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Jennifer J. Turner[a]; Margaret M. Harding[a]
[a] School of Chemistry, The University of Sydney, Australia

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Synthesis and Properties of Chiral Molecular Clefts Related to Tröger's Base

JENNIFER J. TURNER and MARGARET M. HARDING*

School of Chemistry, The University of Sydney, NSW 2006, Australia

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The chiral cavities present in 2,3:6,7-dibenzo-9-oxabicyclononona-2,6-diene,dibenzobicyclo[*b,f*][3.3.1]nona-5a,6a-diene-6,12-dione, bicyclo[3.3.1]nonane and dibenzobicyclo[*b,f*][1,5]diazocines are reminiscent of Tröger's base, which has been widely used as a molecular cleft in supramolecular chemistry. The synthetic methodology to provide key derivatives for elaboration into new supramolecular structures, efficient resolution methods, the introduction of additional recognition groups and applications in supramolecular chemistry of these structurally related molecular clefts are reviewed.

Keywords: Molecular cleft; Tröger's base; Kagan's ether; Host–guest; Molecular recognition; Tweezer

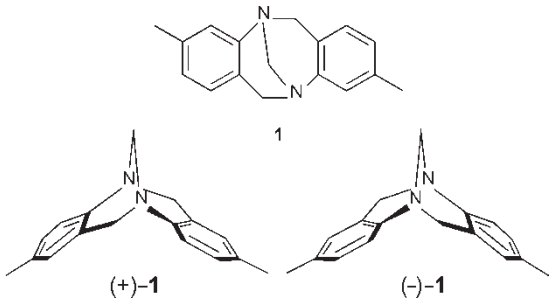

FIGURE 1 The structure of Tröger's base.

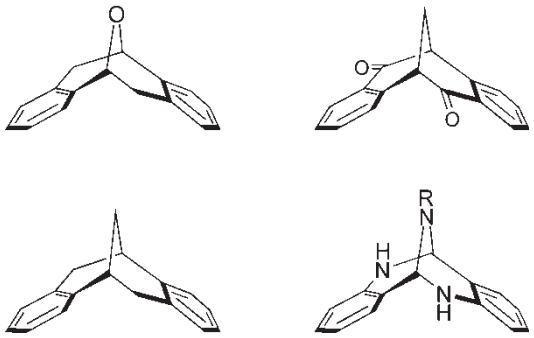

FIGURE 2 Chiral molecular clefts structurally related to Tröger's base. A single enantiomer is shown.

INTRODUCTION

The ability to orient recognition sites in defined and predictable geometries by the use of molecular clefts is highly desirable in the design of supramolecular systems [1,2]. The general term cleft refers to molecules that orient a set of functional groups into a V- or U-shaped cavity [3]. Precise positioning of recognition features on these clefts allows highly specific binding environments to be engineered, and reduced flexibility helps to minimize the entropic penalty associated with binding events [1,2].

Tröger's base **1** [4] (Fig. 1) is a small, chiral molecule [5–7] that has been used widely as a cleft in supramolecular chemistry. The chemistry and applications of **1** are summarized in an excellent review [8] and in the accompanying article in this journal [9]. C_2-symmetrical derivatives of **1** have been designed to recognize heterocycles, amino acid esters and small dicarboxylic acids, using acid, porphyrin and hydrogen-bonding recognition features, respectively. Structural modifications have resulted in clefts that bind DNA, biotin, urea and adenine and macrocyclic hosts that incorporate the cleft have also been designed. In most cases, the inherent chirality in the cleft has not been exploited in molecular recognition studies, although selective binding of guest enantiomers is possible. Despite the spectacular success of Tröger's base [8], limitations to applications of this framework in supramolecular chemistry include access to optically

*Corresponding author. Fax: +61 2 93516650. E-mail: harding@chem.usyd.edu.au

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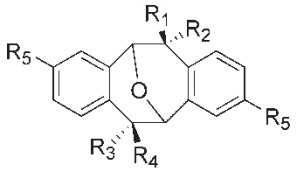
pure ligands and synthetic considerations that restrict the substituents that can be incorporated in cleft derivatives.

