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Tricoordinated Phosphorus-Containing Macrocycles: New Synthetic Strategies

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ABSTRACT

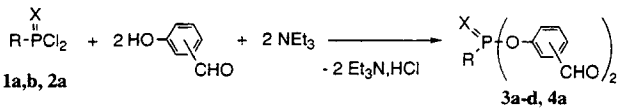
Phosphorus dialdehydes RP $(OC_6H_4CHO)_2$ (R = Ph, Me_2N) react with phosphodihydrazides PhP(Y)-$[N(CH_3)NH_2]_2$ (Y = S, O) to give macrocycles **6a–c** *arising from [2 + 2] cyclocondensation reactions. Treatment of phosphodihydrazone PhP(S)* $[OC_6H_4CH{=}N{-}N(Me)H]_2$ **7** *with phenyldichlorophosphine affords macrocycle* **8** *possessing tri and tetracoordinated phosphorus atoms. Clean desulfurization of thiophosphorus macrocycles* **9** *and* **12** *gives rise selectively to new tricoordinated phosphorus containing macrocycles* **11** *and* **13**.

INTRODUCTION

Despite the fact that a huge amount of work has been devoted to the synthesis and complex forming properties of macrocycle ligands containing N- and O- (hard) donor atoms [1], relatively few examples of such ligands containing P- (soft) donor atoms are known [2]. However, tricoordinated phosphorus-containing macrocycles are very interesting, due in particular to their potential ability to stabilize low oxidation state transition metal complexes [2].

We have already demonstrated that tetracoordinated phosphorus-containing macrocycles [3], multimacrocycles [4], cryptands [5], dendrimers [6], or functionalized phosphorhydrazones [7] can easily be obtained by reacting phosphorhydrazides with aldehydes. This general synthesis has been applied in two cases for the preparation of tricoordinated phosphorus-containing macrocycles, starting from tricoordinated phosphorus dialdehydes. Compounds with $C{-}P^{III}{-}C$ [8] and $N{-}P^{III}{-}O$ [9] moieties in the macrocyclic ring have thus been isolated.

We report here an extension of this method to the synthesis of macrocycles containing $O{-}P^{III}{-}O$ moieties, as well as two new strategies to synthesise previously unknown macrocycles containing the $N{-}N{-}P^{III}{-}N{-}N$ chain.



1a,b, 2a **3a-d, 4a**

1a: X = lone pair, R = Ph
1b: X = lone pair, R = Me_2N
2a: X = S, R = Ph

3: X = lone pair
a: R = Ph, 4-CHO
b: R = Ph, 3-CHO
c: R = Me_2N, 4-CHO
d: R = Me_2N, 3-CHO
4a: X = S, R = Ph, 4-CHO

SCHEME 1

RESULTS AND DISCUSSION

The first method to obtain macrocycles containing $O{-}P^{III}{-}O$ moieties implies the synthesis of tricoordinated phosphorus dialdehydes **3a–d**. These precursors are prepared in good yield by reacting dichlorophenylphosphine **1a** or dichlorodimethylaminophosphine **1b** with the triethylammonium salt of meta or para hydroxybenzaldehyde (Scheme 1). The phosphorus dialdehydes **3a–d** thus obtained

