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Synthesis and Characterization of Two Isomeric, Self-Assembled Arsenic–Thiolate Macrocycles

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The use of labile As–S bond formation in the self-assembly of discrete supramolecular structures is extended. Macrocyclic structures of chemical formula $As_2L_2Cl_2$ (H_2L = α,α′-dimercapto-*p*-xylene) were prepared and characterized. Diastereomeric syn and anti isomers of these macrocycles were selectively crystallized and characterized in the solid state using single-crystal X-ray diffraction. Both the syn and anti macrocycles show close contacts between the arsenic(III) ions and the aromatic carbons, consistent with intramolecular arsenic–π interactions. The dynamic behavior of the isomers in solution is also investigated. *anti*-$As_2L_2Cl_2$·$AsCl_3$ crystallizes in monoclinic space group $P2_1/c$ (No. 14) with $a = 10.6194(5)$ Å, $b = 16.7780(9)$ Å, $c = 8.5725(4)$ Å, $\beta = 100.6830(10)°$, and $Z = 2$. *syn*-$As_2L_2Cl_2$ crystallizes in orthorhombic space group *Pnma* (No. 62) with $a = 10.8881(8)$ Å, $b = 19.3511(14)$ Å, $c = 9.9524(7)$ Å, and $Z = 4$.

Introduction

Self-assembly of discrete supramolecular aggregates utilizing reversible coordinate bonding interactions has provided access to elaborate and precisely designed structures that have generated an enormous amount of interest.[1] Transition metals have been most widely used in designing coordination-driven discrete structures. In contrast, much less work focuses on using main-group elements as directing units for the construction of supramolecular structures.[2] We have been exploring the coordination chemistry of the metalloid arsenic for use in the formation of discrete supramolecular assemblies. Our recent work has demonstrated that As(III) in combination with appropriately designed bridging thiolate ligands can self-assemble into a discrete dinuclear As_2L_3 structure.[3]

Incorporation of As(III) into supramolecular designs provides access to novel structure types, and may confer further reactivity to the resulting structures. Among transition elements, trigonal pyramidal coordination geometries are only rarely and unpredictably observed.[4] However, trigonal pyramidal is the preferred coordination geometry of As(III) with thiolates.[5] Thus the use of As(III) provides access to a structure type mostly unavailable with the transition metals.

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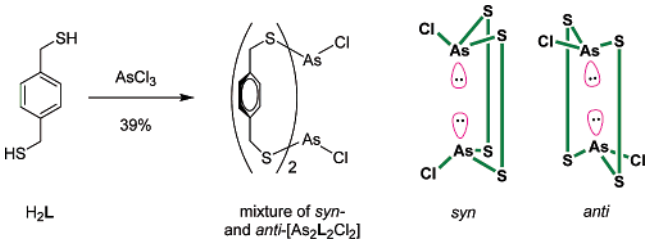
Scheme 1



Furthermore, functionalization of the As(III) ions with spectator blocking ligands is not required because the trigonal pyramidal coordination geometry of As(III) functions as an inherently convergent tripodal structural unit for preparing discrete supramolecular assemblies. Trigonal pyramidal As(III) also features a stereochemically active lone pair, which may provide a handle for functionalization of the resulting supramolecular structures.

The Lewis basic lone pairs on As(III) may also find utility in binding transition metals. For example, arsines have been used as alternatives to phosphine ligands because they act as weaker σ-donors and π-acceptors than their phosphine counterparts.[6] Indeed, arsine ligands have proven superior to phosphines for certain transition-metal-mediated catalyses.[7] Macrocyclic multidentate arsines are often prepared in a stepwise synthesis in which the arsine donor units are installed in separate steps.[8] This requires both the carryover of arsenic derivatives through multiple synthetic steps and the serial use of arsenic reagents. Self-assembly, on the other hand, both provides a highly convergent method of preparation and also postpones the incorporation of arsenic until the last synthetic step.

Herein we expand the use of the reversibility and lability of As−S bonds in the preparation of supramolecular structures. The preparation of isomeric dinuclear arsine macrocycles from a dithiol and an As(III) source is described (Scheme 1). Both syn and anti diastereomers of the macrocycle were structurally characterized in the solid state using single-crystal X-ray diffraction. In both structures, close contacts between the arsenic(III) ions and aromatic carbons were evident, consistent with intramolecular arsenic−π interactions.[3,9] The dynamic behavior of the isomers in solution is also probed.

