# Synthesis and X-Ray Crystal Structures of Silacalix[*n*]phosphinines: The First $sp^2$-Based Phosphorus Macrocycles

**Narcis Avarvari, Nicole Maigrot, Louis Ricard, François Mathey,* and Pascal Le Floch*[a]**

**Abstract:** The synthesis of silacalix[*n*]-phosphinines ($n = 3$, 4) is presented. Three strategies have been investigated. Firstly, the thermal condensation of one equivalent of a 1,3,2-diazaphosphinine **1** with one equivalent of the diyne $(PhCC)_2SiMe_2$; this leads to a mixture of oligophosphinines. A second strategy involves the reaction of a bis(phosphinine) **6** with one equivalent of **1** and with trimethysilylacetylene to give the tetrakis(phosphinine) **10**. More convincing results were obtained from the third approach that first requires the preparation of a precursor **8**, which contains a phosphinine as the central unit and two 1,2-azaphosphinine subunits. The reaction of **8** with one equivalent of diyne, under high dilution conditions, leads to the formation of the dimethylsilacalix[3]phosphinine **3**, which was isolated and characterized by single-crystal X-ray crystallography. The macrocycle **3** is fluxional in solution and adopts a partial cone conformation in the solid state. The same strategy was extended to the synthesis of the dimethylsilacalix[4]-phosphinine **4**, which shows fluxional behavior in solution and adopts an opened-out partial cone conformation in the solid state. In a similar manner, the synthesis of these macrocycles was extended to that of mixed derivatives such as dimethylsilacalix[4]-1,3-phosphinines-2,4-thiophenes **15** and furans **16**. X-ray structure analyses reveal that, like **4**, these macrocycles adopt a opened-out partial cone conformation in the solid state.

**Keywords:** cycloadditions · macrocycles · phosphinines · phosphorus heterocycles · silicon

## Introduction

The synthesis, reactivity, and electronic properties of sp and $sp^2$-hybridized phosphorus compounds have attracted much attention over the last few years.[1a] More than two decades after their discovery, research is now clearly focussed on their use in synthetic phosphorus chemistry and in other fields of interest such as coordination chemistry, catalysis, and long-term projects such as the synthesis of phosphorus-based materials with well-defined structures and unique properties. Although a striking analogy exists between phosphorus and carbon multiple-bonded systems,[1b] it appears that further developments in this area depend on the intrinsic reactivity of the P≡C and P=C bonds. Thus, it is now well established that incorporation of highly reactive molecules, such as phosphaalkenes[3] and phosphaalkynes,[2] into complex structures would be difficult without adequate kinetic stabilization. The situation is different for aromatic derivatives, since the reactivity of the P=C bond is considerably reduced by the thermodynamic stabilization resulting from electronic delocalization.[4] Thus, in molecules such as phosphinines,[5] phospholide anions,[6] and their derivatives (heterophospholes[7] and π-complexes[6]) the unique electronic properties of $sp^2$-hybridized phosphorus atoms (poor σ-donating but good π-accepting ability)[8] can be fully expressed. Recently, in this context, various reports have emphasized that these specific properties can be exploited in homogeneous catalysis[9] and for the stabilization of highly reduced transition metal species.[10] These results account for the current attention brought to the use of such compounds as building blocks in the elaboration of tailored ligands and complex aromatic edifices. As part of a continuing program aimed at the derivatization and use of phosphinines as ligands,[11] we were interested in the synthesis of macrocycles. Our interest centers around the following points. Firstly, it appears that macrocyclic derivatives with strong π-acceptor ligands are still unknown. Indeed, oxygen- and tricoordinate-nitrogen-based macrocycles essentially display pure σ-donor with no π-acceptor properties, whereas sulfur, dicoordinate nitrogen and tricoordinate phosphorus derivatives can be considered as moderate-to-good σ-donors that show some π-acceptor properties. Thus, the synthesis of cavities with strong π-acceptor bonding sites constitutes a very interesting target in itself. Secondly, although a number of phosphorus macrocycles exist,[12] the synthesis is generally associated with multiple steps and low yield. Most importantly, owing to the

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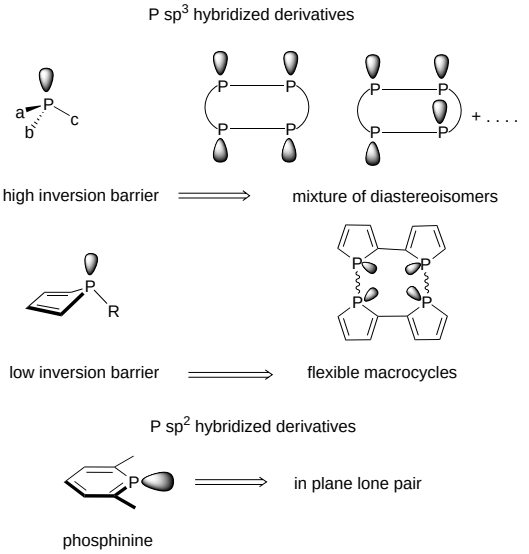
high inversion barrier of pyramidal tricoordinate phosphorus atoms (36 kcal mol$^{-1}$), the usefulness of these macrocycles in coordination chemistry is dramatically reduced by the presence of multiple, inseparable diastereoisomers. Although a significant advance was made in our laboratories some years ago[13] with the use of phospholes (reduced inversion barrier: 16 kcal mol$^{-1}$),[14] the problem of flexible phosphorus macrocycles that display selective coordination is still topical. The use of dicoordinate phosphorus atoms with incorporated in-plane lone pairs of electrons seems to be an original alternative (see Scheme 1). Here we describe a simple synthetic approach to these phosphinine-based macrocycles.

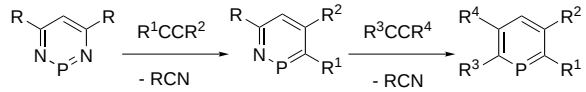



Scheme 1. Phosphorus macrocycles.

**Abstract in French:** *La synthèse des silacalix-[n]-phosphinines (n = 3, 4) est présentée. Trois stratégies synthétiques ont été étudiées. La première qui consiste en la réaction thermique de la diazaphosphinine* ***1*** *avec un équivalent du diyne (PhCC)$_2$SiMe$_2$ conduit à une mixture d'oligomères. Une seconde stratégie faisant intervenir la réaction de la bis(phosphinine)* ***6*** *avec un équivalent de diazaphosphinine* ***1*** *et un équivalent de triméthylsilylacétylène fournit la tétrakis(phosphinine)* ***10****. Des résultats plus significatifs ont été obtenus en utilisant une troisième approche qui nécessite la préparation préliminaire du précurseur* ***8*** *constitué d'une unité centrale de type phosphinine et de deux sous-unités 1,2-azaphosphinines. La réaction de* ***8*** *avec un équivalent de diyne, sous haute dilution, conduit au dimethylsilacalix[3]phosphinine* ***3*** *qui a été isolé et caractérisé par une étude cristallographique. Le composé* ***3*** *qui est fluxionnel en solution adopte une géométrie de type cône partiel à l'état solide. La même stratégie a été étendue à la synthèse du diméthylsilacalix[3]phosphinine* ***4*** *qui lui aussi présente un caractère fluxionnel en solution et adopte une géométrie de type cône partiel à l'état solide. D'une façon identique, la synthèse de ces macrocycles a été généralisée à la préparation de dérivés mixtes du type dimethylsilacalix[4]1,3-phosphinines-2,4-thiophènes* ***15*** *et furanes* ***16****. Ces deux composés adoptent, comme dans le cas de* ***4****, une géométrie de type cône partiel à l'état solide.*

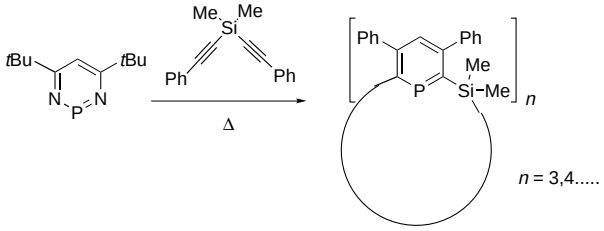
## Results and Discussion

Of the different routes available for the functionalization of the phosphinine nucleus, we decided to use a method that gave good results for the synthesis of $SiMe_2$-linked bis- and tris-phosphinines. This approach relies on the reactivity of 1,3,2-diazaphosphinines towards functional alkynes.[15] In previous reports, we have shown that tetrafunctional phosphinines are easily formed, with nearly quantitative regioselectivity, by means of a thermally promoted cycloaddition/cycloreversion sequence that involves the concomitant loss of two nitrile molecules (Scheme 2).




