for these solvated cations. A particular advantage of preparing lanthanide(II) solutions in AHF is that lanthanide trifluorides are insoluble so that solutions for spectroscopic investigation or for preparation of solid derivatives of lanthanides in oxidation state II are not contaminated by lanthanides in oxidation state III. In a study of the effect of different Lewis acids on the solutions we found that the weak Lewis acid GeF_4 was particularly effective in precipitating the dipositive lanthanide cations from AHF, as it has also proved to be with many dipositive d-transition-metal cations.

On addition of GeF_4, the yellow AHF solution containing Sm^{2+} yielded a stable, stoichiometric yellow solid $SmGeF_6$, which was characterized by chemical determination of the oxidation state as well as by infrared and Raman spectroscopy, by powder X-ray diffraction techniques, and by determination of the magnetic moment. Although, for characterization studies, this compound was handled in a nitrogen-filled glove box, it remained bright yellow in the open atmosphere for a period of over 1 h, gradually taking on the brown color of Sm(III) through hydrolytic oxidation. This simple observation indicates a very low solubility of the compound in polar solvents.

Experimental Procedures

Our earlier report[4] described the reagents used, purification of HF, and manipulation of volatile reagents in vacuum systems and of involatile products in a nitrogen-filled glovebox, as well as removal of surface oxide from metallic Sm and the preparation of a solution of Sm^{2+} and F^- in AHF.

Instrumental Methods. Infrared spectra were obtained (Perkin-Elmer 457) from Nujol mulls between CsI windows.

A Spex-Ramalog instrument was used for recording Raman spectra, 514.5-, 647.1-, and 676.4-nm excitation wavelengths being employed.

X-ray powder photographs were exposed on a Philips Debye-Scherrer camera (PW 1024/10), diameter 114.5 mm, using Cu Kα radiation. Magnetic data were determined by the Gouy method with $HgCo(NCS)_4$ as calibrant.

Isolation of $SmGeF_6$. A solution containing Sm^{2+} and F^- ions was prepared and frozen at −196 °C. An excess of GeF_4 was admitted to the tube, and the contents were allowed to warm to room temperature. Rapid precipitation of $SmGeF_6$ occurred, and the colorless supernatant solution was discarded. The precipitate was washed with fresh AHF (5 mL), which was decanted away, and the solid was dried by being maintained under vacuum for several hours at room temperature. $EuGeF_6$ and $YbGeF_6$ can be recovered in similar fashion from the solutions described in our earlier paper.[4]

Results and Discussion

The oxidation state of the lanthanide was determined by oxidation of solid $SmGeF_6$ with excess acidified MnO_4^- and back-titration with standardized Fe^{2+}. The experimentally determined value was 1.95 (theoretical 2.0), equivalent to a samarium content of 47.1% (calcd, 44.6%).

IR spectra showed bands at 630 (sh), 608 (s), 450 (w), 360 (m), and 330 (m) cm^{-1} in excellent agreement in position, relative intensity, and profile with the spectrum published for $BaGeF_6$.[5] X-ray powder photography indicated that the compound was isomorphous with $BaGeF_6$.[6]

In a Raman experiment conducted at ambient temperature, excitation at 514.5 nm caused thermolysis of the solid sample, but the problem was eliminated when the 647.1- and 676.4-nm lines were used. Intense laser-induced fluorescence occurred. Two lines at 1058 and 904 cm^{-1} together with several weaker features were evident when excitation at 647.1 nm (15 454 cm^{-1}) was employed. When the 676.4-nm (14 784-cm^{-1}) line was used, the lines were shifted to 384 and 233 cm^{-1}, respectively. The shifts effectively mirror the differences in the excitation frequencies used. On converting the energies to wavelengths, we are therefore observing emission from the Sm^{2+} at 694.6 and 687.5 nm, values in excellent agreement with emission near 690 nm reported for Sm^{2+} in host lattices.[7,8]

Emission from the cation so dominated the spectra that scattering from the anion could not be positively identified even when the experiments were conducted at low temperatures.

