Encapsulation of Non-Hydrogen Atoms by *in,in*-Bis(triarylelement)-Containing Cyclophanes

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Keywords: cyclophanes, *in/out* isomerism, non-bonded interactions, through-space coupling

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Abstract: Four unusual *in,in*-cyclophanes have been synthesized—the macrobicyclic *in,in*-bisphosphine **11**, its Ag(I) complex **12**, the *in*-hydroxysilane-*in*-phosphine **16**, and an inseparable mixture of **16** with the *in*-fluorosilane-*in*-phosphine **17**—and the *in,in* geometries have been confirmed by X-ray crystallography. In complex **12**, the silver atom is encapsulated in a hydrophobic cavity, and it experiences strong spin-spin coupling to the phosphorus atoms. In the cyclophanes **16** and **17** an inwardly directed hydroxyl group or fluorine atom is pressed against the lone pair of the opposing, inwardly directed phosphine.

1. Introduction

We recently reported the synthesis and crystallographic characterization of macrobicycles **1-5**, each of which contains two inwardly pyramidalized bridgehead atoms.¹⁻⁴ In every case, the bridgeheads bear either lone pair electrons or hydrogen atoms. All attempts to introduce larger bridgeheads bear either lone pair electrons or hydrogen atoms. All attempts to introduce larger atoms into the interior spaces of these or similar structures, whether by cyclization with larger bridgehead substituents³ or reactions of the bridgehead atoms (e.g., oxygenation),^{1,3} have been unsuccessful, and even the protonation of the *in*-phosphines in compounds **1** and **3** is slow due to the severe steric congestion in these cyclophanes.^{1,3} Indeed, in Alder and East's 1996 review of *in/out* isomerism,⁵ there is not a single example of an *in,in*-macrobicycle that contains an inwardly-directed non-hydrogen atom attached to the bridgehead (i.e., **6**). A later review by Bauer and Habicher⁶ gives three examples of *in,in*-cyclophanes with inwardly directed P=O groups, but in these molecules the phosphorus atoms are separated by three chains of 15 or 16 atoms;^{7,8} thus there is little, if any, steric conflict. A search of the most recent version of the Cambridge Structural Database⁹ (CSD) for similar structures found no additional examples.

Molecules resembling structure **6** are exceptionally rare, but the encapsulation of metal ions by *in,in*-macrobicycles (**7**) is far more common. For example, the CSD contains more than 700 examples of the structure **8**, where M is an alkali or alkaline earth metal ion! However, *transition metal* complexes of this type are only infrequently reported. An extensive search of the CSD found only eight examples of transition metal complexes using [2.2.2]cryptand (i.e., **8**), as well as another eight transition metal complexes that use different cryptands or cryptand-like ligands. All such compounds featured nitrogen atoms at the bridgeheads of the macrobicycles. Only a single complex was found that contained phosphorus atoms at the bridgeheads: a macrobicyclic bis(phosphite) complex of square-planar platinum with *cis* stereochemistry (the P-Pt-P angle is 100.1°),¹⁰ bearing little resemblance to C_3 or D_3 symmetric structures such as **8**.

In this paper we report several unusual "encapsulations" by macrobicycles. First, we describe the preparation of the bisphosphine **11** and its silver complex **12** (Scheme 1), and second, we describe the synthesis of the *in,in*-macrocycles **16** and **17**, the former as the pure *in*-hydroxy compound and the latter as an inseparable mixture of *in*-hydroxy- and *in*-fluorosilanes, both of whose interior atoms must interact with the phosphorus atom on the opposing bridgehead.

2. Results and Discussion

2.1. Synthesis and Structure of Silver Complex **12**.

The synthesis of the bis(phosphine) **11** and its silver complex **12** is illustrated in Scheme 1. Treatment of tris[2-(chloromethyl)phenyl]phosphine¹¹ (**9**) with thiourea, followed by base hydrolysis, gave the corresponding trithiol **10** in excellent yield (96%). A solution of **9** and **10**, each at a concentration of 1 mM in 2:1 benzene-EtOH at reflux, was then treated with KOH to give the *in,in*-bis(phosphine) **11** in 22% yield, a fairly good yield for such a macrocyclization.