Experimental Section

General Procedures. All NMR spectra were measured using a Varian INOVA-500 spectrometer operating at 500.11 and 125.76 MHz for ^{1}H and ^{13}C{^{1}H}, respectively. Spectra were referenced using the residual solvent resonance as an internal standard. Single-crystal X-ray diffraction studies were performed on a Bruker SMART APEX diffractometer. Commercially available reagents were used as received. H_2**L** (α,α'-dimercapto-*p*-xylene) was prepared as reported in the literature.[3,10]

$As_2L_2Cl_2$ (1 and 2). $AsCl_3$ (52 μL, 0.620 mmol) was slowly added to a solution of H_2**L** (103 mg, 0.605 mmol) dissolved in $CHCl_3$ (24 mL). *n*-Pentane (96 mL) was slowly layered onto the $CHCl_3$ solution, and the resulting clear, colorless solution was capped and allowed to stand for 16 h. The solution was decanted, and the colorless crystals were collected, washed with pentane, and allowed to air-dry to yield 66 mg (39% yield) of a polycrystalline material that is a mixture of syn and anti macrocycles.[11] Anal. Found: C, 34.77; H, 2.76. Calcd for $As_2C_{16}H_{16}S_4Cl_2$ (557.31): C, 34.48; H, 2.89. ^{1}H NMR ($CDCl_3$): δ 7.25 (s, 8H, C_6H_4), 7.24 (s, 8H, C_6H_4), 4.28 (d, 4H, CH_2, J = 12.9 Hz), 4.19 (d, 4H, CH_2, J = 12.9 Hz), 4.05 (d, 4H, CH_2, J = 12.9 Hz), 3.96 (d, 4H, CH_2, J = 12.9 Hz). ^{13}C{^{1}H} NMR: δ 137.48, 130.03, 129.80, 35.18.

***anti*-$As_2L_2Cl_2$·$AsCl_3$ (1·$AsCl_3$) Crystal Growth.** A solution of H_2**L** (50 mg, 0.294 mmol) in $CHCl_3$ (5 mL) was combined with another solution of $AsCl_3$ (100 μL, 1.19 mmol) in $CHCl_3$ (5 mL). Slow diffusion of pentane into an aliquot of the reaction mixture over 10 days at 0 °C yielded needles suitable for X-ray diffraction. These conditions selectively yield crystals of the anti macrocycle.

***syn*-$As_2L_2Cl_2$ (2) Crystal Growth.** $AsCl_3$ (48 μL, 0.572 mmol) was added to a solution of H_2**L** (97 mg, 0.570 mmol) in $CHCl_3$ (4 mL). An aliquot of the reaction mixture was diluted to twice its volume with $CHCl_3$. Slow diffusion of pentane into the resulting diluted aliquot over 48 days at 0 °C yielded X-ray quality single crystals of exclusively the syn macrocycle, **2**.

$As_2L_2Cl_2$·THF (1·THF) Crystal Growth. Single crystals suitable for X-ray diffraction were grown by diffusing pentane into a 1 mL solution of H_2**L** (9 mg, 0.053 mmol), $AsCl_3$ (3 μL, 0.035 mmol), and $Ni(BF_4)_2$ (123 mg, 0.53 mmol) in THF at 0 °C.

Results

Slow diffusion of *n*-pentane into a $CHCl_3$ solution of H_2**L** and excess $AsCl_3$ produced single crystals suitable for X-ray diffraction. The structure consists of discrete As_2**L**$_2Cl_2$ anti macrocycles, with the two As−Cl bonds pointing in opposite directions. Figure 1 shows an ORTEP[12] diagram of *anti*-As_2**L**$_2Cl_2$·$AsCl_3$ (**1**·$AsCl_3$), which crystallizes in space group

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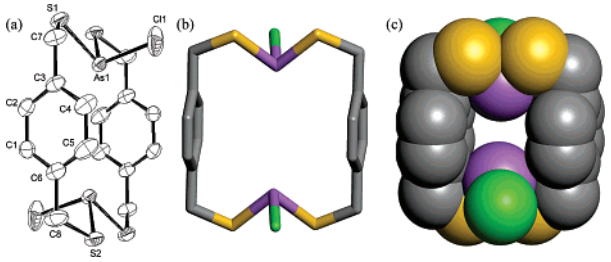

