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in-Cyclophanes Containing Second-Row Elements Poised above Aromatic Rings

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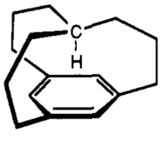
Abstract: The silicon- and phosphorus-containing cyclophanes **2** and **3** were prepared by base-promoted condensation of tris(2-mercaptophenyl)silane and tris(2-mercaptophenyl)phosphine, respectively, with 1,3,5-tris(bromomethyl)benzene. The structures of both cyclophanes were determined by X-ray crystallography. In compound **2**, the distance from the apical silicon to the center of the basal aromatic ring was 3.34 Å, and in **3** the corresponding phosphorus to ring distance was 2.90 Å. The ^{1}H NMR spectrum of **2** was characterized by a high-field Si-H resonance (δ 1.04, 5 ppm upfield from the corresponding resonance in an acyclic model), and the IR spectrum showed a high-frequency Si-H stretching band (2457 cm^{-1}, 280 cm^{-1} above the acyclic model); both features result from the proximity of the *in*-hydrosilane to the aromatic ring. For cyclophane **3**, the ^{13}C NMR spectrum exhibited "through-space" spin-spin coupling of the phosphorus atom with the carbons of the basal aromatic ring ($J_{\mathrm{PC(methine)}}$ = 7.5 Hz and $J_{\mathrm{PC(quaternary)}}$ = 3.5 Hz) and in the ^{31}P NMR spectrum the phosphorus resonance was 32 ppm downfield from that of an acyclic model, both features suggesting an unusual electronic interaction of the phosphine with the base. Due to a strong preference for an *in* geometry (pyramidalization of the phosphine toward the basal ring) and the consequent steric shielding, the phosphine of **3** was quite unreactive: It was not protonated by anhydrous HBr, and even when **3** was heated in refluxing hydrogen peroxide and acetic acid, the corresponding trisulfone was obtained without formation of the phosphine oxide.

The study of functional group interactions resulting from enforced mutual proximity is a major theme of cyclophane chemistry. Our prior investigations of *in*-cyclophanes were confined to compounds (e.g., **1**) containing alkane CH groups projected toward the centers of aromatic rings.[1-3] However, in these molecules there is no evidence of any electronic interaction between the methine hydrogens and the aromatic carbons, despite interatomic distances much less than the sum of their van der Waals radii, and the most unusual features of such cyclophanes are exotic infrared and NMR bands, which are the direct result of steric compression and aromatic ring current effects, respectively.[2,3] We speculated that the incorporation of second-row elements, with their greater polarizability and the presence of potentially accessible d orbitals, into the apical functional groups of *in*-cyclophanes might give rise to more interesting electronic and structural effects. We now report the syntheses of the *in*-cyclophanes **2** and **3** and the structural, spectroscopic, and chemical consequences of the enforced interaction of hydrosilanes and phosphines with aromatic rings.[4]



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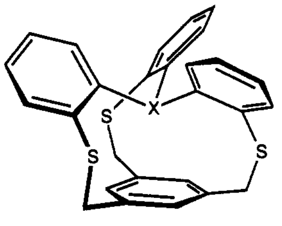
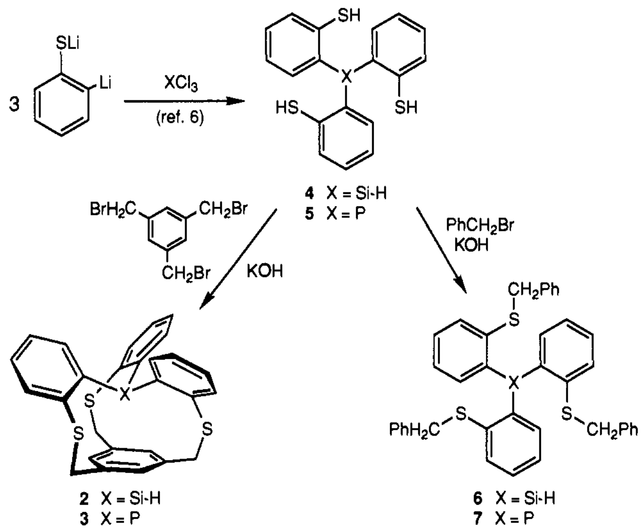


2 X = Si-H
3 X = P

Results and Discussion

Syntheses of Cyclophanes. The preparation of cyclophanes **2** and **3** was greatly simplified by recent findings from the research groups of Martin,[5] Block,[6] and Smith,[7] who have demonstrated the synthetic utility of doubly lithiated thiophenols in a variety of systems. Of specific interest to us were the syntheses of a host of (*o*-mercaptoaryl)silicon[6a,7] and (*o*-mercaptoaryl)phosphorus[6b] compounds, and we used this methodology to prepare tris(2-mercaptophenyl)silane (**4**) and tris(2-mercaptophenyl)phosphine (**5**) directly from trichlorosilane and phosphorus trichloride, respectively (Scheme I).

