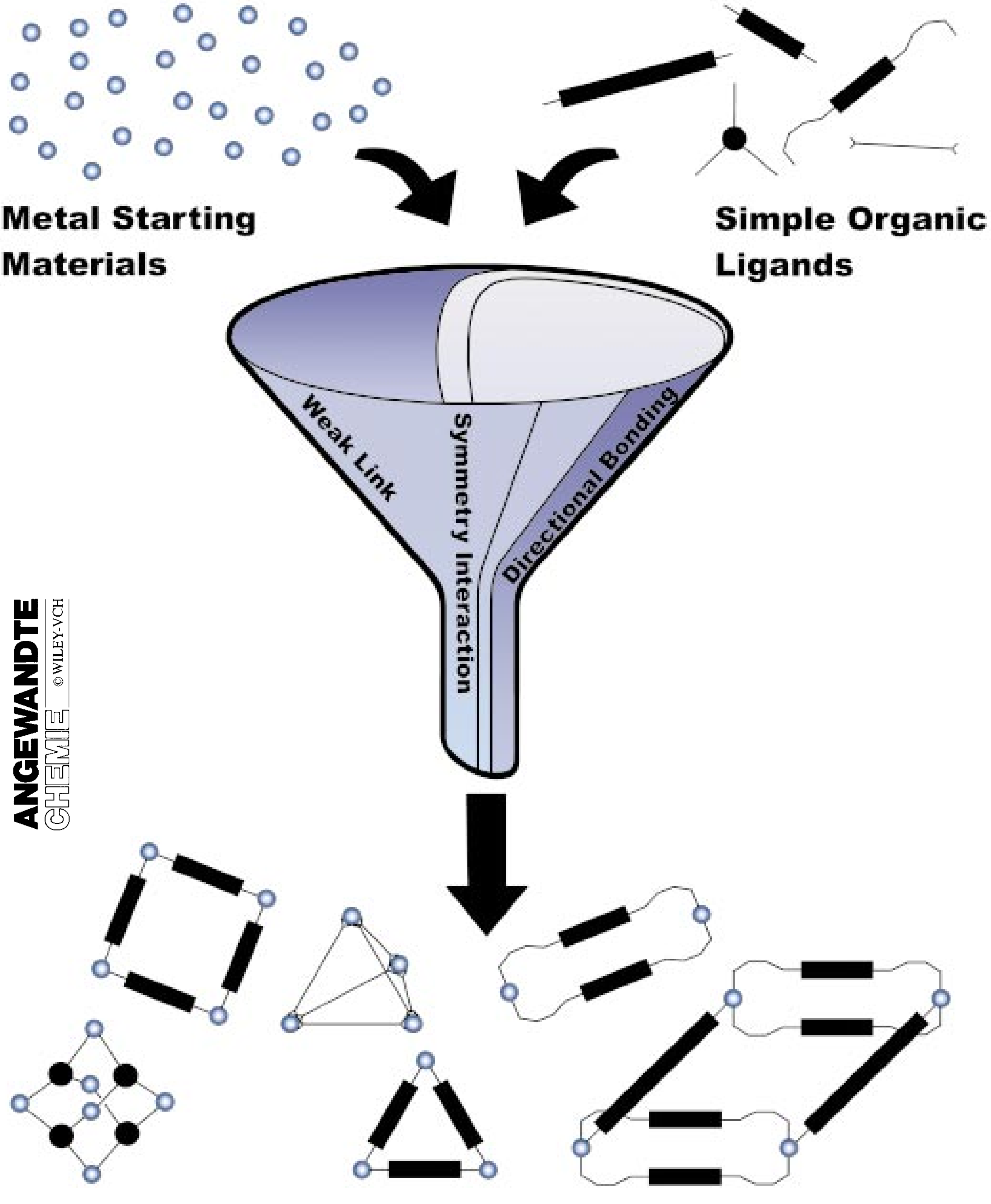
Supramolecular Coordination Chemistry



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Strategies for the Construction of Supramolecular Compounds through Coordination Chemistry

Bradley J. Holliday and Chad A. Mirkin*

Synthetic organic chemists enjoy the luxury of having a large collection of reliable reactions at their disposal for preparing small molecules, mesoscopic structures, and polymers. Coordination chemists, on the other hand, are faced with the fact that transition metal chemistry, when normalized for the number of transition metals, has relatively few high-yielding reactions, when compared to the chemistry of carbon, for preparing even small molecule structures. This lack of control is manifested, in large part, in the weak metal–ligand interactions found in coordination complexes as compared with the strong covalent bonds in organic compounds. Weak bonding often translates into many reaction pathways that are not substantially different from an energetic point of view, and therefore, results in poor selectivity. As a result, many coordination chemists in recent years have come to the realization that it may be easier and more productive to develop straightforward and reliable routes to mesoscopic supramolecular structures by capitalizing on the modest collection of high-yielding reactions in coordination chemistry, the directional bonding afforded by metal centers, and strategies aimed at taking advantage of the weak metal bonds found in coordination complexes. Three emerging synthetic strategies, the symmetry-interaction, directional-bonding, and weak-link synthetic approaches, all use metal centers as structural building blocks to rationally assemble molecular components into supramolecular metallocyclophanes. These three approaches are discussed herein, and the fundamental principles underlying each as well as their capabilities are compared and contrasted.

Keywords: coordination chemistry · nanostructures · supramolecular chemistry · synthetic methods · transition metals

1. Introduction

In the last twenty-five years supramolecular chemistry has developed at a tremendous rate. This expansion has been driven by the growing knowledge regarding synthetic and characterization methods for complex structures.[1–3] Chemistry "beyond the molecule"[1] is as old as life itself and epitomized in nature by the hydrogen-bonded structure of DNA, the elegant ability of enzyme receptor sites to act on one molecule with absolute selectivity, and the control exhibited by metalloproteins, such as hemoglobin, over a metal coordination environment. Only in the past two decades have we begun to develop ways of mimicking the properties and functions of these systems on the most rudimentary levels. Interest in these complex systems lie in the scientific fields of chemistry (recognition and selective transformations), biology (translocation of drugs across membranes), and materials science (construction of macroscopic architectures and devices on the molecular level).[2, 4] In fact, the study of supramolecular systems blurs most of the traditional divisional boundaries of science and thus represents a truly interdisciplinary field.

As chemists, we take on the task of building supramolecular systems by designing rational synthetic schemes that begin with our knowledge of reactivity on the atomic scale (functional groups) and then build up. The development of linear step-wise syntheses, which entail the controlled manipulation of reactive sites on individual molecules, has increased, by many-fold, the number of organic molecules that can now be produced synthetically. The initial work on the synthesis and properties of organic macrocycles as selective hosts[5] paved the way for the synthesis of larger, more complicated arrays, many of which now contain one or more metal atoms. However, as the scale and complexity of target molecules increases, the step-wise synthesis of large discrete supermolecules from molecular building blocks becomes increasingly difficult, often low-yielding, and specific to only a few approaches.[6]

The use of transition metal centers and coordination chemistry for directing the formation of complex structures

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has evolved into one of the most widely used strategies for organizing molecular building blocks into supramolecular arrays. The synthesis of large symmetric structures requires careful consideration of the entropic and enthalpic costs involved. While nature has refined the construction of macromolecules (for example, DNA, RNA, or proteins) utilizing a plethora of relatively weak interactions within each assembly: hydrogen bonding, van der Waals forces, Coulombic interactions, and dipole – dipole interactions, our mastery of these subtle interactions as synthetic tools is in an early stage of development. In supramolecular arrays the use of weak interactions becomes important for two reasons:

1) the weak forces holding the molecules together incorporate a large degree of flexibility into biomolecules which allows conformational changes that are often necessary for function, and
2) the large number of weaker interactions allow for greater specificity through annealing processes which ultimately form the most thermodynamically favorable structure.[7]

The latter observation can be an extremely important consideration when designing supramolecular assemblies and represents a significant advantage that metal-mediated assembly holds over conventional covalent organic synthesis.

The covalent coordination bonds formed to transition metal centers are of intermediate strength relative to the weak interactions discussed above and the strong covalent carbon – carbon bonds of most organic compounds. Significantly, the heteroatom – metal bonds are thermally labile. This property allows one to intentionally select either a thermodynamic or kinetic product through the judicious choice of ligands, transition metals, and reaction conditions. Therefore, defect structures can often be corrected or annealed to the desired product by adjusting reaction times and conditions. In addition to thermal annealing, the metal-directed assembly of supramolecular structures can be aided by chelation effects which can significantly decrease the entropy of formation relative to organic systems which typically couple through one point of contact in the form of a carbon – carbon bond. These characteristics make the formation of large, symmetric supramolecular arrays through transition metal mediated assembly an attractive strategy that has been exploited by many research groups. While the metal – ligand interactions are at the cornerstone of these synthetic strategies, distinct subsets can easily be delineated.

Several general and high-yielding synthetic approaches have emerged from this large body of work. The purpose of this Review is to define and discuss these strategies in the context of the current progress being made in this field. Comprehensive reviews cataloging the molecules synthesized by some of the approaches discussed below have been reported elsewhere.[8–14] Herein, we intend to highlight some of the basic structures which these strategies have produced, review the more extraordinary structures reported in the recent literature, and discuss a relatively new general synthetic approach which has been overlooked in other review articles.

2. Supramolecular Structures Formed through Coordination Chemistry

2.1. The Directional-Bonding Approach

2.1.1. Preface

The directional-bonding approach, as used here, or the "molecular library" approach, as coined by Stang and coworkers,[12] involves the assembly of large metal-containing structures wherein the metal centers act as highly directional corner or side units in the resulting geometric shapes or

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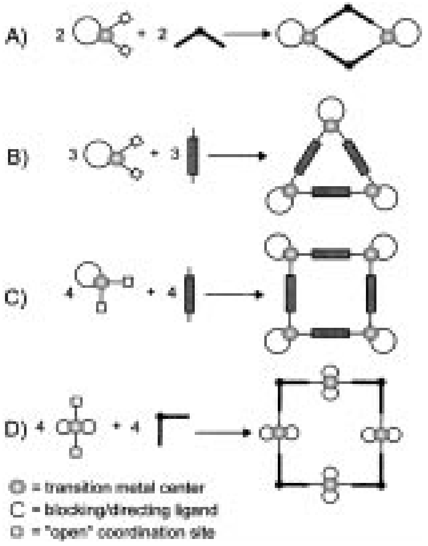
polyhedra. Typically, the metals are introduced into these structures with directing or blocking ligands that only make coordination sites available to incoming ligands with the appropriate angle to form the desired shape (Scheme 1). In this strategy, the target molecule's shape is predetermined by careful selection of the metal starting material, coordinatively inert directing ligands, and rigid bridging ligands. For example, a dinuclear macrocycle can be assembled by using a metal complex with a 60° angle between the coordinately labile sites and a rigid ligand with a 120° kink (Scheme 1 A). This same metal complex can be used to construct a molecular triangle by using a linear ligand system (Scheme 1 B). Finally, there are two complementary ways to construct a molecular square: 1) by using a metal starting material with a 90° angle between the coordination sites and a rigid linear ligand (Scheme 1 C) or 2) by utilizing a metal complex with a 180° geometry and a ligand system with a 90° turn (Scheme 1 D). More complicated polyhedra that can be accessed through this strategy will be discussed in Section 2.1.7.