Scheme 2. From 1,3,2-diazaphosphinines to tetrafunctional phosphinines by two successive [4+2] cycloaddition/cycloreversion processes.

We used this efficient approach for the elaboration of sophisticated bi- and tridentate ligands with bis(alkynyl)silanes as reactants.[15b, c] In an attempt to directly assemble the macrocycles (see Scheme 3), we decided to investigate the reactivity of diazaphosphinines with symmetrical diynes. Part of this work has been already reported as a communication.[16]




Scheme 3. Reaction of 1,3,2-diazaphosphinines with bis(phenylethynyl)-dimethylsilane.

All our experiments were conducted with bis(phenylethynyl)dimethylsilane and with 4,6-di-*tert*-butyl-1,3,2-diazaphosphinine (**1**), which is readily available from the reaction of dimethyltitanocene with pivalonitrile and subsequent treatment with phosphorus chloride in the presence of triethylamine.[15b] Direct condensation of one equivalent of **1** with one equivalent of diyne, at 110–115 °C for 10 hours, led to a mixture of products. $^{31}$P NMR spectroscopic analysis of the crude mixture revealed the presence of multiple signals in the usual range of disubstituted silylphosphinines; this indicated that a variety of oligomers had formed during the reaction. Fortunately, after several purification cycles over silica gel, we were able to obtain a mixture of the two main compounds, **3** and **4**, which appear as singlets at $\delta = 293$ (**3**) and 278 ppm (**4**) in the $^{31}$P NMR spectrum. The most interesting information was given by the mass spectrum, which revealed the presence of two molecular peaks at 912 and 1216 corresponding to molecules with three and four dimethylsilylphosphininyl units (one unit: M = 304). This corresponds to a 12-membered ring ($P_3$) in **3** and a 16-membered ring ($P_4$) in **4**. Unfortunately, the presence of phenyl groups, whose signals overlap with those of phosphinine units in the $^{13}$C NMR spectrum, precluded the



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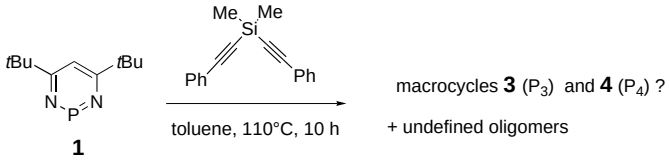
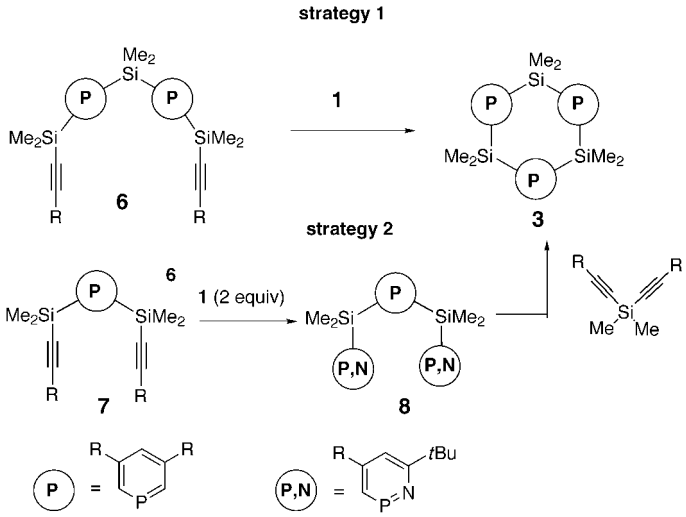
ascertainment of the ring structures. Nevertheless, in line with the two singlets observed in $^{31}P$ NMR, we expected these compounds to possess a symmetrical and cyclic skeleton (Scheme 4).




Scheme 4. Reaction of **1** with bis(phenylethynyl)dimethylsilane to yield a mixture of the macrocyclic derivatives **3** and **4** and oligomers.

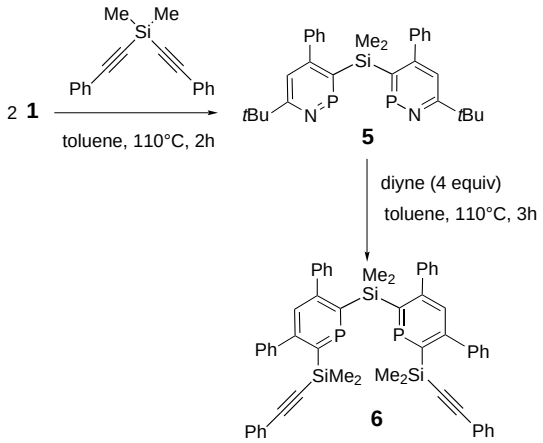
To check this hypothesis, we decided to investigate a more rational synthetic approach to these two compounds. Our first attempts were directed towards the synthesis of the 12-membered ring in **3**. Two strategies were devised (see Scheme 5). The first involved the preliminary synthesis of




Scheme 5. Possible strategies for the synthesis of silacalix[*n*]phosphinines (R = Ph).

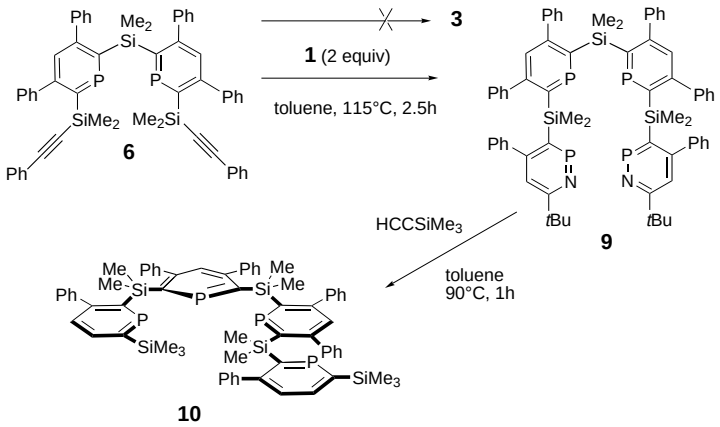
the bis(phosphinine) **6**. This precursor, which bears two phenylethynyldimethylsilyl groups at its extremities, could lead to **3** by ring closure upon reaction with one equivalent of **1**. The second approach relies on the reactivity of the 2,6-bis(phenylethynyldimethylsilyl)phosphinine **7** and the bis(dimethylsilyl-1,2-azaphosphinine)phosphinine **8**; these have both already been used for the preparation of a tris(phosphinine).[15b] In this case, ring closure could occur by the reaction of **8** with one equivalent of diyne.

Precursor **6** is the key synthon for the first approach. Its preparation was easily achieved in a one-pot sequence by reaction of two equivalents of **1** with three equivalents of diyne. Firstly, condensation with one equivalent of diyne led to the bis(1,2-azaphosphinine)dimethylsilyl intermediate **5**, which had been previously characterized and did not need to be isolated. In a second step, **5** was allowed to react with an excess of diyne to give **6**, which was isolated as a very stable, pale yellow solid after chromatography with 60% overall yield (Scheme 6).




Scheme 6. Reaction of diazaphosphinine **1** with bis(phenylethynyl)dimethylsilane to yield the bis(phosphinine) **6**.