Scheme I



The desired cyclophanes **2** and **3** were prepared from **4** and **5**, respectively, by base-promoted condensation with 1,3,5-tris(bromomethyl)benzene[8] under conditions of high dilution (2.8 mM) in refluxing 2:1 benzene-ethanol. The silaphane **2** was formed in low yield (1.1% and 0.5% in two independent runs), but the yield of phosphaphane **3** under the same conditions was sub-

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(1) Pascal, R. A., Jr.; Grossman, R. B. *J. Org. Chem.* **1987**, *52*, 4616.

(2) Pascal, R. A., Jr.; Grossman, R. B.; Van Engen, D. *J. Am. Chem. Soc.* **1987**, *109*, 6878-6880.

(3) Pascal, R. A., Jr.; Winans, C. G.; Van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 3007-3010.

(4) A portion of this work has been reported previously in a preliminary communication: Pascal, R. A., Jr.; West, A. P., Jr.; Van Engen, D. *J. Am. Chem. Soc.* **1990**, *112*, 6406-6407.

(5) Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 654-658.

(6) (a) Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 658-665. (b) Block, E.; Ofori-Okai, G.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 2327-2329.

(7) Smith, K.; Lindsay, C. M.; Pritchard, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 665-669.

(8) Vogtle, F.; Zuber, M.; Lichtenthaler, R. G. *Chem. Ber.* **1973**, *106*, 717-718.

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stantially higher (12% and 15%). The lower yield of the silaphane no doubt results from the extra energy of activation required in the final ring closure to overcome the steric hindrance provided by the *in*-hydrogen (compared with the phosphaphane's lone pair of electrons). Fortunately, the isolation of the relatively soluble, nonpolar cyclophanes from the mostly polymeric byproducts of the cyclization reactions was a simple matter. In order to compare the properties of these cyclophanes with those of nonmacrocyclic model compounds containing similar functional groups, we also synthesized the tris[2-(benzylthio)phenyl]element compounds **6** and **7** by condensation of **4** and **5**, respectively, with benzyl bromide.

Spectroscopic Properties of Silaphane 2. The unusual aspects of the ^{1}H NMR, infrared, and ultraviolet spectra of compound **2** are qualitatively similar to those observed for the "CH" *in*-cyclophanes that we have previously described,[2,3] but these features are highlighted by comparing them briefly with the spectra of the nonmacrocyclic model **6**. In the ^{1}H NMR of **2**, the *in*-hydrogen resonance is found at δ 1.04, more than 5 ppm upfield from the δ 6.13 resonance for the SiH of model **6**, as is to be expected for a proton poised directly above an aromatic ring. The IR spectrum of the model compound shows a fairly broad, medium-strength band at 2177 cm^{-1} due to the Si–H stretching vibration, but in the spectrum of cyclophane **2** only a weak 2457-cm^{-1} band is observed. This hypsochromic shift of 280 cm^{-1} is due to steric compression of the *in*-hydrosilane, and the magnitude of the shift is similar to the 200–400-cm^{-1} frequency enhancements observed for the C–H stretching bands of other *in*-cyclophanes.[2,3] In the UV spectra, the absorption bands for compounds **2** and **6** fall at 286 and 271 nm, respectively. The bathochromic shift for the cyclophane is believed to be due to the bending of the aromatic rings, and such shifts have been frequently observed in small meta- and paracyclophanes.[9]

Spectroscopic Properties of Phosphaphane 3. The NMR spectra of cyclophane **3** indicate an unexpectedly strong electronic interaction between the phosphine and the basal aromatic ring. The proton-decoupled ^{13}C NMR spectrum of **3** provides the first indication of this unusual state of affairs: *All* of the aromatic carbon resonances are doublets, thus demonstrating spin–spin coupling between the phosphorus and the carbons of the basal aromatic ring. The basal-ring methine carbon resonance of **3** was unambiguously assigned (δ 130.0) by means of a ^{1}H–^{13}C heteroscalar correlated 2D NMR experiment, and the basal-ring quaternary carbon was identified (δ 144.66) by selective irradiation of the proton resonances of the adjacent methylene group in the proton-coupled ^{13}C NMR spectrum. For these assignments, the ^{31}P–^{13}C coupling constants are known: 7.5 Hz (basal methine) and 3.5 Hz (basal quaternary). Thus, the phosphorus is more strongly coupled to the basal methine carbons than it is to most of the carbons in the aryl groups of the triarylphosphine (J_{CP} = 40, 22, 4.5, 2, 1.5, and 1 Hz). Furthermore, the coupling to the basal ring is unlikely to result from normal through-bond interactions (five and six bonds) for the reason that no coupling is observed between the phosphorus and the bridging methylene carbons.

Such "through-space" coupling is unprecedented for phosphorus, but fluorine is known to couple to other fluorine,[10,11] and nitrogen[12] atoms via nonbonded interactions. In a recent and relevant example, spin–spin coupling between remote fluorines was found to be enhanced by nonbonded contacts to an intervening aromatic ring;[13] unfortunately, the carbon–fluorine coupling in these materials was not reported. In any event, the ^{31}P–^{13}C spin–spin coupling in **3** must result from a mixing of orbitals on the phosphorus and the basal aromatic ring, and such phenomena are most easily interpreted by means of the theory employed by Mallory and co-workers for the various fluorine systems.[10,12,13] For the FCF system discussed in ref 13, symmetry and orbital energy considerations led the authors to propose that mixing of two fluorine lone-pair orbitals with the π_1 orbital of a phenyl group gives rise to the observed coupling. In the case of phosphaphane **2**, symmetry considerations also lead us to suggest that the ^{31}P–^{13}C coupling results from mixing of the phosphorus lone pair with π_1 of the basal aromatic ring.