Scheme 1. The construction of large structures by the directional-bonding approach. The metal centers have a high directional effect on the resulting geometric shapes. The metals are introduced with directing or blocking ligands.

The corner angles are essential to the closure of the appropriate geometric shape and hence, as defined by Stang and co-workers, the ligands must be "rigid, highly directional multibranched monodentate ligands, which bind to partially coordinatively unsaturated transition-metal complexes via dative bond interactions".[12] Since either the ligand or metal used in this approach has a directing influence, we feel the term "directional-bonding approach" is more descriptive than molecular-library approach, and will be used throughout to describe this approach.

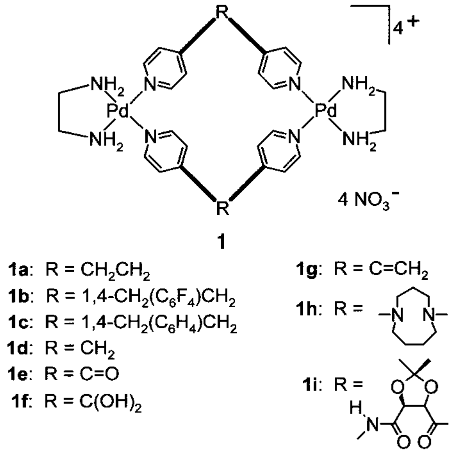
2.1.2. Advantages and Limitations of this Approach

The directional-bonding approach to the synthesis of supramolecular coordination complexes is a general, high-yielding synthetic strategy that grants researchers access to complexes with a wide range of sizes and shapes which can be controlled through rational choices of metals and ligands. The generality of this approach for the incorporation of ligands with many different desirable physical properties for applications has also been demonstrated by various research groups.

However, there are some inherent limitations to this approach. First, the ligand systems used are rigid linking groups which preclude the formation of flexible supramolecular arrays; this rigidity limits the formation of molecular switches or other applications which require conformational changes in the complex other than rotation. Second, the metal centers in the final structures are coordinatively inert, which severely limits applications such as size- and shape-selective metal-based catalysis and use of the metal centers to form more complex structures through further coordination chemistry. Indeed, any catalysis or formation of extended arrays from preformed, discrete supermolecules is ligand based and is encumbered by the limits of organic manipulation on this scale (see Section 1). Finally, the physical properties of both the ligand and metal building blocks are often greatly perturbed as a result of the direct coordination and often conjugation between the transition metal centers and the rigid heteroatom-containing ligands employed in this synthetic strategy. For example, strongly luminescent ligands have been incorporated into several molecular squares only to have the ligand-based luminescence quenched completely by the metal centers.[15, 16]

2.1.3. Dinuclear Macrocycles

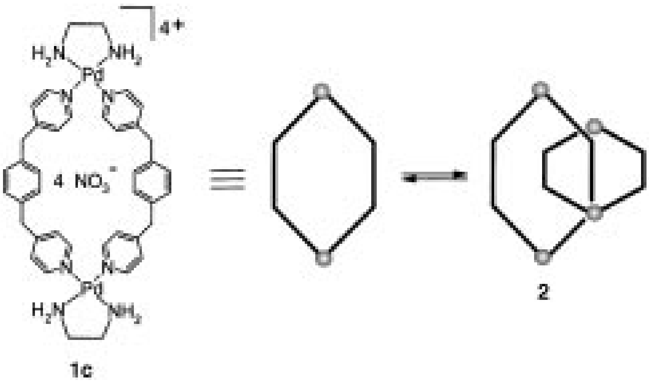
Dinuclear metallomacrocycles containing transition metal atoms in the backbone have been made by the directional-bonding approach. Initial work in this area by Fujita et al. includes the synthesis of a series of ligand systems and the investigation of the dynamic behavior of the macrocycles **1** in solution.[17–21] The ligand systems used are all based on a bis(pyridine) dative donor group and its coordination chemistry with a palladium(II)–ethylenediamine complex. Also, Hosseini and co-workers have prepared analogous metallomacrocycles by incorporating diazacycloalkanes into the organic backbone (**1h**),[22] and Hong and co-workers have reported the synthesis and dynamic guest-induced solution structure of macrocycles possessing a hydrophobic cavity incorporating a chiral group in the backbone (**1i**).[23] The fluorinated version of this system (**1b**) has been shown to



1

1a: R = CH_2CH_2
1b: R = 1,4-$CH_2(C_6F_4)CH_2$
1c: R = 1,4-$CH_2(C_6H_4)CH_2$
1d: R = CH_2
1e: R = C=O
1f: R = $C(OH)_2$
1g: R = C=CH_2
1h: R =
1i: R =

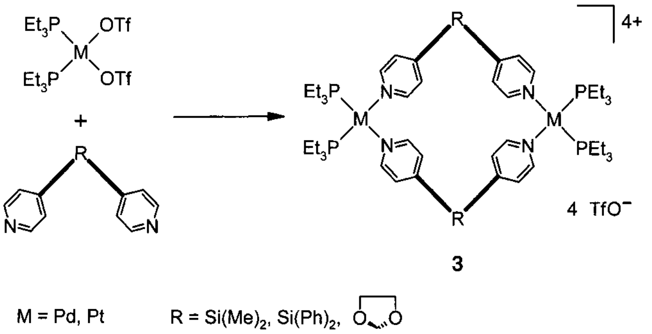
recognize electron-rich aromatic guests in aqueous solutions.[17] Furthermore, dilution studies of complex **1c** in D_2O by ^1H NMR spectroscopy have established the presence of inorganic catenane **2** (two interlocked molecular rings) in equilibrium with the monomeric ring structure (Scheme 2).[18]



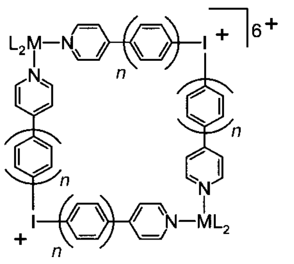
Scheme 2. The monomeric ring structure **1c** is in equilibrium with catenane **2** in D_2O.

By changing to platinum, which forms stronger bonds with the pyridine donors, Fujita et al. have been able to force the equilibrium to a stable inorganic catenane.[19] Finally, Fujita et al. have reported the synthesis of two unique inorganic [2]catenanes formed from molecular rectangles that are remarkably stable in solution, with no evidence of monomer rings even at low concentrations (mM).[21]

In a similar manner, Stang and co-workers have assembled dinuclear macrocycles through dative coordination bonds. They have reported the synthesis of several rhomboids by the reaction of bis(triethylphosphane)platinum(II) and -palladium(II) bistriflates with the corresponding bis(pyridine) ligands (Scheme 3).[24] A single-crystal X-ray diffraction study of the dimethylsilaneplatinum version of rhomboid **3** confirmed its cyclic structure and revealed an internal cavity of 10.9 × 8.0 Å.[24] Stang and co-workers have also reported the synthesis of homodimetallic macrocyclic structures which incorporate iodonium salts as the turn in the organic ligand (**4**; see Table 1 for abbreviations, dppf = 1,1′-bis(diphenylphosphinyl)ferrocene).[25–29] The rigid and highly directional cationic organohalogen salts are ideal for the synthesis of supramolecular arrays by the directional-bonding approach.[30] These iodonium salts have been used as the corners in a number of complexes which can be prepared in good yields (50–100 %) and have been characterized by standard techniques (IR and multinuclear NMR spectroscopies, combustion analysis, and single-crystal X-ray molecular structure determination). Additionally, the incorporation of fullerenes into supramolecular assemblies has been a long-standing goal of many chemists because the unique physical properties of these compounds offer the potential of creating novel materials with rich electronic chemistry.[31] The directional-bonding approach has been used to synthesize a diplatinum complex **5** which contains two bis(pyridine)-functionalized C_{60} molecules.[32]

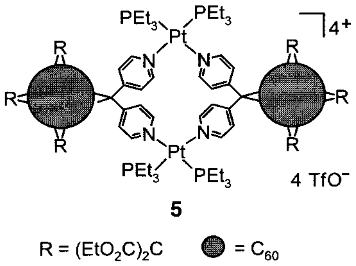


Scheme 3. Synthesis of the various rhomboids through the reaction of bis(triethylphosphane)platinum(II) and -palladium(II) bistriflate with the corresponding bis(pyridine) ligand.[24]



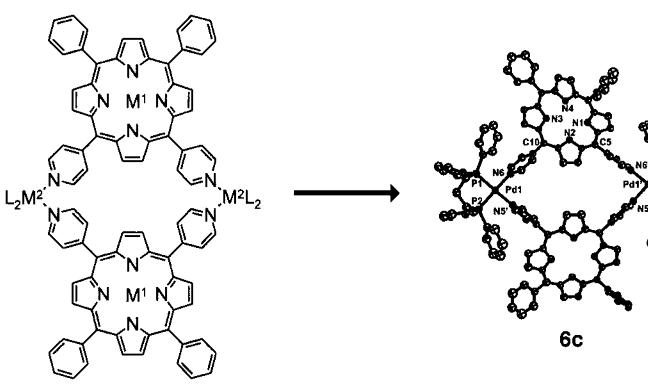
4

4a: M = Pt or Pd, L_2 = dppp, *n* = 0
4b: M = Pt or Pd, L_2 = PEt_3, *n* = 0
4c: M = Pt or Pd, L_2 = dppp, *n* = 1
4d: M = Pt or Pd, L_2 = PEt_3, *n* = 1
4e: M = Pt or Pd, L_2 = binap, *n* = 1
4f: M = Pt or Pd, L_2 = binap, *n* = 0
4g: M = Pt or Pd, L_2 = dppf, *n* = 1
4h: M = Pt, L_2 = diphosphinocalix[4]arene



This synthetic scheme reported by Diederich and co-workers is significant because it demonstrates the covalent attachment of ligating groups onto the surface of C_{60} which allows the incorporation of these molecules into many supramolecular assemblies by the directional-bonding approach.

Building supramolecular structures which incorporate porphyrin subunits is of great interest to many research groups. The rich photochemistry and redox properties (for example, photoinduced electron transfer, luminescence, and light-harvesting) of porphyrins have driven this interest. In addition, when functionalized with the appropriate heteroatom-containing groups, porphyrins have a rich coordination chemistry that allows the inclusion of many different metal centers within the ring and at the periphery. The ability to align the porphyrin chromophores in well-defined geometries, so as to tailor the distances and cofacial interactions between them, paves the way for important studies of the ground-state and excited-state interactions of these molecules. A 5,10-dipyridylporphyrin has two ligating groups oriented at 90° to each other, which makes it ideal for use as a molecular corner in either dimetallic macrocycles or molecular squares (see Section 2.1.5), and allows them to be used as building blocks in the directional-bonding approach.[16, 24, 33] Figure 1 depicts a summary of these structures and the solid-state X-ray crystal structure of one such molecule reported by Stang and co-workers.[24] These molecules can be synthesized in good yields and are well characterized in solution. The solid-state molecular structure of **6c** reveals that these structures possess a large internal cavity measuring 14.1 × 4.8 Å.



