an ill-defined trinuclear copper(II) complex, [Cu$_3$(60)]$^{6+}$, which displays oxidative strand scission of plasmid DNA [126]. The presumably solvated species [Cu$_3$(60)]$^{6+}$ was studied by potentiometric titration, UV spectroscopy, and cyclic voltammetry to reveal that there are three redox-active copper ions in the complex. While the complex demonstrated a moderate binding ability for DNA, it readily cleaves plasmid DNA in the presence of ascorbate. The trinuclear complex is more efficient than a purported mononuclear analogue [Cu(di-2-dipyridylamine)]$^{2+}$ at the same Cu^{2+} concentration, which suggests a possible synergy between three or at least two Cu(II) centres in [Cu$_3$(60)]$^{6+}$ that contributes to its relatively high nucleolytic efficiency.

Silver(I), copper(II) and palladium(II) complexes of 60 were reported by Antonioli et al. [99]. [Ag(60)(NO$_3$)] was prepared by treating 60 with silver nitrate to give crystals of the complex

that was observed in solution by mass spectrometry and in the solid-state by X-ray crystallography to reveal the formation of a 1:1 (metal:ligand) complex. Like silver complexes of 36, only one pyridyl from each pair of pyridyl rings is coordinated to silver and no donors from the third di-2-pyridylamine moiety are coordinated. In liquid–liquid (H$_2$O/CHCl$_3$) extraction experiments of Ag(I) with 60 in the organic phase, the more lipophilic 60 is a better extractant than the ditopic ligands 35–37 [99]. Similar results were also obtained for Cu(II) extraction with the most lipophilic ligands being the best extractant [98].

The synthesis of N,N',N''-1,3,5-tris(di-2-pyridyl)trimesoylamide, 61, has been described but, like other amide ligands of this type, the compound was shown not to be particularly stable when reacted with metal salts, in this case copper(II) perchlorate [127].

The ligand in this series that has attracted the most attention is 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine, 62. This compound was also first reported by Wang et al. and was prepared from the reaction of 1,3,5-trichlorotriazine with di-2-pyridylamine in toluene at reflux overnight (base, KOH; 55% yield, see Scheme 15) [122]. Compound 62 could also be prepared in a slightly higher yield by a one-step synthesis in which 3 equivalents of di-2-pyridylamine were reacted with 1 equivalent of 2,4,6-trichloro-1,3,5-triazine in THF under reflux for 2 days (base, N,N-diisopropylethylamine, DIPEA; 72% yield) [110]. The synthesis of 62 and derivatives with either one or two di-2-pyridylamine arms can be modulated by controlling the temperature of the reaction (Scheme 15) [110].

Wang and co-workers reported 1:1 and 1:2 Zn(II) complexes of 62 which display dynamic behaviour in solution whereby the metal centres move in a carousel-type motion around the ligand from di-2-pyridylamine moiety to the next [141]. The 1:3 complex, [(ZnCl$_2$)$_3$(62)] was insoluble but was proposed not to be dynamic in solution as the metal-hopping behaviour was not possible. X-ray crystallography of the trinuclear Pt(II) complex, [(PtCl$_2$)$_3$(62)], revealed an unusual "bowl" shaped structure, where the complexes stack in a "head-to-tail" fashion in the crystal lattice. This was attributed to the requirement Pt(II) has for square planar geometries as related zinc(II) complexes, where the zinc(II) centres are tetrahedral, do not have a "bowl" shape [141].