Scheme 1^a

^aConditions: (a) thiourea, EtOH, reflux; then KOH, H₂O, reflux; then HCl, 96% (b) **9**, KOH, 2:1 benzene-EtOH, reflux, 22%; (c) Ag(OAc), CHCl₃, ~80%; (d) BCl₃, heptane, then H₂O, 32%; (e) BF₃•Et₂O, CH₂Cl₂, 55%; (f) **10**, KOH, 2:1 benzene-EtOH, reflux, 1% of **16/17** mixture; (g) **10**, KOH, 2:1 benzene-EtOH, reflux, 14% of **16**.

Compound **11** is considerably less soluble than the other *in,in*-cyclophanes that we have prepared,¹⁻⁴ but due to its high symmetry (*C*_{3h}), good NMR spectra were easily obtained. Its ¹H NMR spectrum displays highly broadened, diastereotopic methylene resonances due to the slow flipping of the triarylphosphine caps on the NMR time scale. The ¹³C NMR spectrum shows the

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5 expected seven resonances, but three of these are complex multiplets due to coupling with the
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7 phosphorus atoms. Single crystals of **11** were obtained from acetone-CH₂Cl₂, and its X-ray
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9 structure is illustrated in Figure 1.

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13 When compound **11** was stirred with silver acetate in CDCl₃ overnight, the NMR spectra of the
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15 resulting solution (some residual solid was filtered away) indicated nearly complete conversion to
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17 the silver complex **12**. Most significant is the ³¹P NMR spectrum of the complex, in which very
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19 strong silver-phosphorus coupling is observed [*J*_{AgP} = 482 Hz (¹⁰⁷Ag), 556 Hz (¹⁰⁹Ag)]. The
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21 MALDI-TOF mass spectrum shows a clean molecular ion for the cationic portion of the silver
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23 complex (the acetate counterion is not observed). Many unsuccessful attempts were made to
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25 crystallize complex **12**, but, at last, concentration of a solution in MTBE-CDCl₃ gave satisfactory
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27 crystals. The structure of the complex is also illustrated in Figure 1.

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32 **Figure 1.** Molecular structures of bis(phosphine) **11** (left) and its silver(I) complex **12** (right).
33 Thermal ellipsoids are drawn at the 50% probability level.
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Although compounds **11** and **12** are very similar in shape, from a crystallographic perspective they could hardly be more different. Bis(phosphine) **11** crystallized on a general position in the common monoclinic space group $P2_1/n$ (No. 14). The molecule adopts a conformation of approximate C_{3h} symmetry, and the structure refined without problems to an excellent conventional $R(F) = 0.027$. In contrast, complex **12** crystallized on a special position in the hexagonal space group $P6/m$ (No. 175). In this case, the cationic complex possesses crystallographic C_{3h} symmetry and is well ordered, but the attendant acetate ion and included solvent is highly disordered and compromises the quality of the overall structure. The anion and solvent density was removed by the SQUEEZE/BYPASS procedure,¹² and the structure refined to an acceptable $R(F) = 0.097$.

Only slight distortions are required for the ligand **11** to accommodate the silver ion in complex **12**. In the free ligand, the phosphorus-phosphorus distance is 4.99 Å; in the complex this is reduced slightly to 4.92 Å, and thus the Ag-P bond distances are 2.46 Å each. The sulfur atoms in the bridging thioether chains appear to have only minimal interactions with the silver ion, even though the X-ray software draws three Ag-S “bonds” (see Figure 1). The silver-sulfur distances are 2.92 Å, 0.46 Å longer than the Ag-P bonds, and somewhat greater than the sum of the ionic radius of Ag^+ (0.81 Å¹³) and the van der Waals radius of S (1.80 Å¹⁴). Thus complex **12** is best regarded, electronically at least, as a conventional, linear, divalent Ag(I) complex. However, it must be noted that the flipping of the side chains, a process evident in the ¹H NMR spectrum of **11**, is not observed in spectra of the silver complex **12**, and may reflect a degree of coordination of the silver ion by the sulfur atoms.