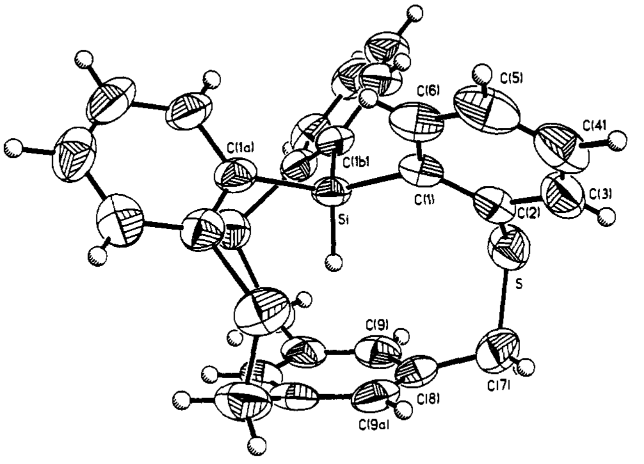

Figure 1. X-ray structure of compound **2**.

The ^{31}P NMR spectrum of compound **3** is also unusual. It shows a single peak at δ 5.0,[14] which is substantially downfield from the δ –26.7 resonance (lit.[6b] δ –26.4) of its precursor **5** or the δ –27.0 resonance of the nonmacrocyclic model compound **7**. In addition, the δ 5.0 resonance is further downfield than any of the resonances observed in a ^{31}P NMR study of 30 triarylphosphines.[15] The observed downfield shift, which is in the opposite direction from that which would result from simple ring-current effects, suggests a more phosphonium-like character for the phosphorus of **2**—typical methyltriarylphosphonium resonances fall in the range of δ 18–26.[16] Might there be net donation of phosphine electron density to the basal ring?

The UV spectra of phosphaphane **2** and model **7** are surprisingly different, and they are illustrated in Figure 3. The spectrum of the model (spectrum B) consists of a single maximum at 210 nm, which tails out to beyond 300 nm by virtue of several indistinct shoulder absorptions. The spectra of compound **2** (spectra A and C) show four distinct absorption bands, with the lowest energy band at 340 nm falling just short of making the cyclophane a colored compound. Our first thought was that the 340-nm feature represented some sort of phosphorus to arene charge-transfer band, but our enthusiasm for this interpretation was dampened by the finding that the absorption maximum scarcely changes with solvent polarity: heptane, 338 nm; chloroform, 341 nm; 2:1 ethanol–chloroform, 340 nm. On the other hand, the long-wave transitions[17] in the UV spectra of triarylphosphines are bathochromically shifted by ortho substitution of the arenes, and this phenomenon is known to be a steric effect on the electronic structure (para substituents of the same sort have no effect on the spectra).[18] The

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[9] Rosenfeld, S. M.; Cho, K. A. [n]Cyclophanes. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vol. 1, p 339 and references cited therein.

[10] Mallory, F. B. *J. Am. Chem. Soc.* **1973**, *95*, 7747–7752 and references cited therein.

[11] Mallory, F. B.; Mallory, C. W.; Ricker, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 4770–4771 and references cited therein.

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[13] Mallory, F. B.; Mallory, C. W.; Baker, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 2577–2581.

[14] All ^{31}P NMR chemical shifts were referenced to an external standard of (CH$_3$O)$_3$P at δ 140.

[15] Grim, S. O.; Yankowsky, A. W. *Phosphorus Sulfur Relat. Elem.* **1977**, *3*, 191–195.

[16] Grim, S. O.; Yankowsky, A. W. *J. Org. Chem.* **1977**, *42*, 1236–1239.

[17] There has been some debate as to whether the strong long-wave band of arylphosphines is best characterized as an n $\rightarrow \pi^*$ or a $\pi \rightarrow \pi^*$ transition. Whatever the description, the unshared pair of electrons on phosphorus is clearly involved. See ref 18b and references cited therein for a discussion of this matter.

[18] (a) Bokanov, A. I.; Rozanel'skaya, N. A.; Stepanov, B. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1974**, *44*, 732–735. (b) Ratovskii, G. V.; Panov, A. M.; Yakutina, O. A.; Sukhorukov, Y. I.; Tsvetkov, E. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1978**, *48*, 1394–1401.