A zinc(II) complex of 62 was also reported by Gamez and Reedijk [139]. When reacted with zinc(II) nitrate, 62 acts as an hexadentate
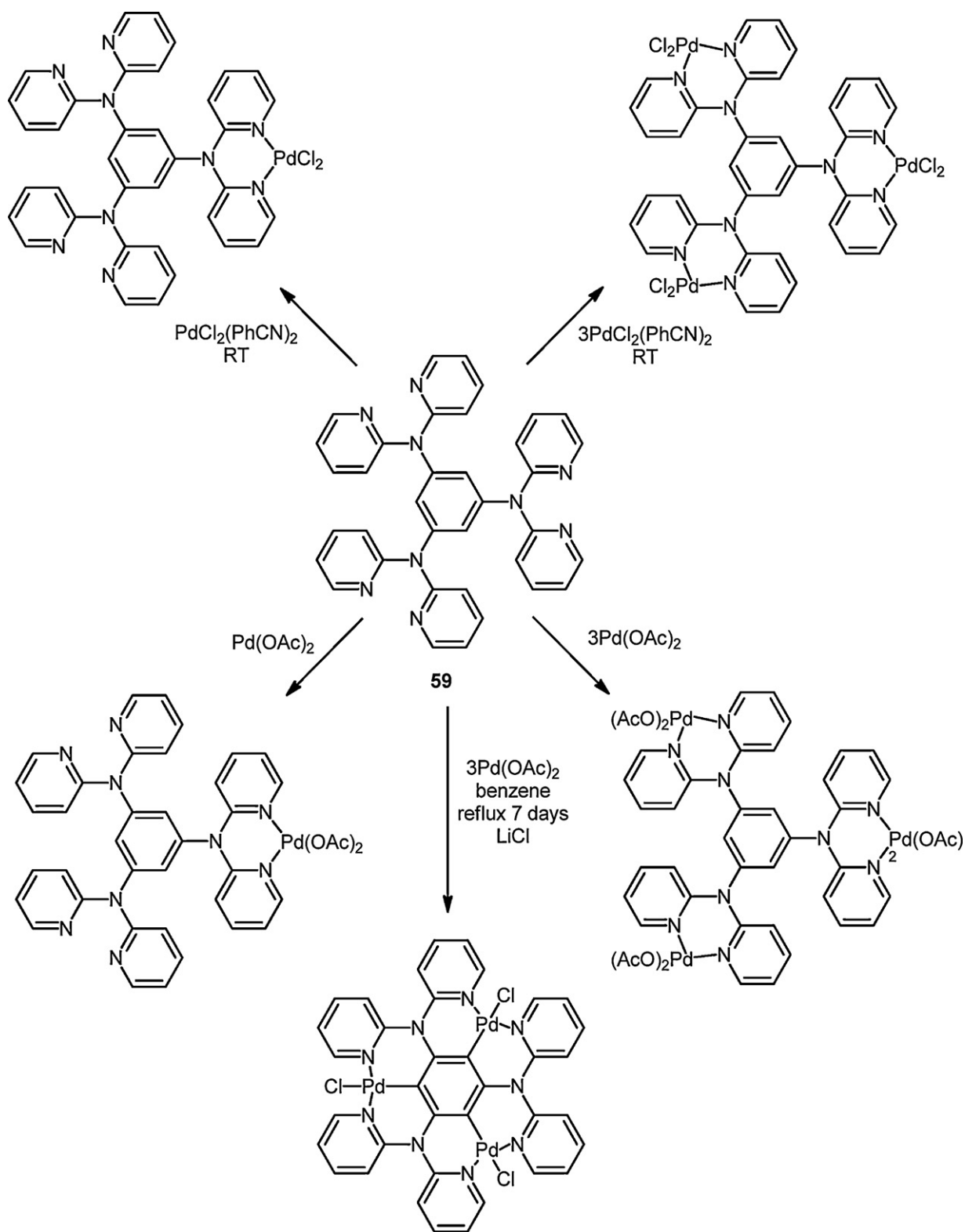
Fig. 7. A representation of the palladium(II) chemistry of **59** (after Refs. [123,124]).

ligand to form $[Zn_4(NO_3)_8(\mathbf{62})_2]$, where each ligand binds to four Zn^{2+} atoms. In the tetranuclear complex of Gamez two of the Zn ions are five coordinated with a trigonal bipyramidal geometry, while the other two Zn ions are six coordinate and link the two ligands together within the complex. This compares with the $[(ZnCl_2)_3(\mathbf{62})]$ complex reported by Wang [141], where all three zinc centres are chelated by the ligand. Reaction with cobalt(II) nitrate gave a dinu-

clear complex $[Co_2(NO_3)_2(\mathbf{62})_2(MeOH)_2](NO_3)_2(MeOH)_2$ where **62** acts as a tetradentate ligand [139].

Gamez and Reedijk also reported that copper(II) nitrate reacts with **62** to give a 1D coordination polymer with a molecular ladder structure, $\{[Cu_5(NO_3)_{10}(\mathbf{62})_2(CH_3CN)_2]\cdot 7CH_3CN\}_n$ [140]. The ligand acts as the T-shaped connectors which are coordinated by three copper centres. Two of the copper centres are five-coordinated
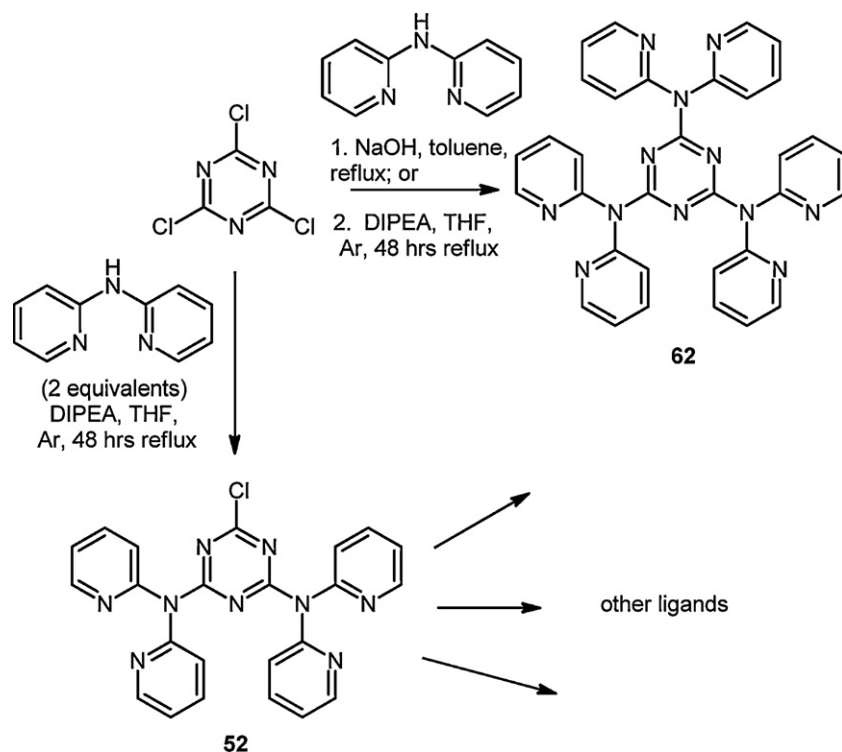
Scheme 15. (after Refs. [110,122]).