Figure 1. Single-crystal X-ray structure of *anti*-$As_2\mathbf{L}_2Cl_2$ macrocycle (**1**·$AsCl_3$). (a) ORTEP representation of **1** with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. (b) Wireframe and (c) van der Waals representations of **1** in the crystal. The cocrystallized $AsCl_3$ molecule is omitted for clarity. Selected bond lengths (Å), interbond angles (deg), and torsion angles (deg): As1−S1, 2.2180(8); As1−S2, 2.2252(8); As1−Cl1, 2.2235(9); As1−C3, 3.165; As1−C2, 3.575; As1−C4, 3.689; As1−S1−C7, 100.41(10); As1−S2−C8, 100.88(12); S1−As1−S2, 87.09-(3); S1−As1−Cl1, 101.17(4); S2−As1−Cl1, 99.54(4); As1−S2−C8−C6, 41.20; As1−S1−C7−C3, 37.37. Arsenic atoms are shown in purple, sulfur in yellow, chlorine in green, and carbon in gray.

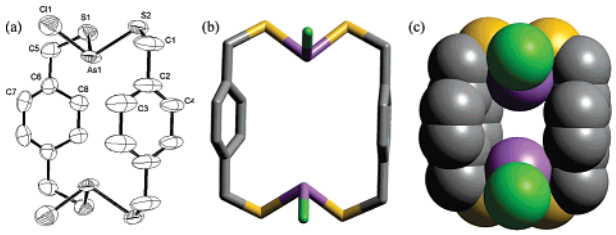

Figure 2. Single-crystal X-ray structure of *syn*-$As_2L_2Cl_2$ macrocycle (**2**). (a) ORTEP representation of **2** with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. (b) Wireframe and (c) van der Waals representations of **2** in the crystal. The rotational disorder of one phenyl group is omitted for clarity. Selected bond lengths (Å), interbond angles (deg), and torsion angles (deg): As1−S1, 2.229(2); As1−S2, 2.1997(19); As1−Cl1, 2.245(2); As1−C2, 3.247; As1−C3, 3.565; As1−C4, 3.893; As1−C6, 3.272; As1−C7, 3.972; As1−C8, 3.350; As1−S1−C5, 98.7(2); As1−S2−C1, 98.3(3); S1−As1−S2, 90.32(9); Cl1−As1−S1, 100.48(8); Cl1−As1−S2, 101.33(9); As1−S2−C1−C2, 50.39; As1−S1−C5−C6, 52.64. Arsenic atoms are shown in purple, sulfur in yellow, chlorine in green, and carbon in gray.

$P2_1/c$ with two macrocycles per unit cell—therefore, the macrocycle has crystallographic C_i symmetry. The two aromatic rings are parallel, and each As(III) center is twisted so that each As(III) atom is slightly closer to one aromatic ring than to the other (As1−As1a = 4.65 Å). These crystallization conditions exclusively yield the anti macrocycle, as confirmed by measuring the unit cells of numerous (>10) single crystals prepared using this method. Long-range As−S interactions (As−S distances ranging from 3.27 to 3.90 Å) between the macrocycle and the cocrystallized $AsCl_3$ may contribute to the selective stabilization of the anti macrocycle under these crystal growth conditions.

Slow diffusion of *n*-pentane into a chloroform solution of $H_2\mathbf{L}$ and $AsCl_3$ in equimolar amounts at slightly higher concentrations (see the Experimental Section) selectively yielded single crystals of the diastereomeric syn macrocycle suitable for X-ray diffraction (Figure 2). The structure consists of discrete dinuclear $As_2\mathbf{L}_2Cl_2$ macrocycles with the chlorine atoms each facing the same side of the macrocycle. *syn*-$As_2\mathbf{L}_2Cl_2$ (**2**) crystallizes with mirror symmetry in space group *Pnma* with four macrocycles per unit cell. The two As(III) centers are oriented directly above one another, with an As1−As1a distance 5.02 Å.

Another crystal structure was obtained from crystals grown from a solution of $AsCl_3$, $H_2\mathbf{L}$, and excess $Ni(BF_4)_2$ in THF.[13] The structure consists of a THF solvate of either disordered *anti*- or *syn*-$As_2\mathbf{L}_2Cl_2$ or a mixture of the two. The carbon atoms of the ligand are well ordered; however, the arsenic coordination sphere is severely disordered. Both the sulfur and chlorine atoms are disordered over two sites, and were modeled with equal site occupancy. As a result of the disorder, it cannot be determined whether *syn*-$As_2\mathbf{L}_2Cl_2$, *anti*-$As_2\mathbf{L}_2Cl_2$, or a combination of the two is present in the crystal structure. The macrocycle crystallizes with four molecules per unit cell, and each molecule sits on a crystallographic inversion center. The As−As distance in this structure is 4.9 Å, which is between the As−As distances of 4.65 and 5.02 Å in the anti and syn macrocycles, respectively.