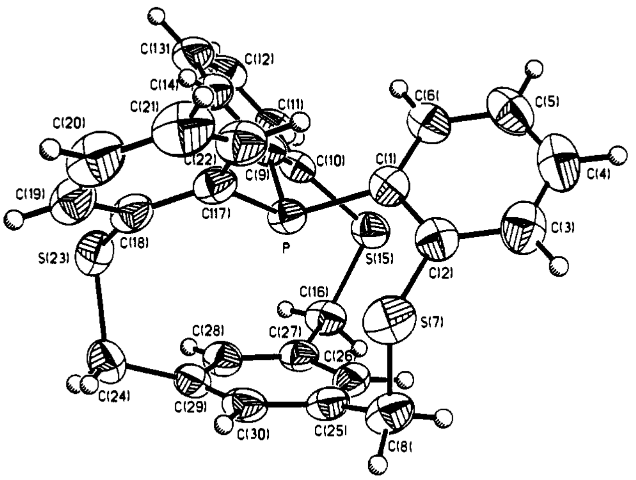


Figure 2. X-ray structure of compound **3**.

observed spectrum of **2**, where the phosphine is not only ortho substituted but also even more conformationally restricted by incorporation into a cyclophane, may represent an extreme example of this sort, but a definite assignment is not possible at this time.

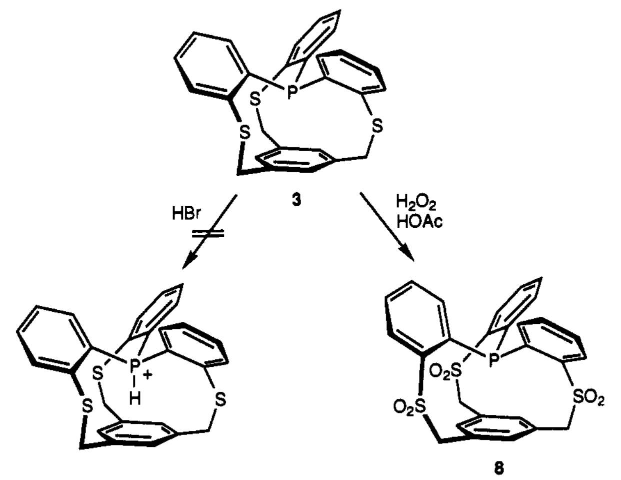
X-ray Crystal Structures of Cyclophanes 2 and **3**. Both cyclophanes yielded single crystals upon evaporation of solutions in chloroform-methanol. The X-ray crystal structures were determined without difficulty, and the molecular structures of **2** and **3** are illustrated in Figures 1 and 2, respectively.

Compound **2** crystallized in the trigonal space group $P\bar{3}$, and the molecule lies on a crystallographic 3-fold axis of symmetry. A casual inspection of the structure shows that the triarylsilane is substantially flattened from a regular tetrahedral geometry, with a C–Si–C bond angle of 112.2° and a C–Si–H angle of 106.5°. However, these angles are not very different from those found in the structure of triphenylsilane itself (average C–Si–C angle 111.0°; average C–Si–H angle 107.9°)[19] and thus do not provide much evidence of strain. Similarly, the basal aromatic ring is only slightly distorted from a normal geometry; the deviation from planarity is less than 0.03 Å. Most of the distortion from an ideal geometry is found in the three linking arms, where the carbons α to the basal aromatic ring are fully 0.39 Å above the ring mean plane and the bond angles about the linking carbon and sulfur atoms are somewhat opened from the normal values. The distance from the silicon to the centroid of the basal aromatic ring is 3.34 Å and from the *in*-hydrogen to the ring is 2.06 Å. However, the latter value reflects the Si–H bond length of 1.29 Å used in the crystallographic model, which is surely an underestimate.[20] A more reasonable Si–H bond length of 1.48 Å[21] would place the hydrogen 1.86 Å from the aromatic ring.

Phosphaphane **3** crystallized in the common monoclinic space group $P2_1/c$, and the molecule resides at a general position. Most aspects of the structure are similar to those of **2**, but the triarylphosphine of **3** is much more strongly pyramidalized than the triarylsilane in **2**. This is to be expected: The average C–P–C bond angle in triphenylphosphine itself is 103.0°,[22] and the average C–P–C angle in **3** is only slightly widened to 104.9°. As a result of the greater pyramidalization of phosphorus and the absence of an obstructing *in*-hydrogen, the distance from the phosphorus to the basal aromatic ring is only 2.90 Å.

Molecular mechanics calculations (MMPI[23]) yield geometries for compounds **2** and **3** that are generally in good agreement with the X-ray structures. In both cases, however, the distance from the apical element to the center of the aromatic ring is somewhat overestimated; for **2**, the calculated distance is 3.43 Å, and for **3**, it is 3.07 Å.

Scheme II



Dynamic NMR Properties of Cyclophanes 2 and 3. The X-ray structures of **2** and **3** show that both molecules adopt chiral, propeller-like conformations, and in the ^{1}H NMR spectra of these compounds the diastereotopic benzylic protons give rise to clean, well-separated AB patterns, indicating that interconversion of the enantiomeric propellers is relatively slow. In the hope of estimating the barriers to enantiomerization, the compounds were heated in DMSO-d_6 solutions while their ^{1}H NMR spectra were recorded at 500 MHz. However, even at 180 °C the AB patterns remain, thus placing a lower limit on the free energy of activation for the enantiomerization of cyclophanes **2** and **3** of approximately 22 kcal/mol.[24] Indeed, the barrier is probably much higher than this, but a resolution of the enantiomers would be required in order to measure it.

