

# Ligand Design in Multimetallic Architectures: Six Lessons Learned

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## ABSTRACT

Metallor-supramolecular chemistry involves the use of combinations of organic ligands and metals for the construction of both discrete and polymeric aggregates. This Account describes some lessons that we have learned about aspects of ligand design in the course of our work in this area. Specifically, we recommend the incorporation of a diverse range of heterocyclic rings and arene cores within the ligands, as well as attention to symmetry considerations, and offer suggestions for the introduction of chirality and flexibility within the ligands and the exploitation of other weak interactions to assist self-assembly processes.

## Introduction

Nitrogen heterocycles are extensively used as bridging ligands in coordination and metallor-supramolecular chemistry.<sup>1</sup> The simplest such ligand is pyrazine (1), which can be employed for the formation of simple binuclear complexes, such as the Creutz–Taube mixed valence ion, or for the construction of larger aggregates, such as discrete molecular squares or extended coordination polymers (Figure 1). Pyrazine acts as a linear bridge between metals separated by ca. 7 Å.<sup>1</sup> By means of ligand design, it is possible to control the distance between the metals and hence the dimensions of the resultant aggregates. For example, 4,4'-bipyridine (2) and the more extended ligands 3–5 lead to metal–metal separations of ca. 11, 13.5, 15, and 20 Å, respectively.<sup>1</sup>

The controlled assembly of discrete metallor-supramolecular architectures usually relies on the use of combinations of linear and angular components that logically self-assemble into predictable structures by means of directional information encoded within the metal and ligand precursors.<sup>2–8</sup> This can be used to assemble simple two-dimensional polygons, such as squares and hexagons, or more complex three-dimensional polyhedra, such as cubes and dodecahedra, as described in several of the accompanying Accounts in this issue. Generally, control over the self-assembly process is achieved by using structurally rigid species. However this approach is limited to relatively few molecular architectures that are highly symmetrical.<sup>2</sup> It is now recognized that access to other topologies is best achieved by incorporating some flex-

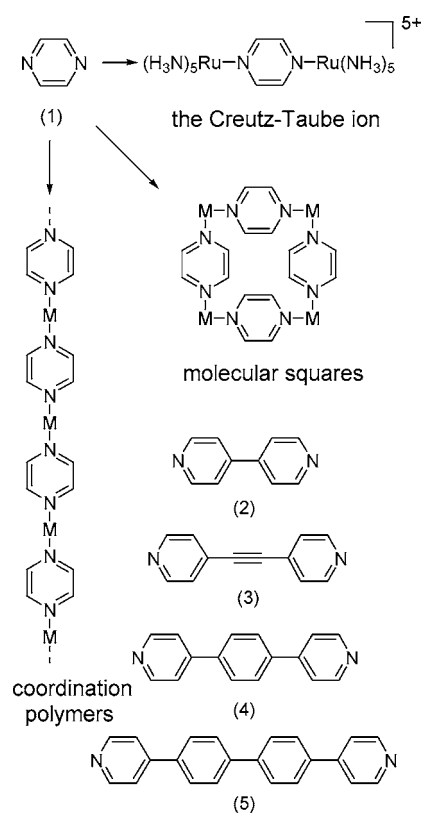


FIGURE 1. Reactions of pyrazine 1 and the structures of linear bridging ligands 2–5.

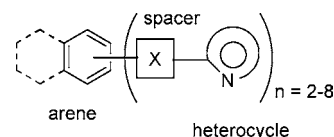


FIGURE 2. Generalized representation of a family of polyheteroaryl substituted arenes.

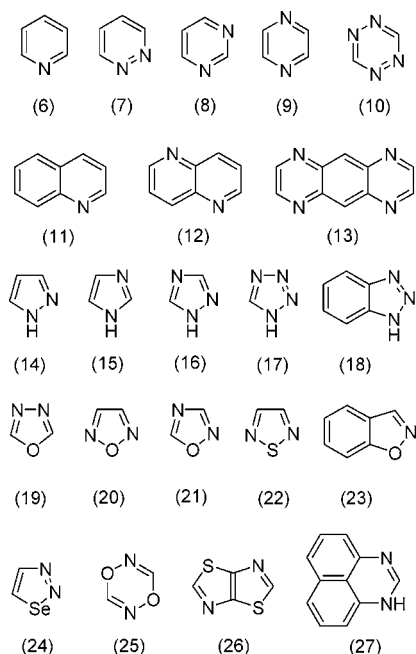
ibility into the ligand in the form of conformationally free subunits, such as short alkyl chains.