2.2. Synthesis and Structure of *in,in*-Cyclophanes **16** and **17**.

Treatment of tris[2-(methoxymethyl)phenyl]silane¹⁵ (**13**) with BCl_3 gave tris[2-(chloromethyl)phenyl]silanol (**14**) in 32% yield. In fact, we have used exactly the same procedure to prepare

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5 tris[2-(chloromethyl)phenyl]silane in 17% yield;² the silanol is the major product, the silane the
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7 minor. This material might have been used immediately to prepare a cyclophane containing an
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9 *in*-hydroxyl, but we were more interested in the possible magnetic interactions of an *in*-fluorine
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11 with an opposing phosphorus atom, and previous attempts to prepare similar *in*-hydroxy
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13 cyclophanes had been frustrated by the intramolecular reaction of the hydroxyl with adjacent
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15 chloromethyl groups to give five-membered rings.¹⁶ For this reason, silanol **14** was treated with
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17 BF₃ etherate to give the fluorosilane **15** in 55% yield, and then a solution of trichloride **15** and
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19 trimercaptophosphine **10**, each at a concentration of 1 mM in 2:1 benzene-EtOH at reflux, was
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21 treated with KOH. The cyclophane fraction was isolated by repeated silica gel chromatography
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23 in a meager 1% yield.
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28 Spectroscopic analysis soon showed that this material was a mixture of the *in*-hydroxy and
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30 *in*-fluoro cyclophanes **16** and **17**, respectively. This is most clearly evident in the ¹H-decoupled
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32 ³¹P NMR spectrum of **16/17**: compound **16** is represented by a singlet at δ -37.5, but **17** yields a
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34 doublet at δ -40.3 with *J*_{FP} = 112 Hz, a very strong through-space coupling constant. NMR
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36 integration indicated a 4:1 mixture of **16** and **17**, and MS analysis showed a 2:1 mixture (assuming
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38 an equal propensity for ionization, which is unlikely).
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43 At first we believed that the hydroxide base had displaced some of the fluoride during the
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45 macrocyclization, but, because our samples of fluorosilane **15** were contaminated with a few
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47 percent of hydroxysilane **14** (compare the ¹H and ¹³C NMR spectra of compounds **14** and **15** in the
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49 Supplementary Data), it was conceivable that the *in*-hydroxy compound **16** arose from the
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51 contaminant **14**. This latter possibility was confirmed by the base-promoted reaction of
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53 phosphine **10** and hydroxysilane **14**, which gave pure **16** in the much more respectable (for a
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55 macrocyclization) 14% yield.
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Thus it seems that compound **16** is formed significantly more easily than **17**, even though the *in*-fluorine of the latter macrocycle is sterically less demanding. We speculate that hydrogen bonding between the hydroxyl group and the phosphine and/or the thiolate anion in a partially cyclized macrocycle (e.g., **18**) may facilitate the final ring closure, but the interaction of a fluorine atom with the lone pair electrons of a phosphine or thiolate at the same stage is purely repulsive. There is no doubt that the phosphine and hydroxyl group interact in compound **16**: in its ^1H NMR spectrum, the hydroxyl proton is visible as a doublet ($J_{\text{PH}} = 4 \text{ Hz}$) at δ 6.50.