copper pseudo-dimers which are bridged by nitrate anions to form 1D polymers. These coordination polymers are linked by six-coordinate copper(II) ions to form the ladder structure and large guest cavities. Despite relatively weak interactions being responsible for the formation of the structure, it was able to be desolvated and to adsorb water without structure collapse. This was not demonstrated for regeneration of the original acetonitrile-filled structure.

Gamez, Reedijk, and co-workers demonstrated that undertaking reactions of copper(II), zinc(II), and cadmium(II) nitrate with **62** at elevated temperature and pressure resulted in new 1D coordination polymers that differ from the materials obtained at room temperature and atmospheric pressure [134]. Notably, a 1D zigzag coordination polymer, $\{[Cu_2(NO_3)_4(\mathbf{62})](H_2O)\}_n$, was obtained when **62** was reacted with copper(II) nitrate under at high temperature and pressure. This differs significantly from the 1D ladder-type polymer, $\{[Cu_5(NO_3)_{10}(\mathbf{62})_2(CH_3CN)_2]\cdot 7CH_3CN\}_n$, obtained under ambient conditions.

A series of dinuclear Fe(II) complexes, $[Fe_2(\mathbf{62})_2(H_2O)_2(solvent)_2](X)_4$ (solvent = CH_3CN or CH_3OH; X = ClO_4^- or BF_4^-) and $[Fe_2Cl_2(\mathbf{62})_2](CF_3SO_3)_2$ have been reported for **62** [134]. These were prepared from different iron(II) salts using different solvents. The two complexes with the formula $[Fe_2(\mathbf{62})_2(H_2O)_2(solvent)_2](X)_4$ have very similar Fe_2L_2 structures but the subtle differences in terminal ligands result in slightly different magnetic behaviour (one complex undergoes partial spin crossover while the other remains high spin). In the complex $[Fe_2Cl_2(\mathbf{62})_2](CF_3SO_3)_2$, which consists of a centrosymmetric dimer in which two octahedral Fe(II) ions are connected by two molecules of **62**, the triazene ring of **62** is involved in coordination of the Fe centres. This is the only time the triazene ring of **62** has been coordinated. Murray and co-workers also reported analogous dinuclear complexes of **62** with the formula $[Fe_2(\mathbf{62})_2(X)_2](ClO_4)_y\cdot(solvent)$ (X = H_2O, Cl^-, y = 4 or 2, respectively) that contain isostructural dinuclear moieties that differ in their associated anions and solvents [111].

Aromí and Gamez have also reported the synthesis of a monomeric iron(II) complex of **62**, $[Fe(SCN)_2(\mathbf{62})_2]$, that was formed by treating $[Fe_2Cl_2(\mathbf{62})_2](CF_3SO_3)_2$ with ammonium thiocyanate, whereby **62** acts as a bidentate ligand [133]. The complex displays a cooperative thermal spin-crossover with a transition temperature close to 200 K. A 1D polymeric material was also obtained when solvothermal methods were employed [131]. Single-crystal X-ray diffraction on the material, formulated as $[Fe_3(BF_4)_2(\mathbf{62})_2(CH_3CH_2CN)_4](BF_4)_4\cdot 4CH_3CH_2CN$, revealed that these chains originate from previously identified dinuclear $[Fe_2]$ building blocks [134] that are connected via their free coordination pockets using additional Fe(II) centres. The material undergoes thermal spin-crossover but exchange of the proprionitrile ligands by water results in a material that remains high-spin at all temperatures.

Palladium(II) complexes of ligand **62**, the so-called 'star-burst' ligands, were reported by Wang [124]. Both 1:1 and 3:1 complexes were obtained for **62**, with the complex $[(Pd(OAc)_2)_3(\mathbf{62})]$, characterised by X-ray crystallography. $[(Pd(OAc)_2)_3(\mathbf{62})]$ displays an "up-and-down" structure in the solid-state which was maintained in solution. Pandey et al. also described the synthesis of ruthenium, rhodium and iridium complexes of **62** [112]. Trinuclear compounds $[\{(\eta^6\text{-arene})RuCl\}_3(\mathbf{62})]Cl_3$ and $[\{(\eta^5\text{-Cp*})MCl\}_3(\mathbf{62})]Cl_3$ (where M = Rh, Ir) were prepared and characterised. Like the corresponding complexes reported for **52**, no evidence for metal–metal communication was observed in these species [112].

