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Phosphorus-Based Functional Groups as Hydrogen Bonding Templates for Rotaxane Formation

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Supporting Information

ABSTRACT: We report on the use of the hydrogen bond acceptor properties of some phosphorus-containing functional groups for the assembly of a series of [2]rotaxanes. Phosphinamides, and the homologous thio− and selenophosphinamides, act as hydrogen bond acceptors that, in conjunction with an appropriately positioned amide group on the thread, direct the assembly of amide-based macrocycles around the axle to form rotaxanes in up to 60% yields. Employing solely phosphorus-based functional groups as the hydrogen bond accepting groups on the thread, a *bis*(phosphinamide) template and a phosphine oxide−phosphinamide template afforded the corresponding rotaxanes in 18 and 15% yields, respectively. X-ray crystallography of the rotaxanes shows the presence of up to four intercomponent hydrogen bonds between the amide groups of the macrocycle and various hydrogen bond accepting groups on the thread, including rare examples of amide-to-phosphinamide, -thiophosphinamide, and -selenophosphinamide groups. With a phosphine oxide−phosphinamide thread, the solid-state structure of the rotaxane is remarkable, featuring no direct intercomponent hydrogen bonds but rather a hydrogen bond network involving water molecules that bridge the H-bonding groups of the macrocycle and thread through bifurcated hydrogen bonds. The incorporation of phosphorus-based functional groups into rotaxanes may prove useful for the development of molecular shuttles in which the macrocycle can be used to hinder or expose binding ligating sites for metal-based catalysts.

INTRODUCTION

Hydrogen bonding has previously been used[1−12] to assemble benzylic amide macrocycles around various amide,[1,2] ester,[1h,3] squaraine,[4] phenolate,[5] urea,[6] pyridone,[7] azodicarboxamide,[8] nitrone,[9] sulfoxide[10] and ion-pair[11] templates to generate rotaxanes and catenanes.[12] Although threading protocols using preformed macrocycles have been successful in some cases,[1j,6,7] the poor solubility of most benzylic amide macrocycles in the nonpolar solvents needed to promote intercomponent hydrogen bonding has meant that the template assembly of building blocks about the thread to form the macrocycle is most often used to construct such rotaxanes.[13] These five-component 'clipping' reactions involve multipoint hydrogen bonding between the open-chain precursor **1** (which in the absence of a suitable template preferentially adopts a linear *syn*−*anti* conformation) and the thread **2** promotes a conformational change that brings the reactive end groups close together, leading to rapid cyclization of **1** about the axle (I, Scheme 1).[1c,d,h] The majority of neutral hydrogen bond accepting groups employed in such threads to date have been amides, squaraine units (which have significant oxocarbon anion character), and esters.[1−4] The hydrogen bond acceptors in the thread have recently been extended to noncarbonyl-based functional groups with significant hydrogen bond basicity such as N^+-O^- and S^+-O^-.[9,10] Accordingly, we decided to determine the effectiveness of employing various P═O, P═S, and P═Se functional groups as a hydrogen bonding template for rotaxane formation (II, Scheme 1). The hydrogen bond basicity of P═S and P═Se functional groups is not well established, and introducing phosphorus-based functional groups into a rotaxane architecture[14] could be useful for developing molecular shuttles that can expose or conceal metal binding sites by changing the position of the rotaxane ring on the thread.

Recently, templates for rotaxane formation based on sulfoxides[10] and nitrone[9] functional groups have been reported. The related phosphorus analogues have proven to be valuable ligands for metal coordination[15] and have found application in both organocatalysis[16] and transition metal catalysis[17] due to their Lewis basicity and hydrogen bonding[18] ability. Accordingly, we investigated the efficacy of some phosphinic, thiophosphinic, and selenophosphinic amides (P═X)NHR; X = O, S, Se)[19] and phosphine oxides as hydrogen bonding templates in rotaxane formation.