Reactivity of Phosphaphane 3. It is difficult even to protonate the phosphorus of **3**. Typical triarylphosphines are protonated by anhydrous HBr in organic solvents, and the ^{31}P NMR resonances of the resulting hydrobromides are shifted substantially downfield.[16] We bubbled anhydrous HBr into deuteriochloroform solutions of cyclophane **3** and model **7**, left the compounds to stand in the fuming solutions overnight, and then recorded the ^{31}P{^{1}H} NMR spectra. The solution of **7**·HBr showed two broad (ca. 50-Hz) resonances at δ 40.5 (major) and δ 49.4 (minor), far downfield from the δ −27.0 resonance of untreated **7**. The presence of two resonances was due to the fact that the sample had undergone partial decomposition. When the sample was neutralized and subjected to chromatographic and ^{1}H NMR analysis, two components were observed: unchanged **7** (~30%) and an unknown decomposition product (~70%). In contrast, the spectrum of cyclophane **3** was essentially unchanged; only a sharp resonance at δ 2.5 was observed in the fuming solution, which is scarcely different from the δ 5.0 resonance observed in ordinary $CDCl_3$; certainly the phosphine of **3** remained (at least predominantly) unprotonated.

In view of the above results, it is perhaps not surprising that treatment of **3** with a 2:1 mixture of acetic acid and 30% hydrogen peroxide at reflux yields the trisulfone **8** (Scheme II); no phosphine oxide was detected (if formed, it would surely be the *out* isomer, very highly strained and perhaps unstable under the reaction conditions).

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(19) Allemand, J.; Gerdil, R. *Cryst. Struct. Commun.* **1979**, *8*, 927–932.

(20) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.

(21) Lukevics, E.; Pudova, O.; Sturkovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis Horwood Limited: Chichester, 1989; p 12.

(22) Daly, J. J. *J. Chem. Soc.* **1964**, 3799–3810.

(23) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907. Some ad hoc parameters were included for phosphorus and sulfur. Silicon parameters were from: Frierson, M. R.; Imam, M. R.; Zalkow, V. B.; Allinger, N. L. *J. Org. Chem.* **1988**, *53*, 5248–5258.

(24) For compound **2**, $\Delta\nu_{AB}$ = 133 Hz and J_{AB} = 13 Hz; the lower limit for k_c (304 s^{-1}) was calculated with use of the equation appropriate for a coupled AB system with equal populations.[25] For the calculation of the lower limit for ΔG_c^* (21.8 kcal/mol), a transmission coefficient of 1 was assumed for the Eyring equation. For compound **3**, $\Delta\nu_{AB}$ = 92 Hz, J_{AB} = 13 Hz, and a similar calculation yields a lower limit for ΔG_c^* of 22.1 kcal/mol.

(25) Kurland, R. J.; Rubin, M. B.; Wise, W. B. *J. Chem. Phys.* **1964**, *40*, 2426–2427.

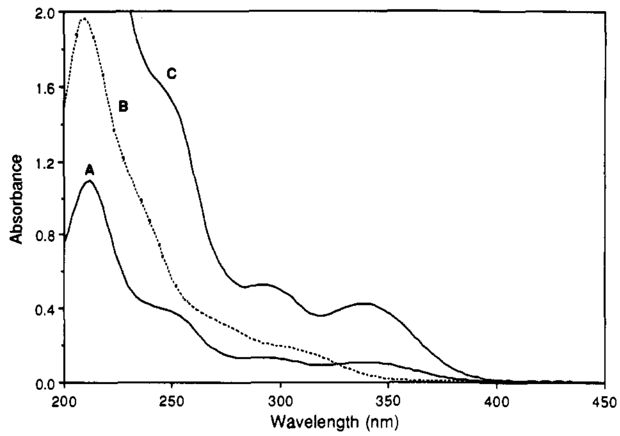
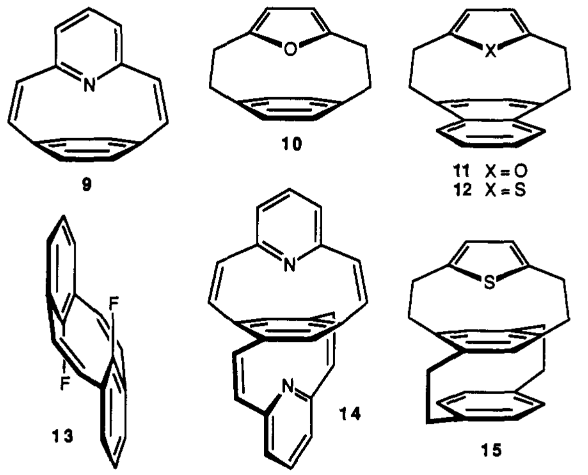


Figure 3. Ultraviolet–visible absorption spectra of phosphines in hexane solution (2.8 × 10^{-5} M): spectrum A, compound **3**; spectrum B, compound **7**; spectrum C, absorbance data of A × 4.