Although the bond distances and bond angles are quite similar in the syn and anti macrocycles, they do have significantly different As−S−C−C dihedral angles. This results in shorter $As-C_{aryl}$ distances in the anti macrocycle compared to those of the syn macrocycle. The shortest $As-C_{aryl}$ distance in the syn macrocycle is 3.25 Å, whereas the shortest $As-C_{ar}$ distance in the anti macrocycle is 3.16 Å. These distances are significantly shorter than the sum of their van der Waals radii, and fit well within the range of known arsenic−π interaction distances in the solid state.[3,9,14,15] The $As-C_{aryl}$ distances in the anti macrocycle are even shorter than those in the previously reported $As_2\mathbf{L}_3$ assembly.[3] According to molecular mechanics models,[16] each arsenic atom should have greater torsional freedom to flex away from the aromatic rings in an $As_2\mathbf{L}_2Cl_2$ macrocycle compared to an $As_2\mathbf{L}_3$ assembly. Surprisingly, the As−π distances are the same (in the syn macrocycle) or shorter (in the anti macrocycle) with two bridging ligands rather than the three bridging ligands in the $As_2\mathbf{L}_3$ assembly. Clearly, As−π interactions are influencing the solid-state structure. This represents a novel example of intramolecular arsenic−arene interactions, suggesting that these interactions may be incorporated as a design element in other supramolecular structures.

NMR spectroscopy was used to characterize the macrocycles in solution. ^{1}H NMR spectral characterization of the mixture showed two aromatic signals and eight methylene signals with the splitting pattern in the methylene region shown in Figure 3. One might interpret this spectrum as resulting from a single diastereomer (*syn*- or *anti*-$As_2\mathbf{L}_2Cl_2$) alone. If the phenyl rings are not freely rotating, but rather are static, then two different aromatic signals would be observed by ^{1}H NMR spectroscopy, matching the observed

(13) See the Supporting Information for full crystallographic details on the severely disordered structure **1**·THF. $Ni(BF_4)_2$ was used as an additive in crystal growth experiments in an attempt to form a Ni(II) inclusion complex. Although this was unsuccessful, a new solvate of the macrocycles was obtained instead.

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Table 1. Crystallographic Data and Refinement Parameters for **1**·$AsCl_3$ and **2**

	1·$AsCl_3$	**2**
empirical formula	$C_{16}H_{16}As_4Cl_8S_4$	$C_{16}H_{16}As_2Cl_2S_4$
formula weight	919.81	557.27
temperature (K)	153(2)	153(2)
wavelength (Å)	0.71073	0.71073
crystal system	monoclinic	orthorhombic
space group	*P*2(1)/*c*	*Pnma*
a (Å)	10.6194(5)	10.8881(8)
b (Å)	16.7780(9)	19.3511(14)
c (Å)	8.5725(4)	9.9524(7)
α (deg)	90	90
β (deg)	100.6830(10)	90
γ (deg)	90	90
volume (Å^3)	1500.91(13)	2096.9(3)
Z	2	4
F(000)	888	1104
crystal size (mm^3)	0.4 × 0.1 × 0.1	0.2 × 0.05 × 0.05
no. of reflections collected	8590	11466
no. of independent reflections	3054 [*R*(int) = 0.0168]	2211 [*R*(int) = 0.0390]
completeness to $\theta = 26.37°$ (%)	99.6	99.7
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	3054/0/145	2211/0/128
goodness-of-fit on F^2	1.034	1.166
R1/wR2 [$I > 2\sigma(I)$]	0.0264/0.0670	0.0629/0.1582
R1/wR2 (all data)	0.0320/0.0693	0.0820/0.1690

pattern. The splitting pattern in the methylene region could then be explained as a result of long-range four-bond coupling between inequivalent aromatic and methylene protons. However, if this long-range coupling were in fact occurring, the observed coupling constants would be unusually large compared to known benzylic coupling constants.[17] In addition, if the methylene protons are coupling to the aromatic protons, by necessity the aromatic protons should display coupling to the methylene signals: two doublets would be observed in the aromatic region instead of the two singlets actually observed. For additional confirmation, selective irradiation of alternately the aromatic and methylene regions yielded no changes in the corresponding splitting patterns; thus, benzylic coupling is not responsible for the observed splitting pattern.