We have long been involved in the synthesis of new heterocyclic ligands for use in coordination, organometallic, and metallor-supramolecular chemistry.<sup>9</sup> Some years ago, we embarked on a project to synthesize a large family of new ligands represented by the generalized structure shown in Figure 2. These ligands are comprised of a central arene core to which are appended a number ( $n$ ) of nitrogen-containing heterocyclic rings attached via flexible spacer groups (X). We have used these ligands for the formation of a diverse array of metal complexes, ranging from simple binuclear species to more complex discrete and polymeric multinuclear aggregates. During the course of this work, we have learned many lessons about aspects of ligand design and synthesis that we now share in this Account. We hope that these ideas will be of value to both new and established researchers in the area.

## Lesson 1: Do Not Just Use Pyridine Rings

The vast majority of ligands used for the formation of metallor-supramolecular species utilize pyridine rings as the

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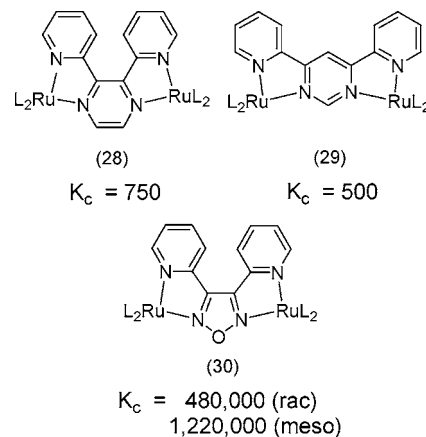


**FIGURE 3.** A selection of the heterocyclic ring systems **6–27** that we have incorporated into chelating and bridging ligands.

metal-coordinating subunit. This undoubtedly stems from the classical role played by pyridine in coordination chemistry, where it forms complexes with almost all metals in the periodic table, often stabilized by back-bonding into the  $\pi^*$ -orbitals of the pyridine ring. For over a century, 2,2'-bipyridine has been used as the classical bidentate chelating heterocyclic ligand<sup>10</sup> and, along with its tridentate analogue 2,2':6',2''-terpyridine,<sup>11</sup> has been incorporated into many bridging ligands.<sup>12</sup> Many other bridging ligands containing 2-, 3-, or 4-substituted pyridines have been synthesized and studied. However, pyridine is just one of many readily available heterocyclic ring systems, which differ in their electronic and structural properties. Most of these are more amenable to synthesis and manipulation than pyridine, but many have been totally ignored by coordination chemists.

Figure 3 shows some of the different heterocycles that we have incorporated into chelating or bridging ligands or both. Some of these, such as pyrazine (**9**), quinoline (**11**), pyrazole (**14**), imidazole (**15**), and 1,2,5-triazole (**16**) have been used by various researchers as useful groups for metal coordination.<sup>1,13,14</sup> Others have never previously been incorporated as subunits into more complex ligands. For example, benzotriazole (**18**) has been much studied as a synthetic auxiliary in organic chemistry<sup>15</sup> but had not been used as a component of chelating or bridging ligands until our recent report of five ligands of this type.<sup>16</sup>

Varying the heterocycles can effect dramatic changes to the physicochemical properties of metal complexes. While it is well-known<sup>13</sup> that six-membered heterocycles, such as pyridine (**6**), are  $\pi$ -deficient and therefore good  $\pi$ -acceptors whereas five-membered aromatic rings, such as pyrazole (**14**), are  $\pi$ -excessive and hence  $\pi$ -donors, there are other more subtle differences that exist between heterocyclic ring systems that can impart significant



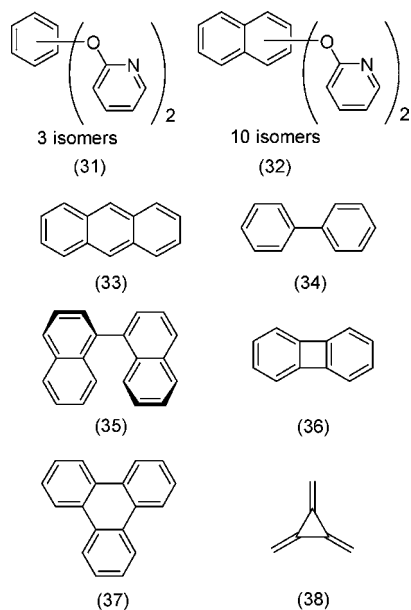
**FIGURE 4.** The structures of three binuclear ruthenium(II) complexes (**28–30**) ( $L = \text{bpy}$ ) and their comproportionation constants,  $K_c$ .

effects upon the properties of their metal complexes. As an example, Figure 4 shows the structures of three binuclear ruthenium(II) complexes, along with the values of the comproportionation constants ( $K_c$ ) that measure the extent of metal–metal interaction between the two ruthenium centers.<sup>17</sup> The first (**28**) incorporates a pyrazine bridge and represents a well-studied complex.<sup>17</sup> The second (**29**) was prepared by us some years ago<sup>18</sup> in the hope that it would exhibit a stronger metal–metal interaction due to the ability of the ligand to adopt a more planar conformation. This proved not to be the case, and the binuclear complex showed a slightly weaker  $K_c$ . The third example (**30**) shows a related complex having a 1,2,5-oxadiazole bridge. This ring system (**20**) is readily synthesized from 1,2-diketones, via their dioximes, but has been strangely ignored by coordination chemists. This binuclear complex exhibits an extraordinary amplification of the metal–metal interaction as evidenced by the value of  $K_c$ .<sup>19</sup> This result is even more remarkable for the fact that the two diastereoisomers (*meso* and *racemic*) of the complex show extremely different values of  $K_c$ . The origin of this behavior is presently unexplained and is the subject of ongoing investigations.