A number of molecular clefts that are structurally related to Tröger's base but differ in the nature of the atoms in the bridging ring and at the bridgehead position have been reported (Fig. 2). This review summarizes the chemistry and applications of these clefts and compares their properties to Tröger's base with a focus on current and potential applications of these alternate clefts in supramolecular chemistry. Molecular clefts have also attracted interest in medicine as the curvature offers a synthetically accessible scaffold that mimics the shape of steroids [10]. Full coverage of this area is beyond the scope of this review but key compounds of interest in supramolecular chemistry are mentioned.

KAGAN'S ETHER CLEFTS

The synthesis of 2,3:6,7-dibenzo-9-oxabicyclonona-2,6-diene **2** (Kagan's ether, Fig. 3) from the treatment of phenylacetaldehyde in fluorosulfuric acid was first reported by Kagan *et al.* in 1977 [11]. The structure of the cleft was confirmed by X-ray crystallography and showed an angle of 93° between the two aryl rings [12]. The proposed mechanism for formation of **2** involved a double *ortho*-aromatic substitution reaction. The use of a very strong acid, fluorosulfuric acid, was essential for the reaction as the use of other mineral acids resulted in the formation of 2-phenylnaphthalene via an aldol condensation step followed by cyclization and dehydration [13,14].

Similar treatment of ethyl 2-formyl-2-phenyl-propionate with fluorosulfuric acid afforded substituted diastereomeric derivatives of Kagan's ether **3** and **4** (60:40, **3**:**4**) in which the ethyl ester and methyl group are substituted at the carbocyclic ring positions [15]. The absolute stereochemistries of these substituents was determined by single X-ray diffraction [15]. A detailed study on a range of phenylacetaldehydes established that the substituted derivatives **5**–**10** can be readily prepared [16]. However, under the same conditions used to generate derivatives **5**–**10**, phenylacetone underwent aromatic electrophilic substitution by fluorosulfuric acid. Independent studies showed that the cyclization to produce **5**–**10** can also be effected trimethyl silyl iodide in place of fluorosulfuric acid [17,18].



	R_1	R_2	R_3	R_4	R_5
2	H	H	H	H	H
3	CO_2Et	Me	Me	CO_2Et	H
4	Me	CO_2Et	Me	CO_2Et	H
5	C_6H_5	H	C_6H_5	H	H
6	Br	H	Br	H	H
7	Me	H	Me	H	H
8	H	Me	H	Me	H
9	H	Me	Me	H	H
10	H	H	H	H	Me

FIGURE 3 The structure of Kagan's ether **2** and derivatives functionalized at bridge positions.

In contrast to the studies of Kagan and coworkers [11,12,15,16], who focused on understanding the mechanism of carbocation rearrangements, Harmata and co-workers, in a series of publications, highlighted the potential for Kagan's ether **2** as a molecular cleft in supramolecular chemistry [19–26]. Initial studies [19] focused on the synthesis of unsymmetrical Kagan's ether derivatives incorporating electron-rich aryl groups that provided more control over the incorporation of substituents on the aryl rings than the published routes to symmetric derivatives.

The novel dimeric derivative **11**, in which the two oxy bridges form a molecular tweezer, has attractive features for molecular recognition as the rigidity afforded by the oxy bridges orients the aryl rings approximately 7 Å apart, the ideal distance for inclusion of aromatics (Fig. 4) [19]. The cleft **11** was prepared in four steps from *o*-2,5-dibromo-*p*-xylene and was characterized by X-ray crystallography [20]. Cocrystallization of a molecule of ethyl acetate occurred in the cavity formed by two molecules of the cleft **11** to afford a stable clathrate structure; the ethyl acetate:**11** ratio remained constant even after 12 h at 0.1 Torr. While crystals of **11** were isolated and studied by X-ray diffraction, the diastereomeric cleft **12** was also formed in the reaction, and was independently characterized by X-ray crystallography [22].

Extension of this basic concept to incorporate dibenzofurans allowed the preparation of rigid clefts in which the aromatic arms are separated by either 7 Å **13** [23] or 10.4 Å **14** (Fig. 4) [23]. In contrast to **11**, which showed no evidence for formation of 1:1 complexes with a range of guests, the deeper cleft present in the bisbenzofuran tweezer **13** resulted in cocrystallization of **13** with trinitrobenzene (**13**:TNB, 1:1, Fig. 4b) with the guest molecule stacked between the aromatic arms of the tweezer [21].