Satisfactory crystals of these compounds were difficult to obtain, but eventually single crystals of the **16/17** mixture were obtained from CHCl_3 solution, and the molecular structure of **17** is illustrated in Figure 2. This material crystallized in the hexagonal space group $P \bar{6}2c$ (No. 190), with two independent molecules in the structure, each located on a special position with crystallographic C_{3h} symmetry. Unfortunately, since **16** and **17** are at most C_3 symmetric, this means that the resulting structure is disordered end-to-end, with the silicon and phosphorus atoms indistinguishable; furthermore, there is the occupational disorder resulting from the presence of both *in*-hydroxysilane **16** and *in*-fluorosilane **17**. However, because the two molecules are so similar in shape, and the two ends of the molecules are so much alike, the disorder is relatively easily modeled, and the structure refined to a very reasonable $R(F) = 0.079$. Nevertheless, the bond distances and angles in this structure cannot possibly be as accurate as those from a well-ordered structure.

Figure 2. Molecular structure of cyclophane mixture **16/17**. One of the two independent molecules is illustrated (molecule 2), only one orientation of the disordered structure is illustrated, and the *in*-atom is illustrated as a fluorine atom, although both fluorine and oxygen are present. Thermal ellipsoids are drawn at the 50% probability level.

For this reason, we examined the structures of compounds **16** and **17** with HDFT calculations. The structures of **16** and **17** were optimized at the B3LYP/6-311++G(2df,2pd) level of theory, and calculations of their NMR spectra, including selected coupling constants, were performed at the same level. (The large basis set is recommended in order to give accurate through-space coupling constants.^{4,17}) As noted above, the X-ray structure contains two independent molecules of **16/17**; molecule 1 is somewhat compressed when compared to the HDFT-calculated geometries, but molecule 2 (illustrated in Figure 2) very closely resembles the calculated structures. The salient geometric parameters for the experimental and calculated structures are found in Table 1. When comparing these data it must be born in mind that the Si-OH and Si-F bond distances were fixed at 1.600 Å and 1.645 Å in the X-ray refinement, and that the experimental Si...P distance reflects contributions from both **16** and **17**.

Table 1. Experimental and Calculated Atom-Atom Distances for Compounds **16** and **17**.

Method	16			17		
	Si-O (Å)	P...O (Å)	Si...P (Å)	Si-F (Å)	P...F (Å)	Si...P (Å)
X-ray molecule 1	1.645 ^a	3.207	4.851	1.600 ^a	3.251	4.851
X-ray molecule 2	1.645 ^a	3.540	5.185	1.600 ^a	3.585	5.185
B3LYP/6-311++G(2df,2pd)	1.641	3.532	5.168	1.613	3.631	5.244

^a Distance was fixed at the indicated value in the X-ray refinement.

The phosphorus-oxygen and phosphorus-fluorine non-bonded contact distances differ by more than 0.3 Å in the experimental structures, with the calculated values more closely resembling the longer distance in molecule 2. We have previously observed that the B3LYP functional overestimates cyclophane non-bonded contact distances,¹⁸ but this is a relatively small effect in comparison to the seemingly very large effect of crystal packing forces on these molecules. The sum of the van der Waals radii of phosphorus and oxygen is 3.35 Å and that of phosphorus and fluorine is 3.35-3.45 Å,¹⁴ so that in molecule 1 the two atoms are perhaps slightly compressed, while in molecule 2 and the calculated geometries they are barely touching.

The through-space coupling of the fluorine and phosphorus atoms in **17** is calculated to be 104 Hz at the B3LYP/6-311++G(2df,2pd) level, in excellent agreement with the experimental $J_{\text{FP}} = 112$ Hz. The experimental value is one of the largest reported through-space ^{19}F - ^{31}P coupling constants. Three larger examples are known: 184 Hz,¹⁹ 144 Hz, and 130 Hz;^{20,21} however, all three are found in 1,8-disubstituted naphthalene derivatives where the F and P atoms are separated by only four bonds. In the present case, the two atoms are separated by *nine* bonds, so that there is really no possibility of an ordinary through-bond coupling mechanism.