Other ring systems shown in Figure 3 have been incorporated into various ligands with similar interesting results. These heterocyclic subunits offer electronic and structural diversity far beyond that provided by pyridine rings.

## Lesson 2: Do Not Just Use Benzene Scaffolds

Numerous ligands have been reported in recent years that use a benzene ring as a spacer unit between coordinating moieties. These range from ones in which the benzene acts as a simple linear spacer unit, as in ligands **4** and **5** (Figure 1), to others in which it provides a central scaffold from which up to six arms radiate outward to metal binding domains. However, benzene is not the only arene core available for such purposes. Figure 5 shows a selection of the units that we have incorporated into our family of ligands and that offer much greater diversity than is provided by a single benzene ring.



**FIGURE 5.** The structure of the 2-pyridyloxy-benzenes (**31**) and -naphthalenes (**32**) and other arene cores (**33–38**).

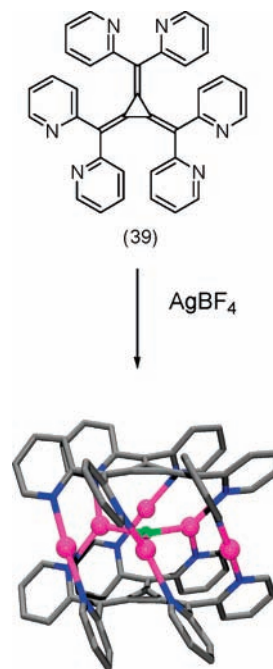
For example, we have prepared many ligands containing 2-pyridyl units linked by flexible oxygen atoms to arene cores. In the case of disubstituted examples, benzene offers only three possible substitution patterns (*ortho*, *meta*, and *para*) for these ligands (**31**). In contrast, there are 10 possible isomers (**32**) for disubstitution in a naphthalene ring, each of which differs in the orientation and spatial separation of the donor units.<sup>20</sup> This diversity increases as one moves to larger polycyclic aromatic cores. In this context, we have also used anthracene (**33**), biphenyl (**34**), 1,1'-binaphthyl (**35**), biphenylene (**36**), and triphenylene (**37**) units as scaffolds for more complex ligands.<sup>9</sup> The 1,1'-binaphthyl unit (**35**) also offers the possibility of chirality associated with atropisomerism.<sup>21</sup>

One interesting scaffold is [3]radialene (**38**), which is isomeric with benzene and which we have used as the central core in the hexasubstituted ligand **39** shown in Figure 6. This ligand is readily prepared in a one-pot reaction and leads to a number of discrete and polymeric metallosupramolecular species.<sup>22,23</sup> For example, its reaction with silver tetrafluoroborate produces a novel  $[M_6L_2F]^{5+}$  assembly in which a planar array of six silver atoms is sandwiched between two of the radialene ligands in a discrete hexagonal prismatic structure, as shown in Figure 6.<sup>22</sup>

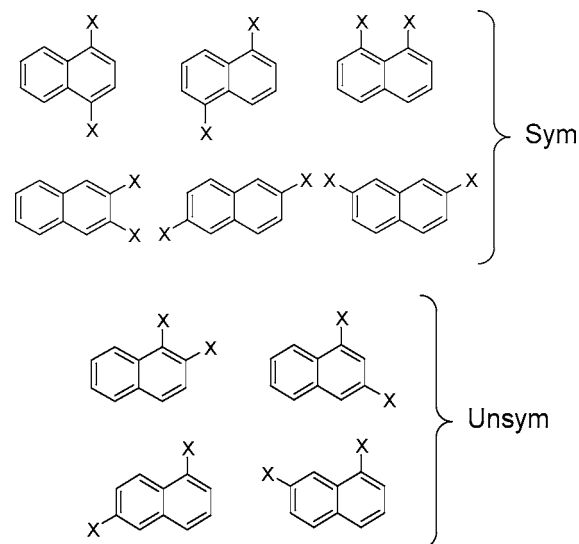
Thus, when new bridging ligands are designed, consideration should be given to aromatic spacers other than benzene, since these offer much greater diversity of orientation, separation, and substitution patterns for attached metal binding groups.