The larger cleft **14**, which contained a flexible biaryl arm, was designed as a mimic of the naturally occurring depsipeptide echinomycin, which acts as a DNA-bisintercalator [23]. Although both *meso*- and *d*,*l*-forms of the biaryl cleft **14** are possible, only the *d*,*l*-isomer was formed and the enantiomers were resolved by chiral HPLC. The structure of **14** was confirmed by X-ray analysis of crystals isolated by slow evaporation of a solution of **14** containing TNB

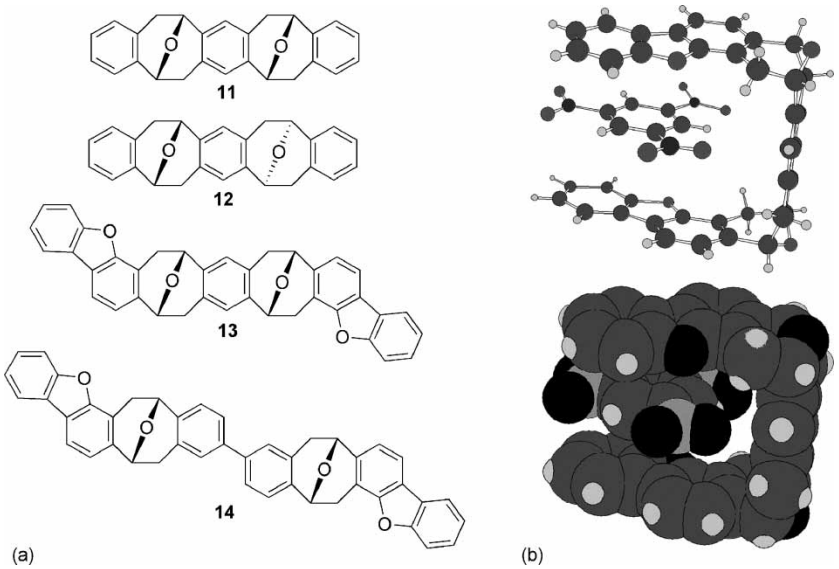


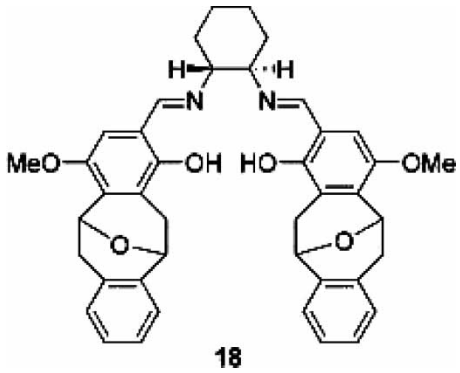
FIGURE 4 (a) Molecular tweezers derived from Kagan's ether via functionalization of the aryl rings. (b) Three-dimensional representation of the 1:1 dinitrobenzene:**13** complex generated from X-ray coordinates [20].

and nitrobenzene. As predicted, the two aromatic chromophores were separated by 10.4 Å and thus able to accommodate binding of two aromatic groups in the cleft, with the biphenyl dihedral angle of 31.4° as expected for biaryl systems.

While the enantiomers of both the Kagan's ether **2** and the bisbenzofuran derivative **13** can be resolved by chiral HPLC, determination of the absolute configuration of the enantiomers is not straightforward. Fleischhauer *et al.* calculated the expected CD spectra for the *RRRR* enantiomer of **13** (shown in the structure presented in Fig. 4) and compared this to the experimentally observed spectrum [27]. Good agreement was found between the calculated spectra computed using MNDO, AMI, PM3 and *ab initio* calculations at the HF/3-21G level using Gaussian 94, and, on this basis, the *RRRR* enantiomer was assigned as the less polar enantiomer to elute on a Pirkle HPLC column.