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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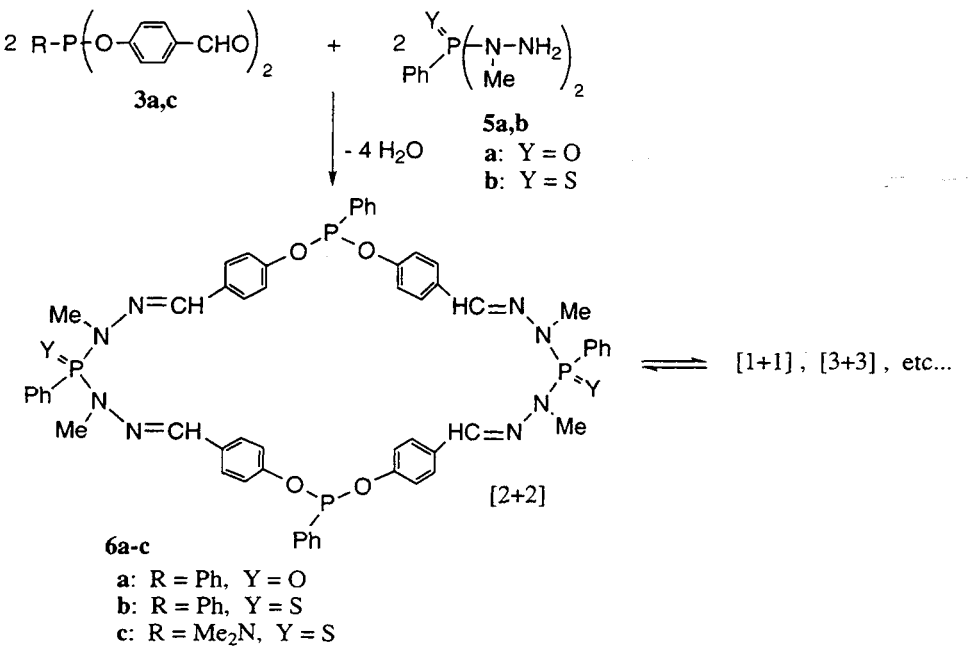
are not very stable, due to the known reaction of the lone pair of tricoordinated phosphorus with aldehyde functions [10], which induces the polymerization of dialdehydes **3a–d** when left several weeks at room temperature. On the other hand, the same synthetic method applied to dichlorophosphine oxides or sulfides (**2a**, for example) yields stable tetracoordinated phosphorus dialdehydes such as **4a** (Scheme 1).

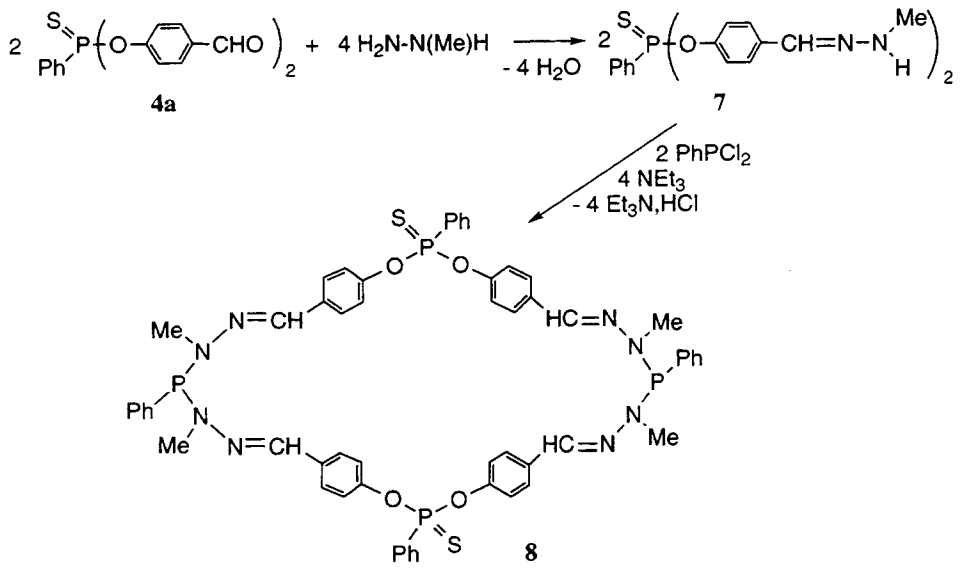
Dialdehydes **3a,c** are generally used in situ to react with phosphodihydrazides **5a,b** [11]. The reaction of dialdehyde **3a**, monitored by ^{31}P NMR spectroscopy, necessitates 4 days to be completed. At this stage, two sharp signals appear in the ^{31}P NMR spectra, corresponding to the $O-P^{III}-O$ (δ = 158) and N–P(O)–N (δ = 22.8) or N–P(S)–N (δ = 78.5) moieties of macrocycles **6a,b**, respectively. The disappearance of NH_2 and CHO functions, shown by ^1H ^{13}C NMR and IR spectroscopies, confirms the formation of a cyclocondensation product. Mass spectrometry proves that macrocycles **6a,b** are obtained by reaction of two equivalents of each reagent i.e., [2 + 2] cyclocondensations (Scheme 2). However, when left several weeks in solution, these macrocycles undergo a ring opening, which induces a broadening of ^{31}P NMR signals. An analogous phenomenon has already been described for other types of macrocycles containing the $O-P^{III}-O$ linkage [12]. This probably explains why we have been unable to isolate the macrocycle **6c** in a pure state. In this case, the reaction is very slow and takes 1 month for completion; one may presume that the rate of ring opening is of the same order of magnitude as the rate of cyclocondensation.