### Lesson 3: Symmetry Considerations Are Important

An important design aspect of bridging ligands is the symmetry, or otherwise, of different metal binding sites. In our experience, it is not advisable to use ligands that

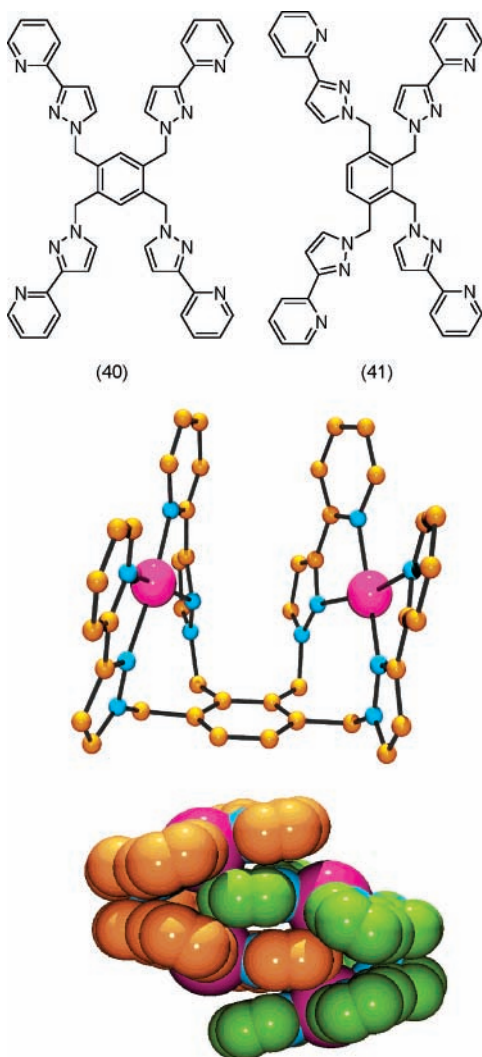


**FIGURE 6.** The structure of the [3]radialene ligand (**39**) and X-ray structure of the  $[M_6L_2F]^{5+}$  reaction product with silver(I) tetrafluoroborate.



**FIGURE 7.** The six symmetrical and four unsymmetrical substitution patterns available to ligands such as **32**.

have slightly different binding sites. This is exemplified by returning to the 10 isomeric disubstituted naphthalenes mentioned earlier. As shown in Figure 7, six of these have symmetrical patterns in that the two metal binding groups are equivalent. The remaining four have donor groups in slightly different environments. Thus, in a self-assembly process each of these latter ligands can be incorporated into the multinuclear complex in either of two ways. Such structural ambiguity means that a single molecular architecture is unlikely to result. Indeed, we have found that ligands based on disubstituted naphthalenes with symmetrical substitution patterns are more likely to give a single crystalline product than their less symmetrical isomers.



**FIGURE 8.** The structures of the isomeric ligands **40** and **41** and the X-ray structure of the dinuclear silver complex of **41** and its self-complementary duplex.

More subtle aspects of symmetry are also worthy of attention. For example, Figure 8 shows two isomeric ligands each of which contains a central benzene ring tetrasubstituted with chelating units attached via methylene linkers. The first (**40**) has a 1,2,4,5-substitution pattern, and hence, all four arms are symmetrically equivalent. We have found that this ligand readily coordinates to up to four metal centers, thereby acting as a 4-fold connector unit, in various complexes.<sup>24</sup> The second ligand (**41**) has a 1,2,3,4-substitution pattern with reduced symmetry. It contains two equivalent outer arms (1,4-substituted) and two equivalent inner arms (2,3-substituted). This different symmetry has interesting consequences. For example, upon reaction with silver(I) salts (tetrafluoroborate, perchlorate, or triflate) this ligand produces binuclear complexes containing two silver atoms each chelated by two adjacent arms.<sup>25</sup> Surprisingly, all four arms lie on the same side of the benzene ring and the complex has a cleft-shape. The reason for this may be seen by examining the space filling diagram (Figure 8) of two such binuclear units, which are found to further assemble into a self-

complementary duplex held in place by other weak forces ( $\pi$ - $\pi$  stacking and C-H $\cdots$ M interactions).<sup>25</sup>