3. Conclusion

The *in,in*-cyclophanes described herein are large enough to contain a non-hydrogen atom in their central cavities, yet small enough that the internal atoms must interact with both ends of the cyclophane. The silver complex **12** is an unusual transition metal complex, given that the silver ion is entirely enclosed by a hydrophobic macrocycle, but it does not display any extraordinary properties. It is likely that other metals can be encapsulated by bisphosphine **11**, but thus far we have been unable to form even the corresponding gold complex. The purely organic atom encapsulations, compounds **16** and **17**, are extremely rare examples of cyclophanes with *in*-non-hydrogen atoms. The pendant internal hydroxyl group and fluorine atom are pressed against the inwardly directed, opposing phosphine lone pair, and the F $\cdots$ P interaction is close enough to result in a very large through-space coupling constant. It is unknown whether even larger *in*-atoms can be enclosed in the same way.

4. Experimental

4.1. General

Tris[2-(chloromethyl)phenyl]phosphine¹¹ and tris[2-(methoxymethyl)phenyl]silane¹⁵ were prepared as described previously. All other solvents and reagents were commercial, reagent grade materials, and they were used without further purification. ¹H NMR spectra were recorded at 300 MHz on a Bruker AVANCE 300 spectrometer, at 400 MHz on a Varian Unity INOVA 400 spectrometer, and at 500 MHz on a Bruker AVANCE 500 spectrometer. ¹³C NMR spectra were recorded at 75 MHz, 101 MHz, and 126 MHz, respectively, on the same instruments. ³¹P NMR spectra were recorded on Varian Unity INOVA spectrometer at 161 MHz. Samples were dissolved in CDCl₃. MALDI-TOF mass spectra were recorded on a Bruker Autoflex III spectrometer, and high-resolution ESI-TOF mass spectra were recorded on an Agilent 6220 spectrometer.

4.2. Data for compounds

4.2.1. Tris[2-(mercaptomethyl)phenyl]phosphine (10). A solution of tris[2-(chloromethyl)phenyl]phosphine (**9**, 408 mg, 1.00 mmol) and thiourea (228 mg, 3.00 mmol) in EtOH (10 mL) was heated at reflux overnight. After cooling, the solvent was removed, and KOH (385 mg) in water (15 mL) was added to the remaining white salt under argon. This solution was heated at reflux for 5 h, cooled to room temperature, acidified with 1 N HCl, and extracted three times with CH₂Cl₂. The combined extracts were dried over Na₂SO₄ and concentrated in vacuo to give the desired trithiol **1** (386 mg, 0.964 mmol, 96%). ¹H NMR (CDCl₃) δ 2.01 (td, *J* = 8 Hz, 2 Hz, 3 H), 3.92 (dd, *J* = 8 Hz, 1 Hz, 6 H), 6.83 (ddd, *J* = 7.5 Hz, 4.5 Hz, 1 Hz, 3 H), 7.16 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1 Hz, 3 H), 7.36 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1 Hz, 3 H), 7.42 (m, 3 H); ¹³C NMR (CDCl₃) δ 28.2 (d, *J*_{PC} = 25 Hz), 127.8, 129.9 (d, *J*_{PC} = 6 Hz), 130.2, 133.5 (d, *J*_{PC} = 10 Hz), 134.6, 146.1 (d, *J*_{PC} =