Chart I



In the Context of Other Cyclophanes. The construction of cyclophanes that places heteroatoms close to aromatic rings is not a new activity. Close contacts between lone-pair electrons and aromatic rings are most often observed in the heterophanes,[26] and illustrated in Chart I are a number of crystallographically characterized phanes that share this feature. In the pyridinophanes **9**[27] and **14**,[28] the nitrogen atoms are only 2.51[29] and 2.52 Å,[30] respectively, from the benzene rings; in the furanophanes **10**[31] and **11**,[32] the oxygen atoms are 2.58[33] and 2.60 Å[34] from the arenes; the fluorine atoms of **13**[35] are ca. 2.6 Å[36] from the mean planes of the opposing rings. Close contacts of second-row elements are much less common, but the thiophene-containing phanes **12**[37] and **15**[38] have sulfur atoms some 2.93[33] and 2.86 Å[39] from the respective arenes.

These and related compounds show substantial bathochromic shifts in their UV spectra, a common feature among cyclophanes, but generally speaking their other spectroscopic properties are not terribly unusual (Figure 3). Certainly the ^{31}P–^{13}C spin–spin coupling observed for **3** appears to have no analogy in other phanes. Compound **13** and related fluorinated cyclophanes[40] are the most likely candidates to display similar phenomena, but their ^{13}C NMR spectra have not been reported. On the other hand, changes in reactivity are well-documented among cyclophanes, and the pyridinophanes share several of the properties of phosphaphane **3**. The pyridine ring of **9** is perpendicular to the basal aromatic ring, with the nitrogen lone pair projected directly toward the ring center,[29] a situation comparable to that in **3**. Indeed, the basicity of the nitrogen is greatly reduced,[28] and no interaction with a europium NMR shift reagent was observed;[28] however, compound **9** and related phanes did form complexes with boron trifluoride and antimony pentafluoride.[27,28] Interestingly, in analogues of **9** with saturated bridges, the basicity of the nitrogens is actually increased by comparison with model compounds and treatment with peracids yields the corresponding *N*-oxides.[28] Compound **14** exhibits structural features and reactivity patterns similar to those of **9**,[28,30] but in addition its photoelectron spectrum shows a very low first ionization potential of uncertain origin.[28]

Conclusion. Compounds **2** and **3** are, to the best of our knowledge, the only examples of cyclophanes containing silicon and phosphorus atoms so close to the π cloud of an aromatic ring, and we have shown that this proximity confers unusual spectroscopic characteristics to both and dramatically reduces the reactivity of the phosphine of **3**. In compound **2**, the interaction of the hydrosilane with the aromatic ring appears to be a purely repulsive nonbonded contact, and the low reactivity of the phosphorus of **3** may reasonably be attributed to steric encumbrance and a preference for an *in* geometry due to bond angle constraints. However, the unusual ^{13}C and ^{31}P NMR properties of **3** indicate that there is an electronic interaction between the phosphine and the basal ring, but unfortunately these data do not tell us if there is an attraction between them (i.e., a bond). The crystallographically observed phosphorus to ring distance is 0.2 Å less than the ca. 3.1-Å gap calculated for **3** by both MMPI (which treats the interaction as purely repulsive) and MNDO,[41] but inasmuch as it is much longer than the corresponding distance in typical (η^6-arene)metal complexes any attractive force between the phosphine and basal ring in **3**, if one exists at all, must be relatively weak.

Experimental Section

1,3,5-Tris(bromomethyl)benzene[8] and tris(2-mercaptophenyl)phosphine[6b] were prepared as described previously.

Tris(2-mercaptophenyl)silane (4). Trichlorosilane (1.3 mL, 13 mmol) in THF (5 mL) was added to a stirred solution of lithium 2-lithiothiophenolate[6a] (56 mmol) in THF (100 mL) at −78 °C under argon. Stirring was continued for 24 h as the reaction mixture warmed to room temperature. Water (25 mL) was added, and the solution was concentrated. The residue was taken up in water (250 mL), the mixture was acidified to pH 2, and it was extracted with methylene chloride (3 × 100 mL). The extracts were dried and concentrated to leave a yellow oil. This was purified by column chromatography on silica gel (3:1, then 1:1, hexanes-benzene) to give compound **4** as a gummy white solid: 0.5 g, 11%; ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.65 (s, 3 H), 6.13 (s, 1 H), 7.24 (ddd, J = 7, 7, 1 Hz, 3 H), 7.34 (dd, J = 7, 2 Hz, 3 H), 7.41 (ddd, J = 7, 7, 2 Hz, 3 H), 7.50 (d, J = 7 Hz, 3 H); MS, m/z 246 (M − C$_6$H$_6$S, 100), 213 (76), 184 (72).