6

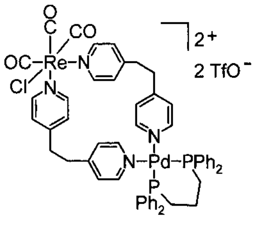
6c

6a: M^1 = 2H, M^2 = Pd, L$_2$ = 2 Cl
6b: M^1 = Zn, M^2 = Pd, L$_2$ = 2 Cl
6c: M^1 = 2H, M^2 = Pd, L$_2$ = dppp
6d: M^1 = Zn, M^2 = Pd, L$_2$ = dppp
6e: M^1 = 2H, M^2 = Pd, L$_2$ = binap

Figure 1. Generalized diagram of dinuclear macrocycle **6** and the X-ray crystal structure of **6c**. Reprinted with permission from ref. [24].

The dinuclear systems discussed above are all homodimetallic systems, but there are two examples of mixed-metal systems reported by Hupp and co-workers and Iengo/Alessio and co-workers.[34, 35] Hupp and co-workers, in an effort to synthesize a molecular square using a flexible ligand system (bis(pyridyl)ethane), isolated compound **7**. Significantly, they found that the luminescence in this system was completely quenched.[34] The stepwise synthesis of compound **8** was reported by Iengo, Alessio, and co-workers.[35] First, the bisporphyrin/ruthenium complexes were isolated in moderate yields (40–70%) followed by reaction with bisphosphanepalladium(II) bistriflates to form the dinuclear complex **8** in good yield (80%). The metalation with zinc resulted in the formation of **8d**. This stepwise synthesis provides a rational route to mixed-metal dinuclear supramolecular complexes.

Finally, there have been relatively few examples of dinuclear metallomacrocycles formed with metal centers other than Pd^{II} or Pt^{II}. Two complexes that incorporate osmium and molybdenum into the framework of the macrocycle by the directional-bonding approach. Jeong et al. have reported the spontaneous assembly of a series of homodimetallic Os^{VI} complexes from osmium tetroxide, 2,3-dimethyl-2-butene, and bis(pyridyl) ligands.[36, 37] In this synthesis, OsO_4 is treated with a 1:1 mixture of the olefin and bis(pyridyl) ligand. The resulting octahedral metal center contains two available coordination sites at 90° to one another to which the pyridyl groups bind. The dinuclear products are formed and isolated in near-quantitative yields. Figure 2 shows the X-ray crystal structure of the 1-naphthol adduct of one such complex. Furthermore, Jeong et al. have prepared a macrocyclic receptor containing hydrogen-bonding groups on the interior of the cavity and have studied the binding of several guest molecules.[36] The synthesis of molybdenum-containing dinuclear macrocycles **9** has been reported by Jones and co-workers.[38–40] The synthetic procedure adopted for this preparation utilizes an octahedral Mo^{III} metal center with bulky Tp or Tp* (Tp = hydrotris(pyrazol-1-yl)borate, TP* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) and nitrosyl ligands as the directing groups which allow binding of the bridging anionic diol or dithiol ligands in the two *cis* coordination sites.



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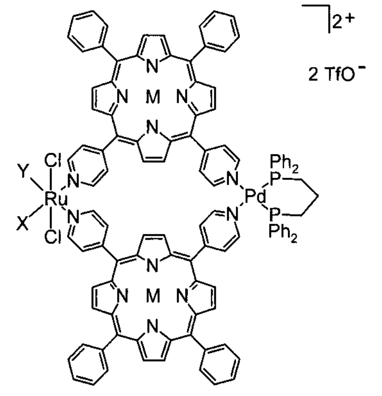


8

8a: X = Y = Me$_2$SO, M = 2H
8b: X= Me$_2$SO, Y = CO, M = 2H
8c: X = Y = CO, M = 2H
8d: X = Y = CO, M = Zn

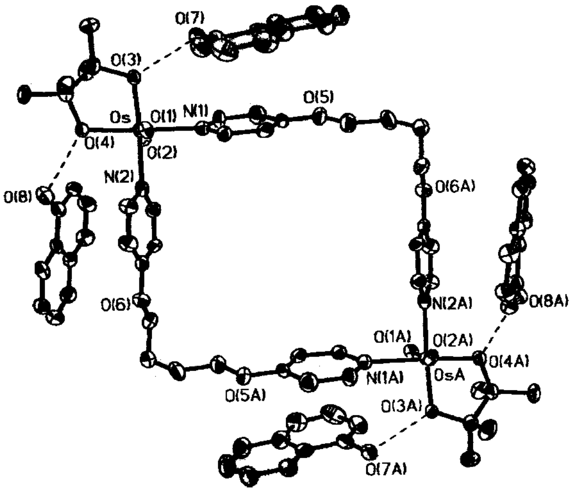
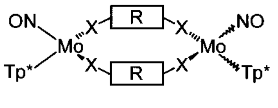


Figure 2. X-ray crystal structure of the 1-naphthol adduct of a dinuclear macrocycle with Os^{VI} metal centers. Reprinted with permission from ref. [36].

As demonstrated by the examples above, the directional-bonding approach can be employed to synthesize a variety of homodimetallic and heterodimetallic macrocyclic compounds



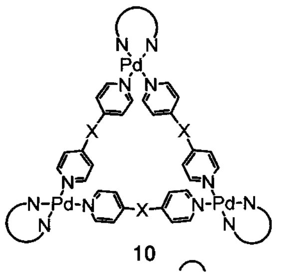
9

9a: R = 1,3-$CH_2(C_6H_4)CH_2$; X = S
9b: R = 1,3-$CH_2(C_6H_4)CH_2$; X = O
9c: R = 1,4-$CH_2(C_6H_4)CH_2$; X = S
9d: R = 4,4'-$(C_6H_4)CH_2(C_6H_4)$; X = O
9e: R = 2,7-$C_{10}H_8$; X = O

by selecting the proper transition metal complexes and ligands as starting materials. The synthetic strategy has been developed and generalized now by a large number of research groups to include a diverse set of metals and ligands. As discussed in Section 1, subtle changes in the protecting ligands on the transition metal center can lead to the formation of different molecular geometries, for example, trinuclear transition metal-containing molecular triangles, which will be considered next.

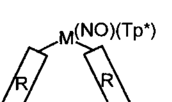
2.1.4. Molecular Triangles

The requirements for the formation of molecular triangles by the directional-bonding approach have been outlined in Section 2.1.1 and are illustrated in Scheme 1. Relatively few examples of trinuclear molecular triangles have appeared in the literature, for example, **10**–**14**. Fujita et al. have shown that molecular triangles **10** are formed in equilibrium with molecular squares.[41] By varying the length of the ligand (see **10a**–**10d**; en = ethylenediamine) and changing the protecting group on the metal starting material (see **10e**) this equilibrium can be adjusted in a predictable way. Additionally, Fujita et al. reported on dilution studies that support the thermodynamic balance they proposed exists between the enthalpically favored squares and the entropically favored triangles.[41] Similar studies of the dynamic solution equilibrium of these systems have been carried out by Hong and co-workers utilizing ligand systems illustrated in structures **10b** and **10f**.[23, 42]

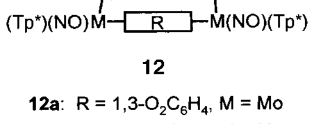


10

10a: X = C≡C; N N = en
10b: X = CH=CH; N N = en
10c: X = C≡C-C≡C; N N = en
10d: X = C_6H_4; N N = en
10e: X = none ; N N = 2,2'-bpy
10f: X =

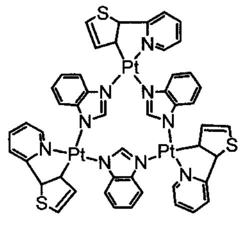


; N N = en

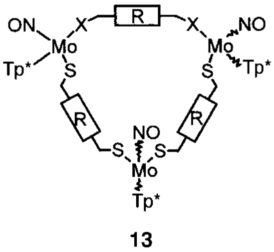


12

12a: R = 1,3-$O_2C_6H_4$, M = Mo
12b: R = 1,4-$O_2C_6H_4$, M = Mo
12c: R = 1,4-$O_2C_6H_4$, M = W

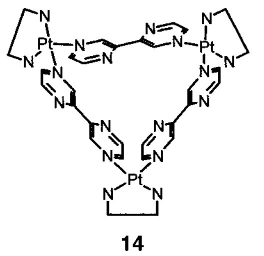


11



13

13a: R = 1,3-$O_2C_6H_4$
13b: R = 1,4-$O_2C_6H_4$



14

The flexibility of the directional-bonding approach has been demonstrated by Chan and co-workers through the rational synthesis of two luminescent molecular triangles (**11**) that, in contrast to the complexes prepared by Fujita et al., incorporate ligands with a 150° bend and metal corners that have coordination sites at 90° to one another, instead of linear or pseudo-linear ligands and metal centers with distorted coordination sites at 60° to each other.[43] Chan and co-workers chose deprotonated benzimidazolate as the edge units and 2-(2′-thienyl)pyridine (in **11**) or 7,8-benzoquinoline (not shown) as the protecting groups on the platinum(II) metal centers. These trimers have been prepared in high yields and are well characterized in solution, the gas phase, and the solid state. Other luminescent molecular triangles have been reported by Sun and Lees.[44, 45] These systems incorporate 1,4-bis(4′-pyridylethynyl)-2,5-dihexyloxybenzene as a ligand with rhenium(I) centers as the vertices of the structure (not shown). The molecular triangles are luminescent at room temperature in solution and show increasing structural features in the spectra at low temperatures.

Jones and co-workers have used Group 10 transition metal centers to expand the directional-bonding approach to a series of molybdenum- and tungsten-containing trinuclear metallomacrocycles (**12** and **13**).[38, 39] These compounds exist as a mixture of structural isomers which differ with respect to the orientation of the protecting ligands relative to one another. The trimers have been well characterized, and the solid-state molecular structure of **12b** has been reported.[38]

Recently, Lippert and co-workers have reported the synthesis of a novel class of trinuclear metallomacrocycles based on 2,2′-bipyrazine (bpz) as an edge group, ethylenediamine as the directing group, and platinum or palladium as the transition metal centers.[46, 47] Significantly, it has been demonstrated that triangle **14** is the kinetic product of the reaction of $[(en)Pd(H_2O)_2](NO_3)_2$ with bpz; longer reaction times and elevated temperature lead to the formation of the mononuclear product $[(en)Pt(bpz)](NO_3)_2$.[46] It is important to note that the ligand groups in **14** are oriented approximately perpendicular to the plane defined by the three metal atoms. This arrangement not only creates a larger interior cavity for possible host–guest interactions (anionic guests have been shown to bind inside this cavity), but it also orients the remaining coordination sites of the bpz ligands above and below the plane defined by the three metal centers. Rotation about the C–C single bond of the bpz ligand (from the conformation shown) allows for the chelation of three additional transition metals, thereby locking the structure into one conformation and resulting in a hexanuclear molecular triangle. Lippert and co-workers have also reported the synthesis of the Pt_6, Pd_6, and Pt_3Pd_3 triangles as well as more complex structures which can be formed from them.[47]

The triangular structures reviewed thus far are based on trinuclear species with single metal centers at each geometric vertex. The syntheses of molecular triangles where transition metal dimers form the corners also have been reported; Figure 3 depicts two such structures. These structures are classified under the directional-bonding approach because the metal centers are introduced with directing groups present which predetermine the final molecular shape. It is important to note that despite being introduced as dimeric complexes, the metal centers maintain their role as the geometric cornerstones of the structures. Each metal center still has two available coordination sites which are oriented at the appropriate angles to form the desired geometric shape. The synthesis and characterization of complex **15** was reported by Cotton et al.[48] Quantitative formation of **15** was achieved while attempting to construct the corresponding molecular square with rhodium dimer corners. Süss-Fink et al. have synthesized the trimeric structure **16**, which incorporates diruthenium complexes as the corners and tartaric acid as the edges of the triangle.[49] The molecular triangle **16a** can be formed as three different isomers depending on which diastereomer of tartaric acid is used as the starting material. All of the isomers can be obtained in about 80% yield. The triphenylphosphane complex **16b** is synthesized by a ligand substitution reaction on the preformed triangle **16a**.