The compound has a magnetic moment, $\mu_{eff} = 3.13\ \mu_B$, at 293 K. Surprisingly little magnetic data has been reported for Sm^{2+}. The ion is isoelectronic with Eu^{3+} for which moments in the range 3.4–3.5 are usually found.[2b] In contrast, moments for Sm^{3+} are usually near 1.6 μ_B.[2c]

We believe that the data confirm the formulation of the samarium compound as $SmGeF_6$, and together with the solids isolated by adding GeF_4 to the solutions previously reported as containing Eu^{2+} and Yb^{2+},[4] we have prepared a new series of compounds that are easily synthesized at or below room temperature that contain divalent lanthanide ions: $LnGeF_6$ (Ln = Sm, Eu, Yb).

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Contribution from the Laboratoire de Chimie de Coordination du CNRS, UPR 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex, France, and Laboratoire de Chimie des Agroressources, Institut National Polytechnique de Toulouse, Ecole Nationale Supérieure de Chimie de Toulouse, 118 route de Narbonne, 31077 Toulouse Cedex, France

Reactivity of Polyaza Diphosphorus Macrocycles

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Introduction

We recently described an easy synthesis of polyaza diphosphorus macrocycles[1] by reacting phosphodihydrazides with 1,2, 1,3, 1,4, 1,6, or 1,11 dicarboxaldehydes.[2] These reactions do not require high dilution or drastic conditions since these derivatives are obtained in nearly quantitative yield when both reactants are stirred in methanol for 3 h at room temperature. Another significant advantage of this type of reaction is the formation of *free* macrocycles. This was not the case for the other known reactions leading to phosphorus Schiff base large-membered rings: all the reported experiments involved template reactions and therefore led to macrocycle complexes.[3]

The possibility to form easily these first free P–N–N-containing macrocycles prompted us to investigate both their reactivity and their complexation properties.

We herein report some examples of the reactivity of these macrocycles involving either imino functions or phosphoryl and thiophosphoryl groups. We also demonstrate that these molecules possess tailored internal cavities and allow one to prepare selectively macrocyclic hydrazino phosphonium salts. To our knowledge, no examples of cyclic or even linear (alkylhydrazino)phosphonium salts have been reported so far.

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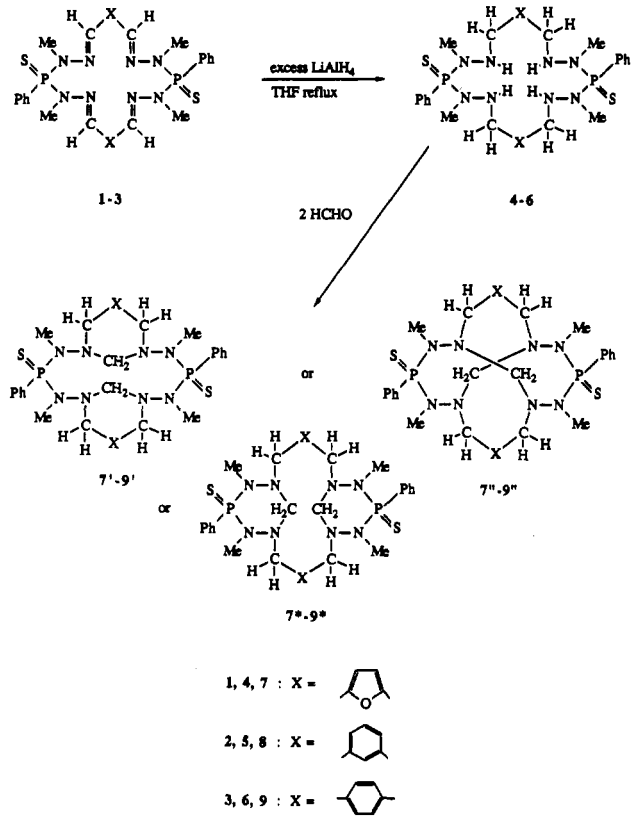
Scheme I