25 Hz) (7 of 7 expected resonances); HRMS (ESI) 401.0616 (M + H), calcd for C₂₁H₂₂PS₃ 401.0621.

4.2.2. *in, in*-Bis(phosphine) 11. Tris[2-(chloromethyl)phenyl]phosphine (**9**, 383 mg, 0.939 mmol) and tris[2-(mercaptomethyl)phenyl]phosphine (**10**, 376 mg, 0.939 mmol) were mixed in 2:1 benzene-ethanol (900 mL), and the solution was heated to reflux under argon. An argon-saturated solution of KOH (253 mg, 4.5 mmol) in ethanol (50 mL) was added slowly over 3 h. After 16 h, the solution was cooled, and the solvent was evaporated under reduced pressure to leave a white solid. The solid was extracted twice with chloroform, and the combined extracts were concentrated to yield a light yellow liquid. This material was chromatographed on silica gel (solvent, 1:1 hexanes-benzene) to give compound **11** as a white solid (144 mg, 0.206 mmol, 22%). A portion of this material was purified further by preparative silica gel TLC (solvent, 1:1 hexanes-benzene), and the resulting solid was recrystallized from acetone-CH₂Cl₂ to give single crystals of **11** suitable for X-ray analysis. ¹H NMR (CDCl₃) δ 3.4-4.8 (br, 12 H), 6.78 (dd, *J* = 7.5 Hz, 1 Hz, 6 H), 7.14 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1 Hz, 6 H), 7.28 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1 Hz, 6 H), 7.37 (m, 6 H); ¹³C NMR (CDCl₃) δ 38.0 (m; AA' component of AA'XX' system, where the X's are ³¹P nuclei), 127.9, 129.4, 130.5, 134.7, 136.2 (m; as above), 142.0 (m; as above) (7 of 7 expected resonances); HRMS (ESI) 699.1522 (M + H), calcd for C₄₂H₃₇P₂S₃ 699.1532.

4.2.3. Ag(I)•11 Acetate (12). Silver acetate (1.0 mg, 6.0 μmol) was added to a solution of compound **11** (2.0 mg, 2.9 μmol) in CDCl₃ (1 mL). The solution was stirred at room temperature for 16 h. Residual solid was filtered away, and the filtrate was mixed with *tert*-butyl methyl ether. Slow concentration of the solution gave compound **12** as crystals (*ca.* 2 mg) suitable for X-ray analysis. ¹H NMR (CDCl₃) δ 2.23 (s, 3 H), 4.17 (d, *J* = 10.5 Hz, 6 H), 4.24 (d, *J* = 10.5 Hz, 6 H), 6.75 (m, 6 H), 7.33 (m, 6 H), 7.56 (m, 12 H); ¹³C NMR (CDCl₃) δ 29.7, 39.2 (m; AA' component of AA'XX' system, where the X's are ³¹P nuclei), 129.7, 132.7, 132.8, 134.4 (6 of 9 expected resonances; the two quaternary carbons of **12** and the acetate carbonyl are invisible; in addition,

the resonances at δ 129.7, 132.8, and 134.4 are clearly broadened due to unresolved long-range coupling to P and Ag); ^{31}P NMR (CDCl_3) δ -28.9 (dd, $J_{\text{AgP}} = 556$ Hz [^{109}Ag coupling]), $J_{\text{AgP}} = 482$ Hz [^{107}Ag]); MS (MALDI-TOF) m/z 805 ($\mathbf{11} \cdot ^{107}\text{Ag}^+$, 82), 807 ($\mathbf{11} \cdot ^{109}\text{Ag}^+$, 100).

4.2.4. Tris[2-(chloromethyl)phenyl]silanol (14). Boron trichloride (1 *M* in heptane, 100 mL, 100 mmol) was added to tris[2-(methoxymethyl)phenyl]silane (**13**, 1.76 g, 4.49 mmol) in a round bottom flask under argon. The mixture was stirred at room temperature for 2 h and then heated at reflux for 3 h. After cooling to room temperature, CHCl_3 and water were added. The organic layer was separated, and the aqueous phase was extracted again with CHCl_3 . The combined extracts were dried over Na_2SO_4 and concentrated to dryness. The resulting white solid was chromatographed on silica gel (solvent, 3:1 CHCl_3 -hexanes) to give compound **14** as a white solid (616 mg, 1.46 mmol, 32%). ^1H NMR (CDCl_3) δ 3.90 (br, 1 H), 4.72 (s, 6 H), 7.27 (m, 6 H), 7.50 (m, 3 H), 7.56 (d, $J = 7.5$ Hz, 3 H); ^{13}C NMR (CDCl_3) δ 47.1, 128.2, 131.0, 131.5, 134.4, 137.0, 143.9 (7 of 7 expected resonances); HRMS (ESI) 443.0179 ($\text{M} + \text{Na}$), calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_3\text{NaOSi}$ 443.0168.