Silaphane 2. Tris(2-mercaptophenyl)silane (**4**; 0.5 g, 1.4 mmol) and 1,3,5-tris(bromomethyl)benzene (0.5 g, 1.4 mmol) were mixed in 2:1

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benzene–ethanol (500 mL), and the solution was heated to reflux under argon. An argon-saturated solution of KOH (0.27 g, 4.2 mmol) in ethanol (50 mL) was added dropwise over 1 h. After 12 h, the solution was cooled and filtered, and the solvent was evaporated. The residue was chromatographed on silica gel (3:2 hexanes–benzene), and the fractions containing compound **2** were combined and further purified by preparative TLC (silica gel, 7:3 hexanes–benzene) to give cyclophane **2** as a white solid: mp > 350 °C (darkens above 250 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.04 (s, 1 H), 3.74 (d, J = 13 Hz, 3 H), 3.92 (d, J = 13 Hz, 3 H), 6.78 (s, 3 H), 7.26 (m, 6 H), 7.41 (m, 3 H), 7.72 (d, J = 8 Hz, 3 H); UV ($CHCl_3$) λ_{max} (log ϵ) 286 nm (4.3); IR (cm^{-1}) ν_{max} 3046 (m), 2919 (s), 2852 (m), 2457 (w, Si–H), 1444 (m), 1417 (s), 1247 (m), 1210 (m), 1125 (s), 1104 (m), 1039 (m), 860 (m), 790 (s), 754 (s), 701 (m); MS, m/z 470 (M$^+$, 3), 361 ($M - C_6H_5S$, 17), 327 (5), 85 (65), 83 (100); exact mass 470.0647, calcd for $C_{27}H_{22}S_3Si$ 470.0653.

Tris[2-(benzylthio)phenyl]silane (6). Tris(2-mercaptophenyl)silane (**4**; 0.5 g, 1.4 mmol), benzyl bromide (0.72 g, 4.2 mmol), and a solution of KOH (0.28 g, 4.2 mmol; in 6 mL of ethanol) were added to an argon-saturated solution of benzene and ethanol (2:1, 30 mL). After it was stirred for 16 h at room temperature, the solution was concentrated and the residue was taken up in methylene chloride and washed with brine. The organic layer was dried and concentrated, and the residual yellow oil was chromatographed on silica gel (3:1 hexanes–benzene) to give pure compound **6** as a colorless oil, which slowly solidified upon standing: 362 mg, 42%; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.93 (s, 6 H), 6.21 (s, 1 H), 7.07 (m, 6 H), 7.16 (m, 15 H), 7.31 (m, 6 H); UV ($CHCl_3$) λ_{max} (log ϵ) 271 nm (4.0); IR (cm^{-1}) ν_{max} 3050 (m), 3026 (m), 2920 (s), 2855 (m), 2177 (m, Si–H), 1571 (m), 1552 (m), 1493 (s), 1450 (s), 1421 (s), 1262 (m), 1242 (m), 1126 (m), 1105 (s), 1070 (m), 1043 (m), 1028 (m), 813 (s), 803 (s), 787 (s), 746 (s), 700 (s); MS, m/z 626 (M$^+$, 0.5), 535 ($M - C_7H_7$, 100), 443 ($M - 2C_7H_7 - H$, 53), 335 ($M - 2C_7H_7 - C_6H_5S$, 67), 245 (70), 91 (85); exact mass ($M - C_7H_7$ ion) 535.1029, calcd for $C_{32}H_{27}S_3Si$ 535.1044.

Phosphaphane 3. Tris(2-mercaptophenyl)phosphine (**5**; 1.43 g, 4.0 mmol) and 1,3,5-tris(bromomethyl)benzene (1.43 g, 4.0 mmol) were mixed in 2:1 benzene–ethanol (1.5 L), and the solution was heated to reflux under argon. An argon-saturated solution of KOH (1.1 g, 19 mmol) in ethanol (70 mL) was added dropwise over 1 h. After 12 h, the solution was cooled, precipitated salt was removed by filtration, and the solvent was evaporated. The residue was chromatographed on silica gel (solvent, 2:1 hexanes–toluene) to yield compound **3** (290 mg, 15.4%). Single crystals, mp 315–320 °C dec, were obtained upon crystallization from chloroform–methanol: ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.78 (d, J = 13 Hz, 3 H), 3.84 (d, J = 13 Hz, 3 H), 6.81 (d, J = 8 Hz, 3 H), 6.84 (s, 3 H), 7.20 (t, J = 8 Hz, 3 H), 7.29 (t, J = 8 Hz, 3 H, collapses to doublet upon irradiation at δ 7.71), 7.71 (dd, J = 8 Hz, J_{PH} = 4 Hz, 3 H); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) δ 44.5 (s), 129.0 (d, J_{PC} = 1 Hz), 129.6 (d, J_{PC} = 1.5 Hz), 130.0 (d, J_{PC} = 7.5 Hz), 134.7 (d, J_{PC} = 2 Hz), 138.6 (d, J_{PC} = 40 Hz), 139.5 (d, J_{PC} = 4.5 Hz), 144.66 (d, J_{PC} = 3.5 Hz), 144.69 (d, J_{PC} = 22 Hz); UV (heptane) λ_{max} (log ϵ) 212 nm (4.6), 250 (sh, 4.1), 292 (3.7), 338 (3.6); UV ($CHCl_3$) λ_{max} (log ϵ) 292 nm (3.8), 341 (3.7); MS, m/z 472 (M$^+$, 100), 439 ($M - SH$, 33), 406 ($M - 2SH$, 15), 323 (35), 215 (42), 162 (43), 131 (79); exact mass 472.0556, calcd for $C_{27}H_{21}PS_3$ 472.0543.