The remaining explanation is that both the syn and anti macrocycles are present in solution. Each diastereomer gives rise to one aromatic signal and two doublets corresponding to an AB system resulting from geminal coupling between the diastereotopic methylene protons. This is consistent with the expected C_{2v} and C_{2h} symmetric discrete structures expected in solution for the syn and anti macrocyclic structures, respectively. The ^{1}H NMR spectrum of the equilibrium mixture indicates that one diastereomer is slightly more stable than the other. Molecular mechanics minimizations performed on the syn and anti macrocycle structures indicate an energy difference of less than 0.5 kcal mol^{-1}.[16] One may speculate, however, that the stronger As$-\pi$ interactions observed in the crystal structure of the anti macrocycle persist in solution, resulting in a slightly higher stability for this diastereomer.

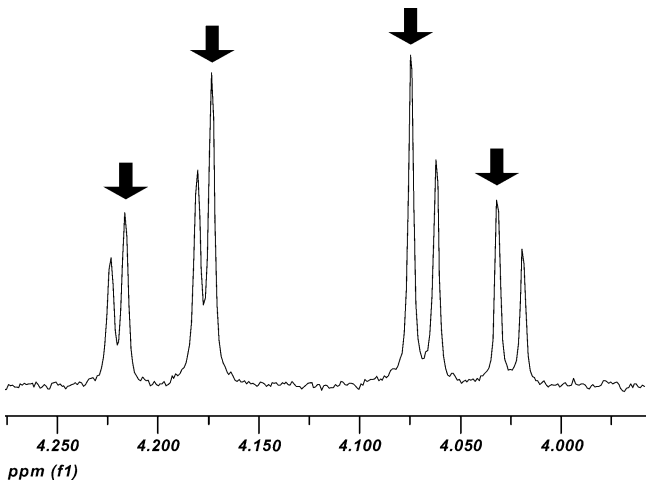

Figure 3. ^{1}H NMR spectrum of the equilibrium mixture of syn and anti macrocycles. Signals resulting from the thermodynamically favored macrocycle are marked with arrows.

Interconversion between the syn and anti macrocycles must occur in solution. When 10 single crystals each verified by single-crystal X-ray diffraction to consist of a single diastereomer were collected and dissolved, equilibration to a mixture of syn and anti macrocycles was found to occur in less time than that required for dissolution and insertion into the NMR spectrometer (less than 15 min). Variable-temperature ^{1}H NMR spectroscopy did not permit quantification of the interconversion process between the diastereomeric macrocycles. No signal coalescence was observed at high temperatures (130 °C) in d_4-tetrachloroethane. Low-temperature ^{1}H NMR spectroscopy similarly showed no changes down to −60 °C in CD_2Cl_2. At −80 °C, however, some broadening of a single aromatic signal was observed. This may be attributable to slowed rotation of the phenyl rings in one of the diastereomers, perhaps as a result of the As$-\pi$ interaction. Therefore, although interconversion of the syn and anti macrocycles is not observed in solution on the NMR time scale between −60 and 130 °C, equilibration is fast over the course of several minutes.[18]

Discussion

When $AsCl_3$ and H_2**L** are combined in the absence of base, the macrocycles (**1** and **2**) are the dominant product initially

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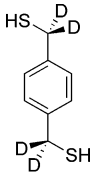
formed even in the presence of excess H_2**L** (Scheme 1). Presumably, the HCl generated as a byproduct of binding the dithiolate to $AsCl_3$ inhibits formation of As_2**L**$_3$. This is an alternative route to dithiomonochloroarsenites, which are typically prepared from bidentate chelating dithiolate complexes.[14,19] In further support of the assertion that the macrocycles are the kinetic product, heating of a solution of the macrocycles in the presence of excess H_2**L** produced the three-fold symmetric As_2**L**$_3$ assembly.