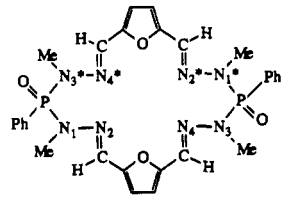


Results and Discussion

Reduction and Bridging. No reduction occurs, even under drastic conditions, when the 20-membered rings **1** and **2**, or the 22-membered ring **3**, are treated with sodium borohydride. On the other hand, compounds **1–3** are cleanly reduced with lithium aluminum hydride in THF (Scheme I). The new macrocycles, **4–6**, are isolated as white powders in 20% yield for **4**, 60% yield for **5**, and 35% yield for **6**. Their structure is deduced from ^{31}P, ^{1}H, and ^{13}C NMR and IR spectroscopies, mass spectrometry, and microanalysis. An expected slight deshielding effect is observed in ^{31}P NMR from +77.7–78.2 (compounds **1–3**) to +81.4–81.6 (compounds **4–6**) ppm. ^{1}H NMR spectra are well resolved, and all the protons can be uniquely assigned (see Experimental Section for details). Particularly pertinent as a consequence of the reduction is the absence of imino protons and the presence of hydrazino protons (from 3.19 to 3.50 ppm, depending on the macrocycle) and methylene groups (3.69–3.90 ppm). Moreover, macrocycles **4–6** exhibit characteristic $^{13}C\{^{1}H\}$ NMR features (for example, doublets ($^{3}J_{CP}$) for the CH_2 groups at 46.5 (**4**), 53.20 (**5**), and 53.21 (**6**) ppm). Broad NH vibration frequencies bands are also observed in IR spectroscopy (3240–3270 cm^{-1}, association with P=S). Lastly, mass spectrometry confirms the formation of derivatives **4–6**.

Internal cavities of macrocycles **4–6** can be easily tailored. Addition of 2 equivs of formaldehyde to THF solutions of these compounds (1 equiv) leads quantitatively to new macrocycles **7–9** obtained as yellow or white powders. Spectroscopic data are in favor of structures resulting from the intramolecular bridging of the NH groups (see Experimental Section). Indeed, ^{1}H NMR spectra display singlets between 4.1 and 4.38 ppm (depending on the model) for the two bridged methylene groups, while ^{13}C NMR spectra confirm the presence of new sp^3 carbon atoms in the final product (δ from 58.7 to 68.2 ppm). Mass spectrometry allows us to preclude dimers arising from intermolecular bridging between NH groups of two macrocycles.

Therefore, three structures can be postulated for these polycyclic derivatives: that resulting from the bridging of nitrogen atoms owning to two different phosphorhydrazino groups, viz. **7′–9′**, that arising from bridging of nitrogen atoms accross the ring viz. **7″–9″**, or that coming from the direct bridging of nitrogen atoms of the same phosphorhydrazino fragment, viz. **7*–9*** (Scheme I). Unfortunately, all attempts to get suitable crystals for an X-ray structure determination have failed. Nevertheless, the following arguments can be evoked in favor of structures **7*–9***: (i) it is usually easier to obtain six-membered rings rather than eight- or nine-membered rings, (ii) ^{31}P chemical shifts of compounds **7–9** are close to those observed for perhydro-1,2,4,3-tetrazaphosphorines and 2,3,4,5-tetrahydro-1,2,4,5,3-tetrazaphosphorines,[4] and (iii) interatomic distances observed for the macrocycle **10**, N(2)–N(4)* = 2.860 Å, N(2)–N(4) = 6.088 Å, and N(2)–N(2)* = 6.910 Å,[5] strongly suggest that the bridging is much more likely between nitrogen atoms of the same $-P(N-NH)_2$ moieties even though these distances are presumably slightly different in **4–6**, in which imino functions are reduced. It is obvious from models that the large macrocycle cannot distort enough to allow CH_2 group bridging nitrogen atoms across the ring.