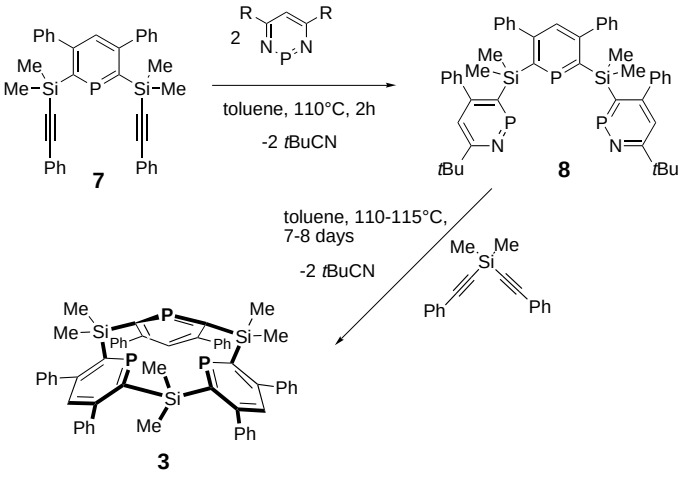
The structure of **6** was unambigously established on the basis of NMR spectroscopic data and mass spectrometry experiments. Contrary to our expectations, the reaction of **6** with one equivalent of **1**, even under high dilution conditions, did not give the expected macrocycle **3**. After two hours of heating at 115 °C, a $^{31}P$ NMR spectroscopic analysis of the crude mixture showed that only half of precursor **6** had been consumed and no traces of **1** could be detected. Additionally, the presence of a simplified AA′XX′ spin pattern (see Experimental Section) indicated the formation of a compound that contained two phosphinine and two 1,2-azaphosphinine units. Indeed, it is known that $^{31}P$ NMR resonances of 1,2-azaphosphinines always appear at lower fields than those of phosphinines.[15b] Unfortunately, the compound turned out to be too sensitive towards hydrolysis to be isolated. We suspected that it could be the intermediate bis(1,2-azaphosphinine)-bis(phosphinine) (**9**), resulting from the reaction of diazaphosphinines on the two alkynes functions, and so we carried out the condensation of **9** with an excess of trimethylsilylacetylene to isolate a stable derivative. As expected, the tetrakis(phosphinine) **10** was isolated as the sole phosphorus compound, which confirmed our initial hypothesis (Scheme 7). The structure of **10**, which is the first ligand to contain four P=C bond sites, was unambigously confirmed on the basis of NMR data, mass spectrometry and elemental analysis.




Scheme 7. Synthesis of tetrakis(phosphinine) **10**.

Undoubtedly, the failure of our strategy in the synthesis of macrocycle **3** can be ascribed to the difference in reactivity between 1,2- and 1,3,2-diazaphosphinines. As we had already noticed, the latter are much more reactive. Thus, in the case of precursor **6**, the ring-closure process, which requires the successive transformation of one molecule of **1** into an 1,2-azaphosphinine and then into a phosphinine unit, is kinetically disfavored compared with the formation of oligomer **9**, which only involves the formation of two 1,2-azaphosphinine units. A second approach, the condensation of one equivalent of diyne with one equivalent of **9**, was also unsuccessful. Although macrocycle **4** was detected in the $^{31}$P NMR spectrum of the reaction mixture, the presence of numerous unidentified side-products precluded its isolation. However, despite these failures, it is clear that **6** could be an intermediate of great synthetic utility in the synthesis of defined phosphinine-based oligomers with an even number of units.

More convincing results were obtained by the second strategy, which involved the transformation of two azaphosphinines units into two phosphinines. The preparation of precursor **8** was carried out by the procedure reported for the synthesis of the tris(phosphinine) [see Scheme 3]. A series of preliminary experiments showed that the equimolar reaction between the diyne and **8** requires high dilution conditions (best fit: $5 \times 10^{-3}$ mol L$^{-1}$) to discourage the formation of linear oligomers. Furthermore, in order not to slow down the kinetics, periodical evaporation of the solvent is necessary to maintain a regular concentration of the two reactants. With this procedure, macrocycle **3** was formed after 7–8 days of heating at 110–115 °C, as monitored by $^{31}$P NMR spectroscopy. Purification of **3**, which was recovered as a very air stable yellow solid, was easily achieved by chromatography on silica gel. Although the yields were modest (20%), the formation of **3** was achieved through a one-pot procedure from precursor **7** (Scheme 8).




Scheme 8. Synthesis of silacalix[3]phosphinine **3**.

The structure of **3** was initially established by NMR experiments, mass spectrometry, and elemental analysis. As expected, the chemical shift observed in the $^{31}$P NMR spectrum is identical to that of the compound isolated in the reaction of **1** with the diyne (see Scheme 4); this confirmed our starting hypothesis. Interestingly, **3** resonates as a singlet in the $^{31}$P NMR spectrum, which suggests that the macrocycle is fluxional in solution. Unfortunately, we could not obtain thermodynamic information on the energy barrier required for the interconversion of **3**, since its low solubility in common organic solvents precluded variable low-temperature NMR spectroscopic experiments. Definitive evidence for the cyclic structure of **3** was given by an X-ray crystal study. Crystals of suitable size were grown by slow diffusion of pentane into a toluene solution of **3** at room temperature. Crystallographic data are listed in Table 1 and an ORTEP view of **3** is presented

Table 1. Crystallographic data for compounds **3** and **4**.

| | **3** | **4**·2 $C_7H_8$ |
|---|---|---|
| formula | $C_{57}H_{51}Si_3P_3$ | $C_{97}H_{92}Si_4P_4$ |
| $M_r$ | 913.22 | 1404.91 |
| crystal system | triclinic | orthorombic |
| space group | $P\bar{1}$ | $Pna2_1$ |
| $a$ [Å] | 9.609(1) | 25.148(3) |
| $b$ [Å] | 16.257(2) | 13.171(1) |
| $c$ [Å] | 17.594(2) | 23.546(2) |
| $\alpha$ [°] | 108.27(2) | 90.00(2) |
| $\beta$ [°] | 98.71(2) | 90.00(2) |
| $\gamma$ [°] | 106.32(2) | 90.00(2) |
| $V$ [Å$^3$] | 2416.9(1.7) | 7799.2(3) |
| $Z$ | 2 | 4 |
| color | yellow | colorless |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.255 | 1.194 |
| $T$ [°C] | −150 | −150 |
| diffractometer | Enraf-Nonius CAD4 | |
| radiation | $Cu_{K\alpha}$ ($\lambda = 1.54184$ Å) | $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) |
| $2\theta$ range [°] | 114.5 | 60.0 |
| Total reflections | 7029 | 12306 |
| Independent reflections | 6560 | 11589 |
| Standard reflections | 5040 ($F_o^2 > 2.0\sigma(F_o^2)$) | 5574 ($F_o^2 > 2.0\sigma(F_o^2)$) |
| $R(F)$ [%] | 3.8 | 4.5[a] |
| $R(wF)$ [%] | 5.4 | 5.7[b] |
| $\Delta/\sigma$ (max) | 0.01 | 0.02 |
| $\Delta(\rho)$ [e Å$^{-3}$] | 0.39(5) | 0.39(6) |
| GOF | 1.12 | 1.01[c] |

[a] $R_F = \Sigma(F_0 - F_c)/\Sigma(F_0)$. [b] $R_w = [\Sigma(w(F_0 - F_c)^2)/\Sigma(wF_0^2)]^{1/2}$. [c] GOF = $[\Sigma(w(F_0 - F_c)^2)/\{(\text{no. of reflections}) - (\text{no. of parameters})\}]^{1/2}$.

in Figure 1. In the solid state, **3** adopts a partial cone-type structure. Two phosphorus-atom lone pairs (P1 and P2) point towards the top of the cavity and are located above the plane defined by the three silicon atoms ($\theta = 49.28°$ for P1 and $\theta = 71.32°$ for P2), the third one (P3) points below this plane ($\theta = -46.03°$). Since no molecular-modelling simulations have yet been undertaken, it is difficult to assert at this stage that this particular geometry corresponds to an energy minimum or if it results from packing forces in the crystal. Apparently, there is significant strain in the macrocycle, as reflected by the rather small C–SiMe$_2$–C [$\theta = 104.9(1) - 105.8(1)°$] and P–C–Si [111.2(2) – 114.1(2)°] bond angles. In good agreement with this observation, connections between the phosphinine subunits and linkers (C–Si bond lengths) appear to be rather long [$d = 1.908(3) - 1.914(3)$ Å].