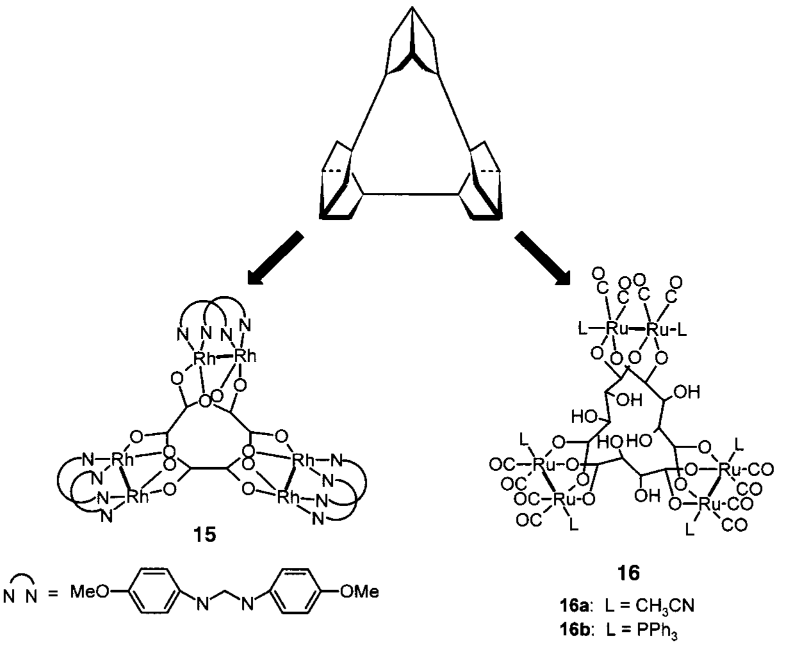


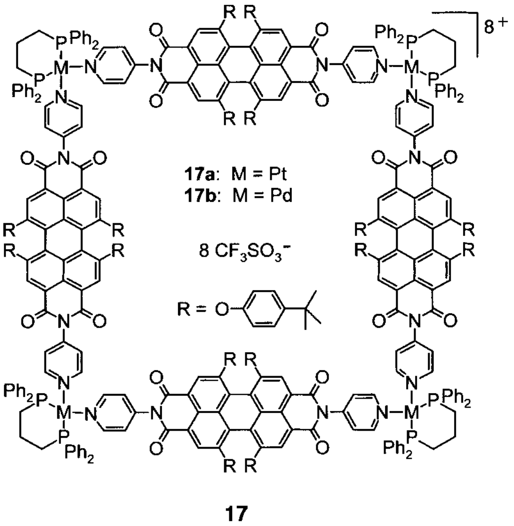
Figure 3. Simplified diagram (top) and molecular structures of molecular triangles **15** and **16**.

The synthesis of molecular triangles by the directional-bonding approach has been demonstrated by several research groups and represents the important link between enthalpic and entropic considerations when targeting discrete geometric shapes through the directed-assembly of edges and corners.

2.1.5. Molecular Squares

Of the geometric shapes accessible through the directional-bonding approach, squares have been the most widely reported. The requirements for the formation of a square metallocyclophane from molecular components has been outlined in Section 2.1.1 (see Scheme 1C and D). The formation of molecular squares over oligomeric or polymeric products in high yields is enthalpically driven in that the resulting shape is essentially strain free. Furthermore, the incorporation of a large number of ligand systems and transition metals is easily understood as a result of the relatively simple requirements for each. The ligands must be rigid, linear or pseudo-linear, difunctional, and capable of bridging, while the metal centers must have open coordination sites at either 90° or 180° to one another (*cis* square planar or octahedral metal centers). Many commercially available or easily synthesized compounds meet these requirements. Molecular squares made by the directional-bonding approach have been thoroughly reviewed elsewhere.[8, 11–13, 50] Table 1 summarizes the molecular components used to assemble squares and the resulting properties that have been successfully imparted to the squares.

Notable structures that are outlined above include the final entry in Table 1; the construction of a molecular square with nanometer-scale dimensions in high yield (90-95%) from a perylenebisimide derivative and Pt^{II} and Pd^{II} corners.[77] The resulting tetranuclear metallomacrocycle **17** is significant for several reasons:



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1) the square is exceptionally large, with a metal–metal diagonal length of 3.4 nm,
2) the dipyridylperylene ligand retains its photophysical properties after being bound to the metal centers ($\Phi_F = 0.88$), and
3) the organic ligands also exhibit reversible electrochemistry in the final Pt^{II} complex.

Table 1. Components used in the formation of molecular squares by the directional-bonding approach.

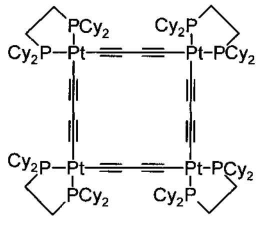
Ligand(s)	Directing group(s)	Transition metal center(s)	P	Ref.
$P(OPCH_2)_3P$	$(CO)_4$	Cr and Mo,W and Mo		[51]
4,4′-bpy	en	Pd or Pt	1	[41, 52, 53]
	dppp	Pd or Pt		[54]
	crown ether bisphosphane	Pt		[29]
	calix[4]bisphosphane	Pt	4	[29]
	dppp and $(CO)_3Cl$	Pd and Re	5	[34]
	2,2′-bpz	Pd		[55]
	$O_2(mes)_2$	Os		[56]
bis(4-pyridyl)acetylene	en	Pd		[41]
P-benzonitrile	dppp or PEt_3	Pd and/or Pt		[57, 58]
diazapyrene	Et_3P	Pd or Pt		[59]
	1,1′-bis(diphenylphosphanyl)ferrocene	Pd or Pt	3	[27]
	crown ether bisphosphane	Pt		[29]
diazaperylene	Et_3P	Pd or Pt		[59]
dicyanobenzene	dppp	Pd		[59]
2,6-diazaanthracene	binap	Pd or Pt	2	[28, 60]
2,6-diazaanthracene-9,10-dione	binap	Pd or Pt	2	[28, 60]
$[\{[CC(C_5H_4N)](C_6H_4)(PPh_3)_2Pt\}_2]$	dppp	Pt		[26]
5,15-dipyridylporphyrin (2H or Zn)	dppp or binap	Pd or Pt		[15, 33]
	$(CO)_3Cl$	Re	5,6	[61, 62]
4-pyridyl acetate	dppp or PEt_3	Pt and Ti		[63]
4-ethynylpyridine	dppp and/or PEt_3	Pd and/or Pt	1	[58, 64]
	dppp and/or PEt_3 and/or diop	Pd and/or Pt	2	[65]
1,2-$C_2B_{10}H_{12}$ or 3-phenyl-1,2-$C_2B_{10}H_{11}$	–	Hg	2	[66]
2-hydroxybenzoxazole	–	Al		[67]
functionalized zinc porphyrin	porphyrin	Zn		[68]
uracilate	en	Pt		[69]
4,4′-bpy, pyrazine, or 1,2-bis(4-pyridyl)ethylene	$(CO)_3Cl$	Re	5, 6, 1	[70, 71, 72]
cyanide	$Cl/C_{10}H_{14}$	Rh and Co		[73]
1,3-dihydroxybenzene or 1,4-dihydroxybenzene	Tp*/NO	Mo or W		[38]
butadiyne and bis(tri-*n*-butylphosphane)platinum dibutadiyne	d(cy)pe	Pt		[74]
t-dppen	$(CO)_2bpy$	Re	5	[75]
1,2-bis(4-pyridyl)ethylene	en	Pd	1	[41, 42]
	$(CO)_3Cl$	Re	5	[45]
	$(CO)_3Cl$ and 1,1′-bis(diphenylphosphanyl)ferrocene	Re and Pd	5, 3	[45]
1,4-dipyridylbutadiyne	$(CO)_3Cl$	Re	5	[44, 45]
benzene-1,4-dicarboxylic acid	dicarboxylic acid and 4-*tert*-butylpyridine	Rh_2		[76]
oxalate, tetrafluoroparaphthalate, or ferrocene-1,1′-dicarboxylate dianion	DarF	Mo_2		[48]
perylenebisimide	dppp	Pt or Pd	3,5	[77]

P = Properties the resulting square possesses. 1 = host–guest interactions, 2 = chiral, 3 = redox-active, 4 = molecular transport, 5 = luminescence, 6 = molecular separations.. dppp = 1,3-bis(diphenylphosphanyl)propane, bpy = 2,2′-bipyridine, binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, bpz = 2,2′-bipyrazine, diop = 4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane, dppen = 1,2-bis(diphenylphosphanyl)ethene, DarF = *N,N′*-diarylformamidinate anion, d(cy)pe = 1,2-bis(dicyclohexylphosphino)ethane.

These properties give complex **17** the potential to be used as a sensitive host for large functional guest molecules which can be monitored by electro- and photochemistry.

Additional structures have been reported by other groups which incorporate ethynyl groups and transition metals into the sides of the final square to provide binding sites for other metal atoms and ligands. Tessier, Youngs, and co-workers have reported the synthesis of a butadiyne linked/Pt^{II} molecular square **18** (Cy = cyclohexyl) and a derivative that introduces a platinum metal center into each side of the square (**19**).[74] Both structures can be synthesized in good yield (80–98%), and silver binding studies have been reported for compound **18**. Introduction of 1.5 equivalents of AgOTf to a solution containing square **18** results in the bonding of a silver atom across each corner of the square in a tweezer fashion. Additional structures containing ethynyl–metal linkages and metal centers on the edges have been reported by Stang and co-workers.[26] These structures incorporate diplatinum building blocks into the linear edges. The resulting squares are very large (4.3–4.8 nm on the diagonal) and also have been shown to bind silver atoms across the corners.

The synthesis of molecular squares by the directional-bonding approach has become a widely used technique for the high-yield formation of discrete tetranuclear metallocyclophanes, some with nanometer dimensions. The incorporation of functional organic groups into the interconnecting ligands has allowed the synthesis of squares with a wide range of desirable chemical and physical properties. However, the exploitation of these properties in the development of sensors and catalysts has yet to be demonstrated and represents an important frontier for those working with these types of complexes.