10

Alkylation and Silylation. We tried to obtain macrocyclic salts by reacting species **1–3** with methyl trifluoromethanesulfonate and **10–12** with trimethylsilyl trifluoromethanesulfonate. Alkylation or silylation might take place either on imino nitrogen atoms or on phosphoryl and thiophosphoryl groups. Actually, methylation only occurs on sulfur even when the reaction is performed with a large excess of CF_3SO_3Me affording macrocyclic cations **13–15** (Scheme II). ^{1}H NMR spectra are fully consistent with these assignments. In particular, the SMe groups appear as a doublet (δ 2.4 ppm) with a larger phosphorus proton coupling constant ($^{3}J_{PH}$ = 16 Hz) than that observed for the NMe groups ($^{3}J_{PH}$ = 9–10 Hz). The shift of the P=S vibration frequencies from 730 (neutral macrocycles) to 630 (cationic species) cm^{-1} in the IR spectra is also consistent with the methylation of sulfur atoms. No evidence for the alkylation of imino nitrogen atoms has been found.

Similarly, silylation preferentially takes place on phosphoryl groups when derivatives **10–12** are treated with 2 equiv of $CF_3SO_3SiMe_3$ (deshielding effect of 6 ppm in ^{31}P NMR). The resulting salts **16–18** are extremely unstable and even at 0 °C decompose into numerous products evidenced by ^{31}P NMR that have not been identified so far.

Reaction with NaOCl. Macrocyclic Schiff bases can be used as catalysts for oxidation reactions when the oxygen source is a smooth oxidant such as PhIO or ROOH. The trivial oxidant NaOCl is also able to act as an excellent oxygen donor in catalytic oxygenation reactions, viz. epoxidation and hydroxylation. Surprisingly, the thiophosphoryl macrocycles **1–3** are cleanly transformed into the corresponding phosphoryl derivatives by treatment with aqueous NaOCl while no reaction occurs when compounds **10–12** already possessing phosphoryl groups are reacted with NaOCl.

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$$\mathbf{1\text{-}3} \xrightarrow{\text{aqueous NaOCl}} \mathbf{10\text{-}12}$$

No clear evidence has been found for the formation of different isomers for macrocycles **1–3**, **4–6**, **7–9**, and **13–18**, even if broad signals are observed in ^{31}P NMR spectra (different arrangements of phenyl groups and sulfur or oxygen should allow at least two diastereoisomers per macrocycle).

Experimental Section

General Procedures. All experiments were performed under dry argon atmosphere. Dry, oxygen-free solvents were used at all times. ^1H NMR spectra were recorded on a Bruker WM250 or a Bruker AC80 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AC80 or a Varian FT 80A spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. Downfield shifts are expressed with a positive sign. ^{31}P NMR spectra were obtained on a Bruker AC80 spectrometer. Downfield shifts are expressed with a positive sign in ppm relative to external 85% H_3PO_4. IR spectra were recorded on a Beckman IR10 spectrometer and a Perkin-Elmer lattice spectrometer (Mol 598), using a polystyrene film for calibration. Mass spectra were obtained on a Ribermag R10 10E instrument or a Varian MAT 311A instrument.

Reduction of Macrocycles 1–3. To a solution of $LiAlH_4$ (12 mmol) in 50 mL of THF at 0 °C was added dropwise a solution of macrocycle **1–3** (1 mmol) in 5 mL of THF. The mixture was stirred for 7 h at 80 °C. Excess $LiAlH_4$ was decomposed by addition of 1 mL of water at 0 °C. After filtration of the precipitate through Celite, the organic layer was dried over sodium sulfate and concentrated to give a powder. The crude products **4–6** were purified by successive extractions with chloroform/hexane (1:2) and chloroform/toluene (1:2).