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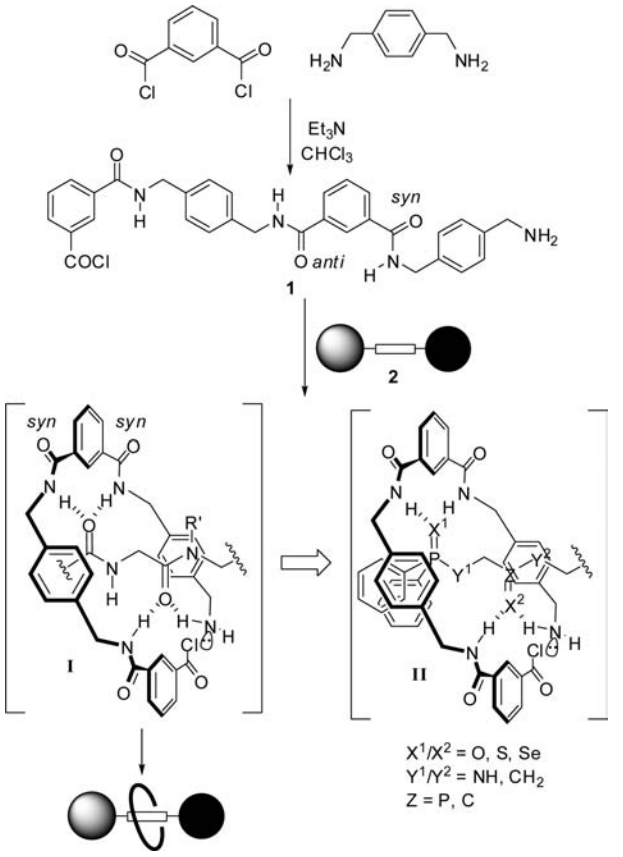
Scheme 1. Hydrogen Bonding Modes of Dipeptide and *Bis*phosphorus−Derived Templates in Rotaxane Synthesis

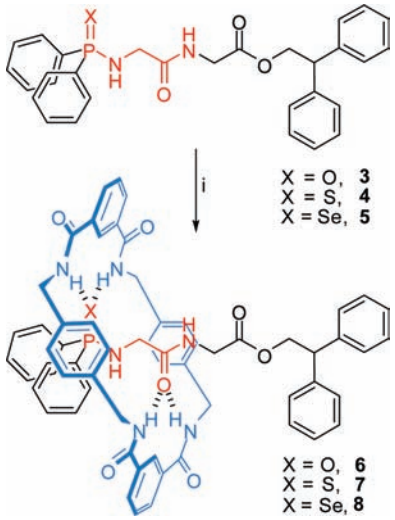


RESULTS AND DISCUSSION

Suitable phosphinamide (**3**), thiophosphinamide (**4**), and selenophosphinamide (**5**) threads, which feature the chalcogen atoms in a spatial orientation similar to that of the carbonyl groups in a glycylglycine motif (Scheme 1), were prepared in three steps from commercially available glycylglycine ethyl ester hydrochloride (see Supporting Information). Pleasingly, upon addition of a 5-fold molar excess of isophthaloyl dichloride, *p*-xylylenediamine and triethylamine in anhydrous chloroform each thread afforded the corresponding [2]rotaxane, **6**−**8**, through the hydrogen bond-directed five-component 'clipping' reaction (Scheme 2). The phosphinamide [2]rotaxane **6** was obtained in 60% yield, similar to that (62%) obtained for the previously reported[1d] glycylglycine analogue, indicating that the phosphinamide group (with a large, sp^3-hybridized P^+-O^- group) is able to function almost as effectively as one of the amide groups in the hydrogen bond-directed template reaction. Somewhat unexpectedly, the thiophosphinamide and selenophosphinamide [2]rotaxanes **7** and **8** were also formed in reasonable yield, 18 and 20% respectively, from the reactions with the corresponding P═S and P═Se threads (**4** and **5**).