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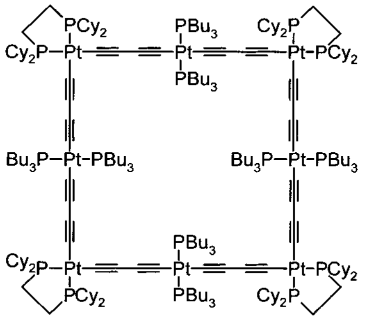

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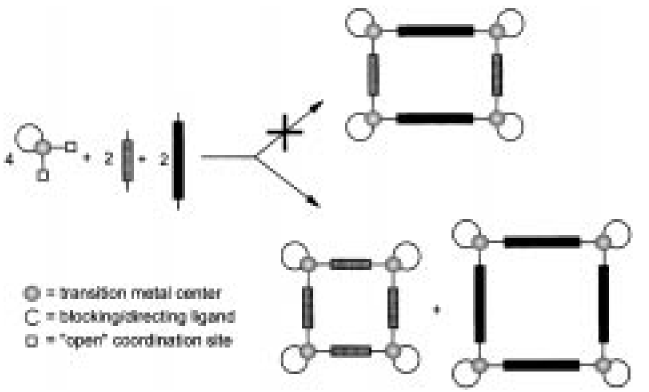
2.1.6. Molecular Rectangles

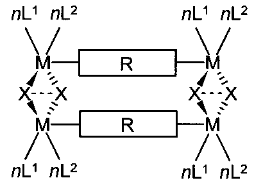
Molecular rectangles (tetranuclear metallocyclophanes constructed with two different lengths of bridging ligands) can be synthesized through a stepwise modification of the directional-bonding approach. While one of the advantages of this synthetic strategy for molecular squares is the spontaneous assembly of such structures from a mixture of ligands (edges) and metals (corners) in one step, the one-step synthesis of rectangles is not possible.

The strong enthalpic driving force, which makes possible the high-yield formation of squares over polymers and oligomers, also makes the statistical formation of rectangles from a mixture of two ligands and metal starting materials unfavorable. In fact, in studies aimed at evaluating the likelihood of the one-pot formation of molecular rectangles from a mixture of metal precursors and two rigid ligands which differ in length, only the two types of molecular squares formed rather than the molecular rectangles (Scheme 4).[13, 78]



Scheme 4. From a mixture of metal-containing precursors and two rigid ligands of different length only the two molecular squares are formed, not the molecular rectangle.[13, 78]

Hupp and co-workers have reported the preparation of a series of rhenium- and manganese-based molecular rectangles, which are synthesized in two steps. First, the shorter edge of the rectangle is assembled from a rhenium starting material and (a) bridging ligand(s), for example, sulfides, selenides, bipyrimidine (bpym), or bisbenzimidazolate (BzIm). This dimer is then treated with a longer bridging ligand to form the target rectangles **20a–h** (see Table 2).[78, 79] These rectangles can be prepared in moderate to good yields (50-80 %) and have been well characterized in solution. Additionally, the solid-state X-ray crystal structure of rectangles **20a**, **20e**, and **20h** have been reported. Structurally similar molecular rectangles have also been reported by Sullivan and co-workers (**20i–l**).[80] These structures utilize alkoxide bridging ligands to form the dimer on the shorter end of the rectangle. Complexes **20i–l** have been isolated in near-quantitative yield and are well characterized. Notably, rectangles **20i–l** show luminescence in the solid state and complexes **20g** and **20h** show luminescence both in solution and the solid state. These compounds are in contrast to the compounds initially reported by Hupp and co-workers which exhibit no luminescence in either solution or the solid state. Süss-Fink and co-workers have also reported the synthesis of a ruthenium molecular rectangle (**20m**) comprised of 4,4′-bpy and oxalate ligands with a *p*-cymene blocking ligand.[81] Again, this complex was prepared in a step-wise fashion from the corresponding methanol dimer and 4,4′-bpy.



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20: See Table 2.

Table 2. Molecular rectangles synthesized by the directional-bonding approach (see **20**).

20	M	L^1	*n*	L^2	*n*	X	R
a	Re	CO	3	–	–	$SCH_2CH_2CH_3$	4,4′-bpy
b	Re	CO	3	–	–	$SCH_2CH_2CH_3$	pz
c	Re	CO	3	–	–	SC_6H_5	4,4′-bpy
d	Re	CO	3	–	–	SeC_6H_5	4,4′-bpy
e	Re	CO	3	–	–	bpym	4,4′-bpy
f	Re	CO	3	–	–	bpym	bpe
g	Re	CO	3	–	–	BzIm	4,4′-bpy
h	Mn	CO	3	–	–	BzIm	4,4′-bpy
i	Re	CO	3	–	–	OH	4,4′-bpy
j	Re	CO	3	–	–	OCH_3	4,4′-bpy
k	Re	CO	3	–	–	OCH_2CH_3	4,4′-bpy
l	Re	CO	3	–	–	OCH_2CH_2OH	4,4′-bpy
m	Ru	*p*-Pr*i*C_6H_4Me	1	–	–	C_2O_4	4,4′-bpy
n	Re	CO	3	Br	1	pz	4,4′-bpy
o	Re	CO	3	Br	1	bpe	4,4′-bpy
p	Re	CO	3	Br	1	pz	bpe
q	Ir	Cp*	1	–	–	Cl	pz
r	Rh	Cp*	1	–	–	Cl	pz
s	Ir	Cp*	1	Cl	1	pz	$CN(C_6H_4)NC$
t	Rh	Cp*	1	Cl	1	pz	$CN(C_6H_4)NC$

Two recent reports of the synthesis of molecular rectangles have appeared by Lu and co-workers and Yamamoto and co-workers. Lu has reported the stepwise synthesis of neutral molecular rectangles that are luminescent in solution at room temperature. These complexes (**20n–p**) are constructed from rhenium metal centers and pyridyl bridging ligands.[82] Finally, Yamamoto and co-workers have assembled rectangles **20q–t** from Cp*MCl$_2$ (M = Rh or Ir) building blocks and either pyrazine and/or diisocyanide bridging units.[83] These simple two-step routes to molecular rectangles demonstrate the important control offered by the directional-bonding approach over the shape of the resulting complex.

2.1.7. Molecular Cages and Higher Order Structures

The directional-bonding approach has been extended to include the synthesis of more complex polynuclear three-dimensional structures. The simplest of these structures is the cagelike structure that results from the coordination of two tridentate bridging ligands to three transition metal centers (Figure 4A). These complexes have been reported by several groups and exhibit interesting host–guest properties.[10, 11, 84–88] Fujita and co-workers have reported the synthesis of cage molecules based on palladium(II) ions and 1,3,5-tris(4-pyridylmethyl)benzene.[84, 89] Interestingly, these trinuclear cages only form in high yields in the presence of a suitable guest molecule to template the reaction (namely, sodium *p*-methoxybenzoate). Fujita et al. have also reported the synthesis of trinuclear complexes with asymmetric tridentate ligands which assemble as two interlocked cages.[88] Additional cage structures have been reported that incorporate novel functional groups into the tridentate ligand to enhance host–guest interactions. Shinkai and co-workers have synthesized a tridentate ligand which branches off a homooxacalix[3]arene core.[85, 90] The cage formation is based on N donor ligands and palladium(II) metal centers. The resulting molecular cage showed reversible inclusion of a C$_{60}$ molecule in solution. Other research groups have formed molecular cages based on tridentate P donor ligands and transition metal centers. Lindner et al. have reported the synthesis of 1,3,5-tris(4-diphenylphosphanylmethyl)-benzene and its cage complex with platinum(II) dicloride.[86] The target complex was isolated in 38% yield, and underwent ligand substitution reactions at the transition metal center without significant decomposition. Finally, a tetranuclear cage molecule based on tetracyanocavitand and Pt^{II} and Pd^{II} metal centers has been synthesized by Jacopozzi and Dalcanale.[87] They demonstrated that the cages can be formed reversibly in quantitative yields through the addition of excess of N donor ligands which bind strongly to the metal centers.

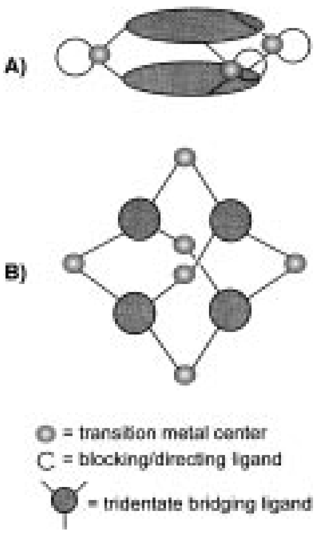


Figure 4. Molecular cages prepared by the directional-bonding approach.

The formation of structures such as that depicted in Figure 4B have been reported by several research groups.[91–94] These cage molecules are assembled in solution from a mixture of ten components: six metal centers and four ligands. The ligands are based on 1,3,5-substituted arene rings with pendant pyridyl or pyrazole groups, and the transition metal centers are platinum or palladium(II) with *cis* coordination sites open for complexation. Fujita and co-workers have demonstrated the unique properties of these nanometer-scale cages, for example, reversible pH-dependent binding of a molecular guest,[93] encapsulation of large neutral guests,[92] selective binding of *cis* over *trans* isomers of azobenzene and stilbene molecules on the basis of cavity size and packing,[94] synthesis of labile siloxanes,[95] and as reverse phase-transfer reagents for aqueous-phase catalysis.[96]

Other two- and three-dimensional shapes have been synthesized using the principles of the directional-bonding approach. They include hexagons,[97] dodecahedra,[98] cuboctahedra,[99] hexahedra,[100] rectangular boxes,[101] compounds with an adamantane-type geometry,[102] cubes,[73, 103] tubes,[104] bowls,[105] and grids.[106] The expansion of this synthetic strategy into the third dimension and the organization of complex structures through simple metal–ligand coordination bonds demonstrates a powerful ability to rationally design and synthesize complex nanoscale structures in high yield and represents an important aspect of supramolecular chemistry today.

2.2. The Symmetry-Interaction Approach

2.2.1. Preface

The symmetry-interaction approach has been developed as a transition metal templated, high-yield strategy for the rational design of high symmetry coordination clusters. In this strategy, multibranched chelating ligands are used in conjunction with sources of transition or main group metals which are free of strongly coordinating ligands. With this combination of starting materials, the formation of a given supramolecular shape is driven by the inherent symmetry of the coordination sites available on the metal center. Therefore, careful consideration must be given to the preferred coordination environment of the metal to be used and the binding mode of the chelating ligand. Additionally, the orientation of the multiple chelation sites with respect to one another within the ligand must be carefully chosen to ensure the closure of discrete clusters over formation of oligomers and polymers. The chelation effect of the ligands used in this approach provides stronger overall binding constants to the metal centers than monodentate ligands, but the metal/ligand combinations must be chosen carefully in order to maintain coordinative lability. This approach, like the directional-bonding approach, targets the thermodynamic products of the reaction which makes thermal annealing of defect structures an important feature of the synthetic strategy. Finally, the symmetry interactions with which one must contend (for example, metal geometry, ligand orientation, and ligand–ligand steric interactions) when designing a supramolecular assembly utilizing this method can be considerably more complicated than the other two approaches presented in this Review. This added level of complexity has facilitated the extensive use of computer modeling to predict whether target architectures are possible products of a given combination of metals and ligands. Comprehensive reviews on this topic have recently been reported;[12, 14] supramolecular shapes available through this approach will therefore only be highlighted briefly below.