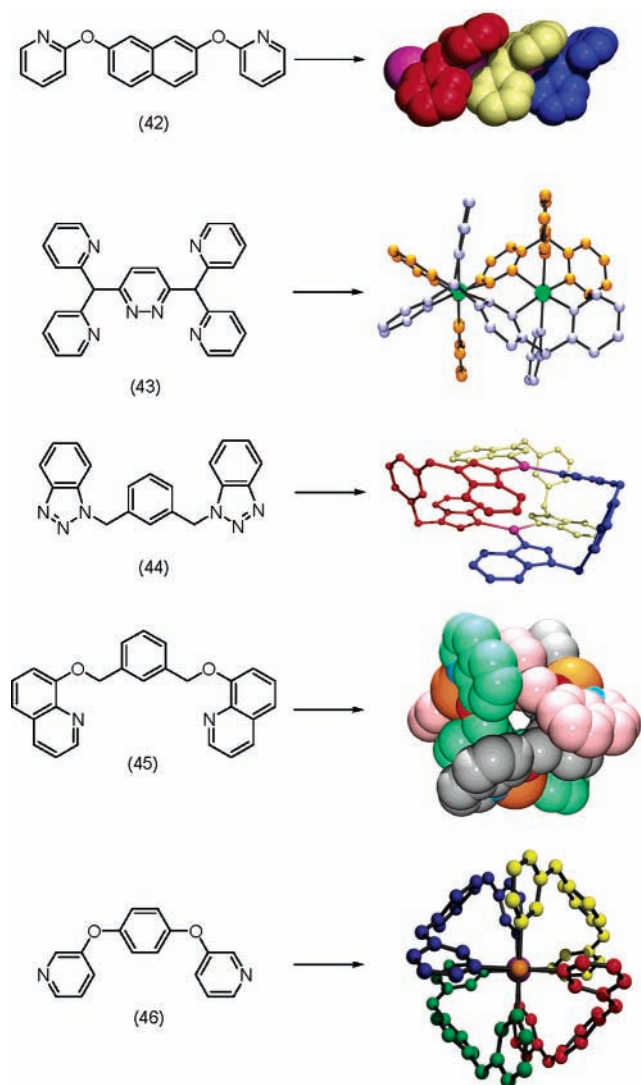
Symmetry, therefore, is an important aspect of ligand design. While it is acceptable to use unsymmetrical ligands with metal binding domains that are sterically or electronically very different or both, we have found that it is not advisable to use ligands with similar binding groups in slightly different environments for use in the assembly of complex molecular architectures.

#### Lesson 4: Be Flexible with Ligand Design

As mentioned above, the most common approach to the rational design of two- and three-dimensional metallo-supramolecular species has been to use appropriate combinations of *rigid* angular and linear components. However, many topologies are not accessible through such an approach. We have often incorporated *flexible* linker units into our bridging ligands to access other architectures. These can be single-atom spacers, such as methylene groups or ether oxygen atoms, or longer spacers, such as three-atom propylene groups.<sup>26</sup> An obvious disadvantage of the inclusion of flexible subunits is that the ligand itself can adopt different conformations as a consequence of rotations about single bonds. This can lead to a loss of control in the design and assembly of the resulting metal-containing aggregates.

Flexible bridging ligands with two metal binding domains often form binuclear  $M_2L_2$  dimetallo-cycles for thermodynamic reasons, because this maximizes both the enthalpic and entropic return. Another common outcome for such ligands is helicate formation, a structural motif that has played an important role in the historical development of metallosupramolecular chemistry.<sup>27,28</sup> Helicates are obtained by wrapping strands of organic ligands around metals in a helical fashion. Some flexibility within the ligand is required for introduction of the twist associated with the helical shape.

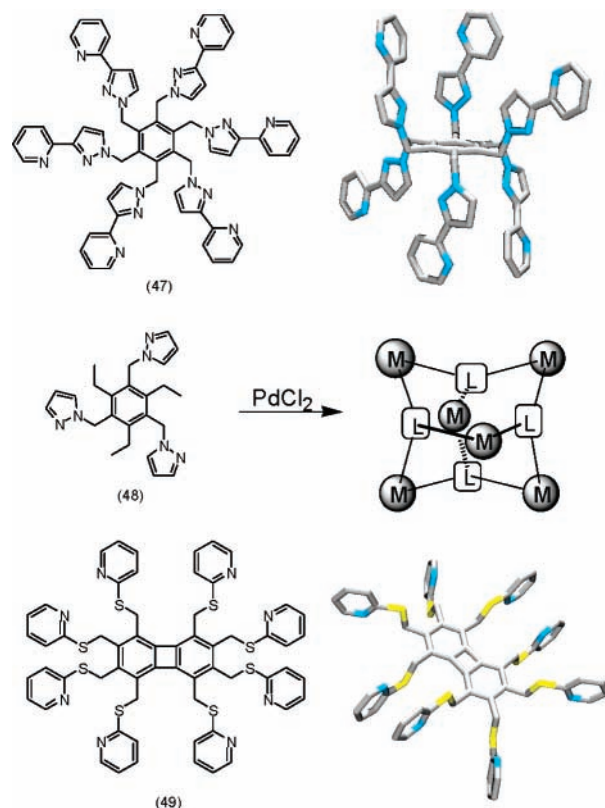
Figure 9 shows the structures of five of our ligands that form various types of helicates. The first (**42**) has a naphthalene core with two 2-pyridyl groups attached via ether linkages. It reacts with silver nitrate to form a single-stranded helical coordination polymer.<sup>29</sup> The second (**43**) has a pyridazine core with four pyridyl groups attached via two methine linkages and forms a highly contorted, binuclear double-stranded helicate upon reaction with nickel tetrafluoroborate.<sup>30</sup> The third ligand (**44**) has two 1-benzotriazolyl groups attached via methylene spacers to a central *meta*-disubstituted benzene ring. It forms a highly compact binuclear triple-stranded helicate.<sup>31</sup> The fourth ligand (**45**) has two 8-quinolinyl substituents attached to a central benzene ring through two-atom flexible spacer groups. This reacts with silver(I) triflate to form a trinuclear circular helicate that is stabilized by multiple aryl embraces.<sup>32</sup> The fifth, very simple ligand (**46**) has two 3-pyridyl substituents and was used to prepare the first example of a quadruple-stranded helicate.<sup>33</sup> Such a structure was achieved by the bridging of two square-planar palladium(II) centers in a helical fashion using four of the