Single crystals of each of the three rotaxanes (**6**−**8**) were obtained by slow diffusion of hexane vapor into solutions of the rotaxanes in chloroform and the solid-state structures determined by X-ray crystallography (Figures 1−3). The three crystal structures show broadly similar features: the macrocycle hydrogen bonds to the amide carbonyl and the O/S/Se atom of the phosphorus functional group rather than the ester moiety, which is a poor hydrogen bond acceptor.[1h,20] The macrocycle adopts a distorted boat-like conformation with one amide hydrogen bonding to the O/S/Se atom of the phosphorus functional group with the other isophthalamide unit adopting bifurcated hydrogen bonds to the single amide group of the thread. The fourth amide

Scheme 2. Synthesis of Phosphinamide, Thiophosphinamide, and Selenophospinamide [2]Rotaxanes 6−8[a]



[a] Reagents and conditions: (i) isophthaloyl dichloride (5-fold excess), *p*-xylylenediamine (5-fold excess), Et_3N, $CHCl_3$, RT, 4 h, 60% (**6**), 18% (**7**), 20% (**8**). The intercomponent hydrogen bonding shown for the [2]rotaxanes is one of several intramolecular hydrogen bonding modes that are likely to be present for the rotaxane molecules in solution.[1d,f−h,n,q,t,8−10] It does not necessarily correspond to the hydrogen bond motifs found in the solid-state structures (see Figures 1−5) where intermolecular hydrogen bonding modes (and, in Figure 5, the participation of solvate molecules) are also available.

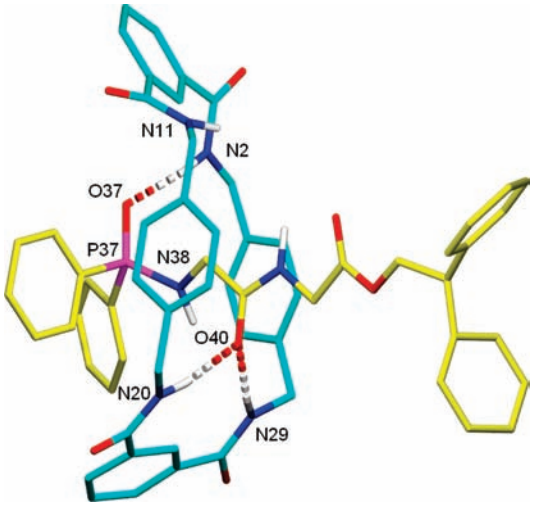


Figure 1. X-ray crystal structure of phosphinamide rotaxane **6**. Selected bond lengths [Å]: P37−O37, 1.48. Intercomponent hydrogen bond distances [Å]: O37−H2N, 1.87; O40−H20N, 2.20; O40−H29N, 2.05. Intercomponent hydrogen bond angles [deg]: N2−H−O37, 161.4; N20−H−O40, 170.5; N29−H−O40, 159.7.

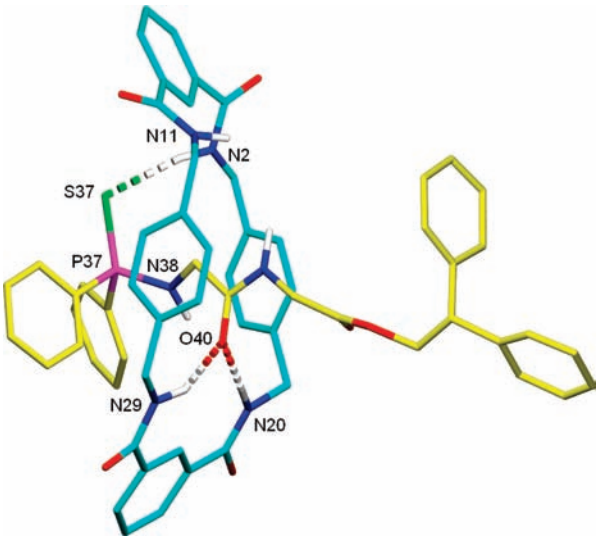


Figure 2. X-ray crystal structure of thiophosphinamide rotaxane **7**. Selected bond lengths [Å]: P37−S37, 1.95. Intercomponent hydrogen bond distances [Å]: S37−H2N, 2.40; O40−H20N, 2.19; O40−H29N, 2.07. Intercomponent hydrogen bond angles [deg]: N2−H−S37, 168.6; N29−H−O40, 153.6; N20−H−O40, 173.5.