4: yellow powder; mp >195 °C dec; 20% yield. ^{31}P NMR ($CDCl_3$): δ 81.5. ^1H NMR ($CDCl_3$): δ 2.9 (d, $^3J_{PH}$ = 10.2 Hz, 12 H, P–N–CH_3), 3.5 (s, 4 H, NH), 3.9 (s, 8 H, CH_2), 6.4 (s, 4 H, C_4OH_2), 7.5 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 36.3 (d, $^2J_{PC}$ = 9 Hz, P–N–CH_3), 46.5 (d, $^3J_{PC}$ = 6 Hz, P–N–N–CH_2), 108.4 (s, C–C–O), 125.9–133.2 (m, C–C–O and C_6H_5). IR (KBr): 3270 (br, ν (NH)) cm^{-1}. Mass spectrum: *m/e* 644 (M^+). Anal. Calcd for $C_{28}H_{38}N_8O_2P_2S_2$: C, 52.17; H, 5.9; N, 17.39. Found: C,51.98; H, 5.58; N, 17.21.

5: white powder; mp 105 °C; 60% yield. ^{31}P NMR ($CDCl_3$): δ 81.6. ^1H NMR ($CDCl_3$): δ 2.85 (d, $^3J_{PH}$ = 11.2 Hz, 12 H, P–N–CH_3), 3.19 (s, 4 H, NH), 3.69 (s, 8 H, CH_2), 6.82–8.01 (m, 18 H, C_6H_4 and C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 35.74 (d, $^2J_{CP}$ = 8 Hz, P–N–CH_3), 53.20 (d, $^3J_{CP}$ = 7 Hz, P–N–N–CH_2), 127.46–137.73 (m, C_6H_4 and C_6H_5). IR (KBr): 3250 (br, ν(NH)) cm^{-1}. Mass spectrum: *m/e* 664 (M^+). Anal. Calcd for $C_{32}H_{42}N_8P_2S_2$: C, 57.83; H, 6.32; N, 16.86. Found: C, 57.37; H, 6.25: N, 16.67.

6: white powder; mp 124–126 °C; 60% yield. ^{31}P NMR ($CDCl_3$): δ 81.4. ^1H NMR ($CDCl_3$): δ 2.81 (d, $^3J_{PH}$ = 11.1 Hz, 12 H, P–N–CH_3), 3.32 (s, 4 H, NH), 3.72 (s, 8 H, CH_2), 6.97–7.9 (m, 18 H, C_6H_4 and C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 36.08 (d, $^2J_{CP}$ = 8 Hz, P–N–CH_3), 53.21 (d, $^3J_{CP}$ = 8 Hz, P–N–N–CH_2), 127.69–129.37 (m, C_6H_5), 132.6–137.14 (m, C_6H_4). IR (KBr): 3240 (br, ν (NH)) cm^{-1}. Mass spectrum: *m/e* 664 (M^+). Anal. Calcd for $C_{32}H_{42}N_8P_2S_2$: C, 57.83; H, 6.32: N, 16.86. Found: C, 57.48; H, 6.07; N, 16.59.

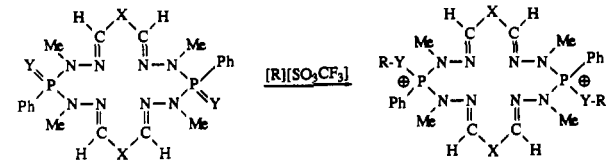
Addition of Formaldehyde to Macrocycles 4–6. To a solution of macrocycles **4–6** (2.3 mmol) in 8 mL of THF was added formaldehyde (4.6 mmol, 30% aqueous solution). After the mixture was stirred for 1 h at room temperature, the solution was evaporated to dryness and the residue extracted with chloroform/ether (1:2). Evaporation of the solvents afforded macrocycles **7–9** as yellow or white powders.

7: yellow powder; mp >210 °C dec; 93% yield. ^{31}P NMR ($CDCl_3$): δ 64.4. ^1H NMR ($CDCl_3$): δ 3.01 (d, $^3J_{PH}$ = 10.3 Hz, 12 H, P–N–CH_3), 3.76 (s, 8 H, P–N–N–CH_2), 4.38 (s, 4 H, N–CH_2–N), 6.45 (s, 4 H, C_5OH_2), 7.42 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.70 (br s, P–N–CH_3), 51.50 (br s, P–N–NCH_2), 68.2 (s, N–CH_2–N), 110.57 (s, C–C–O, 125.8–132.13 (, C_4OH_2 and C_6H_5). Mass spectrum: *m/e* 668 (M^+). Anal. Calcd for $C_{30}H_{38}N_8O_2P_2S_2$: C, 53.89; H, 5.68; N, 16.76. Found: C, 53.51; H, 5.26: N, 16.57.