Meyer and colleagues reported anion–π interactions in a tricopper(II) complex of **62** [137]. During an investigation of structural and magnetic properties of metal complexes containing **62**, a copper(II) chloride complex, $[(CuCl)_3(\mathbf{62})][CuCl_4]Cl$, was obtained (Fig. 8). This complex has an interesting trigonal prismatic type structure with two ligands connected by three five-coordinate copper(II) centres, but the most notable feature of the complex is that it shows chloride–triazine anion–π interactions with metric parameters very close to those predicted theoretically for s-triazine. The distance between the centroid of the triazine ring and the chlorine
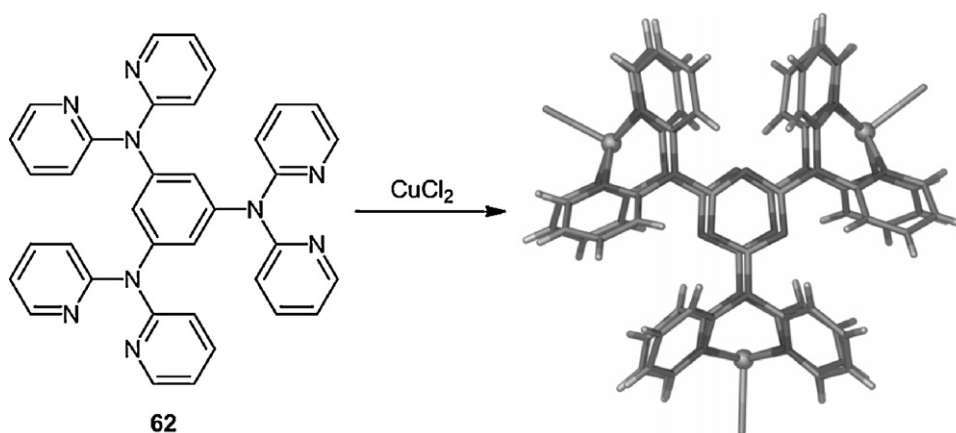
Fig. 8. The synthesis of a carousel complex of the type reported by Meyer [137], Aromí [130], and Guo [132]. The anions display particularly close contacts, less that the sum of the van der Waals radii, with the central triazine ring of the ligands in these complexes.

atom is 3.17 Å and the angle of the Cl⁻···centroid axis to the plane of the ring is 87°. The experimental parameters are in excellent agreement with values obtained from *ab initio* molecular orbital calculations for the parent chloride-1,3,5-triazine species (3.2 Å and 90°) [144]. Gamez and Reedjik have also reported unusual anion–π interactions for coordinated nitrate anions within Cu(II), Zn(II) and Cd(II) coordination polymers formed from **62** [135].

Aromí et al. have undertaken a detailed study of anion–π interactions involving **62** [130]. Two tricopper carousel complexes, $[Cu_3Cl_3(\mathbf{62})_2](ClO_4)_3$ (Fig. 8) and $[Cu_3Br_3(\mathbf{62})_2](ClO_4)_3$, and a tetranuclear complex $[Cu_4(N_3)_4(ClO_4)_2(\mathbf{62})_2(DMF)_4](ClO_4)_2$ were prepared by reacting **62** with $Cu(ClO_4)_2$ and CuX_2 salt mixtures (X⁻ = Cl⁻, Br⁻, or N₃⁻). The tetranuclear complex consists of two equivalents of **62** bridged via coordination to Cu(II) and disposed face-to-face in a parallel manner and mutually shifted in one direction. The non-coordinated ClO_4^- anions display anion···π interactions with the triazine rings which were studied by *ab initio* calculations. A further carousel-type copper(II) complex of **62**

through bis-bidentate moieties of **62** and bidentate oxalato groups, while $[Cu_6(NO_3)_3(ox)_3(\mathbf{62})_2(H_2O)_9](NO_3)_3\cdot 4H_2O$ contains discrete cage-like hexacopper(II) units connected by three bis-bidentate oxalate ligands.

Wang reported Cu(I) and Ag(I) complexes of a series of ligands, including **62** [129]. The complexes isolated for **62** were $\{[Cu(PPh_3)_2]_2(\mathbf{62})]\}(BF_4)_2$ and $[(AgNO_3)_3(\mathbf{62})]\cdot 2H_2O$. In $\{[Cu(PPh_3)_2]_2(\mathbf{62})\}(BF_4)_2$ the ligand acts as a tetradentate bridging moiety to connect the two $[Cu(PPh_3)_2]$ units that are coordinated by two arms in a 6-membered ring chelating manner common to this class of ligand.