To the best of our knowledge, macrocycle **3** is only the second example of a calix[3]-type structure, the first one being the S-linked calix[3]azine reported by Mascal et al in 1997.[17] Encouraged by this initial result, we then turned our attention



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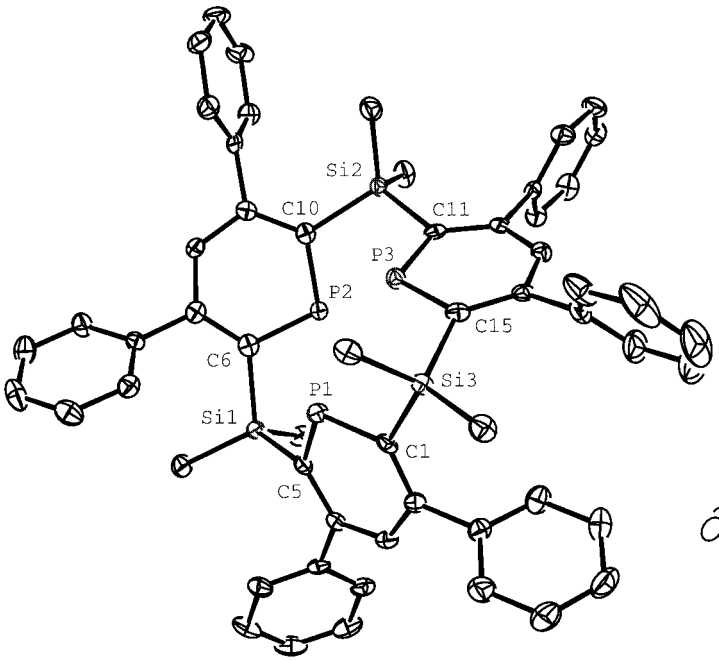
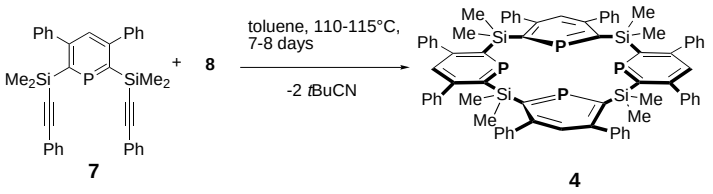



Figure 1. ORTEP diagram of macrocycle **3**. Ellipsoids are scaled to 50 % of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for the assignment of the NMR spectra. Selected bond lengths [Å] and angles [°]: P1–C1 1.751(3), P1–C5 1.739(2), C6–P2 1.746(2), C5–Si1 1.908(3), Si1–C6 1.910(3), P2–C10 1.738(3), C10–Si2 1.908(2), Si2–C11 1.913(3), C11–P3 1.742(3), P3–C15 1.749(3), C15–Si3 1.908(3), Si3–C1 1.914(2); P1–C1–C2 120.9(2), C6–P2–C10 106.1(1), P2–C10–Si2 114.1(2), C10–Si2–C11 105.1(1), Si2–C11–P3 113.5(1), C11–P3–C15 106.9(1), C1–P1–C5 105.8(1), P3–C15–Si3 111.1(1), P1–C5–Si1 114.0(1), C15–Si3–C1 104.9(1), Si1–C6–P2 113.1(2).

towards the synthesis of the calix[4] derivative **4**, the formation of which was discussed earlier (see Scheme 4). To limit the number of precursors, we adopted a strategy similar to that used for the synthesis of **3** by using one equivalent of phosphinine **7** instead of diyne. The formation of **4** occured under comparable conditions (high dilution, controlled concentration) by heating an equimolar mixture of **7** and **8** at 110–115 °C for 7–8 days. As in the case of **3**, the formation of undefined oligomers was unavoidable. Nevertheless, the low solubility of **4** in solvents such as acetone considerably simplified the different purification steps. Macrocycle **4** was obtained as a very air-stable powder with a 20 % overall yield (Scheme 9).




Scheme 9. Synthesis of silacalix[4]phosphinine **4**.

All accessible NMR spectroscopic data confirmed the proposed structure of **4**. Firstly, its $^{31}$P NMR chemical shift is identical to that recorded in our first experiment (see Scheme 4). Like **3**, this signal appears as a singlet; this confirms the fluxional behavior of **4** in solution. Again, the low solubility of **4** in common organic solvents precluded the realization of variable-temperature $^{31}$P NMR experiments. The cyclic structure of **4** was definitively ascertained by an X-ray structure analysis that was carried out on crystals obtained from the slow diffusion of pentane into a toluene solution of the compound at room temperature. These crystals contain two molecules of toluene per macrocycle. Crystallographic data are listed in Table 1 and an ORTEP view of **4** is presented in Figure 2.

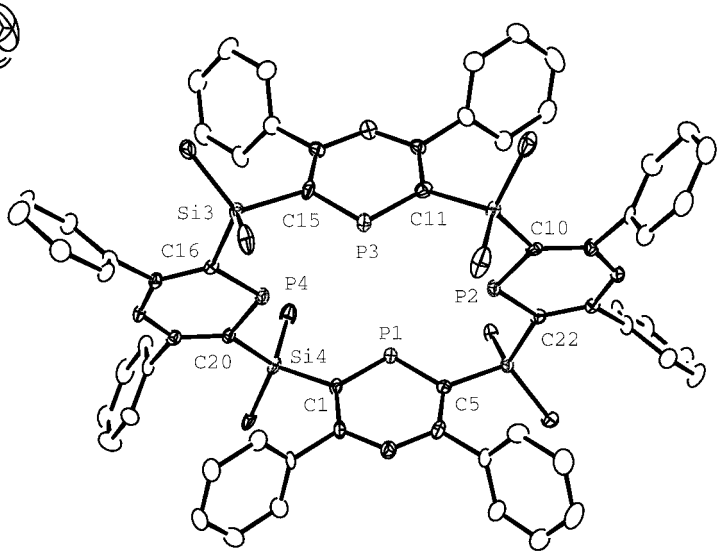
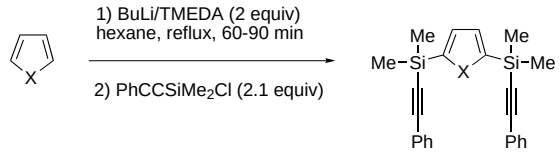



Figure 2. ORTEP diagram of macrocycle **4**. Ellipsoids are scaled to 50 % of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for the assignment of the NMR spectra. Selected bond lengths [Å] and angles [°]: P1–C1 1.734(5), P1–C5 1.746(5), C5–Si1 1.885(5), Si1–C22 1.898(5), C22–P2 1.747(5), P2–C10 1.739(5), C10–Si2 1.894(5), Si2–C11 1.895(5), C11–P3 1.739(6), P3–C15 1.740(5), C15–Si3 1.899(6), Si3–C16 1.883(5), C16–P4 1.742(5), P4–C20 1.736(5), C20–Si4 1.899(5), Si4–C1 1.900(5); C10–Si2–C11 109.4(2), Si2–C11–P3 115.6(3), C11–P3–C15 106.3(3), P3–C15–Si3 113.3(3), C15–Si3–C16 108.0(2), C5–P1–C1 106.3(2), P1–C5–Si1 115.2(3), C5–Si1–C22 108.2(2), Si1–C22–P2 114.1(3), C22–P2–C1 105.0(2), Si3–C16–P4 114.7(3), C16–P4–C(20) 105.4(2), P4–C20–Si4 112.5(3), C20–Si4–C1 108.7(2), Si4–C1–P1 115.4(3), P2–C10–Si2 113.2(3).