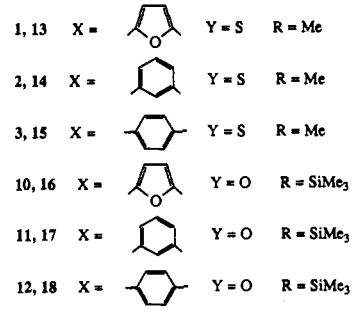
8: white powder; mp 179 °C; 94% yield. ^{31}P NMR ($CDCl_3$): δ 64.26. ^1H NMR ($CDCl_3$): δ 2.84 (d, $^3J_{PH}$ = 11 Hz, 12 H, P–N–CH_3), 3.67 (br s, 8 H, P–N–N–CH_2), 4.37 (s, 4 H, N–CH_2–N), 6.85–8.01 (m, C_6H_4 and C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.51 (br s, P–N–CH_3), 57.50 (s, P–N–N–CH_2), 68.11 (s, N–CH_2–N), 125.65–137.52 (m, C_6H_4 and C_6H_5). Mass spectrum: *m/e* 688 (M^+). Anal. Calcd for $C_{34}H_{42}N_8P_2S_2$: C, 59.30; H, 6.10; N, 16.27. Found: C, 59.11; H, 5.84; N, 15.96.

9: white powder; mp 185 °C; 96% yield. ^{31}P NMR ($CDCl_3$): δ 64.3. ^1H NMR ($CDCl_3$): δ 2.82 (d, $^3J_{PH}$ = 11.2 Hz, 12 H, P–N–CH_3), 3.66 (br s, 8 H, P–N–N–CH_2), 4.1 (s, 4 H, N–CH_2–N), 6.97–7.42 (m, C_6H_4 and C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.73 (br s, P–N–CH_3), 52.92 (s, P–N–N–CH_2), 58.7 (s, N–CH_2–N), 125.6–137.6 (m, C_6H_4 and C_6H_5). Mass spectrum: *m/e* 688 (M^+). Anal. Calcd for $C_{34}H_{42}N_8P_2S_2$: C, 59.30; H, 6.10; N, 16.27. Found: C, 59.15; H, 6.00; N, 16.02.

Scheme II



1-3 , 10-12 **13-18**



Alkylation of Macrocycles 1–3 with Methyl Trifluoromethanesulfonate. To a solution of macrocycles **1–3** (1.57 mmol) in 10 mL of dichloromethane was added methyl trifluoromethanesulfonate (3.14 mmol). The yellow solution turned red. After the mixture was stirred for 2 h at room tempera ture, the solvent was removed to yield an oily residue, which was washed several times with acetonitrile. Unstable red powders were thus obtained.

13: red powder; 96% yield. ^{31}P NMR (CD_3CN): δ 75.3; ^1H NMR (CD_3CN): δ 2.4 (d, $^3J_{PH}$ = 16 Hz, 6 H, P—S—CH_3), 3.27 (d, $^3J_{PH}$ = 9.6 Hz, 12 H, P—N—CH_3), 6.9 (s, 4 H, C_4OH_2), 7.7 (m, 10 H, C_6H_5), 8.08 (s, 4 H, HC=N). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 14.4 (br s, P—S—CH_3), 34.02 (br s, P—N—CH_3), 117 (s, *C*—C—O), 121.9 (q, $^1J_{CF}$ = 320.6 Hz, CF_3SO_3), 134.70–137.46 (m, C—*C*—O and C_6H_5), 151.5 (s, *C*=N). IR (KBr): 637 (m, ν(P=S)) cm^{-1}. Anal. Calcd for $C_{32}H_{36}F_6N_8O_8P_2S_4$: C, 39.83; H, 3.76; N, 11.62. Found: C, 39.62: H, 3.71; N, 11.41.