Phosphaphane Trisulfone (8). Compound **3** (16 mg, 0.034 mmol) was heated in a refluxing solution of acetic acid (2 mL) and 30% hydrogen peroxide (1 mL) for 20 h. Evaporation of the solvent left highly insoluble compound **8**, which was, however, recrystallized from hot DMSO: 19 mg, 98%; mp > 350 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.66 (d, J = 14 Hz, 3 H), 4.89 (d, J = 14 Hz, 3 H), 6.91 (d, J = 8 Hz, 3 H), 7.50 (t, J = 8 Hz, 3 H), 7.51 (s, 3 H), 7.57 (t, J = 8 Hz, 3 H), 8.07 (dd, J = 8 Hz, J_{PH} = 4 Hz, 3 H); MS, m/z 568 (M$^+$, 33), 440 ($M - 2SO_2$, 48), 439 ($M - 2SO_2 - H$, 58), 376 ($M - 3SO_2$, 100); exact mass 568.0224, calcd for $C_{27}H_{21}O_6PS_3$ 568.0238.

Tris[2-(benzylthio)phenyl]phosphine (7). Tris(2-mercaptophenyl)phosphine (**5**; 0.25 g, 0.7 mmol) was dissolved in 1:1 benzene–ethanol (20 mL), and the solution was saturated with argon. KOH (0.12 g, 2.1 mmol) in ethanol (1 mL) and then benzyl bromide (0.39 g, 2.3 mmol) were added, and the solution was stirred at room temperature for 90 min. Benzene and water were added, and the organic phase was separated, dried over $MgSO_4$, and concentrated to give compound **7** as a colorless oil (0.5 g). A portion of this material was crystallized from chloroform–ethanol: mp 101–102 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.17 (s, 6 H), 6.71 (ddd, J = 8, 3, 2 Hz, 3 H), 7.11 (td, J = 8, 2 Hz, 3 H), 7.2 (m, 21 H), 7.30 (ddd, J = 8, 4, 2 Hz, 3 H); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) δ 40.4 (d, J_{PC} = 8.5 Hz), 126.9 (s), 127.6 (s), 128.3 (s), 129.0 (s), 129.2 (d, J_{PC} = 1 Hz), 132.7 (d, J_{PC} = 3 Hz), 134.0 (s), 137.5 (s), 140.8 (d, J_{PC} = 30 Hz), 140.9 (d, J_{PC} = 10.5 Hz); UV (heptane) λ_{max} (log ϵ) 210 nm (4.8), 270 (sh, 4.1), 300 (sh, 3.9); UV ($CHCl_3$) λ_{max} (log ϵ) 262 nm (sh, 4.3), 302 (sh, 3.9); MS, m/z 628 (M$^+$, 3), 537 ($M - C_7H_7$, 100), 445 ($M - 2C_7H_7 - H$, 4), 413 ($M - C_7H_7 - C_7H_7SH$, 11), 355 (81), 323 (34); exact mass 628.1474, calcd for $C_{39}H_{33}PS_3$ 628.1482.

X-ray Crystallographic Analysis of Cyclophane 2. A single crystal of **2** measuring 0.02 mm × 0.30 mm × 0.38 mm was used for X-ray measurements. Crystal data: $C_{27}H_{22}S_3Si$; trigonal, space group $P\bar{3}$; $a = b$ = 13.217 (1) Å, c = 8.326 (1) Å, V = 1265.1 (3) Å^3, Z = 2, D_{calcd} = 1.24 g/cm^3. Intensity measurements were made with $3° \leq 2\theta \leq 114°$ with use of graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at 214 K on a Nicolet R3m diffractometer. A total of 1136 unique reflections were measured, of which 1018 were considered to be observed [$|F_o| > 3\sigma(F_o)$]. The structure was solved by direct methods with the SHELXTL software. Refinement converged at R = 0.050, R_w = 0.056. Full details are given in the supplementary material.

X-ray Crystallographic Analysis of Cyclophane 3. A single crystal of **3** measuring 0.13 mm × 0.15 mm × 0.48 mm was used for X-ray measurements. Crystal data: $C_{27}H_{21}PS_3$; monoclinic, space group $P2_1/c$; a = 16.635 (2) Å; b = 9.2834 (14) Å, c = 16.593 (2) Å, β = 118.308 (8)°, V = 2256.1 (4) Å^3, Z = 4, D_{calcd} = 1.39 g/cm^3. Intensity measurements were made with $3° \leq 2\theta \leq 114°$ with use of graphite-monochromated Cu Kα radiation (λ = 1.54178 Å) at room temperature on a Nicolet R3m diffractometer. A total of 3041 unqiue reflections were measured, of which 2826 were considered to be observed [$|F_o| > 3\sigma(F_o)$]. The structure was solved by direct methods with the SHELXTL software. Refinement converged at R = 0.033, R_w = 0.037. Full details are given in the supplementary material.

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Supplementary Material Available: Crystallographic data and processing descriptions, final atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **2** and **3** (18 pages). Ordering information is given on any current masthead page.