Macrocycle **4** adopts a opened-out partial cone conformation[18] in the solid state. Two opposing phosphinine subunits (P2 and P4) lie almost in the plane defined by the four silicon atoms ($\theta = 5.68°$ for P2 and $\theta = 7.63°$ for P4), whereas the other two subunits (P1 and P3) are located in two roughly parallel planes ($\theta = 2.45°$) that are perpendicular to the first ($\theta = 88.37°$ for P1 and $\theta = 89.56°$ for P3). Interestingly, these two phosphorus atoms point in opposite directions, probably to minimize interactions with the other two lone pairs. Unlike **3**, no strain is apparent in **4**, as reflected by the C–$SiMe_2$–C bond angles which fall in the usual range [108.0(2)–109.4(2)°]. As a consequence, the C–$SiMe_2$ bond lengths are slightly shortened [1.883(5)–1.900(5) Å] compared with **3**. The most interesting information is provided by the cavity size, which is given by the internal P–P bond distances. Surprisingly, the distance between P1 and P3, which are both located in two parallel planes, is shorter than that between the two opposing atoms P2 and P4. At 5.650 and 5.788 Å, respectively, these distances appear to be rather significant

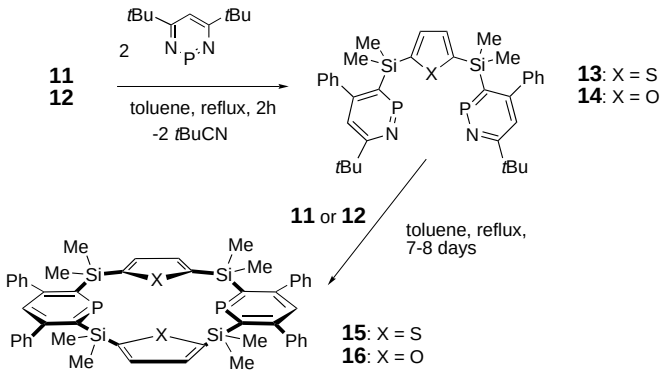
and we believe that the four $SiMe_2$ joints give sufficient flexibility to **4** to accommodate the coordination of various metallic centers. In conclusion, we note that **4** is a new example of a heterosilacalix macrocycle, a class of compounds which is still rather rare[19] in comparison with the C, B, S and Ge-bridged heterocalix derivatives.[20]

The strategy devised for the synthesis of **3** and **4** can be easily extended to that of silacalix[4]phosphinines derivatives containing other heterocycles. We first explored the incorporation of furan and thiophene units, which could play an interesting role as hemilabile ligands in the coordination chemistry of these cavities. A prerequisite to these syntheses is the preparation of 2,5-bis(phenylethynyldimethylsilyl)furan and thiophene; this was readily achieved by the classical approach of the reaction of the corresponding 2,5-dilithio derivatives with phenylethynyldimethylchlorosilane (Scheme 10).




Scheme 10. Synthesis of 2,5-bis(phenylethynyldimethylsilyl)thiophene **11** and furan **12**.

Diynes **11** and **12**, which were unknown before this work, were obtained in fair to excellent yield and were characterized by NMR spectroscopy and mass spectrometry. As in the case of **4**, the formation of the corresponding macrocycles can be achieved in a one-pot sequence. In a first step, **11** or **12** was heated under reflux for two hours with two equivalents of **1** to give the bis(azaphosphinines) **13** or **14** (Scheme 11). In the second part of the syntheses, **13** or **14** was then heated under reflux with an additional equivalent of **11** or **12**, respectively. As in the preparation of **3** and **4**, the use of high dilution and control of the concentration of both reactants was necessary to minimize the amount of linear oligomers. After conventional purification on silica gel, **15** and **16** were separated from traces of oligomers by washing with acetone and were isolated as white, air-stable, and poorly soluble powders in 20% yield (Scheme 11).




Scheme 11. Synthesis of mixed-thiophene **15** and -furan **16** silacalix[4]-phosphinine macrocycles from the diazaphosphinine **1** and precursors **11** and **12**.

All NMR spectroscopic data support the proposed macrocyclic structures. Like **3** and **4**, the presence of singlets in $^{31}P$ NMR spectra [$\delta = 272$ (**15**) and 278 ppm (**16**)] indicates that **15** and **16** are fluxional in solution. Unfortunately, like their congeners, their poor solubility in common organic solvents precluded the use of variable temperature NMR experiments.

Definitive evidence for their structure was given by X-ray crystal analysis of the two compounds. In both cases, suitable crystals were obtained by slow diffusion of pentane into a toluene solution of **15** or **16**. Crystallographic data for both compounds are presented in Table 2 and ORTEP views in Figures 3 (**15**) and 4 (**16**). Both structures are centrosymmetrical and adopt a opened-out partial cone conformation with the two phosphinine subunits lying in two perfectly parallel planes ($\theta = 0°$); these planes are nearly perpendicular to the plane that bears the heterocycles ($\theta = 84.27°$ for **15** and 82.16° for **16**). The fact that in both structures the heterocycles face each other is an interesting problem that is difficult to rationalize without molecular-mechanics calculations. Nevertheless, we propose that this specific conformation results from the minimization of the repulsion between the two phosphorus-atom lone pairs. Apparently, the strain within the two macrocycles is comparable with that observed in the case of **4** (compare the C–Si–C and P–C–Si bond angles and C–$SiMe_2$ bond lengths). The most important information is provided by the internal heteroatom–heteroatom bond distances. The cavity size of the mixed sulfur-phosphorus derivative **15** is clearly smaller than that of its oxygen counterpart **16** [$d(S{-}S) = 4.826$ versus $d(O{-}O) = 6.05$ Å]. Undoubtedly, this results from the lengthening of the C–

Table 2. Crystallographic data for compounds **15** and **16**.

| | **15** | **16** |
|---|---|---|
| formula | $C_{50}H_{50}Si_4P_2S_2$ | $C_{50}H_{50}Si_4O_2P_2$ |
| $M_r$ | 889.38 | 857.25 |
| crystal system | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ [Å] | 7.288(2) | 7.383(1) |
| $b$ [Å] | 12.411(3) | 12.475(2) |
| $c$ [Å] | 13.532(3) | 13.53(2) |
| $\alpha$ [°] | 99.11(2) | 100.90(1) |
| $\beta$ [°] | 95.94(2) | 98.82(1) |
| $\gamma$ [°] | 101.91(2) | 101.85(1) |
| $V$ [Å$^3$] | 1170.7(1.2) | 1150.46(62) |
| $Z$ | 1 | 1 |
| color | colorless | colorless |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.261 | 1.237 |
| $T$ [°C] | −150 | −150 |
| diffractometer | Enraf-Nonius CAD4 | |
| radiation | $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) | $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) |
| $2\theta$ range [°] | 60.0 | 60.0 |
| Total reflections | 7077 | 6991 |
| Independent reflections | 6809 | 6706 |
| Standard reflections | 4348 ($F_o^2 > 2.0\sigma(F_o^2)$) | 4994 ($F_o^2 > 2.0\sigma(F_o^2)$) |
| $R(F)$ [%] | 4.0 | 3.5[a] |
| $R(wF)$ [%] | 4.8 | 5.4[b] |
| $\Delta/\sigma$ (max) | 0.01 | 0.02 |
| $\Delta(\rho)$ [e Å$^{-3}$] | 0.38(7) | 0.48(5) |
| GOF | 1.01 | 1.11[c] |

[a] $R_F = \Sigma(F_0 - F_c)/\Sigma(F_0)$. [b] $R_w = [\Sigma(w(F_0 - F_c)^2)/\Sigma(wF_0^2)]^{1/2}$. [c] GOF = $[\Sigma(w(F_0 - F_c)^2)/\{(\text{no. of reflections}) - (\text{no. of parameters})\}]^{1/2}$.



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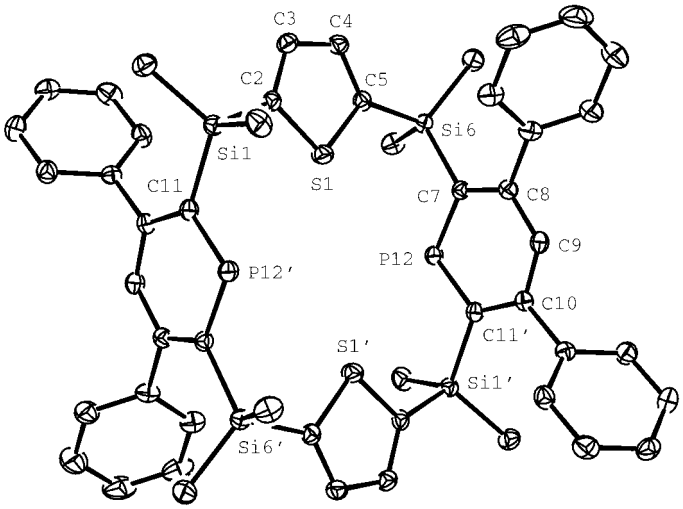


Figure 3. ORTEP diagram of macrocycle **15**. Ellipsoids are scaled to 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for the assignment of the NMR spectra. Selected bond lengths [Å] and angles [°]: P12–C7 1.738(2), C11′–P12 1.742(2), C7–Si6 1.892(2), Si6–C5 1.867(2), C5–S1 1.725(2), S1–C2 1.725(2), C2–Si1 1.867(2), Si1–C11 1.891(2); C11′–P12–C7 105.9(1), C7–Si6–C5 106.6(1), Si6–C5–S1 120.9(1), C5–S1–C2 94.2(1), S1–C2–Si1 120.1(1), C2–Si1–C11 107.41(9), Si1–C11–P12′ 114.4(1), P12–C7–Si6 114.4(1).