**FIGURE 9.** Five flexible ligands (42–46) that lead to various types of metal helicates.

ligands shown. This helicate has a central cavity within which lies an anion (iodide in the example shown). Furthermore, we have shown that the encapsulated anion can be exchanged for different anions and that in the process the helicate adjusts its size and shape in response to that of the encapsulated species.<sup>34</sup>

The loss of control associated with the use of flexible ligands can be partly compensated by a number of subtle approaches. One of these is to make use of preorganization.<sup>35</sup> This involves controlling the conformations of the free ligand by orienting substituents with respect to a given reference plane. The most common way to do this is to make use of the fact that six bulky substituents attached to a single benzene ring will tend to arrange themselves on alternating faces of the ring. An example of this is ligand (47) shown in Figure 10, where six pyridylpyrazole units are attached via methylene groups to a central benzene ring. The X-ray crystal structure of the free ligand shows the alternating orientations of the arms.<sup>36</sup> This concept can be used to preorganize different sets of substituents on opposite faces, three in the 1,3,5-



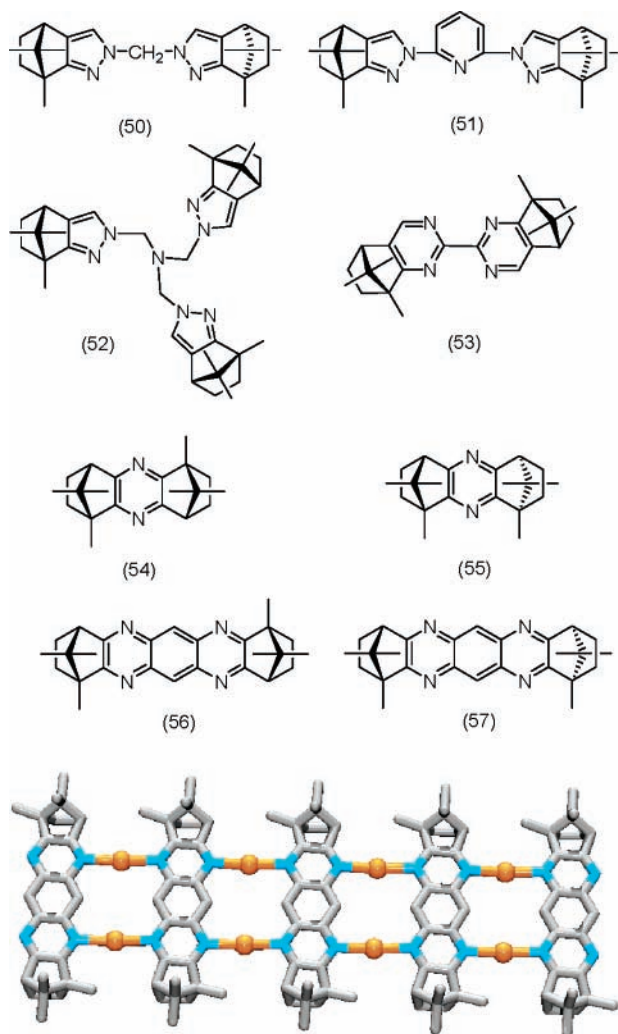
**FIGURE 10.** X-ray crystal structures of two multiply armed ligands, 47 and 49, showing the preorganization of the substituents, and the formation of an adamantanoid cage from 48.

positions on one face and three different ones in the 2,4,6-positions.<sup>35</sup> We used this concept to prepare one of the first examples of  $M_6L_4$  adamantanoid cages from ligand 48<sup>37</sup> and a new class of metal-encapsulating ligands.<sup>38</sup> We have recently extended this approach to larger systems, such as ligand 49 shown in Figure 10. This has eight 2-pyridyl substituents attached by flexible two-atom spacers to a central biphenylene core. Once again the crystal structure of the free ligand, which could potentially adopt many conformations, shows that it has the eight arms locked into a specific conformation in which the donor groups alternate on opposite faces of the central core.<sup>39</sup>

Thus, the use of flexible ligands can provide access to interesting molecular architectures without complete loss of control in the self-assembly process.