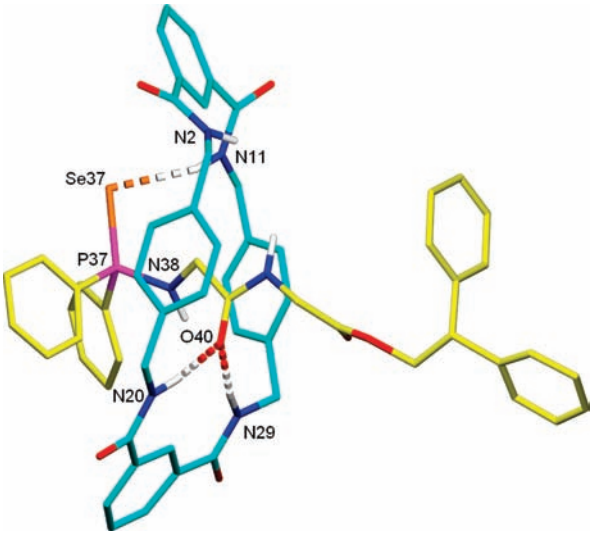
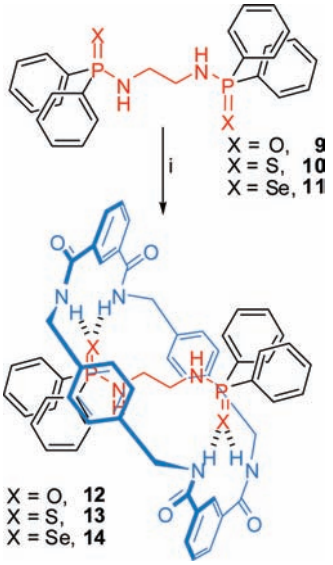


Figure 3. X-ray crystal structure of selenophosphinamide rotaxane **8**. Selected bond lengths [Å]: P37−Se37, 2.10. Intercomponent hydrogen bond distances [Å]: Se37−H11N, 2.54; O40−H20N, 2.09; O40−H29N, 2.12. Intercomponent hydrogen bond angles [deg]: N11−H−Se37, 153.2; N20−H−O40, 173.3; N29−H−O40, 169.4.

group of the macrocycle engages in intermolecular hydrogen bonding to an adjacent rotaxane molecule in the crystal. In comparison to the short P═O···HN hydrogen bond (O37−H2A, 1.87 Å) in the phosphinamide rotaxane **6**, the corresponding P═S···HN and P═Se···HN hydrogen bonds in the thiophosphinamide and selenophosphinamide rotaxanes are relatively long (S37−H2A, 2.40 Å (**7**); Se37−H11N, 2.54 Å (**8**)). While the differences in hydrogen bond length can be largely attributed to the increasing atomic radius of sulfur and selenium (O^{2-} 1.26 Å; S^{2-} 1.70 Å; Se^{2-} 1.84 Å), weaker intercomponent hydrogen bonding is consistent with the lower yields obtained in the

Scheme 3. Synthesis of *Bis*(phosphinamide) [2]Rotaxane 12 (and Attempted Synthesis of the Corresponding *Bis*-(thiophosphinamide) and *Bis*(selenophospinamide) [2]Rotaxanes 13 and 14)[a]



[a] Reagents and conditions: (i) isophthaloyl dichloride (5-fold excess), *p*-xylylenediamine (5-fold excess), Et_3N, $CHCl_3$, RT, 4 h, 18% (**12**), 0% (**13**), 0% (**14**).