To date, there are limited examples of the direct functionalization of the aromatic rings in Kagan's ether to provide entry into derivatives for molecular recognition studies. As in the case of Tröger's base, this has in part been related to the lack of a general method to incorporate electron-withdrawing halogens into the rings, which would allow access to diverse metal-catalyzed cross-coupling reactions (although it should be noted that this limitation has recently been addressed in the case of **1** [28]). In the case of Kagan's ether, the preparation of optically pure bistriflates **16** via the bisphenols **15** [26] (Fig. 5) provide alternate derivatives that may be used to introduce further functionality by metal-catalyzed cross-coupling reactions. The bispyridyl ligand **17** was prepared via this route and assembly of the molecular square shown in Fig. 5 in the presence of palladium(II) was proposed on the basis of NMR and mass spectroscopic data [25].

Recently, a new synthetic route to the chiral salicylaldehyde derivative of Kagan's ether **18** has been reported [29]. This and related ligands required the preparation of differentially substituted Kagan's ether derivatives (not shown). While the ligands were designed as new synthetic catalysts, the chirality present in the two clefts in **13** and also the bridging imine ligands offer significant potential for further development into molecular receptors that may have interesting recognition properties.



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CARBOCYCLIC DIONE CLEFTS AND DERIVATIVES

The synthesis of dibenzobicyclo[*b,f*][3.3.1]nona-5a,6a-diene-6,12-dione **19** (Fig. 6) was reported in 1975 as part of a study aimed at establishing the relationship between structure and chiroptical properties of various triptycene derivatives and

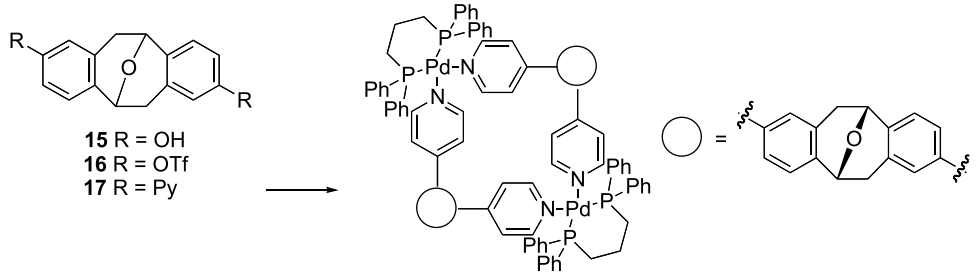


FIGURE 5 Proposed assembly of a metallomacrocycle from optically pure pyridyl-substituted (+)-ligand **17** [25].

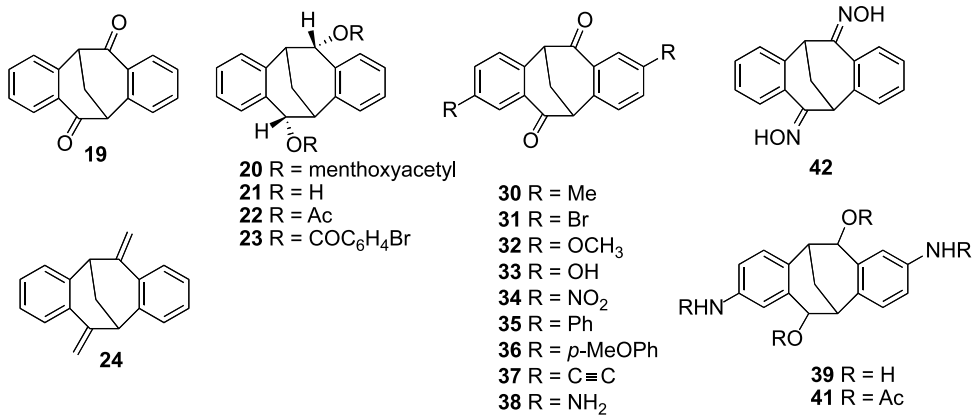


FIGURE 6 Key derivatives of carbocyclic dione **19**.

related compounds [30] and followed initial reports by Stetter and Reischl [31]. Resolution of the enantiomers was achieved by classic crystallization and separation of diastereomeric menthol esters **20** [30]. Stereoselective reduction of the ketones by hydride attack at the less hindered face of the cleft afforded the corresponding diols **21**, which were further functionalized as esters (**22** and **23**) for characterization. The absolute stereochemistry of the clefts was proven by correlation with optically pure starting materials with known absolute configuration. The dione **19** can also be converted to the bisalkene **24** by a Wittig reaction. This derivative can be resolved using enantioselective gas chromatography [32], but there are no reports of further reaction of the alkenes to produce new clefts.