While the s-triazene derivative **62** has attracted significant attention, a tri-s-triazine or cyamelurine derivative **63** has gone without investigation for nearly 50 years [142]. This was first prepared in 1962 by refluxing di-2-pyridylamine with cyameluric chloride in xylene to give bis(di-2-pyridylamino)-chlorotri-s-triazine, which in turn could be finally converted into **63** by treatment with di-2-pyridylamine in refluxing decaline (Eq. (4)):

$$(4)$$
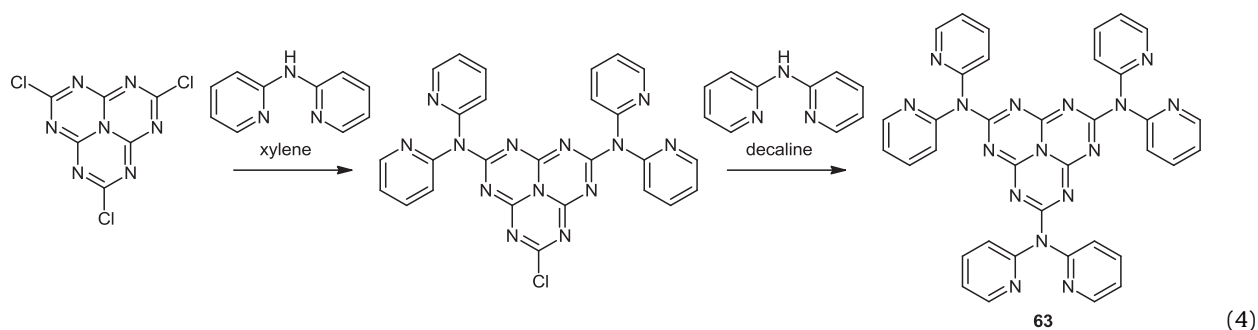
with the triazine cores being in a quasi eclipsed conformation, $[Cu_3(\mathbf{62})_2(H_2O)_3](ClO_4)_6\cdot 2H_2O$, was reported by Julve et al. [128].

Guo and co-workers reported an isostructural tricopper(II) complex $[(CuCl)_3(\mathbf{62})_2]Cl_3\cdot 2H_2O$ with a carousel-type structure [132]. The trinuclear complex is stable at physiological relevant conditions, can bind to DNA through electrostatic attraction and cleave, at micromolar concentrations, supercoiled pBR322 DNA into its nicked and linear forms. Further studies of the reactions of **62** with CuCl₂ by Meyer and co-worker [136] revealed under different conditions both a discrete $[(CuCl_2)_3(\mathbf{62})(DMSO)_3]$ complex and 1D coordination polymer $[(CuCl_2)_3(\mathbf{62})(DMSO)]_n$ were obtained. Variable temperature magnetic studies revealed weak antiferromagnetic coupling within the trinuclear moieties of the complexes. Two copper(II) coordination polymers of **62** and oxalate (ox) have also been reported [128]. $\{[Cu_4(NO_3)_2(ox)_2(\mathbf{62})_2(H_2O)_2](NO_3)_2\cdot 2H_2O\}_n$ is a layered structure of copper(II) ions which are connected

As part of a larger study on blue-luminescent star-shaped compounds, Wang et al. reported the synthesis of **64a** and **64b** from 1,3,5-tris(*p*-bromophenyl)benzene or 2,4,6-tris(*p*-bromophenyl)-1,3,5-triazine, and di-2-pyridylamine in 85% and 60% yields, respectively [122]. Reactions with ZnCl₂ yielded two zinc complexes, namely $[(ZnCl_2)_3(\mathbf{64a})]$ and $[(ZnCl_2)_3(\mathbf{64b})]$ [141]. Compound $[(ZnCl_2)_3(\mathbf{64a})]$ displays three different crystal motifs, depending on the solvent and the solvent ratio used during crystallization. Increasing amounts of benzene in the solvent mixture resulted in greater inclusion of benzene in the crystal lattice. In the structures the three ZnCl₂ units in $[(ZnCl_2)_3(\mathbf{64a})]$ are all located on the same side of the central phenyl ting and chelated by the dipyridylamino groups with a typical tetrahedral geometry. The packing reveals extensive π-stacking interactions in the structure involving the central phenyl ring of **64a** and the benzene solvate molecules. Highly insoluble 1:3 Pt(II) complexes of **64a** and **64b**,

[(PtCl$_2$)$_3$(**64a**)] and [(PtCl$_2$)$_3$(**64b**)] were also reported but their insolubility precluded further investigation.

Wang also reported the synthesis of the larger star-shaped ligands 1,3,5-tris{4′-[4″-(2,2′-dipyridylamino)]biphenyl}benzene, **65a**, and 1,3,5-tris{4′-[4″-(2,2′-dipyridylamino)]biphenyl}triazine, **65b**, by Suzuki couplings in 54% and 56% yields, respectively [143]. The Pt(II) complexes were synthesised by the reactions of [PtPh$_2$(SMe$_2$)]$_n$ with the ligands **64a**, **64b**, **65a**, and **65b**. The relatively labile bridging dimethylthioether ligand in the Pt(II) starting material was replaced by the chelating 2,2′-dipyridylamino moiety in the resulting complexes. While the complexes were relatively insoluble, they were all characterised as the M$_3$L species employing chelation to the metal centres by the three dpa moieties from the respective ligands.

3.6. Other ligands

In studies of linked di-2-pyridylamine derivatives Antonioli and co-workers have reported the synthesis of an octadentate tetratopic derivative, 1,2,4,5-tetrakis(di-2-pyridylaminomethyl)benzene, **66** (Table 9), possessing four di-2-pyridylamine arms [98]. Compound **66** was prepared by reaction of di-2-pyridylamine with 1,2,4,5-tetrakis(bromomethyl)benzene in 34% yield. No complexes were reported for this compound but liquid–liquid (H$_2$O/CHCl$_3$) extraction experiments involving copper(II) showed **66** was the most efficient extractant of the six ligand systems investigated in their broader study. This was correlated with the high lipophilicity of the compound.