The obtention of macrocycles **6** is of interest since one of them (**6b**) has recently allowed us to prepare the first phosphorus spherand [5a], but the instability of the O–P–O moieties prompted us to explore the synthesis of macrocycles containing other types of tricoordinated phosphorus atoms including the $N-N-P^{III}-N-N$ linkage. These macrocycles are not accessible from a reaction similar to those reported in Scheme 2, involving P^{III} dihydrazides $RP[N(Me)NH_2]_2$, since this type of compound is still unknown. To circumvent this difficulty, we elaborated two synthetic strategies. The first one is a "game of building blocks": the reaction of methyl hydrazine with the phosphorus dialdehyde **4a** yields the phosphodihydrazone **7**, then reaction of the N–H functions of **7** with dichlorophenylphosphine in the presence of triethylamine rapidly results in the formation of a cyclocondensation product, **8** (Scheme 3). **8** is characterized in its ^{31}P NMR spectrum by two sharp signals: δ = 82.4 corresponding to the O–P(S)–O moieties and δ = 102.1 corresponding to the $N-N-P^{III}-N-N$ moieties. In this case also, mass spectrometry proved a [2 + 2] cyclocondensation reaction leading to the first macrocycle possessing the $N-N-P^{III}-N-N$ linkage.

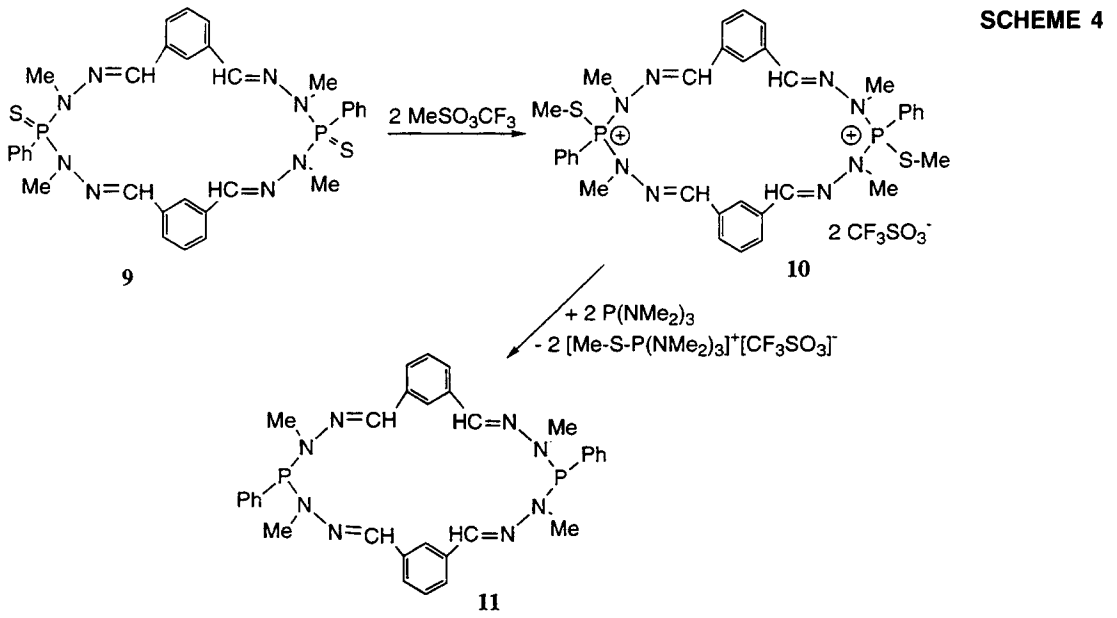
The second method to synthesize macrocycles of this type proceeds with thiophosphoryl macrocycles as starting reagents. We have already demonstrated that methyl trifluoromethanesulfonate specifically adds to the thiophosphoryl groups of macrocycles such as **9** [3a–c,e] to yield dicationic macrocycles such as **10** [3e,f,k,8]. Methylation weakens the phosphorus–sulfur bond and allows desulfurization to take place using bases such as