A range of dipodands and crown ethers of the dione **19** have be prepared [33–35] and their effectiveness as enantioselective transporters of chiral molecules through bulk liquid membranes assessed. Representative examples are given by structures **25**–**29** (Fig. 7). Chloroform solutions of the ligand to be tested were separated from an inner aqueous phase (0.1 M HCl) and an outer phase (0.08 M HCl), which contained $LiPF_6$ and the racemic guest, with the transport monitored by ultraviolet spectroscopy, and the enantiomeric excess of the guest molecule transported was monitored by circular dichroism. All of the dipodands showed enantiomeric selectivity towards chiral primary ammonium salts, with the R substituent strongly influencing the degree of selectivity. Optimal transport properties were exhibited by the dipodand **27**, which produced 84% optically pure amine from transport experiments with either racemic 1,2-diphenylethylamine hydrochloride or racemic phenylglycinate hydrochloride.

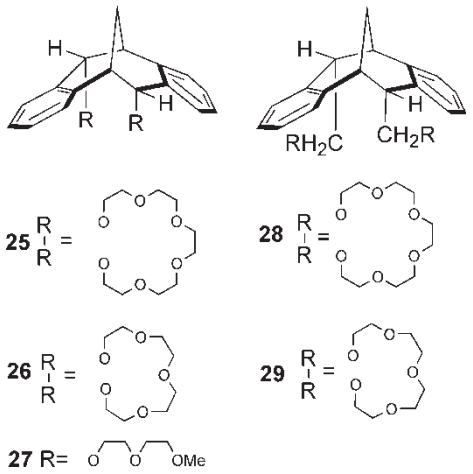


FIGURE 7 Selected podand and crown ether derivatives of the carbocyclic dione **19** that have been studied as transporters of chiral amines.

Our group has prepared a range of functionalized derivatives (compounds **30**–**42**) of dione **19** that have significant potential as building blocks in supramolecular chemistry (Fig. 6) [36–38]. Using similar methodology to Tatemitsu *et al.* [30], the racemic 2,8-dimethyl **30** and 2,8-dibromo **31** derivatives were synthesized by a three-step sequence from the corresponding *p*-benzyl nitrile, with the bridgehead formed in the final step by an intramolecular Friedel–Crafts acylation reaction using concentrated sulfuric acid [36,37]. The mechanism of the reaction tolerates *ortho*-, *para*-, mildly activating aromatic substituents and hence the direct preparation of phenol or nitro clefts using this methodology was not possible. However, the use of polyphosphoric acid in the final cyclization step has allowed the preparation of the methyl ether **32** [10] and related clefts [39], which upon demethylation afforded the bisphenol **33** [39]. Incorporation of electron-withdrawing nitro groups, valuable precursors for the preparation of amides, was possible by direct nitration of **19**, which gave the 2,8-dinitrodione **34** in good yield [36]. The prediction of directive effects in **19** and its derivatives is not straightforward, and similar nitration of the dimethyl dione **30** also occurred to give a single regioisomer.

Although the functionalized derivatives **30**–**38** could be resolved by conversion to diastereomeric derivatives using similar procedures to those reported by Tatemitsu *et al.* [30], this resolution method is time-consuming and not ideal for the preparation of large quantities of material. We have reported an optimal procedure to resolve the enantiomers of **30** and **31** using chiral HPLC [36,37]. The absolute configuration of the enantiomers was determined by comparison of the CD spectra with spectra reported by Tatemitsu *et al.* [30]. However, although chiral HPLC was effective in resolving the enantiomers of **30** and **31**, no resolution of the enantiomers of the derivatives **32** or **33** was observed under the same conditions using a range of solvent systems [40]. An alternate route to optically pure bisphenols, (+)-**33** and (−)-**33** [40], through the resolved bromoclefts **31** involved conversion to the corresponding pinacol boronate esters and hydrolysis under standard Miyaura conditions [41]. In addition to allowing the preparation of optically pure bisphenols **33**, this methodology provides a significantly improved route to the bisphenols compared with the alternate route involving polyphosphoric acid cyclization to form the bismethoxy cleft **32** followed by demethylation to produce **33** [10,39]. A number of isomeric bisphenols have also been reported [10].