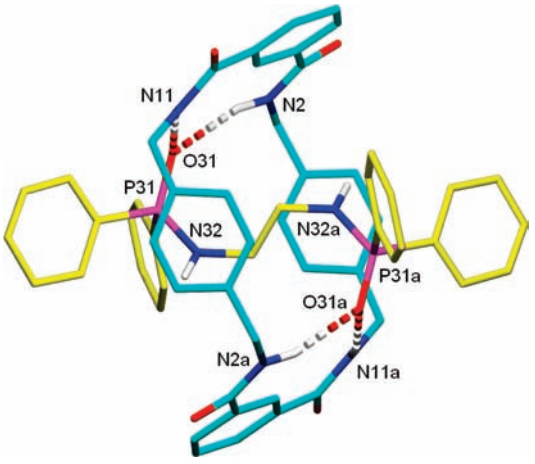


Figure 4. X-ray crystal structure of *bis*(phosphinamide) rotaxane **12**. Selected bond lengths [Å]: P31−O31 = P31a−O31a, 1.45. Intercomponent hydrogen bond distances [Å]: O31−HN2 = O31A−HN2a, 2.20; O31−H11 = O31a−HN11a, 2.38. Intercomponent hydrogen bond angles [deg]: N2−H−O31 = N2a−H−O31a, 160.0; N11−H−O31 = N11a−H−O31a, 165.6.

synthesis of the P═S and P═Se rotaxanes (Scheme 2). A search of the CCDC database revealed only one other example[21] of amide-to-phosphinamide hydrogen bonding and one example[22] of amide-to-thiophosphinamide hydrogen bonding. As far as we are aware, there are no previous examples of amides hydrogen bonding to P═Se functional groups.[23]

Having shown that one amide carbonyl of the rotaxane-forming glycylglycine template (Scheme 1) can be successfully substituted by phosphinamide, thiophosphinamide and

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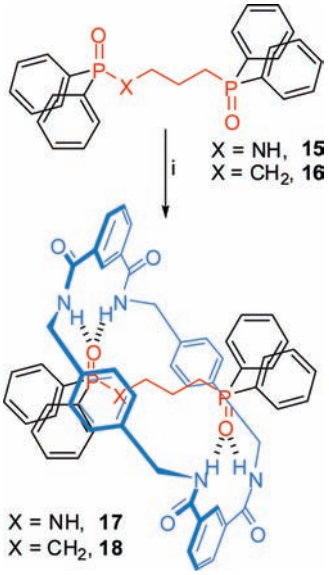
Scheme 4. Synthesis of Phosphinamide−Phosphine Oxide [2]Rotaxane 17 (and Attempted Synthesis of *Bis*(phosphine oxide) [2]Rotaxane 18)[a]



[a] Reagents and conditions: (i) isophthaloyl dichloride (5-fold excess), *p*-xylylenediamine (5-fold excess), Et_3N, $CHCl_3$, RT, 4 h, 15% (**17**), 0% (**18**).

selenophosphinamide functionalities, we investigated the efficacy of employing two such groups in the thread. Symmetrical *bis*(phosphinamide) thread **9**, and the analogous thio- and seleno- analogues, **10** and **11**, were synthesized from 1,2-diaminoethane and the corresponding chalcogen chlorodiphenylphosphine derivatives (see Supporting Information) and subjected to the rotaxane-forming reaction conditions employed previously (Scheme 3). Although no rotaxane could be detected in the reactions involving the *bis*(thiophosphinamide) or *bis*-(selenophosphinamide) threads, the *bis*(phosphinamide) rotaxane **12** was isolated in 18% yield. Single crystals of the rotaxane were obtained by layering a saturated $CDCl_3$ solution with hexanes and the solid state structure determined by X-ray crystallography (Figure 4).

The X-ray crystal structure of **12** shows that, somewhat remarkably, given the size and (tetrahedral) arrangement of the phosphorus functional groups, the rotaxane molecules adopt a co-conformation in which both phosphinamide moieties are able to form bifurcated hydrogen bonds (2.20−2.38 Å) with the macrocycle isophthalamide groups (Figure 4). The macrocycle is able to satisfy this hydrogen bonding arrangement while adopting a low-energy chair conformation.