A tetratopic di-2-pyridylamine containing ligand that has attracted significantly more study is *N,N′*-{2,4-di[(dipyridin-2-yl)amine]-1,3,5-triazine}ethylenediamine, **67** [110]. The synthesis of **67** is relatively easily accomplished from 2-chloro[4,6-(dipyridin-2-ylamino)]-{1,3,5}triazine **52** by taking advantage of the differential substitution of triazine derivatives at 0°, room temperature and elevated temperatures. Compound **67** could be reacted with copper(II) chloride to give a infinite zigzag coordination polymer in which trinuclear copper complexes of **67** are bridged by chloride anions [145]. As is commonly observed with this class of ligand, the copper centres are chelated by the di-2-pyridyl arms of the ligand, with the central copper centre involved in coordination of two arms from different triazine rings and the external copper centres coordinated by one di-2-pyridyl arm each. Compound **67** was also reacted with copper(II) nitrate to give a novel hexanuclear copper complex [Cu$_6$(NO$_3$)$_{12}$(**67**)$_2$(H$_2$O)]·½(acetone)·½(CH$_3$CH$_2$CH$_2$OH) [146]. The complex consists of two trinuclear complexes bridged by a nitrate anion. The crystal structure revealed the presence of six structurally different copper centres with square-pyramidal CuN$_2$O$_3$ and trigonal-bipyramidal CuN$_4$O environments.

In addition to the discrete complex and 1D polymer previously reported, Gamez and Masciocchi utilised a solvothermal synthetic procedure to prepare another coordination polymer [Cu$_3$(NO$_3$)$_6$(**67**)]$_n$ [147]. The coordination environment of the ligand is quite similar to the copper(II) chloride complex of this ligand, where a nitrate bridges (nitrato-O,O′ bridging mode) between the discrete trinuclear complexes to give the 1D polymer. The 1D polymers are involved in weak interchain head-to-tail π-stacking

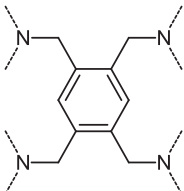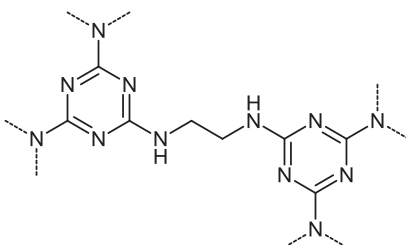**Table 9**
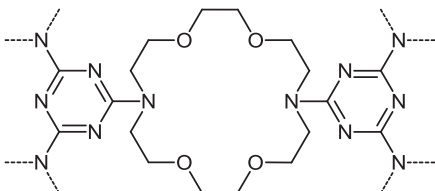Other dpa-containing bridging ligands.
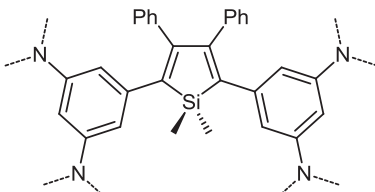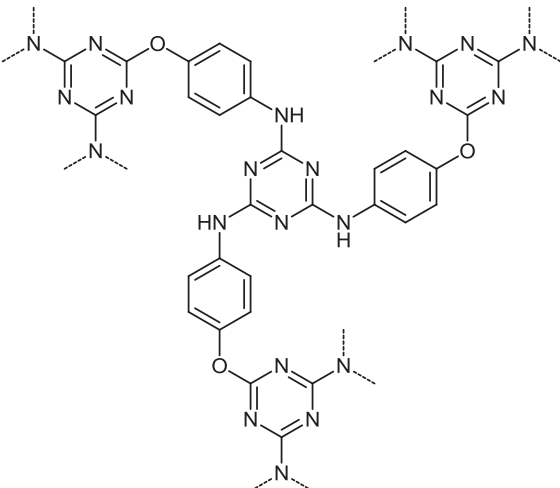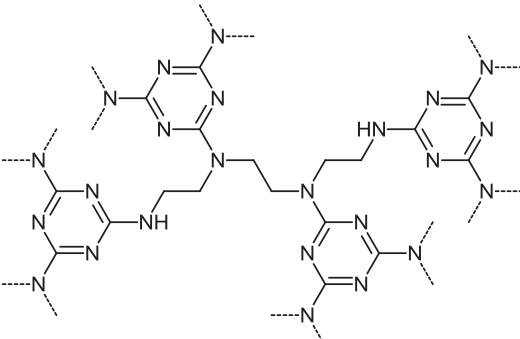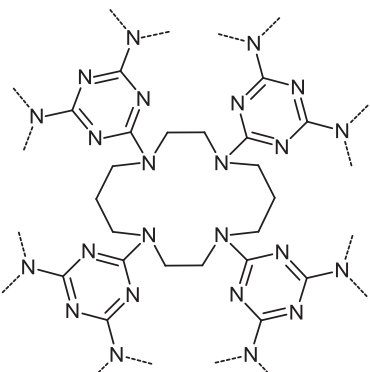
Number	X—▭—X	Reference
66		[98]
67		[110,138,145–148]
68		[149]
69		[103]