2.2.2. Advantages and Limitations of the Symmetry-Interaction Approach

The symmetry-interaction synthetic strategy has granted researchers access to a variety of elegant shapes and architectures (for example, helicates, tetrahedra, and adamantoid structures) through the predictable coordination chemistry of multibranched chelating ligands with transition and main group metal centers. The added complexity that is inherent in this approach has, until recently, defined the synthesis of novel complexes as mostly resulting from trial and error. While Raymond et al. and Saalfrank et al., among others, have made significant strides towards developing a rational synthetic scheme, the subtle interactions driving the formation of these architectures is not fully understood.[12, 14]

The compounds formed through this approach are, by definition, supramolecular clusters, the structure of which are usually relatively compact. While some host–guest interactions have been demonstrated by these complexes, the relatively small dimensions of the interior cavities typically prohibits the encapsulation of large guest molecules.

2.2.3. Dinuclear Structures

Dinuclear structures formed using the symmetry-interaction model have been classified into three categories for the purposes of this review: macrocycles formed with chelating ligands, helical structures, and dinuclear metallocryptands (Figure 5, **A**, **B**, and **C**, respectively). Although structure **C** is not formed with chelating ligands, it is still classified by the symmetry-interaction model as a consequence of the lack of blocking ligands present on the metal starting materials. The formation of the resulting structures is therefore driven by the coordination symmetry about the metal center. Dinuclear macrocycles which contain a variety of metal centers, such as Cu[107–109] and Zn,[108, 110, 111] have been reported (Figure 5, **A**). These structures possess desirable supramolecular properties, such as host–guest interactions,[107, 110] and the ability to form more complex structures, such as catenanes[110] has been reported (Figure 5). Homodimetallic helicates are the most widely reported dinuclear structures formed by this model. Several research groups have reported the synthesis of structures analogous to **B** (Figure 5). The most common ligands incorporated into these coordination clusters are based on catecholamide and hydroxamate units. The research groups of Albrecht,[112] Stack,[113] Raymond,[114] Rice/Ward,[115] Yoshida,[116] James,[117] Bünzli,[118] and Lehn[119] have reported dinuclear helicates assembled by utilizing the principles of the symmetry-interaction approach. Dinuclear metallacryptands (**C**, Figure 5) have also been reported. These structures are assembled with ligands which contain a central binding site which allows the encapsulation of a guest (usually an alkali earth metal cation) into the center of the final structure. Saalfrank et al. have reported such a complex based on iron(III) ions.[120] This complex contains a pyridyl unit on the interior of the cage for guest binding. Similar structures which possess a dipyridyl binding site have also been reported.[121] Catalano et al. have recently synthesized a series of structural analogues assembled from gold(I), silver(I), platinum(0), or palladium(0) ions and 2,9-bis(diphenylphosphanyl)-1,10-phenanthroline.[122]

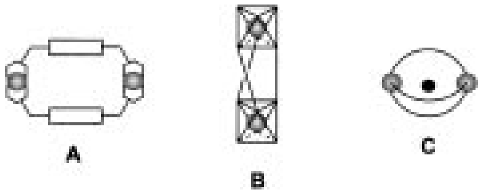


Figure 5. Dinuclear structures prepared by the symmetry-interaction approach.

2.2.4. Three-Dimensional Structures

Two types of three-dimensional structures have most commonly been prepared utilizing the symmetry-interaction synthetic strategy. The first class of coordination clusters are molecular tetrahedra (Figure 6 **A**), such as those reported by Raymond et al.[123] These structures were synthesized from catecholamide or hydroxamate derivatives and aluminum(III), iron(III), or gallium(III) metal centers. Other examples of molecular tetrahedra have been reported by Saalfrank et al.[124] and McCleverty, Ward, and co-workers.[125]

Figure 6. Tetranuclear structures prepared by the symmetry-interaction approach.

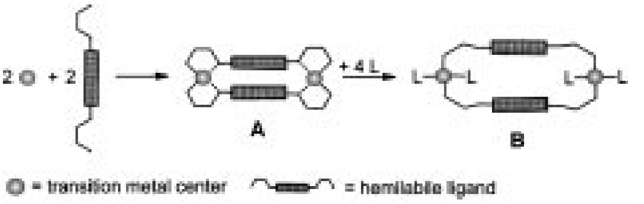
The second class of coordination clusters with adamantoid structures (Figure 6, **B**) have been reported by Saalfrank et al. A series of these structures has been prepared incorporating tetracarboxylate ligands and magnesium(II), manganese(II), cobalt(II), iron(III), or nickel(II) centers.[126] The redox properties of these complexes as well as their guest-encapsulation properties have been investigated. In addition to the three-dimensional structures highlighted here, other architectures prepared with this methodology include triangles,[127] squares,[128] cylindrical structures,[129] molecular grids,[130, 131] and circular helicates.[132]

2.3. The Weak-Link Approach

2.3.1. Preface

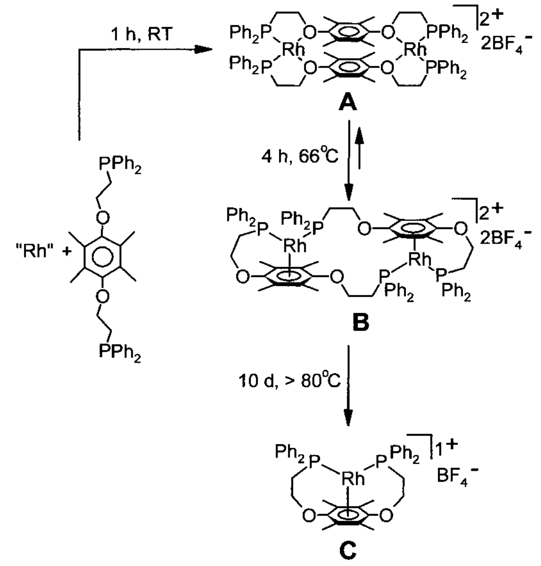
The weak-link synthetic strategy for two- and three-dimensional structures offers one the ability to prepare supramolecular architectures from flexible ligands and transition metal starting materials free of directing ligands to yield structures with coordination sites that are available for further chemistry. In this approach, hemilabile ligands[133] are used to bond to transition metal centers in a bidentate fashion in such a way that one of the metal–ligand bonds is stronger than the other, and formation of the dinuclear complex **A**, rather than mononuclear complex, is favored (Scheme 5). The formation of this intermediate is driven by the formation of favorable five- or six-member chelate rings, the chelation effect of the bidentate ligand which directs the formation of dinuclear structures, and the π–π interactions between the central bridging units (typically arenes) in the ligands. This intermediate structure is typically formed in high, if not quantitative, yield and often can be isolated and fully characterized. The target dinuclear metallocyclophane **B** (Scheme 5) is formed by introducing the condensed intermediate **A** to a ligand that preferentially binds to the metal center rather than the groups forming the weak links; this process results in the selective displacement of the weak links and, in most cases, quantitative formation of the desired product. It is important to note that this approach is conceptually different from the directional-bonding and symmetry-interaction approaches and yields structures that are not accessible by those approaches. Some of the notable differences are:

1) flexible metal-linking ligands can be used in place of rigid aromatic groups,
2) the metal centers in the condensed intermediate and, often, even in the metallocyclophane structures, have coordination sites that can be used for host–guest chemistry or the construction of more elaborate architectures, and
3) the reactions used in the weak-link approach are under kinetic rather than thermodynamic control; indeed, the 1:1 ligand:metal complex is typically the thermodynamic product, but because of large activation barriers it can be prohibited from forming through the careful choice of reaction conditions.



Scheme 5. The formation of the dinuclear complex **A** is favored by using hemilabile difunctional ligands.

Mirkin and co-workers have recently reported the slow conversion, at elevated temperature, of a dirhodium intermediate (**A**) based on a 2,3,5,6-tetramethylbenzene (durene) ligand to the monomeric piano-stool species (**C**) via an arene–rhodium structure (**B**, Scheme 6).[134] A preliminary conclusion has been made on the basis of these results that the bidentate chelating properties of the symmetrical hemilable ligands used in the weak-link approach are essential for complexing the metal precursors and directing the formation of the condensed intermediate (**A**). Once formed, **A** can convert into other more-stable dinuclear forms (for example, **B**), but there is a relatively large energetic barrier to the formation of the mononuclear thermodynamic product (**C**). This process ensures the high-yield formation of a set of dinuclear intermediates that can be converted into a single macrocyclic product.



Scheme 6. At high temperature the dinuclear intermediate **A**, a dirhodium complex with durene ligands, is converted into monomer **C** via the arene–rhodium structure **B**.

2.3.2. Advantages and Limitations of this Approach

The weak-link approach is a general synthetic strategy which grants access to sophisticated two- and three-dimensional supramolecular architectures through control over the coordination environment of transition metal centers with hemilabile ligands. Furthermore, the approach demonstrates the use of relatively subtle coordination chemistry principles to incorporate greater flexibility and impart utility to the metal centers in the final structure. The metal centers do not merely act as the corners of the structures but remain useful as dynamic building blocks for the construction of more-complex architectures and for potential applications (for example, catalysis and host–guest chemistry). A significant attribute of this approach is the ability to perform ligand substitution reactions at the metal centers of the target macrocycles while maintaining the supramolecular structure (see Section 2.3.3). This ability allows one to control the electronic and steric properties of the metal centers contained within the supramolecular architectures in a systematic fashion.

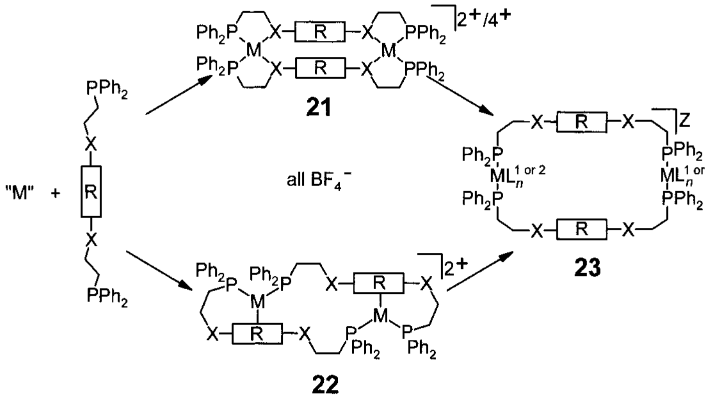
In contrast to the directional-bonding approach, the weak-link approach can be used to incorporate structurally flexible ligands into supramolecular coordination complexes. By targeting the condensed intermediate discussed above, which is relatively rigid, the entropic cost of using flexible ligands is reduced in the initial organization of the molecular components. Upon expansion of the intermediate structure into an open macrocycle, the flexible portion of the ligand system is liberated from the metal and imparts flexibility to the entire metallocyclophane structure. This feature of the approach facilitates the synthesis of flexible supramolecular complexes with dynamic structural properties.