We next turned our attention to employing phosphine oxide groups in the template site. Keeping the interhydrogen bond-acceptor distance similar to the *bis*(phosphinamide) system, the phosphinamide−phosphine oxide thread **15** and *bis*(phosphine oxide) thread **16** were prepared (see the Supporting Information) and each subjected to the standard rotaxane-forming conditions (Scheme 4). Although no rotaxane could be detected using the *bis*(phosphine oxide) thread **16**, we were delighted to isolate the [2]rotaxane **17** in 15% yield from the reaction featuring the phosphinamide−phosphine oxide template (Scheme 4). This is consistent with other studies[24] that suggest that phosphinamides are more strongly polarized than phosphine oxides and therefore

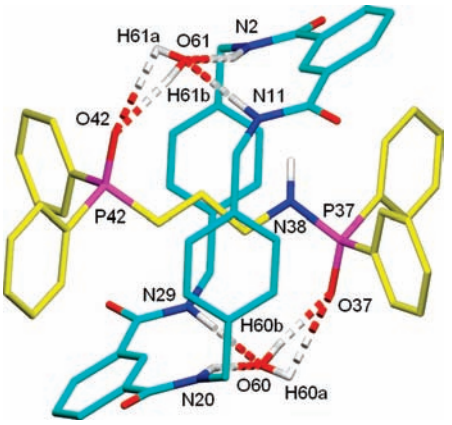
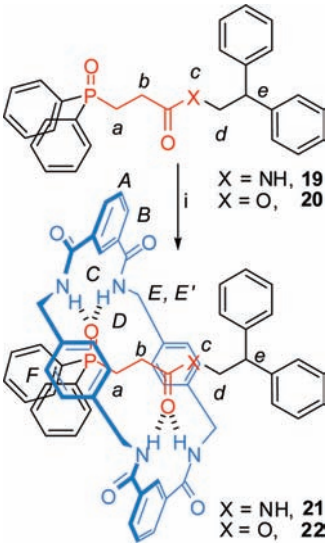


Figure 5. X-ray crystal structure of phosphinamide−phosphine oxide rotaxane **17**. Selected bond lengths [Å]: P37−O37, 1.50; P42−O42, 1.50. Hydrogen bond distances [Å]: O37−H60a, 1.94; O37−H60b, 2.68; O60−H20N, 2.35; O60−H29N, 2.17; O42−H61a, 1.95; O42−H61b, 2.68; O61−HN2, 2.35; O61−HN11, 2.17. Hydrogen bond angles [deg]: O60−H60a−O37, 128.5; O60−H60b−O37, 79.3; N20−H−O60, 175.1; N29−H−O60, 161.5; O61−H61a−O42, 128.4; O61−H61b−O42, 79.2; N2−H−O61, 175.1; N11−H−O61, 161.5.

Scheme 5. Synthesis of Phosphine Oxide-Based [2]Rotaxanes 21 and 22[a]



[a] Reagents and conditions: (i) isophthaloyl dichloride (5-fold excess), *p*-xylylenediamine (5-fold excess), Et_3N, $CHCl_3$, RT, 4 h, 42% (**21**), 6% (**22**).

the phosphinamide phosphoryl oxygen is more negatively charged and should be a better hydrogen bond acceptor. However, the different steric requirements of the groups adjacent to the P═O unit in the thread—sp^2-NH for the phosphinamide; sp^3-CH_2 in the phosphine oxide—may also contribute to the differences in the effectiveness of the templates orienting the open-chain macrocycle precursor (**II** in Scheme 1) about the thread.

Single crystals of rotaxane **17** were obtained by layering a saturated $CDCl_3$ solution with hexanes, and the solid-state

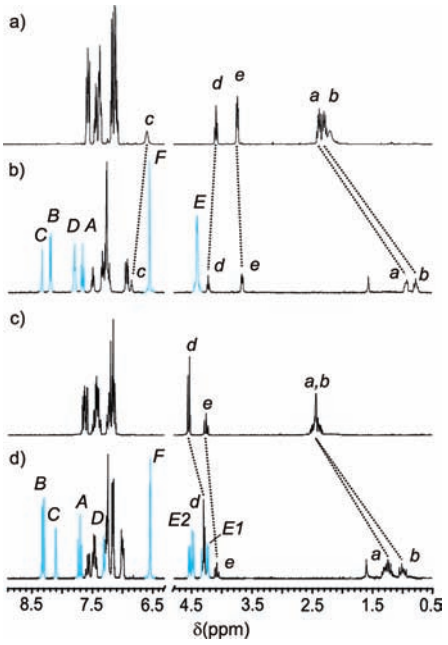


Figure 6. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of (a) phosphine oxide−amide thread **19**, (b) phosphine oxide−amide-based [2]-rotaxane **21**, (c) phosphine oxide−ester thread **20**, (d) phosphine oxide−ester-based [2]rotaxane **22**. The assignments correspond to the lettering shown in Scheme 5.