SCHEME 2





SCHEME 3



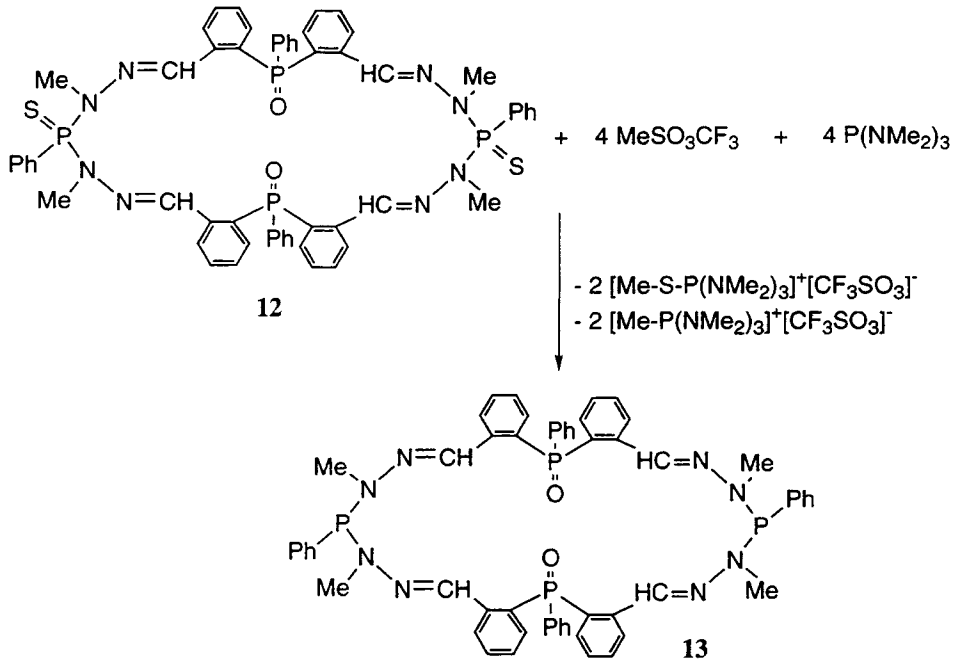
SCHEME 4

hexamethyl-phosphorus triamide [13]. The tricoordinated phosphorus-containing macrocycle **11** is thus isolated in good yield (Scheme 4) and characterized in its ^{31}P NMR spectrum by a single signal at δ = 101.3 (N–N–P^{III}–N–N). This reaction is specific, since we have tried to perform the same experiment with the oxo analogue of **9** (P=O functions instead of P=S functions); the P=O functions are not methylated and the starting oxo macrocycle is recovered intact after addition of $P(NMe_2)_3$.

This specificity has also been observed when we tried to add first, four equivalents of methyl trifluoromethanesulfonate, then four equivalents of hexamethylphosphorus triamide to the tetraphosphorus macrocycle **12** [8], which possesses two phosphoryl and two thiophosphoryl functions. The ^{31}P NMR spectrum of the crude reaction products exhibits four singlets corresponding to the thiophosphonium ion $[Me–S–P(NMe_2)_3]^+$ (δ = 67.3), the phosphonium ion issued from the direct reaction of unreacted $MeSO_3CF_3$ with $P(NMe_2)_3$ ($[MeP(NMe_2)_3]^+$: δ = 58.8) and the macrocycle **13** (δ = 102.8, N–N–P^{III}–N–N; δ = 33.6, C–P(O)–C). These values evidence that no reduction of the P=O bonds occurred, as proved also by mass spectrometry of the isolated macrocycle **13** (m/z = 993 [M + 1]$^+$).

The easy and specific desulfurization of thiophosphoryl groups in the reaction with $MeSO_3CF_3$/$P(NMe_2)_3$ allows us to consider macrocycles con-

SCHEME 5



taining P^{IV} = S as stable and easy to handle precursors of P^{III}-containing macrocycles. The investigation of the complexation properties of these new classes of macrocycle toward low oxidation state transition metals is underway.

EXPERIMENTAL

All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker AC 80 and AC 200 spectrometers. ^{31}P NMR chemical shifts are reported in δ values relative to 85% H_3PO_4. Mass spectra were obtained by fast atom bombardment on a Finniganmat TSQ 700 spectrometer.