The coordinatively labile transition metal centers in the target supramolecular structures formed by the weak-link synthetic strategy offer the ability to tailor both the electronic and steric properties of the resulting host structure through simple coordination chemistry. In the case of Rh^{I} and Pd^{II} centers, reaction of the condensed intermediate with neutral ancillary ligands will result in formation of dinuclear macrocycles with 2+ and 4+ charges, respectively. The use of anionic ligands to open the condensed intermediates can be used to produce macrocycles of neutral or anionic charge. This tailorability of complex electronic properties in the final step of synthesis is an extremely useful feature of this approach. Additionally, like the directional-bonding approach, simple modifications of the ligand systems provide control over the macrocycle shape, size, and physical properties (for example, luminescence, redox activity, or chirality).

A potential disadvantage of this approach has been eluded to earlier. As discussed above, the condensed intermediate structures are the kinetic products of the reactions, with the mononuclear 1:1 metal:ligand complexes typically being the thermodynamic products. This, in principle, will result in some thermal instability of the supramolecular structures formed by this approach. However, for the systems studied thus far, the energy barrier for dimer to monomer conversion is exceptionally high and, therefore, product selection is relatively easy to control. Indeed, the desired products exhibit long-term stability over a moderate temperature range (RT to 100 °C).

2.3.3. *Dinuclear Macrocycles*

Mirkin and co-workers have utilized this synthetic strategy to produce a series of homodimetallic macrocyclic structures.[134–139] The structures reported thus far have been prepared from hemilabile ligands derived from phosphanyl alkyl ether, thioether, and amine groups. These ligands bind to many late transition metal centers such as rhodium(I) and palladium(II) with the strong binding groups being the phosphines and the weak binding groups being the ethers, thioethers, or amines. The initial structure prepared by this approach was synthesized from phosphanyl alkyl ether, **21a** containing a durenyl group (Scheme 7 and Table 3).[135] This condensed intermediate was opened into a dinuclear 26-membered ring (**23a**) by treating it with carbon monoxide (1 atm; Scheme 7). This strategy has been expanded to include other aromatic groups such as benzene and 4,4′-biphenyl, with the latter resulting in a 34-membered ring.[134] In both of these cases the stable intermediate structure formed is a "slipped" macrocycle in which the ether–rhodium weak links are replaced by arene–rhodium weak links (**22a** and **22b**, respectively, Scheme 7). Upon addition of a stronger



21a: R = 1, 4-$C_6(CH_3)_4$; X = O; M = Rh
21b: R = 9, 10-$C_{14}H_8$; X = O; M = Rh
21c: R = 1, 4-C_6H_4; X = S, M = Rh
21d: R = 1, 4-C_6H_4; X = N(CH_3); M = Rh
21e: R = 1, 4-$C_6(CH_3)_4$; X = O; M = Pd
21f: R = 1, 4-C_6H_4; X = S, M = Pd

22a: R = 1, 4-C_6H_4; X = O, M = Rh
22b: R = 4, 4'-$(C_6H_4)_2$; X = O, M = Rh

23: See Table 3.

Scheme 7. Preparation of macrocycles with homodinuclear metal centers starting from hemilabile ligands.

Table 3. Homodimetallic macrocycles prepared by the weak-link approach (see Scheme 7).

23	R	X	M	L^1	$n(L^1)$	L^2	$n(L^2)$	Z
a	1,4-$C_6(CH_3)_4$	O	Rh	CO	3	–	–	2+
b	1,4-C_6H_4	O	Rh	CO	3	–	–	2+
c	4,4′-$(C_6H_4)_2$	O	Rh	CO	3	–	–	2+
d	9,10-$C_{14}H_8$	O	Rh	CO	3	–	–	2+
e	1,4-$C_6(CH_3)_4$	O	Rh	CO	1	CH_3CN	1	2+
f	1,4-C_6H_4	O	Rh	CO	1	CH_3CN	1	2+
g	4,4′-$(C_6H_4)_2$	O	Rh	CO	1	CH_3CN	1	2+
h	9,10-$C_{14}H_8$	O	Rh	CH_3CN	2	–	–	2+
i	9,10-$C_{14}H_8$	O	Rh	CH_3CN	1	2,6-$(CH_3)_2(C_6H_3)NC$	1	2+
j	9,10-$C_{14}H_8$	O	Rh	CH_3CN	1	$(CH_3)_3CNC$	1	2+
k	1,4-C_6H_4	S	Rh	CO	1	Cl	1	0
l	1,4-C_6H_4	O	Rh	CO	1	Cl	1	0
m	1,4-$C_6(CH_3)_4$	O	Rh	CO	1	Cl	1	0
n	1,4-C_6H_4	S	Rh	CO	2	I	1	0
o	1,4-C_6H_4	N(CH_3)	Rh	CO	1	–	–	2+
p	1,4-C_6H_4	N(CH_3)	Rh	CO	1	CH_3CN	1	2+
q	1,4-C_6H_4	O	Pd	CH_3CN	2	–	–	4+
r	1,4-$C_6(CH_3)_4$	O	Pd	CH_3CN	2	–	–	4+
s	1,4-C_6H_4	O	Pd	CN	2	–	–	0
t	1,4-$C_6(CH_3)_4$	O	Pd	CN	2	–	–	0
u	1,4-C_6H_4	S	Pd	CN	2	–	–	0

binding ligand such as carbon monoxide these rhodium–arene weak links have been selectively broken to form the analogous open structures **23b** and **23c**. Significantly, the incorporation of 4,4′-biphenyl into these structures demonstrates that the macrocycle size can be expanded by adjusting the size of the initial aromatic group in the ligand system. Ligand substitution reactions have also shown that the transition metal centers in the target macrocycle remain coordinatively labile towards incoming ligands, such as acetonitrile, as evidenced by the formation of the stable carbon monoxide/acetonitrile adducts **23e**–**g** (Scheme 7).[134, 135]

Fluorescent aromatic units have also been incorporated into macrocyclic structures with this approach. Mirkin and coworkers have reported the synthesis of a dinuclear rhodium macrocycle that has an anthracene functionality in the backbone of the macrocycle (**21b** and **23h**, Scheme 7).[136] Notably, the condensed intermediate **21b** exhibits fluorescence in solution which is significantly increased upon expansion to macrocyclic structures **23h**–**j** (Scheme 7). Also, the fluorescence signatures of these complexes are sensitive to molecules bound inside the macrocyclic cavity, thus pointing towards potential sensor applications (see Section 3.2).

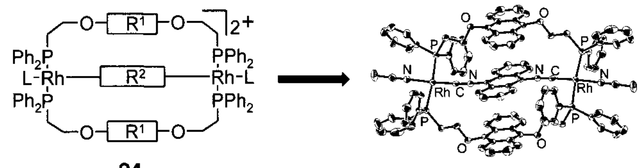
Dinuclear macrocycles containing thioether weak links also have been prepared through this approach.[137] Structure **21c** was prepared from a ligand derived from 1,4-benzenedithol. Compound **21c** is an exceptionally stable condensed intermediate as a consequence of the stronger rhodium–sulfur bonds (compared to the rhodium–oxygen bonds in **21a** and **21b**). Consequently complex **21c** does not form open macrocycles when introduced to excess acetonitrile or even carbon monoxide. However, **21c** has been opened through a novel halide-induced ring-opening reaction which forms the neutral chloride/carbon monoxide complex **23k** (Scheme 7).[137] The generality of this ring-opening reaction has been demonstrated by extending it to several analogous ether-containing ligand systems and other halides (**23l**–**n**, Scheme 7).

The incorporation of redox-active groups into this ligand system is straightforward and has been accomplished with the synthesis of a ligand based on Wurster's reagent (*N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine).[139] This ligand allows the templated synthesis of a homodimetallic macrocyclic structure which has sensitive indicators for the formation of inclusion complexes and the ability to precisely control the electronic environment of the internal cavity. The condensed structure **21d** is formed in quantitative yield, and the amine groups display the anticipated intermediate reactivity towards incoming ligands (relative to the ether and thioether systems). Specifically, reaction with CO alone forms structure **23o**, with one amine and one CO ligand about each metal center (displacement of only one amine from each rhodium center). Access to the fully "opened" macrocycle is accomplished by the addition of excess CH_3CN in the presence of CO to yield macrocycle **23p** (Scheme 7). This system holds promise for the electrochemical control of supramolecular host–guest chemistry, and its properties are currently being investigated.[139]

The weak-link synthetic strategy has also been used to prepare isostructural macrocycles with two palladium(II) centers.[138] These structures were formed in quantitative yields by combining the hemilabile ligands discussed above with a source of "naked" palladium(II) ions ($[Pd(CH_3CN)_4][BF_4]_2$). Analogous intermediates, **21e** and **21f**, were isolated and characterized and these compounds exhibit similar reactivity to the dirhodium(I) complexes, thus allowing the formation of **23q** and **23r** (Scheme 7). Finally, the closed palladium(II) complexes react with cyanide ligands to produce neutral macrocycles **23s**–**u** (Scheme 7). Thus far, the generality of the weak-link approach for the synthesis of dinuclear macrocycles of varying size, physical property, and charge has been demonstrated. The coordinative unsaturation of the metal centers in the macrocyles makes this system ideal for designing receptor sites with tailorable molecular recognition properties and, perhaps, catalysts with size- and shape-dependent reactivities and selectivities.