structure was determined by X-ray crystallography (Figure 5). Remarkably, the hydrogen bonding motifs and relative positions of the isophthalamide macrocycle and the phosphinamide−amide based thread in the crystal structure of rotaxane **17** are very different from the other phosphorus rotaxanes and, indeed, to all other amide-based rotaxanes reported to date. There are no direct intercomponent hydrogen bonds between the macrocycle and thread in the solid-state structure of **17** (Figure 5). Rather, both isophthalamide units of the macrocycle engage in bifurcated hydrogen bonding with water molecules which, in turn, act as hydrogen bond donors in a set of bifurcated hydrogen bonds to the oxygen atom of the phosphinamide and phosphine oxide groups on the thread. Although rotaxanes **6**−**8** and **12** all have water molecules as solvates in their X-ray crystal structures, only **17** sacrifices direct intracomponent hydrogen bonding and employs water as a 'bridge' to hydrogen bonding in a manner reminiscent of the role water often plays to connect hydrogen bonding groups in the binding of substrates in the active sites of enzymes and antibodies.[25]

Finally, we investigated the efficacy of a phosphine oxide unit with an amide or ester group as the other hydrogen bond-accepting moiety in the template site (Scheme 5). Reaction of phosphine oxide−amide thread **19** or phosphine oxide−ester thread **20** under the rotaxane-forming reaction conditions afforded the corresponding [2]rotaxanes **21** and **22** in 42% and 6% yields, respectively (Scheme 5). Esters are much poorer hydrogen bond acceptors than amides,[1h,20] and so the modest yield of **22** is unsurprising.

Although single crystals suitable for X-ray analysis could not be obtained for either rotaxane **21** or **22**, the ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of the rotaxanes and the corresponding threads (**19** and **20**) give some information regarding the intercomponent hydrogen bonding in the interlocked structures in solution (Figure 6). Comparison of the spectra in Figure 6 shows that in both rotaxanes the co-conformations of the mechanically interlocked components are dominated by hydrogen bonding that locates the xylylene groups of the macrocycles over the ethylene spacer (note the large shifts in protons H_a and H_b). The strength of hydrogen bonding between the components of **21** and **22**, however, is very different, reflected in the relative chemical downfield shifts of the macrocycle amide protons (H_D) in **21** (δ 7.79) and **22** (δ 7.31). Furthermore, the H_C protons of the macrocycle which are positioned in the shielding region of a carbonyl group when bifurcated hydrogen bonding occurs, are shielded to a greater degree in **21** (δ 8.33) than in **22** (δ 8.12).

CONCLUSIONS

Replacing one or both amide groups of the classical glycylglycine template for rotaxane formation with hydrogen bond acceptors based on various phosphorus-containing functional groups can result in effective motifs for the hydrogen bond−directed synthesis of [2]rotaxanes. In addition to P═O-based phosphinamide and phosphine oxide functional groups, thio- and selenophosphinamides can act as sufficiently good hydrogen bond acceptors to form rotaxanes in combination with an amide group in the template site. Phosphinamides can successfully substitute for both amide groups, even though this results in a significant change in both steric size and shape (sp^2 to sp^3) of the hydrogen bond-accepting groups at the template site. X-ray crystal structures and ^{1}H NMR spectroscopy reveal information about the intramolecular hydrogen bonding networks between the components in both solution and the solid state. As well as increasing the diversity of templates available for the assembly of benzylic amide macrocycle rotaxanes, such templates may prove useful for the assembly of rotaxanes and molecular shuttles in which the macrocycle can be used to hinder or expose binding ligating sites for metal-based catalysts.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures and spectroscopic data for all compounds synthesized, and full crystallographic data for rotaxanes **6**−**8**, **12**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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