General Procedure for the Synthesis of the Dialdehydes **3a–d** *and* **4a**

Freshly distilled triethylamine (0.77 mL, 5.52 mmol) was added to a solution of meta or para hydroxybenzaldehyde (0.675 g, 5.55 mmol) in tetrahydrofuran (40 mL). After the solution had been stirred for 30 minutes at room temperature, 2.76 mmol of dichlorophosphine (**1a**: 0.375 mL, 0.494 g; **1b**: 0.403 g; **2a**: 0.428 mL, 0.582 g) was added at 0°C. The mixture was stirred for 2 hours at room temperature. After filtration, the solvent was evaporated and the resulting oil was washed with acetonitrile/hexane (20/20).

Bis(O-p-formylphenyl)phenyl Phosphonite **3a**. **3a** was isolated as a pale yellow oil (75% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 159.0; ^1H NMR ($CDCl_3$) δ 6.87–7.91 (m, 13H, C_6H_5, C_6H_4), 9.77 (s, 2H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 115.4–131.6 (unresolved m, C_6H_5, C_6H_4), 161.0 (s, C-1-O-P), 190.3 (s, CHO). IR (THF): 1697 cm^{-1} ($\nu_{C=O}$).

Bis(O-m-formylphenyl)phenyl Phosphonite **3b**. **3b** was isolated as a yellow oil (72% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 160.3; ^1H NMR ($CDCl_3$) δ 7.13–7.74 (m, 13H, C_6H_5, C_6H_4), 9.75 (s, 2H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 115.0–137.0 (unresolved m, C_6H_5, C_6H_4), 157.0 (s, C-1-O-P), 191.1 (s, CHO). IR (THF): 1697 cm^{-1} ($\nu_{C=O}$).

Dimethylamido-bis(p-formyl phenyl) Phosphite **3c**. **3c** was isolated as a red oil (70% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 138.4; ^1H NMR ($CDCl_3$) δ 2.61 (d, $^3J_{HP}$ = 9.6 Hz, 6H, CH_3) 6.97 (d, $^3J_{HH}$ = 8.4 Hz, 4H, C_6H_4), 7.64 (d, $^3J_{HH}$ = 8.4 Hz, 4H, C_6H_4), 9.70 (s, 2H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 33.9 (d, $^2J_{CP}$ = 20.7 Hz, CH_3), 119.1 (d, $^3J_{CP}$ = 9.2 Hz, C-2), 130.9 (s, C-3), 157.9 (d, $^2J_{CP}$ = 5.8 Hz, C-1), 189.7 (s, CHO). IR (THF): 1697 cm^{-1} ($\nu_{C=O}$).

Dimethylamido-bis(m-formyl phenyl) Phosphite **3d**. **3d** was isolated as a red oil (73% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 140.1; ^1H NMR ($CDCl_3$) δ 2.68 (d, $^3J_{HP}$ = 9.6 Hz, 6H, CH_3) 7.21–7.43 (m, 8H, C_6H_4), 9.83 (s, 2H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 34.1 (d, $^2J_{CP}$ = 20.6 Hz, CH_3), 119.7 (d, $^3J_{CP}$ = 8.7 Hz, C-6), 124.4 (s, C-3), 125.6 (d, $^3J_{CP}$ = 7.8 Hz, C-2), 129.7 (s, C-4), 137.3 (s, C-5), 153.0 (d, $^2J_{CP}$ = 5Hz, C-1), 190.9 (s, CHO). IR (THF): 1691 cm^{-1} ($\nu_{C=O}$).

Bis(O-p-formylphenyl)phenyl Thiophosphonate **4a**. **4a** was isolated as a pale yellow oil (80% yield).

$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 82.1; ^1H NMR ($CDCl_3$) δ 6.80–7.91 (m, 13H, C_6H_5, C_6H_4), 9.61 (s, 2H, CHO); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 119.9–139.3 (unresolved m, C_6H_5, C_6H_4), 149.8 (d, $^2J_{CP}$ = 7.2 Hz, C-1-O-P), 190.8 (s, CHO). IR (THF): 1695 cm^{-1} ($\nu_{C=O}$).

General Procedure for the Synthesis of Macrocycles **6a–c**

A solution of phenyl(thio)phosphonic dihydrazide **5a,b** (1 mmol, **5a**: 0.214 g, **5b**: 0.230 g) in THF (20 mL) was added to a solution of dialdehyde **3a,c** (1 mmol, **3a**: 0.350 g, **3b**: 0.317 g) in THF (20 mL), in the presence of molecular sieves (4 Å). The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After 4 days (for **6a, b**) or 1 month (for **6c**), the solution was filtered and the solvent was evaporated under vacuum. The resulting powder was washed several times with THF/pentane (1/3).