2.3.4. Three-Tiered Metallocyclophanes

The dinuclear metallocyclophanes discussed above have the potential to be used as building blocks to form more complex supramolecular structures. For example, the coordinatively labile metal centers incorporated into the macrocycle skeleton allow arrays to be built up through simple coordination chemistry. Judicious choice of difunctional ligands of the appropriate length to span the interior cavity of the macrocycles can lead to the formation of three-tiered metallocyclophanes. Complexes **24a**–**d**, in which aryl diisocyanides or dinitriles have been used to bind across the center of the macrocycles have been reported (Figure 7).[134–136] These structures form in quantitative yield from the corresponding macrocycles and difunctional ligands. The aromatic groups of the incoming ligands and the dirhodium macrocycles align in a parallel-planar or cofacial fashion. The ability to place chromophores and fluorophores in such a well-defined geometric arrangement is appealing for the study of the chemical and photophysical interactions of these molecules. The fluorescent anthracene-containing macrocycle **23h** (see Section 2.3.3) binds 1,4-phenylene- and 9,10-anthracene-diisocyanide to form fluorescent triple-layered metallocyclophanes (**24c** and **24d**) in quantitative yield. These compounds exhibit charge-transfer behavior between the aromatic fluorophores (Figure 7).[136] It is important to note that cyclo-



24 **24d**

24a: R^1 = 1, 4-$C_6(CH_3)_4$, R^2 = 1, 4-$(CN)_2C_6H_4$, L = CH_3CN
24b: R^1 = 1, 4-$C_6(CH_3)_4$, R^2 = 1, 4-$(NC)_2C_6H_4$, L = CO
24c: R^1 = 9, 10-$C_{14}H_8$, R^2 = 1, 4-$(CN)_2C_6H_4$, L = CH_3CN
24d: R^1 = 9, 10-$C_{14}H_8$, R^2 = 1, 4-$(CN)_2C_{14}H_8$, L = CH_3CN

Figure 7. Three-tiered metallocyclophanes prepared by the weak-link approach (left). X-ray crystal structure of complex **24d** (right). Reprinted with permission from ref. [136].

phanes containing anthracene units have been prepared through conventional stepwise organic synthesis, but these syntheses involve many steps and give extremely low overall yields (5–7 steps, 1–10% yields).[140] Additionally, organic triple-layered structures have been prepared by stepwise synthesis and their charge-transfer behavior studied, but none have incorporated three anthracene units and all suffer the same multiple-step synthetic pathways and low yields (5–8 steps, 10–40% yields).[141]

2.3.5. Molecular Cylinders

As discussed above, the transition metals in the homodimetallic structures accessed through the weak-link approach allow for further chemistry at the metal centers. For example, the triple-layered structures (**24**) were formed by reaction of difunctional ligands of the appropriate dimensions to span across the interior of the macrocycle. If a rigid difunctional ligand is used which is too large to fit in the interior of the macrocycles, then the ligand links two macrocycle building blocks to form a molecular cylinder (Figure 8). Two such structures, which were formed using 4,4′-biphenyldicarbonitrile and -diisocyanide as the linker units, have been reported.[142] The X-ray crystal structure analysis of one of these cylinders revealed an interior cavity of 1100 Å^3. This structure, which has the complexity of a small protein, is a beautiful example of the versatility of the weak-link approach. The structure was assembled in three simple synthetic steps and formed in quantitative yield. The size and complexity of these structures, combined with the tailorability of their structural parameters, which are accessible by the weak-link approach makes it ideal for designing receptors for mesoscale substrates.

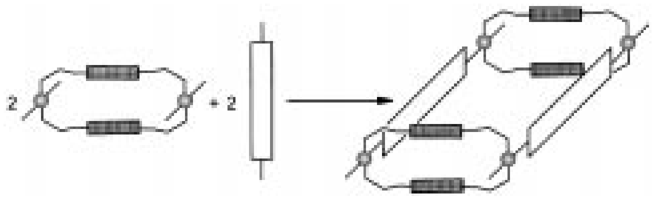


Figure 8. The joining of two macrocycles with rigid difunctional ligands to form a molecular cylinder.

3. Summary and Outlook

The directed assembly of supramolecular arrays from discrete molecular building blocks is a topic of significant interest with tremendous potential in the areas of catalysis, molecular electronics, sensor design, and optics. As demonstrated in this Review, one is now able to design and synthesize a myriad of supramolecular coordination complexes with a great deal of control over the complex shape, size, physical properties, and internal cavity dimensions on the basis of the general principles of a few high-yielding reactions in coordination chemistry, which have been exploited in the outlined strategies. A goal of this field now lies in the realization of the promise these strategies offer for designing and preparing structures with exquisitely tailorable recognition properties. While workers in this field have made major strides in the development of synthetic methods for complex structures, the realization of applications of such structures has lagged behind the progress made in reaction development. The recent advances in these areas towards some of the goals outlined above will be briefly discussed.

3.1. Supramolecular Catalysis

The area of supramolecular chemistry in general has potential to affect the field of catalysis, especially with regard to selective transformations of substrates in complex mixtures. The design and construction of large molecules with well-defined cavities opens the possibilities of host–guest and inclusion chemistry and, therefore, the ultimate goal of selective substrate activation and catalysis. While the synthesis of supramolecular structures, constructed by both covalent and coordination chemistry, has flourished over the past decade, the report of catalytic transformations performed by these systems has lagged behind such developments.[143] There are some inherent limitations in supramolecular coordination chemistry which are to blame for this lack of progress. Namely, the majority of the complexes reported that have been assembled utilizing the principles of coordination chemistry have only taken advantage of the transition metal centers as building blocks. Therefore, such complexes often have coordinatively inert, saturated metal centers, which precludes their involvement in catalytic transformations without concomitant destruction of the supramolecular complex.

There are several examples in the recent literature where the internal cavity of covalently linked supramolecular structures has been exploited to arrange reactants and stabilize reactive intermediates involved in organic transformations.[144] Notably, an example of a supramolecular coordination complex being used to facilitate a metal-mediated catalytic transformation was recently reported by Fujita and co-workers.[96] In this report a cage structure was used as a reverse phase-transfer catalyst for the Wacker oxidation of olefins in aqueous media by free $[Pd(en)(NO_3)_2]$. While this work represents a significant advance, the long-standing goal of utilizing transition metal centers incorporated in the backbone of supramolecular coordination complexes as active catalytic species has not been realized.

3.2. Supramolecular Complexes as Sensors and Sieves

As described above, a wide range of chromophores, fluorophores, and redox-active functionalities have been successfully incorporated into supramolecular frameworks. When their physical properties are retained, these groups can act as sensitive indicators of guest binding and weak host–guest interactions within the supramolecular cavities. Combined with the rich host–guest chemistry demonstrated by many of these systems they are well-suited for sensing applications.

Initial work reported by Fujita and co-workers on shifts in the ^{1}H NMR spectra showed that electron-rich aromatic molecules have an affinity for the interior of di- and tetranuclear macrocyclic structures.[17, 52] These first demonstrations, while not ideal for the design of sensing systems, led to more recent work in which guest binding is detected through luminescence[13, 136] and/or electrochemistry.[145, 146]

Both metal- and ligand-based luminescence have been exploited for this application. For example, host–guest interactions can be followed by changes in the emission profiles of molecular squares with rhenium corner fragments by monitoring shifts in the metal-to-ligand charge transfer (MLCT) bands.[13] A series of dinuclear macrocycles have also been reported which can detect anion binding through the emission from a Ru-bpy group.[145] If dipyridylporphyrin ligands are used as the walls of tetrarhenium squares then the photophysics of the resulting squares are dominated by the porphyrin chromophore and it can be used to report host–guest binding events.[13] Ligand-based luminescence has also been used to detect guest inclusion which involves direct coordination of the guest molecule to the metal centers.[136] While these systems provide proof-of-concept towards the design of sensors with supramolecular coordination compounds, practical sensor arrays based on this chemistry have not yet been demonstrated.

Beer and co-workers have prepared a series of homo- and heterodimetallic macrocycles which take advantage of both luminescence and electrochemical properties to detect the binding of anions inside the cavity.[145, 146] The electrochemical response, as monitored by both cyclic and square-wave voltammetry, shows cathodic perturbations of the reporting redox-active groups upon binding of anionic guests. The shifts ranged from 10–125 mV depending on the host–guest combination.[145]

The host–guest properties of supramolecular coordination compounds in the solid state have also been exploited in the design of molecular sieves and sensors. Hupp and co-workers have reported the synthesis of a series of rhenium-based molecular squares with cavity dimensions that depend on the bridging ligand employed (see Section 2.1.5). These squares can be cast into uniform mesoporous thin films which are stable in aqueous media.[62, 71] X-ray crystal structure data show that, in the solid state, the squares stack on top of one another to generate pores which have the dimensions of the original square. By adjusting the size of the squares used, Hupp and co-workers have demonstrated the size-selective sieving of a mixture of redox-active molecules by electrochemical detection. Additionally, Hupp and co-workers have recently reported the use of these mesoporous thin films of molecular squares as selective sensors for volatile organic compounds in the gas phase.[72] A quartz-crystal microbalance was utilized to detect the binding of analytes inside the molecular squares.

3.3. Towards Molecular Electronics

Molecular electronics, the miniaturization of electronic circuits to the molecular level, has been an ultimate goal of supramolecular chemistry since its inception.[4, 147] This area of application represents the most challenging of those discussed here. While the synthesis of supramolecular structures with variable physical properties has developed greatly, the construction of molecular circuits requires several key technological advances to be realized:

1) the synthesis of compounds and complexes which display changes in physical properties that can be precisely controlled through external stimuli,
2) the development of techniques to deposit these molecules, or supermolecules, with exact control over their position and orientation, and
3) the ability to address individual molecules, or even atoms, selectively.

The largest advances in this area have been towards the first goal, although recent advances in nanolithography for molecular systems look quite promising.[148] The work of Stoddart and co-workers in this field has produced numerous examples of supramolecular systems prepared through covalent organic chemistry which display specific molecular motion which can be controlled by photochemical and electrochemical changes.[149] Additionally, Lindsey, Bocian, and co-workers have reported the synthesis of porphyrin arrays that act as molecular optoelectronic gates.[150] In this area, supramolecular coordination chemistry has produced few examples of complexes which demonstrate the required properties. A notable exception was recently reported by Lehn, Gütlich, and co-workers. The synthesis of a $\mathrm{Fe}^{\mathrm{II}}_4$ [2 × 2] supramolecular grid which exhibits a spin-crossover that is triggered by temperature, pressure, or light, represents an important advance.[131] This grid complex, synthesized by the principles of the symmetry-interaction approach, is constructed by the combination of 4,6-bis(2′,2″-bipyrid-6′-yl)-2-phenylpyrimidine and $\mathrm{Fe(ClO_4)_2 \cdot 6\,H_2O}$ in acetonitrile at room temperature. The four iron atoms in the resulting molecular grid can be present in either a high-spin (HS) or low-spin (LS) state. The spin state of the iron atoms can be switched by several external perturbations including light, pressure, and temperature. The availability of three distinct magnetic levels (3HS/1LS, 2HS/2LS, and 1HS/3LS) makes this unique system a "multiply switchable multilevel device."[131] The application of supramolecular coordination complexes towards the goal of molecular electronics and information storage has great potential and will continue to be the focus of intense investigation.

3.4. Conclusions

The next decade will see rapid advances in the development and utilization of supramolecular coordination complexes as designer catalysts, small and intermediate-sized molecular receptors in sensor devices, molecular transport agents, new materials for molecular electronics, novel light-harvesting structures for solar energy conversion, and perhaps even molecular machines.[151] The driving force behind the intense interest in the metal-directed synthesis of supramolecular compounds lies in the ease with which many of these structures can be prepared. Indeed, the basic chemical principles of using metals with predetermined coordination numbers and angles as building blocks and functional units is generally appealing when compared to the tedious, multistep synthetic organic approaches. However, the relatively weak heteroatom bonds (compared to the strong covalent bonds of organic systems) are thermally labile and require additional considerations in order to assure the formation of stable products in high yield. These ideas have been refined into several distinct synthetic approaches. The directional-bonding, symmetry-interaction, and weak-link approaches now provide rational synthetic routes to supramolecular coordination compounds with tailorable physical dimensions, functionalities, substrate-binding capabilities, and chemical properties.

4. Addendum

Since the submission of this manuscript significant progress has been made in this rapidly expanding field. Two review articles of supramolecular coordination chemistry, its progress, and future directions have been recently published by Ward[152] and Andrews and Raston.[153] Other relevant work[154–176] is listed in the Literature Section with keywords or referenced to the relevant section of this review.

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