## Lesson 5: Fuse Chiral Appendages

An important aspect of molecular design is the ability to include chirality. In the case of metallocsupramolecular architectures, this can be achieved with either the metal or ligand components or a combination of both. Although there has been much recent progress in our ability to control the chirality of octahedral metal centers,<sup>40</sup> it is more common to use chiral ligands for the formation of dissymmetric supramolecular species. Chiral ligands can be obtained either by resolution of synthetic compounds, such as those derived from 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) and 1,1'-bi-2-naphthol (BINOL),<sup>21,41</sup> or by synthetic modification of the many natural products



**FIGURE 11.** A selection of chiral ligands derived from camphor and the X-ray structure of the silver coordination polymer of **56**.

from the chiral pool. Amino acids, carbohydrates, terpenes, and alkaloids have provided many useful chiral ligands for asymmetric catalysis or as building blocks for supramolecular species.<sup>42</sup> Chiral appendages to heterocyclic rings can either be attached through freely rotating single bonds or be fused onto the heterocyclic rings to provide a less mobile chiral environment. We are of the opinion that the latter method is preferable for chiral ligands intended for use in both asymmetric catalysis and self-assembly processes.

We have prepared many new ligands derived from the readily available monoterpene camphor.<sup>9</sup> These all contain a bornane unit fused to a heterocyclic ring with a nitrogen donor adjacent to the ring junction. These nitrogen atoms lie in a highly asymmetric environment. In a similar context, von Zelewsky and co-workers have prepared a large library of ligands (Chiragens) that contain pinane units fused to various heterocycles.<sup>43</sup> Figure 11 shows a selection of ligands that we have prepared and includes bidentate (**50**),<sup>44</sup> tridentate (**51**),<sup>45</sup> tripodal (**52**),<sup>46</sup> and binucleating (**53**)<sup>47</sup> examples.

We have also prepared chiral derivatives of pyrazine as linear bridging ligands for use in the construction of

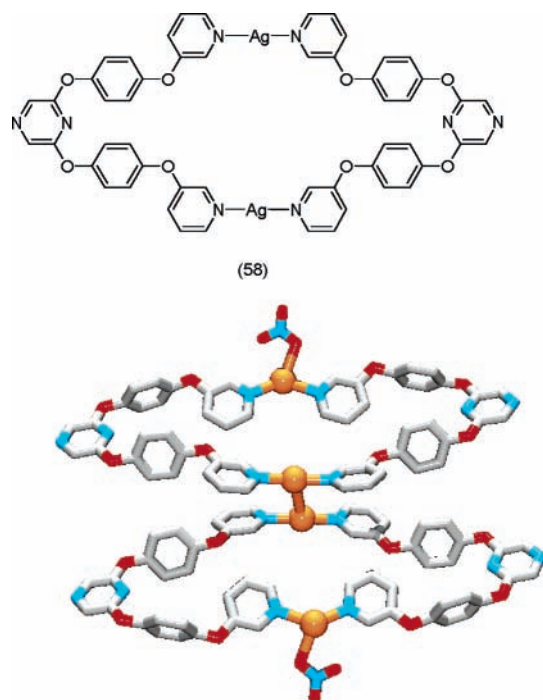
chiral coordination polymers. Once again (lesson 3), aspects of symmetry are important. The isomeric ligands **54** and **55** are both homochiral  $C_2$ -symmetric ligands. However, they differ in the orientation of this symmetry element. In ligand **54**, the  $C_2$ -axis lies perpendicular to the central pyrazine ring, and hence the two nitrogen donors are symmetrically equivalent. In contrast, the  $C_2$ -axis in ligand **55** passes through the two nitrogen atoms, which have very different steric environments. Thus, reactions of **54** with linear metal connectors (such as Ag or  $Cu_2I_2$  units) leads to nondirectional polymers,<sup>48</sup> whereas analogous reactions of **55** result in the self-assembly of chiral directional coordination polymers.<sup>49</sup> A similar relationship exists between the two isomers **56** and **57**, which represent a new class of doubly bridging linear ligands. Ligand **56** reacts with silver nitrate to produce the antiparallel railtrack assembly shown,<sup>49</sup> while the analogous complex of **57** would be unidirectional.

These chiral bridging ligands have monoterpene subunits fused to heterocyclic rings in a structurally rigid environment, which we consider to be the preferred way to append chirality to ligands.