There are several possible mechanisms for interconversion between the *syn*- and *anti*-As_2**L**$_2Cl_2$ macrocycles. Interconversion may occur through pyramidal inversion at one As(III) center;[20] however, this process alone would most likely involve an energy barrier too high to occur at room temperature in this system. The pyramidal inversion barrier of AsH_3 and AsF_3 has been calculated to be greater than 39 and 45 kcal/mol, respectively.[21] The pyramidal inversion barrier of chiral tertiary alkylarsines has been measured at not less than 42 kcal/mol.[22] This barrier to pyramidal inversion has been empirically related to the electronegativity of the substituents,[23] suggesting that trithiolatoarsines may have pyramidal inversion barriers similar to those of trialkylarsines because of the similar electronegativities of C and S.[24] Given the high calculated and measured barriers of related arsines, direct arsine inversion in this system seems unlikely to be the mechanism of interconversion.

However, the presence of HCl in solution may catalyze pyramidal inversion at the arsenic center. There is some evidence that chiral chlorophosphines undergo racemization much faster than expected.[25] HCl is believed to catalyze the racemization.[26] Furthermore, isotope exchange studies have found that HCl acts as a powerful catalyst for halide exchange with $AsCl_3$.[27] Thus, chloroarsines may exhibit special stereochemical nonrigidity in the presence of HCl. In the present work, HCl is generated as a side product of the reaction between $AsCl_3$ and H_2**L** and may initially contribute to the fast interconversion of syn and anti macrocycles. However, when single crystals containing exclusively one diastereomer are dissolved in dry $CDCl_3$ passed through basic alumina to remove any HCl present, rapid interconversion to the equilibrium mixture still occurs.

Chart 1



H_2D_4**L**

A third possible mechanism of interconversion would involve complete or partial ligand dissociation. To test this hypothesis, macrocycles labeled with deuterium at the methylene positions were prepared from H_2D_4**L** (α,α′-dimercapto-α,α,α′,α′-tetradeutero-*p*-xylene) and $AsCl_3$. A large excess of the protio-ligand was added, and the sample was monitored. None of the protio-ligand was found to exchange with the deuterated ligands on the macrocycle over a period of days. This result does not, however, rule out the possibility that interconversion of the syn and anti macrocycles is accomplished through the dissociation of a single As−S bond, without exchange of an entire dithiolate ligand.

Some evidence for the lability of the As−S bond is provided by the observed dependence of speciation on concentration. Slow evaporation of a $CHCl_3$ solution of the macrocycles leads to formation of an intractable white solid. It appears that at high concentrations, the macrocycles rearrange into a coordination polymer or oligomer. Consistent with other reports of the intractability of coordination polymers formed with thiolates and heavy metals,[28] the insolubility of this material precluded definitive characterization. However, extraction of this solid does yield a mixture of **1** and **2** in solution, albeit in much lower quantity. **1** and **2** are isolated as pure solids only through bulk crystallization.

Conclusion

This pair of interconverting diastereomers suggests a potential supramolecular approach to measuring pyramidal inversion barriers. Pyramidal inversion barriers are typically obtained by measuring the rate of racemization of enantiomerically enriched species or monitoring interconverting diastereomeric systems. For example, diastereomeric diphosphines and diarsines have been employed for measuring inversion at trivalent phosphorus and arsenic.[29,30] A third approach to measuring pyramidal inversion barriers that uses a system of interconverting diastereotopic supramolecular assemblies, such as that described here, may provide access to related measurements. For example, this system may provide a means of estimating the influence of As−π interactions on the rate of pyramidal inversion.[30]

(18) Unfortunately, the very small chemical shift differences between the two diastereomers (approximately 0.01 ppm) hindered observation of interconversion by 2D NMR techniques that require selective irradiation of one of two sets of signals. Interestingly, the syn and anti macrocycles do dissolve at different rates. A nonequilibrium ratio of diastereomers was once observed by NMR spectroscopy while using $CDCl_3$ to redissolve a sample of the macrocycles that had evaporated to dryness (from $CDCl_3$).

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The macrocycles possess a conformation appropriate for acting as arsine donors to transition metals. Rigid bidentate trans-spanning ligands are rare,[31] and these macrocycles may preferentially bind metals in a preorganized trans geometry. Future work will explore the coordination chemistry of the macrocycles as ligands and the use of the $As_2\mathbf{L}_2Cl_2$ macrocycles as synthons for the construction of larger architectures.

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Supporting Information Available: X-ray data in CIF format for **1**·$AsCl_3$, **2**, and **1**·THF. This information is available free of charge via the Internet at http://pubs.acs.org.

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