14: red powder; 92% yield. ^{31}P NMR (CD_3CN): δ 75.2. ^1H NMR (CD_3CN): δ 2.41 (d, $^3J_{PH}$ = 16.4 Hz, 6 H, P—S—CH_3), 3.36 (d, $^3J_{PH}$ = 9.6 Hz, 12 H, P—N—CH_3), 7.55–8.16 (m, 22 H, HC=N, C_6H_4 and C_6H_5). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 14.15 (br s, P—S—CH_3), 30.7 (br s, P—N—CH_3), 121.8 (q, $^1J_{CF}$ = 320.6 Hz, CF_3SO_3), 125.2–135 (m, C_6H_4 and C_6H_5), 136.3 (s, *C*=N). Anal. Calcd for $C_{36}H_{40}F_6N_8O_6P_2S_4$: C, 43.90; H, 4.10; N, 11.38. Found: C, 43.66; H, 4.01; N, 11.22.

15: red powder; 90% yield. ^{31}P NMR (CD_3CN): δ 75.33. ^1H NMR (CD_3CN): δ 2.45 (d, $^3J_{PH}$ = 16.3 Hz, 6 H, P–S–CH_3), 3.36 (d, $^3J_{PH}$ = 10.2 Hz, 12 H, P–N–CH_3), 7.54–8.11 (m, 22 H, HC=N, C_6H_4 and C_6H_5). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 14.27 (br s, P–S–CH_3), 31.1 (br s, P–N–CH_3), 121.6 (q, $^1J_{CF}$ = 320.5 Hz, CF_3SO_3), 126.2–135.3 (m, C_6H_4 and C_6H_5), 136.21 (s, *C*=N). Anal. Calcd for $C_{36}H_{40}F_6N_8O_6P_2S_4$: C, 43.90; H, 4.10; N, 11.38. Found: C, 43.56; H, 4.04; N, 11.26.

Silylation of Macrocycles 10–12 with Trimethylsilyl Trifluoromethanesulfonate. To a solution of macrocycles **10–12** (0.24 mmol) in 10 mL of dichloromethane at 0 °C was added trimethylsilyl trifluoromethanesulfonate (0.48 mmol). The yellow solution turned orange. The mixture was stirred for 0.5 h at 0 °C. Removal of the solvent in vacuo afforded an oil, which was quickly washed with acetonitrile. Salts **16–18** thus obtained are extremely unstable even at 0 °C.

16: orange oil; 70% yield. ^{31}P NMR (CD_3CN): δ 30.7. ^1H NMR (CD_3CN): δ 0.6 (s, 18 H, Me_3Si), 3.01 (d, $^3J_{PH}$ = 7.6 Hz, 12 H, P–N–CH_3), 6.4 (s, 4 H, C_4OH_2), 7.63 (m, 10 H, C_6H_5), 8.01 (s, 4H, HC=N).

17: orange oil; 68% yield. ^{31}P NMR (CD_3CN): δ 30.76; ^1H NMR (CD_3CN): δ 0.58 (s, 18 H, Me_3Si), 3.47 (d, $^3J_{PH}$ = 8.8 Hz, 12 H, P–N–CH_3), 7.79 (m, 18 H, C_6H_4 and C_6H_5), 8.26 (s, 4 H, HC=N).

18: orange oil. ^{31}P NMR (CD_3CN): δ 30.73. Due to the high instability of this compound, further characterization failed.

Treatment of Macrocycles 1–3 with NaOCl. To a solution of macrocycles **1–3** (0.4 mmol) in 3 mL of dichloromethane at room temperature, was added aqueous NaOCl (1 mmol). After the mixture was stirred for 8 h, the solvent was removed and the residue extracted with 20 mL of THF. Macrocycles **10–12**[1] were obtained in almost quantitative yields.