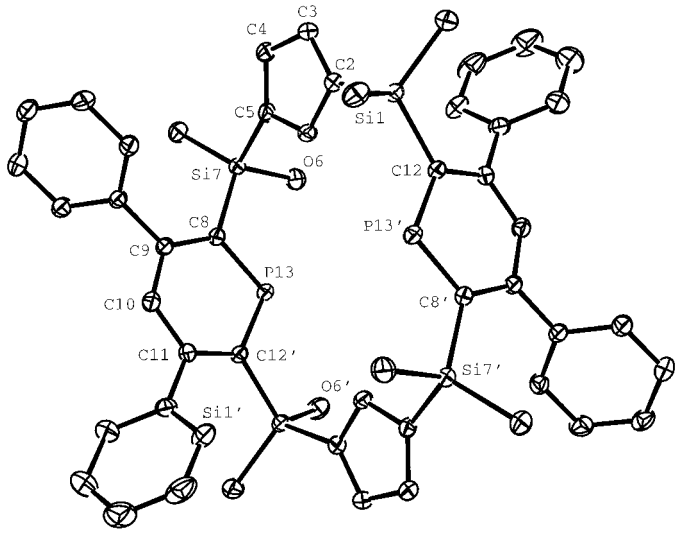


Figure 4. ORTEP diagram of macrocycle **16**. Ellipsoids are scaled to 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for the assignment of the NMR spectra. Selected bond lengths [Å] and angles [°]: P13–C12′ 1.738(1), C8–Si7 1.889(1), C8–P13 1.741(2), Si7–C5 1.866(2), C5–O6 1.385(2), O6–C2 1.382(2), C2–Si1 1.868(2), Si1–C12 1.893(2); C8–P13–C12′ 105.9(7), P13–C8–Si7 114.21(7), C8–Si7–C5 110.81(6), Si7–C5–O6 117.7(1), C5–O6–C2 108.0(1), O6–C2–Si1 119.3(1), C2–Si1–C12 110.31(7), Si1–C12–P13′ 114.60(7).

heteroatom bond lengths [$d$(C–S) = 1.725(2) and $d$(C–O) = 1.382(2) Å], which by closing the internal C–S–C angle ($\theta$ = 94.2°, compare with 108.0° for furan) brings the sulfur atoms closer to the center of the cavity. However, simple geometrical considerations show that this difference cannot totally explain the observed shortening. It is likely that repulsion between the two lone electron pairs of the more electronegative oxygen atoms also plays a significant role.

## Conclusions

We have described simple synthetic procedures for the synthesis of a new class of phosphorus macrocycles. Silacalix[*n*]phosphinines are the first macrocyclic structures to contain dicoordinate phosphorus atoms. The synthesis of mixed sulfur and oxygen derivatives demonstrate that this method is versatile enough to permit the synthesis of other phosphinine-based macrocycles of different sizes and shapes by the inclusion of different types of spacers. We believe these macrocycles to be sufficiently flexible to encapsulate metals with coordination spheres of different geometries and our future efforts will focus on studies of their host–guest properties. Preliminary results have shown that square-planar complexes of ligand **4** can be formed without difficulty.[16] We also believe that silacalix[*n*]phosphinines, whose cavities made of strongly π-acceptor phosphorus atoms are unique, should play a significant role in coordination chemistry and catalysis with complexes that contain electron-rich metal centers.

## Experimental Section

All reactions were routinely performed under an inert $N_2$ atmosphere by Schlenk techniques and with dry deoxygenated solvents. Dry THF, toluene, hexane, and pentane were obtained by distillation from Na/benzophenone. Dry Celite was used for filtration. NMR spectra were recorded on a Bruker AC 200 SY spectrometer. Chemical shifts are expressed in parts per million downfield from the external standards TMS ($^1$H and $^{13}$C) and 85% $H_3PO_4$ ($^{31}$P). Mass spectra were obtained at 70 eV with a HP 5989 B spectrometer coupled with a HP 5890 chromatograph by the direct inlet method. The following abreviations are used: s singlet, d doublet, t triplet, m multiplet, br broad, v virtual. Elemental analyses were performed by the Service d'analyse du CNRS, at Gif sur Yvette (France). Diazaphosphinine **1**,[15b] $(PhCC)_2SiMe_2$,[21] $PhCCSiMe_2Cl$,[22] 2,5-dilithiofuran, and 2,5-dilithiothiophene[23] were prepared according to published procedures.

**Bis(4-phenyl-6-*tert*-butyl-1,2-azaphosphinine-3-yl)dimethylsilane (5) and bis [3,5-diphenyl-6-(phenylethynyldimethylsilyl)phosphinine-2-yl)dimethylsilane] (6):** A solution of diazaphosphinine **1** (0.52 g, 2.50 mmol) and bis(phenylethynyl)dimethylsilane (0.26 g, 1.25 mmol) in toluene (10 mL) was heated under reflux for 2 h. Complete formation of bis(1,2-azaphosphinine) **5** was confirmed by $^{31}$P NMR spectroscopy. After the addition of toluene (30 mL) and bis(phenylethynyl)dimethylsilane (1.28 g, 5 mmol), the resulting mixture was further heated under reflux for 3 h. The formation of **6** was monitored by $^{31}$P NMR spectroscopy. After the solution was cooled to room temperature, Celite (1.50 g) was added, and the solvents were removed under vacuum. The resulting brown powder was then deposited onto a silica-gel column for chromatography. A first fraction, eluted with hexane/toluene (95:5), yielded excess diyne. A second fraction, eluted with hexane/toluene (70:30), yielded phosphinine **6**, which was recovered as a pale yellow solid (0.65 g, 60%) after evaporation of solvents and precipitation with methanol; m.p. >180 °C (decomp); $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta$ = 274 (s); $^1$H NMR (200.13 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.28 (s, 12 H, 2 $SiMe_2$), 0.49 (s, 6 H, $SiMe_2$), 6.94–7.53 (m, 32 H, 6 Ph, 2 H4); $^{13}$C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta$ = 2.1–2.3 (v t, X part of an ABX system, $\Sigma^3J$(C,P) = 10 Hz, 2 $SiMe_2$ from $SiMe_2$C≡CPh), 4.70 (t, $^3J$(C,P) = 13 Hz, $SiMe_2$), 95.5–95.6 (v t, X part of an ABX system, $\Sigma^3J$(C,P) = 5 Hz, 2 *C*≡CPh), 107.4 (s, 2 C≡*C*Ph), 124.1 (s, 2 C *ipso* of C≡C*Ph*), 128.0–132.5 (m, CH of Ph), 132.9–133.3 (v t, X part of an ABX system, $\Sigma^3J$(C,P) = 21 Hz, 2 C4), 145.7 (s, 2 C *ipso* of Ph), 145.8 (s, 2 C *ipso* of Ph), 154.1–154.5 (m, 2 C3, 2 C5), 160.6 (d, $^1J$(C,P) = 89 Hz, 2 C6), 165.0 (dd, $^3J$(C,P) = 5 Hz, $^1J$(C,P) = 91 Hz, 2 C2); MS (70 eV, EI):*m*/*z* (%): 868 (80) $[M]^+$, 766 (5) $[M - CCPh]^+$, 709 (8) $[M - CCPh - SiMe_2]^+$; $C_{56}H_{50}P_2Si_3$ (869.22): calcd C 77.38, H 5.80; found: C 77.31, H 5.97.