Macrocycle **6a**. White powder (62% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 22.8 (s, N–P(O)–N), 158.1 (s, O–P–O); ^1H NMR ($CDCl_3$) δ 3.15 (d, $^3J_{HP}$ = 7.2 Hz, 12H, N–CH_3), 6.84–7.94 (m, 40H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.4 (d, $^2J_{CP}$ = 10 Hz, N–CH_3), 119.0–132.1 (unresolved m, C_6H_5, C_6H_4), 136.1 (d, $^3J_{CP}$ = 12.8 Hz, HC=N), 154.1 (d, $^2J_{CP}$ = 7 Hz, C-1-O-P); MS: 1057 $[M + 1]^+$. Anal. calcd for $C_{56}H_{52}N_8O_6P_4$: C, 63.66; H, 4.92; N, 10.60. Found: C, 63.59; H, 5.01; N, 10.69.

Macrocycle **6b**. White powder (59% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 78.5 (s, N–P(S)–N), 158.5 (s, O–P–O); ^1H NMR ($CDCl_3$) δ 3.19 (d, $^3J_{HP}$ = 8 Hz, 12H, N–CH_3), 6.82–7.91 (m, 40H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.6 (d, $^2J_{CP}$ = 10 Hz, N–CH_3), 113.9–132.5 (unresolved m, C_6H_5, C_6H_4), 136.2 (d, $^3J_{CP}$ = 13 Hz, HC=N), 154.6 (d, $^2J_{CP}$ = 8 Hz, C-1-O-P); MS: 1089 $[M + 1]^+$. Anal. calcd for $C_{56}H_{52}N_8O_4P_4S_2$: C, 61.78; H, 4.78; N, 10.29. Found: C, 61.85; H 4.71; N, 10.36.

Macrocycle **6c**. White powder, not isolated in pure state. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 78.2 (s, N–P(S)–N), 138.9 (s, O–P–O); ^1H NMR ($CDCl_3$) δ 2.74 (brs, 6H, $N(CH_3)_2$), 3.22 (d, $^3J_{HP}$ = 8 Hz, 12H, P–N–CH_3), 6.9–8.1 (m, 30H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.6 (d, $^2J_{CP}$ = 9.3 Hz, P–N–CH_3), 34.2 (d, $^2J_{CP}$ = 20.6 Hz, $N(CH_3)_2$), 119.2–133.0 (unresolved m, C_6H_5, C_6H_4), 136.3 (d, $^3J_{CP}$ = 11.1 Hz, HC=N), 153.4 (d, $^2J_{CP}$ = 6.2 Hz, C-1-O-P).

Synthesis of the Bis(O p-(2-methylhydrazono)formylphenyl)phenylthio Phosphonate **7**. A solution of methylhydrazine (50 mmol, 1.33 mL) in THF (20 mL) was added at 0°C to a solution of the dialdehyde **4a** (25 mmol, 9.55 g) in THF (200 mL) in the presence of molecular sieves (4 Å). The mixture was stirred overnight at room temperature, then filtered and evaporated to dryness to give a yellow glue. This glue was extracted with ether (50 mL), and the resulting solution was filtered and evaporated to give a white powder (80% yield).

7. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 82.5; ^1H NMR ($CDCl_3$) δ 2.77 (s, 6H, N–CH_3), 5.54 (s, 2H, NH), 7.08–8.23 (m, 15H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 34.0 (s, N–CH_3), 121.1–133.4 (unresolved m, C_6H_5, C_6H_4), 135.7 (s, HC=N), 149.3 (d, $^2J_{CP}$ = 9 Hz, C-1-O-P). Anal. calcd for $C_{22}H_{23}N_4O_2PS$: C, 60.29; H, 5.25; N, 12.78. Found: C, 60.41; H, 5.21; N, 12.69.

Synthesis of the Macrocycle **8**. Dichlorophenylphosphine (2.38 mmol, 0.32 mL) was added at room temperature to a solution of phosphodihydrazone **7** (2.38 mmol, 1.042 g) and triethylamine (4.76 mmol, 0.66 mL) in THF (50 mL). The resulting mixture was stirred overnight, then filtered and evaporated to dryness to give a yellow powder. This powder was first washed with ether (50 mL), then extracted with toluene (20 mL). The toluenic solution was evaporated to dryness to give a pale yellow powder (75% yield).