Table 9 (*Continued*)

Number	X——▭——X	Reference
70		[110,138]
71		[150]
72		[138,151]

interactions within the crystal structure. Interestingly, in the presence of moisture, $[Cu_3(NO_3)_6(\mathbf{67})]_n$ is readily converted into the hydrated $[Cu_3(NO_3)_5(\mathbf{67})](NO_3) \cdot H_2O$ form which consists of isolated $[Cu_3(NO_3)_5(\mathbf{67})]^+$ and $(NO_3)^-$ ions that accommodate water molecules in the crystal lattice. A copper(II) nitrate complex of **67** was also investigated as an oxidation catalyst as part of a study of a series of polynucleating di-2-pyridylamine ligands and copper(II) nitrate [138].

Gamez and Reedijk also reported four discrete Zn(II) and Cd(II) complexes of **67** [148]. The complexes, $[Zn(NO_3)_2(\mathbf{67})]$, $[Cd(NO_3)_2(\mathbf{67})]$, $[Zn_3(NO_3)_6(\mathbf{67})] \cdot CH_3CN$ and $[Cd_3(NO_3)_6(\mathbf{67})] \cdot CH_3CN$ were prepared solvothermal reactions. In this work the solid-state structures of these coordination compounds were tuned by the crystallisation solvent; in methanol, the mononuclear materials crystallised, whereas in acetonitrile, the trinuclear species were obtained. The mononuclear complexes were isostructural by X-ray crystallography with the metal centre

chelated by one di-2-pyridylamine arm from each triazine unit of **67**. The trinuclear complexes are very similar to the trinulear copper(II) complexes previously reported, but lack the bridging anions required to form polymeric coordination materials.

A related tetratopic ligand, **68**, possessing four di-2-pyridylamine arms was prepared by Gamez and Reedijk using a similar approach to the one employed in the synthesis of **67** [149]. 2-Chloro[4,6-(dipyridin-2-ylamino)]-{1,3,5}triazine **52** was reacted with 4,13-diaza-18-crown-6 to give **68** in excellent 89% yield (Scheme 16). Reaction of zinc(II) chloride with **68** led to the formation the tetranuclear complex $[Zn_4Cl_8(\mathbf{68})] \cdot (CH_3CN)_2(H_2O)_{1.5}$, whereby each zinc centre is tetrahedral and coordinated by one di-2-pyridylamine arm and two chloride counterions. Interestingly, an acetonitrile guest molecule, located in the cavity of the crown moiety, forms a lone pair electron-deficient π interaction in the solid-state and this interaction was further studied by computational means.
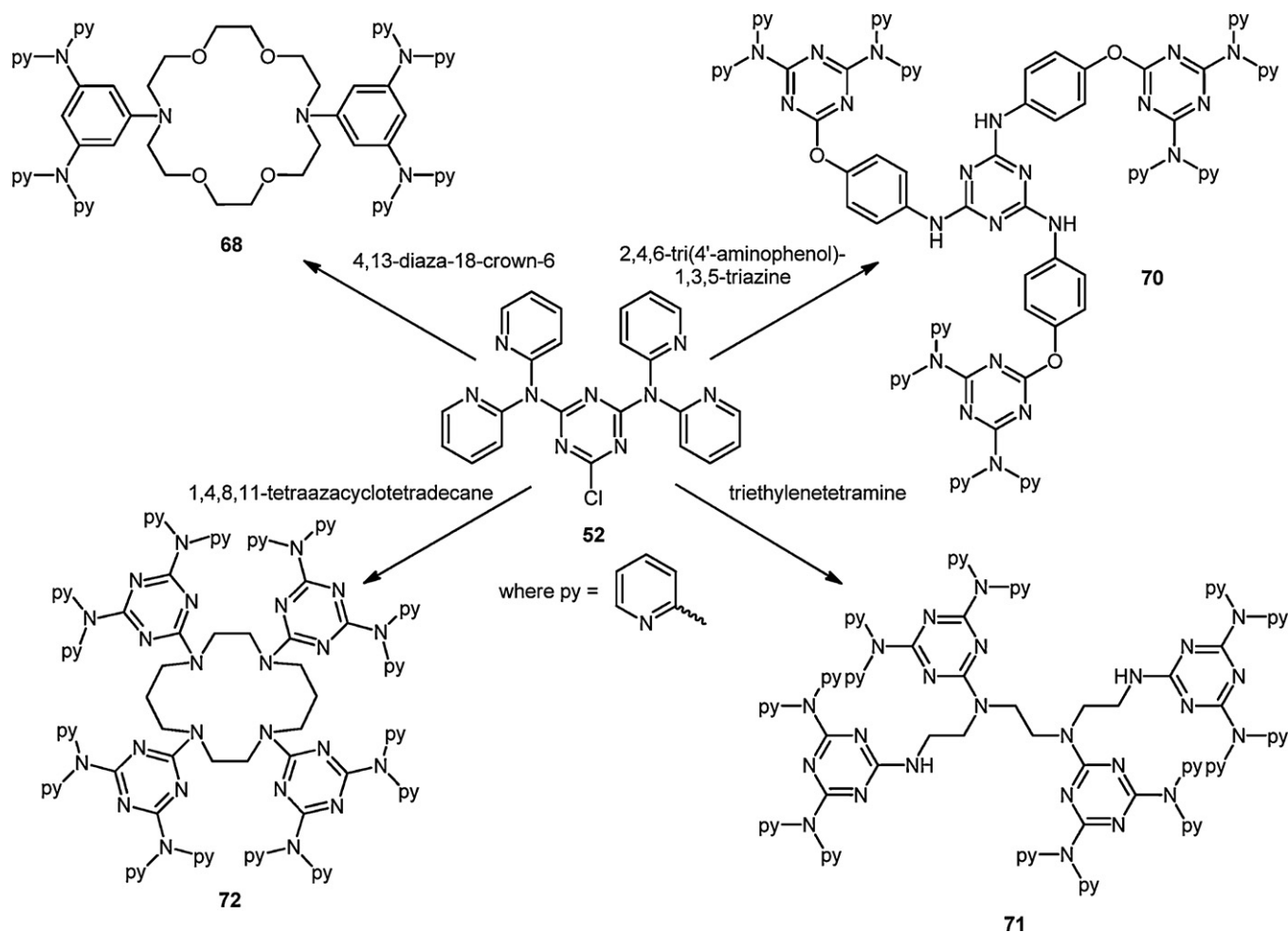
Scheme 16. (after Refs.[110,138,149–151]).