4.2.5. Tris[2-(chloromethyl)phenyl]fluorosilane (15). Tris[2-(chloromethyl)phenyl]silanol (**14**, 1.05 g, 2.49 mmol) was dissolved in CH_2Cl_2 (50 mL), BF_3 etherate (3 mL) was added dropwise, and the solution was stirred at room temperature overnight. The resulting material was chromatographed on silica gel (solvent, 3:1 CHCl_3 -hexanes) to give compound **15** as a white solid (585 mg, 1.38 mmol, 55%). ^1H NMR (CDCl_3) δ 4.64 (s, 6 H), 7.34 (m, 6 H), 7.57 (ddd, $J = 7$ Hz, 7 Hz, 2 Hz, 3 H), 7.63 (d, $J = 7.5$ Hz, 3 H); ^{13}C NMR (CDCl_3) δ 46.2 (d, $J_{\text{FC}} = 3$ Hz), 128.1, 130.7, 131.3 (d, $J_{\text{FC}} = 16$ Hz), 132.3, 136.9 (d, $J_{\text{FC}} = 4$ Hz), 144.1 (7 of 7 expected resonances); HRMS (ESI) 445.0123 ($\text{M} + \text{Na}$), calcd for $\text{C}_{21}\text{H}_{18}\text{Cl}_3\text{FNaSi}$ 445.0125.

4.2.6. *in*-Hydroxysilane-*in*-phosphine 16. Tris[2-(chloromethyl)phenyl]hydroxysilane (**14**, 166 mg, 0.375 mmol) and tris[2-(mercaptomethyl)phenyl]phosphine (**10**, 150 mg, 0.374 mmol) were