**Bis[3,5-diphenyl-6-(4′-phenyl-6′-*tert*-butyl-1′,2′-azaphosphinine-3′-yl)dimethylsilylphosphinine-2-yl]dimethylsilane (9) and bis[3,5-diphenyl-6-(3′-phenyl-6′-trimethylsilylphosphinine-2′-yl)dimethylsilylphosphinine-2-yl]-dimethylsilane (10):** A solution of diazaphosphinine **1** (0.21 g, 1.0 mmol) and bis(phosphinine) **6** (0.43 g, 0.5 mmol) in toluene (5 mL) was heated to 115 °C for 2.5 h. After this period, the formation of **9** was completed, trimethysilylacetylene (0.98 g, 1.0 mmol) was added, and the reaction mixture was heated to 90 °C for 1 h. After the solution was cooled, Celite (1.5 g) was added and the solvent and excess trimethylsilylacetylene were removed under vacuum. As described above, tetrakis(phosphinine) **10** was purified by chromatography with hexane/toluene (80:20) as eluent. After evaporation of the solvents, **10** was recovered as a pale yellow solid (0.36 g, 63 %); m.p. 170 °C (decomp).

**Compound 9**: $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta = 304$ (v d, AA′XX′, $^4J(P_A,P_X) = 8$ Hz, $J(P_A,P_{X'}) = J(P_X,P_{X'}) = 0$ Hz, $^4J(P_A, P_{A'})$ = not estimated, $P_A$ of azaphosphinine), 276 (v d, $^4J(P_A,P_X) = 8$ Hz, $P_X$ of phosphinine).

**Compound 10**: $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta = 265$ (d, $^4J$(P,P) = 7 Hz, P1 and P4), 276 (d, $^4J$(P,P) = 7 Hz, P2 and P3); $^1$H NMR (200.13 MHz, $CDCl_3$, 25 °C): $\delta = 0.33$ (br s, 18 H, 3 $SiMe_2$), 0.41 (s, 18 H, 2 $SiMe_3$), 6.91 – 7.21 (m, 34 H, 6 Ph, 4 H4), 8.01 (t, 2 H, $^3J$(H,H) = $^3J$(H,P) = 8.42 Hz, 2 H5); $^{13}$C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 0.7$ (d, $^3J$(C,P) = 6 Hz 2 $SiMe_3$), 4.3 – 4.9 (m, 3 $SiMe_2$), 127.8 – 132.9 (m, CH of Ph, 4 C4), 138.20 (d, $^2J$(C,P) = 11 Hz, 2 C5 external units), 146.00 (br s, 6 C *ipso* of Ph), 153.0 – 153.8 (m, 4 C3, 2 C5 central units), 163.1 – 168.7 (m, 4 C2, 4 C6); MS (70 eV, EI):*m*/*z* (%): 1153 (8) $[M]^+$, 1079 (2) $[M - SiMe_3]^+$; $C_{68}H_{72}P_4Si_5$ (1153.64): calcd C 70.77, H 6.24; found: C 70.92, H 6.18.

**Dimethylsilacalix[3](3,5-diphenylphosphinine-2,6-diyl) (3):** Phosphinine **7** (0.56 g, 1,0 mmol) was added to a Schlenk tube containing a solution of diazaphosphinine **1** (0.42 g, 2.0 mmol) in toluene (10 mL). The resulting mixture was heated under reflux and the formation of bis(1,2-azaphosphinine) **8** was monitored by $^{31}$P NMR spectroscopy. After 2 h, the reaction was completed and the resulting dark-brown solution was cooled to room temperature. Toluene (200 mL) and bis(phenylethynyl)dimethylsilane (0.26 g, 1.0 mmol) were then added and the solution was heated to 110 – 115 °C . The formation of **3** was monitored by $^{31}$P NMR spectroscopy. In order to maintain a steady concentration of **1** and **7**, small volumes (approx. 20 mL) of solvent were evaporated each day. After 7 – 8 days, the formation of **3** was completed. The resulting solution was then quickly filtrated on a short column of silica gel, and Celite (2.0 g) was added. After evaporation of the solvents, **3** was purified by chromatography on silica gel with hexane/toluene (85:15) as eluent and recovered as a yellow solid (0.18 g, 20 %); m.p. 200 – 202 °C; $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta = 293$ (s); $^1$H NMR (200.13 MHz, $CDCl_3$, 25 °C): $\delta = -0.08$ (s, 18 H, 3 $SiMe_2$), 7.13 – 7.37 (m, 33 H, 3 Ph, 3 H4); $^{13}$C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 3.2$ (s, 3 $SiMe_2$), 127.9 – 129.5 (m, CH of Ph), 131.6 – 132 (v dd, $\Sigma J$(C,P) = 21 Hz, C4), 146.4 (s, C3′ and C5′), 151.9 – 152.1 (v dd, $\Sigma J$(C,P) = 9 Hz, C3 and C5), 163.1 – 164.9 (m, $\Sigma J$(C,P) = 90 Hz, C2 and C6); MS (70 eV, EI):*m*/*z* (%): 912 (100) $[M]^+$, 608 (5) $[M - C_{19}H_{17}PSi]^+$; $C_{57}H_{51}P_3Si_3$ (913.21): calcd C 75.00, H 5.59; found: C 75.12, H 5.48.

**Dimethylsilacalix[4](3,5-diphenylphosphinine-2,6-diyl) (4):** Phosphinine **7** (0.56 g, 1,0 mmol) was added to a Schlenk tube containing a solution of diazaphosphinine **1** (0.42 g, 2.0 mmol) in toluene (10 mL). The resulting mixture was heated under reflux for 2 h and the formation of bis(1,2-azaphosphinine)phosphinine **8** was monitored by $^{31}$P NMR spectroscopy. Toluene (200 mL) and phosphinine **7** (0.56 g, 1.0 mmol) were then added and the solution was heated to 110 – 115 °C. The formation of **4** was monitored by $^{31}$P NMR spectroscopy. As described above for the synthesis of **3**, small volumes of solvent (approx. 20 mL) were evaporated each day. After 7 – 8 days, the formation of **4** was completed. After the reaction mixture was cooled to room temperature, the brown solution was quickly filtrated on a short column of silica gel with toluene as eluent. After evaporation of toluene, acetone (10 mL) was layered onto the oil obtained. This operation allowed the separation of polyphosphinines, which are soluble in acetone, from **4**, which is insoluble. After filtration and drying under vacuum, **4** was recovered as a white solid (0.24 g, 20 %) poorly soluble in common organic solvents; m.p. >220 °C (decomp); $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta = 278$ (s); $^1$H NMR (200.13 MHz, $CDCl_3$, 25 °C): $\delta = -0.04$ (s, 24 H, 4 $SiMe_2$), 7.02 – 7.36 (m, 44 H, 8 Ph, 4 H4); $^{13}$C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 4.4 - 4.7$ (v dd, $\Sigma J$(C,P) = 14 Hz, 4 $SiMe_2$), 127.7 – 129.9 (m, CH of Ph), 132.8 – 133.2 (v t, $\Sigma J$(C,P) = 20 Hz, C4), 146.20 (s, C3′ and C5′), 153 – 153.2 (v t, $\Sigma J$(C,P) = 9 Hz, C3 and C5), 165.65 (d, $^1J$(C,P) = 88.2 Hz, C2 and C6); MS (70 eV, EI):*m*/*z* (%): 1216 (12) $[M]^+$, 912 (100) $[M - C_{19}H_{17}PSi]^+$; $C_{76}H_{68}P_4Si_4$ (1217.61): calcd C 75.00, H 5.59; found: C 75.14, H 5.47.

**2,5-Bis(phenylethynyldimethylsilyl)thiophene (11):** A solution of butyl lithium (1.6 M in hexane; 40 mmol, 25 mL) was added dropwise at room temperature to a solution of thiophene (1.64 g, 20 mmol), TMEDA (4.64g, 40 mmol) in hexane (20 mL). The resulting mixture was then heated under reflux for 90 min. After cooling to −20 °C, phenylethynyldimethylchorosilane (8.50 g, 43,70 mmol) was added, and the resulting solution was heated under reflux for 2 h. After cooling to room temperature, hexane and TMEDA were evaporated, and the residue was chromatographed on silica gel with hexane/toluene (90:10) as eluent. After evaporation of the solvents, **11** was recovered as a yellow solid. Yield: 6.8 g (85 %); m.p. 120 – 122 °C; $^1$H NMR (200.13 MHz, $CDCl_3$, 25 °C): $\delta = 0.55$ (s, 12 H, 2 $SiMe_2$), 7.25 – 7.50 (m, 10 H, 2 Ph), 7.51 (s, 2 H, H3 and H4); $^{13}$C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 1.0$ (s, 2 $SiMe_2$), 92.2 (s, *C*≡CPh), 107.4 (s, C≡*C*Ph), 123.4 (s, C *ipso* of Ph), 128.9 (s, CH of Ph), 129.5 (s, CH of Ph), 132.8 (s, CH of Ph), 137.2 (s, C3 and C4), 143.9 (s, C2 and C5); MS (70 eV, EI):*m*/*z* (%): 400 (100) $[M]^+$; $C_{24}H_{24}Si_2S$ (400.69): calcd C 71.94, H 6.04; found: C 72.08, H 6.07.