A tetratopic silole derivative **69** was reported by Hirsch and Gerbier [103]. As described earlier, their approach was to prepare derivatives functionalised with dipyridylamine, as a hole-transporting group, on the silole ring. The tetratopic species was prepared from 3,5-bis(2,20-dipyridylamino)bromobenzene and the silole core by a Suzuki coupling reaction.

Gamez and Reedijk have additionally described hexatopic and octatopic di-2-pyridylamine ligands, **70**, **71**, and **72**, which were prepared by reaction of 2-chloro[4,6-(dipyridin-2-ylamino)]-{1,3,5}triazine **52** with 2,4,6-tri(4′-aminophenol)-1,3,5-triazine, triethylenetetramine, and 1,4,8,11-tetraazacyclotetradecane, respectively [110,138,150,151]. Copper(II) nitrate complexes of **70** and **72** have been studied as oxidation catalysts, with the dendrimer-like complex of **72** showing the best activity [138]. It is worth noting that while these ligands possess multiple di-2-pyridylamine arms, the flexibility of the core structure results in the coordination of more than one arm to each ligand. Thus, the two ligands with eight di-2-pyridylamine arms, **71** and **72** both coordinate to only four metal centres in complexes that have been reported.

Evidence for anion–π interactions were obtained for a copper(II) chloride complex of **72** [151], [Cu$_4$Cl$_4$(**72**)]Cl$_4$·(H$_2$O)$_{13}$. In the cationic tetranuclear complex the four s-triazinyl groups attached to the macrocycle core stack two by two in a parallel fashion. This allows the copper centre to be coordinated by two 2,2′-dipyridylamino units belonging to two different s-triazine rings. The most fascinating feature of this complex is its encapsulation of two chloride anions, which are guests in the two host cavities

formed by four pyridine rings of **72**. The pyridine centroid···Cl distances vary from 3.466(5) to 3.697(5) Å, which are longer than the values calculated for the s-triazine moiety. Solvothermal reaction of **71** with copper(II) nitrate in acetonitrile also gave a tetranuclear complex [Cu$_4$ (NO$_3$)$_4$(**71**)](NO$_3$)$_4$·12H$_2$O that displays anion–π interactions involving the electron-deficient aromatic rings of the ligand [150]. In this case a nitrate anion lies close to perpendicular to a triazine ring of the ligand.

4. Conclusions

This review has outlined the structural versatility of bridging heterocyclic ligands containing either di-2-pyridylamino or di-2-pyridylmethyl chelating motifs. Bridging ligands of this type can be successfully synthesised in concise, often one or two-step, synthetic approaches from readily or commercially available precursors. The bridging ligands covered in this review form a range of complexes whereby a range of predominantly chelating but also bridging motifs are demonstrated for one dpa or dpm subunit within the ligand. By incorporating multiple dpa or dpm arms into the ligand two, three and four metal centres can be bridged with chelation of each metal centre by an arm.

The ability to bridge multiple metal atoms in a variety of ways has opened up opportunities to exploit these complexes to investigate metal–metal interactions (e.g. electronic and magnetic), in the study of anion–π interactions, and as structural and functional enzyme active site models. Such compounds have also been studied in materials chemistry for their luminescence properties

or as porous materials. While not as well established as 2,2′-bipyridyl ligands, the relative synthetic ease with which dpm- and dpa-containing bridging ligands can be prepared, and their useful properties, will see increasing study of their coordination chemistry.

Acknowledgements

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