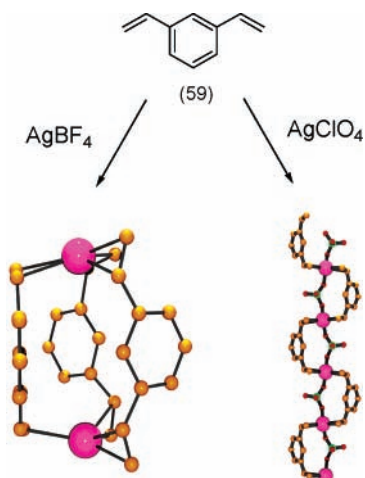
## Lesson 6: Use Multiple Interactions

The primary interaction in metallosupramolecular self-assembly processes is that between a metal atom and a heteroatom donor (nitrogen in the examples discussed above). The strength of this interaction is very dependent on the specific metal involved and varies between relatively weak bonds (for  $d^{10}$  metals such as silver(I)) to much stronger bonds (such as those involving platinum(II) or ruthenium(II)). However, in most cases these are not the only interactions that are responsible for controlling the final shape and structure of the full multinuclear architecture. Other weak interactions usually play important roles in providing thermodynamic stability to the complete assembly. Individually these may be weak, but the combined thermodynamic return from multiple interactions can be very significant. Nature employs this approach to hold together the strands of DNA, protein assemblies, and the majority of cellular machinery.

Most of the structures described above involve stabilizing secondary interactions, such as  $\pi$ - $\pi$  interactions<sup>50</sup> (including multiple aryl embraces<sup>51</sup>), various types of weak hydrogen bonds<sup>52-54</sup> (including C-H $\cdots$ N interactions, C-H $\cdots$ M agostic interactions), or other weak noncovalent interactions with noncoordinated anions, solvate, or guest molecules. For example, the central arene core present in the family of ligands represented in Figure 2 is very often involved in  $\pi$ - $\pi$  interactions within the larger aggregates formed.<sup>55</sup> We have been particularly fond of the use of silver as a component in such constructions and have often encountered assemblies within which silver-silver interactions have played important structural roles. These interactions are comparable in magnitude to normal hydrogen bonds.<sup>56</sup> For example, the binuclear triple-stranded helicate obtained from ligand **44**, shown in Figure 9, further assembles into dimeric units held



**FIGURE 12.** The large dimetallamacrocycle **58** and its dimerization through a  $\text{Ag}\cdots\text{Ag}$  interaction to form a  $[\text{M}_4\text{L}_4(\text{NO}_3)_2]^{2+}$  assembly.



**FIGURE 13.** X-ray structures of discrete  $[\text{M}_2\text{L}_3]^{2+}$  and polymeric  $[\text{ML}(\text{ClO}_4)]_n$  silver complexes obtained from *meta*-divinylbenzene (**59**).

together only by silver–silver interactions.<sup>31</sup> Another intriguing example is shown in Figure 12. In the course of other work, we had occasion to prepare the large  $\text{M}_2\text{L}_2$  dimetallamacrocycle **58** and were surprised to find that it also underwent further aggregation into a dimeric species held together by unsupported  $\text{Ag}\cdots\text{Ag}$  interactions.<sup>57</sup>

Another weak interaction that thus far has been virtually ignored in supramolecular chemistry is that between alkenes and silver atoms. We have recently embarked on a project to exploit this type of interaction as a new supramolecular synthon.<sup>58</sup> Figure 13 shows how *meta*-divinylbenzene (**59**) can be used as a bridging ligand to produce either a discrete  $\text{M}_2\text{L}_3$  molecular cage (with silver tetrafluoroborate) or a linear coordination polymer (with silver perchlorate).

These and other weak interactions, some of which may not yet have been identified, play important roles in defining the structures of metallosupramolecular architectures. A challenge for the future is to logically incorporate these weaker interactions into ligand design for use in heterosupramolecular chemistry.

## Conclusion

It is exactly a decade since the term “metallosupramolecular chemistry” was coined.<sup>59</sup> Since then there has been an exponential increase in the level of publication in this area. New ligands are regularly being reported for use as components in the construction of novel molecular architectures of increasing complexity. We have been active in the area of ligand design and synthesis and in this Account have shared some of the lessons that we have learned throughout the course of this research. We hope that these ideas will be useful to workers in the field. It remains to be seen whether such metallosupramolecular compounds will find truly useful applications as functional resources in material science and nanotechnology.<sup>60–63</sup>

*I am indebted to the many talented co-workers who have carried out the work described in this Account and whose names appear in the references. I also thank the Foundation for Research, Science and Technology, the Royal Society of New Zealand Marsden Fund, and the University of Canterbury for generous funding.*

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