Compared with Kagan's ether and Tröger's base, the ketones in the bicyclononane core of **19** provide chemical handles for the introduction of a range of molecular recognition groups for applications in supramolecular chemistry [36–38]. Incorporation of hydrogen-bonding features oriented towards the interior of the cleft is readily effected by reduction and condensation chemistries on ketone groups, giving rise to the corresponding diol **21** and the dioxime **42**. In terms of the aryl group functionality, the dibromo **31** and dinitro **34** derivatives are key building blocks for supramolecular chemistry as these two derivatives, both available in optically pure form, allow direct access to a range of functionalized molecular clefts. Thus, palladium-catalyzed coupling of the dibromo derivative afforded the disubstituted phenyl **35**, anisole **36** and acetylene **37** derivatives, and reduction of the dinitro derivative **34** using different reaction conditions gives the amino-dione **38** or amide-hydroxyl derivative **39**; subsequent acetylation of **39** furnishes amino-diol **41** [36–38]. X-ray crystal structures of a number of derivatives such as the dimethyl **30**, dibromo **31**, di(*p*-methoxyphenyl) **36** and dinitro **34** show cleft angles between the planes between the aromatic rings of 84–104°, thus indicating that the cleft dimensions may be modulated by the aromatic substituents [36].

We recently reported the synthesis of the racemic and optically pure ligand **40**, in which two 6,6′-disubstituted bipyridines are connected by methyleneoxy linkers to the molecular cleft **19** (Fig. 8) [36–38]. The addition of zinc(II) to the racemic molecular cleft (±)-**40** results in the formation of [2 + 2] metallomacrocycles in which the (+) and (−) ligands undergo self-recognition to form a pair of enantiomeric metallomacrocycles (only two of the four metallomacrocycles formed are shown in Fig. 8). This remarkable self-assembly and slow equilibration on the NMR timescale is a direct result of the incorporation of the cleft in the ligand design, which orients the metal-binding groups (including the oxygen in the linker) in restricted locations. The assembly involving the racemic ligand is one of the few examples where enantiomeric ligand–ligand self-recognition has been achieved in the assembly of metallomacrocycles, and provides the opportunity to further tailor the ligand design to generate new chiral metallomacrocycles.

BICYCLO[3.3.1]NONANE CLEFTS

Several derivatives of bicyclo[3.3.1]nonane have been reported. These clefts contain a fully saturated bridge system containing only carbon atoms. Thus, bisindole **43** [42] and 4-oxo-5-azaindole **44** [43] clefts have been reported. An attractive feature of these clefts is the relatively short synthesis and access to optically pure forms by using optically pure bicyclo[3.3.1]nonane-2,6-dione. The corresponding hydrocarbon was