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5 mixed in 2:1 benzene-ethanol (315 mL), and the resulting solution was heated to reflux under
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7 argon. An argon-saturated solution of KOH (90 mg) in ethanol (40 mL) was added slowly over 3
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9 h. After 26 h, the solution was cooled, and the solvent was removed under reduced pressure.
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11 The residue was extracted twice with hot CHCl₃, and the combined extracts were concentrated and
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13 chromatographed on a silica gel column (solvent, 3:2 hexanes-benzene). Concentrations of the
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15 appropriate fractions gave pure cyclophane **16** (38 mg, 0.053 mmol, 14%). ¹H NMR (CDCl₃) δ
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17 3.90 (br, 3 H), 4.14 (br, 6 H), 4.59 (br, 3 H), 6.50 (d, *J* = 4 Hz, 1 H), 6.75 (ddd, *J* = 7.5 Hz, 4 Hz, 1
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19 Hz, 3 H), 7.98 (dt, *J* = 7 Hz, 1 Hz, 3 H), 7.13 (m, 6 H), 7.32 (dd, *J* = 7.5 Hz, 1 Hz, 3 H), 7.38 (m, 12
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21 H); ¹³C NMR (CDCl₃) δ 37.8 (d, *J*_{PC} = 26 Hz), 40.3, 126.4, 127.7, 129.4, 130.2, 130.4, 130.7 (d,
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23 *J*_{PC} = 5 Hz), 134.3 (d, *J*_{PC} = 11 Hz), 134.7, 135.7, 136.7, 141.6 (d, *J*_{PC} = 28 Hz), 143.8 (14 of 14
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25 expected resonances). HRMS (ESI) 713.1588 (M + H), calcd for C₄₂H₃₈OPS₃Si 713.1592.
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33 Tris[2-(chloromethyl)phenyl]fluorosilane (**15**, 170 mg, 0.401 mmol) and tris[2-(mercapto-
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35 methyl)phenyl]phosphine (**10**, 160 mg, 0.399 mmol) were mixed in 2:1 benzene-ethanol (360 mL),
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37 and the resulting solution was heated to reflux under argon. An argon-saturated solution of KOH
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39 (74 mg) in ethanol (50 mL) was added slowly over 5 h. After 16 h, the solution was cooled, and
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41 the solvent was removed under reduced pressure to leave a yellow solid. This solid was extracted
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43 twice with CHCl₃, and the combined extracts were concentrated to give a light yellow liquid.
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45 This material was chromatographed on silica gel (solvent, 1:1 hexanes-benzene), and the fractions
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47 containing compounds **16** and **17** were combined and further purified by preparative silica gel
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49 TLC (solvent, 1:1 hexanes-benzene) to give the inseparable **16/17** mixture as a white solid (3 mg,
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51 0.004 mmol, 1%). Evaporation of a CHCl₃ solution gave crystals suitable for X-ray analysis.
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53 NMR analysis showed that the sample was predominantly compound **16** (NMR integration gives
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55 *ca.* 4:1 **16:17**) and the reported ¹H and ¹³C NMR spectra are those of **16**. Subspectra for **17** were
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57 partly observed in the ¹H NMR spectrum and invisible in the ¹³C NMR spectrum. ¹H NMR
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59 (CDCl₃) δ 3.89 (br, 3 H), 4.13 (br, 6 H), 4.56 (br, 3 H), 6.48 (d, *J* = 4 Hz, 1 H), 6.73 (ddd, *J* = 7.5 Hz,
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4 Hz, 1 Hz, 3 H), 7.96 (d, $J = 7$ Hz, 3 H), 7.12 (m, 6 H), 7.30 (dd, $J = 7.5$ Hz, 1 Hz, 3 H), 7.38 (m, 12 H); ^{13}C NMR (CDCl_3) δ 38.0 (d, $J_{\text{PC}} = 26$ Hz), 40.6, 126.6, 128.0, 129.7, 130.5, 130.6, 130.9 (d, $J_{\text{PC}} = 5$ Hz), 134.6 (d, $J_{\text{PC}} = 11$ Hz), 134.9, 135.9, 137.0, 141.9 (d, $J_{\text{PC}} = 28$ Hz), 144.0 (14 of 14 expected resonances). ^{31}P NMR and mass spectral analysis showed distinct spectra for compounds **16** and **17**. For **16**: ^{31}P NMR (CDCl_3) δ -37.5; HRMS (ESI) 713.1615 ($\text{M} + \text{H}$), calcd for $\text{C}_{42}\text{H}_{38}\text{OPS}_3\text{Si}$ 713.1592. For **17**: ^{31}P NMR (CDCl_3) δ -40.3 (d, $J_{\text{FP}} = 112$ Hz); HRMS (ESI) 715.1629 ($\text{M} + \text{H}$), calcd for $\text{C}_{42}\text{H}_{37}\text{FPS}_3\text{Si}$ 715.1548.

4.3. Computational Methodology

Quantum calculations were performed using Gaussian 09,²² and its built-in default parameters for integral accuracy, and wave function and gradient convergence were employed. The B3LYP and B3PW91 functionals²³⁻²⁵ with the 6-311++G(2df,2pd) basis set²⁶ were employed for calculations in this study. Full geometry optimizations were performed at the specified level of theory, and NMR spectral data were calculated at the same level as the optimizations by using the GIAO method [keywords NMR=(SPINSPIN,MIXED)].

Acknowledgment

This work was supported by National Science Foundation Grant CHE-1265507, which is gratefully acknowledged. The X-ray diffractometer used in this work was purchased with funds from National Science Foundation Grant MRI-1228232.

Supplementary Data

(1) ^1H and ^{13}C NMR spectra of compounds **10**, **11**, **12**, **14**, **15**, **16**, and **16/17**; ^{31}P NMR spectra of compounds **12** and **16/17**; atomic coordinates of the HDFT-calculated structures of compounds **16**

and **17.** (2) Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1503001-1503003. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Figure(s)

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