**2,5-Bis(Phenylethynyldimethylsilyl)furan (12):** A solution of butyl lithium (1.6 M in hexane; 40 mmol, 25 mL) was added dropwise at room temperature to a solution of furan (1.31 g, 20 mmol) and TMEDA (4.64g, 40 mmol) in hexane. After addition, the mixture was heated to 70 °C for 1 h. After cooling to −20 °C, phenylethynyldimethylchorosilane (8.50 g, 43.70 mmol) was added, and the resulting mixture was then heated to 70 °C for 2 h. After cooling and evaporation of hexane and TMEDA, the residue was chromatographed on silica gel with hexane/toluene (90:10) as eluent. After evaporation of the solvents, **12** was recovered as a yellow oil, which crystallized upon standing. Yield: 4.45 g (58 %); m.p. 110 – 112 °C; $^1$H NMR (200.13 MHz, $CDCl_3$, 25 °C): $\delta = 0.58$ (s, 12 H, 2 $SiMe_2$), 6.91 (s, 2 H, H3 and H4), 7.24 – 7.55 (m, 10 H, 2 Ph); $^{13}$C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = -0.6$ (s, 2 $SiMe_2$), 91.6 (s, *C*≡CPh), 107.1 (s, C≡*C*Ph), 121.9 (s, C3 and C4), 123.5 (s, C *ipso* of Ph), 128.9 (s, CH of Ph), 129.5 (s, CH of Ph), 132.8 (s, CH of Ph), 162.40 (s, C2 and C5); MS (70 eV, EI):*m*/*z* (%): 384 (100) $[M]^+$; $C_{24}H_{24}Si_2O$ (384.63): calcd C 74.95, H 6.29; found: C 74.77, H 6.28.

**2,5-(4′-Phenyl-6′-*tert*-butyl-1′,2′-azaphosphinine-3′-yl)dimethylsilylthiophene (13) and dimethylsilacalix[4]-1,3-(3′,5′-diphenylphosphinine-2′,6′-diyl)-2,4-(thiophene-2′,5′-diyl) (15):** A solution of diazaphosphinine **1** (0.84 g, 4.0 mmol) and 2,5-bis(phenylethynyldimethysilyl)thiophene (0.80 g, 2.0 mmol) in toluene was heated under reflux for 2 h. After this period, the formation of 2,5-bis(1,2-azaphosphininyl)thiophene **13** was completed. Toluene (380 mL) and a second equivalent of diyne (0.80 g, 2.0 mmol) were added, and the resulting solution was further heated under reflux. Periodically, small amounts of solvents (40 mL) were evaporated to maintain a steady concentration of **1** and **11**. After 7 – 8 days, the reaction was completed, and the resulting solution was filtrated on a short silica gel column with toluene as eluent. After evaporation of toluene, acetone (15 mL) was added to precipitate macrocycle **15** and to solubilize the polyphosphinines formed. After filtration and drying, **15** was recovered as a white solid (0.35 g, 20 %). M.p. >220 °C (decomp).

**Compound 13**: $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta = 304$.

**Compound 15:** $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta = 272$ (s); $^1$H NMR (200.13 MHz, $CDCl_3$, 25 °C): $\delta = 0.29$ (d, 24 H, $^4J$(H,P) = 1.73, 4 $SiMe_2$), 7.14 – 7.33 (m, 26 H, 4 Ph, 2 H3 and 2 H4 of thiophene, 2 H4 of phosphinine); $^{13}$C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 1.9$ (d, $^3J$(C,P) = 12 Hz, 4 $SiMe_2$), 128.1 – 132.8 (m, CH of Ph and 2 C4 of phosphinine), 135.3 (s, 2 C3 and 2 C4 of thiophene), 145.9 (s, C3′ and C5′ of Ph), 148.7 (s, C2 and C5 of thiophene), 154.5 (d, $^2J$(C,P) = 11 Hz, C3 and C5 of phosphinines), 163.1 (d, $^1J$(C,P) = 89 Hz, C2 and C6 of phosphinines); MS (70 eV, EI):*m*/*z* (%): 888 (100) $[M]^+$ 444 (30) $[M/2]^+$; $C_{50}H_{50}P_2S_2Si_4$ (889.37): calcd C 67.57, H 5.63; found: C 67.49, H 5.69.

**2,5-(4′-Phenyl-6′-*tert*-butyl-1′,2′-azaphosphinine-3′-yl)dimethylsilylfuran (14) and of dimethylsilacalix[4]-1,3-(3′,5′-diphenylphosphinine-2′,6′-diyl)-2,4-(furan-2′,5′-diyl) (16):** A solution of diazaphosphinine **1** (0.61 g, 2.92 mmol) and 2,5-bis(phenylethynyldimethysilyl)furan **12** (0.56 g, 1.46 mmol) in toluene (15 mL) was heated under reflux for 2 h. After this period, the formation of 2,5-bis(1,2-azaphosphininyl)furan **14** was completed. Toluene (380 mL) and a second equivalent of diyne (0.56 g, 1.46 mmol) were then added, and the resulting solution was further heated



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under reflux. Periodically, small amounts of solvents (40 mL) were evaporated to maintain a steady concentration of **14** and **12**. After 7–8 days, the reaction was completed, and the resulting solution was filtrated on a short silica-gel column with toluene as eluent. After evaporation of toluene, acetone (15 mL) was added to precipitate **16** and to solubilize the polyphosphinines formed. After filtration and drying, **16** was recovered as a white solid. Yield: 0.25 g (20%); m.p. >220 °C (decomp).

**Compound 14**: $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta = 304$ (s).

**Compound 16**: $^{31}$P NMR (81.01 MHz, $CDCl_3$, 25 °C): $\delta = 278.30$ (s); $^1$H NMR (200.13 MHz, $CDCl_3$, 25 °C): $\delta = 0.22$ (s, 24H, $4SiMe_2$), 6.60 (s, 4H, 2H3 and 2H4 of furan), 7.16–7.32 (m, 22H, 4Ph, 2H4 of phosphinine); $^{13}$C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 0.5$ (d, $^3J$(C,P) = 12 Hz, $4SiMe_2$), 120.8 (s, 2C3 and 2C4 of furan), 128.1 (CH of Ph), 128.4 (CH of Ph), 129.6 (CH of Ph), 132.9 (d, $^3J$(C,P) = 20 Hz, 2C4 of phosphinine), 145.95 (s, 2C3′ and 2C5′ of Ph), 154.7 (d, $^2J$(C,P) = 11 Hz, 2C3 and 2C5 of phosphinine), 161.8 (d, $^1J$(C,P) = 89.4 Hz, 2C2 and 2C6 of phosphinine), 164.7 (s, 2C2 and 2C5 of furan); MS (70 eV, EI):*m*/*z* (%): 856 (100) $[M]^+$; $C_{50}H_{50}P_2O_2Si_4$ (857.24): calcd C 70.09, H 5.84, found: C 69.92, H 5.93.

**X-ray structure determination of 3, 4, 15, and 16:**
Crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane into toluene solutions of the compounds. Data were collected at $123 \pm 0.5$ K on an Enraf Nonius CAD4 diffractometer equipped with a graphite monochromator. The crystal structures were solved and refined with the Nonius MOLEN package. All structures were solved by direct methods. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement and anisotropic temperature factors were used for all other atoms. Relevant crystallogaphic details for each compound are summarized in Tables 1 and 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-112703 and CCDC-112706. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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