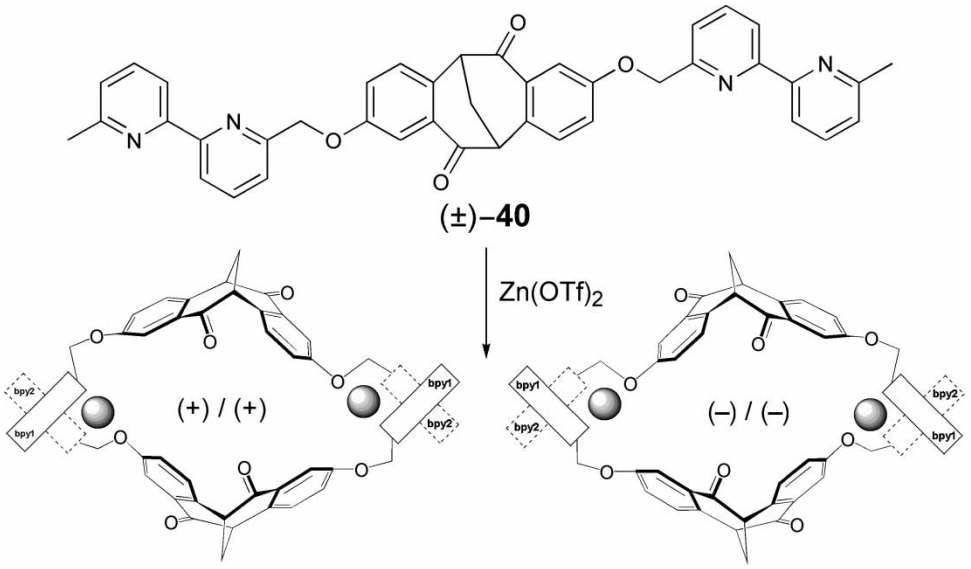


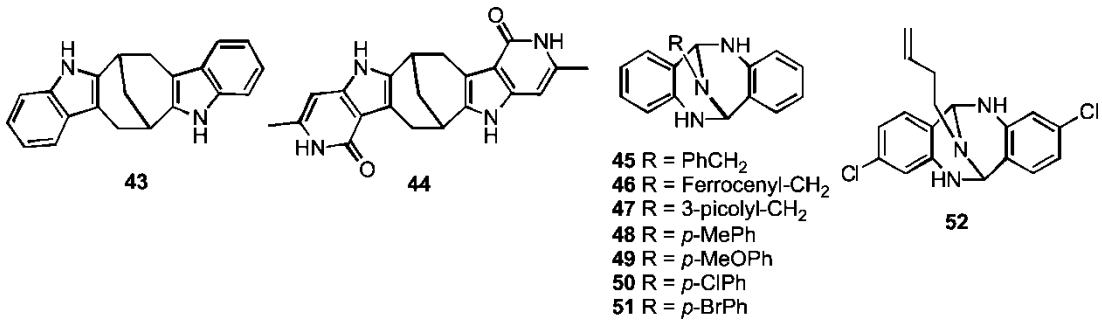
FIGURE 8 Assembly of enantiomeric helical complexes formed from either two (−)-**40** or two (+)-**40** ligands. Slow exchange of ether oxygen coordination to zinc(II) occurs on the NMR timescale [40].

formed in acid-catalyzed cyclodehydration studies with benzyltetraols [44].

The cleft shape of the bicyclo[3.3.1]nonane core has been proposed as a structural motif that mimics the curvature of the estradiol steroidal framework [10]. Several structural analogues were prepared (not shown) and relative binding affinities for the estrogen receptors α and β determined [10].

of *o*-tosylaminobenzaldehyde with nitrogen bases and aminobenzenesulfonamides [47,48].

The bisarylchloride derivative **52** and several related derivatives were prepared as part of studies directed towards the synthesis of the martinellines class of natural products [49,50]. These derivatives allow access to a range of derivatives through palladium cross-coupling reactions using recently



TRIAZINE CLEFTS

The triazine clefts differ from previous examples of clefts as the bridgehead nitrogen allows functionalization on the surface of the cleft, as well as through alkylation of the two ring nitrogens. N-substituted derivatives, illustrated by compounds **45**–**51**, were readily prepared by treatment of the relevant amine with *o*-(triphenylphosphoranylideneamino)benzaldehyde [45,46]. Crystal structures were obtained of two derivatives **45** and **46**, but attempts to resolve the enantiomers on different supports failed, and rapid racemization was proposed to explain this result. A number of tri-N-substituted derivatives have also been reported as products from reactions

developed catalysts [51] that are effective with aryl chlorides and do not require more active leaving groups.

SUMMARY

The chirality, cleft dimensions and chemistry of both the aryl rings and cleft ring atoms of the chiral molecular clefts shown in Fig. 2 offer unique opportunities for elaboration into new supramolecular structures. Compared with Tröger's base, however, there are limited applications of these clefts in supramolecular chemistry to date. The development of high yielding methods for functionalization and

resolution of enantiomers of the carbocyclic dione **19**, coupled with the additional opportunity to introduce recognition groups through the ketones are particularly attractive features of this system compared with Tröger's base. The incorporation of molecular clefts into the design of new heterocyclic ligands for metallosupramolecular chemistry offers the opportunity to produce novel chiral ligands that may be used to direct stereoselective metal self-assembly processes. In addition, the synthetic methodology now exists to allow the preparation of water-soluble clefts and ligands for studies in self-assembly.

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