8: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 82.4 (s, O–P(S)–O), 102.1 (s, N–P–N); ^1H NMR ($CDCl_3$) δ 3.16 (d, $^3J_{HP}$ = 6 Hz, 12H, N–CH_3), 7.16–8.17 (m, 40H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 36.6 (d, $^2J_{CP}$ = 15.1 Hz, N–CH_3), 121.6–133.8 (unresolved m, C_6H_5, C_6H_4), 134.1 (d, $^3J_{CP}$ = 12 Hz, HC=N), 149.9 (d, $^2J_{CP}$ = 8.6 Hz, C-1-O-P); MS: 1089 $[M + 1]^+$. Anal. calcd for $C_{56}H_{52}N_8O_4P_4S_2$: C, 61.81; H, 4.78; N, 10.29. Found: C, 61.93; H, 4.83; N, 10.33.

Synthesis of the Macrocycle **11**. Methyl trifluoromethanesulfonate (0.189 mmol, 0.022 mL) was added to a solution of macrocycle **9** (0.0945 mmol, 0.062 g) in dichloromethane (5 mL). A yellow oil was formed (the dicationic macrocycle **10**) and stirred for 2 hours. Then, the addition of hexamethyl phosphorus triamide (0.189 mmol, 0.035 mL) induced the disappearance of the oil to obtain a clear solution. This solution was stirred for 2 hours, then evaporated to dryness to give a yellow powder which was extracted with toluene (20 mL). Evaporation of the toluenic solution gave **11** as a pale yellow powder (90% yield).

11: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 101.3; ^1H NMR (C_6D_6) δ 2.94 (d, $^3J_{HP}$ = 8 Hz, 12H, N–CH_3), 7.0–8.1 (m, 22H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 36.7 (d, $^2J_{CP}$ = 14 Hz, N–CH_3), 125.0–139.9 (unresolved m, C_6H_5, C_6H_4), 136.1 (brs, HC=N); MS: 593 $[M + 1]^+$. Anal. calcd for $C_{32}H_{34}N_8P_2$: C, 64.88; H, 5.74; N, 18.91. Found: C, 64.97; H, 5.79; N, 18.83.

Synthesis of the Macrocycle **13**. Methyl trifluoromethane sulfonate (0.8 mmol, 0.096 mL) was added to a solution of macrocycle **12** (0.2 mmol, 0.210 g) in dichloromethane (8 mL). The resulting solution was stirred for 2 hours. Then, hexamethyl phosphorus triamide (0.8 mmol, 0.150 mL) was

added and the solution stirred for 3 hours. This solution was evaporated to dryness to give a yellow powder which was extracted with toluene (40 mL). Evaporation of the toluenic solution gave **13** as a white powder (75% yield).

13: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 33.6 (s, C–P(O)–C), 102.8 (s, N–P–N); ^1H NMR ($CDCl_3$) δ 2.72 (d, $^3J_{HP}$ = 9 Hz, 12H, N–CH_3), 7.0–8.2 (m, 40H, C_6H_5, C_6H_4, HC=N); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 35.8 (d, $^2J_{CP}$ = 13 Hz, N–CH_3), 126.6–140.1 (unresolved m, C_6H_5, C_6H_4), 137.8 (brs, HC=N); MS: 993 $[M + 1]^+$. Anal. calcd for $C_{56}H_{52}N_8O_2P_4$: C, 67.72; H, 5.88; N, 11.29. Found: C, 67.63; H, 5.81; N, 11.21.

REFERENCES

[1] R. M. Izatt, K. Pawlack, J. S. Bradshaw, R. L. Bruening, *Chem. Rev., 91*, 1991, 1721 and references included.

[2] (a) A. M. Caminade, J. P. Majoral, *Chem. Rev., 94*, 1994, 1183 and references included; (b) F. Laporte, F. Mercier, L. Ricard, F. Mathey, *J. Am. Chem. Soc., 116*, 1994, 3306.

[3] (a) J. P. Majoral, M. Badri, A. M. Caminade, M. Delmas, A. Gaset, *Inorg. Chem., 27*, 1988, 3873; (b) J. P. Majoral, M. Badri, A. M. Caminade, A. Gorgues, M. Delmas, A. Gaset, *Phosphorus, Sulfur and Silicon, 49–50*, 1990, 413; (c) M. Badri, J. P. Majoral, A. M. Caminade, M. Delmas, A. Gaset, A. Gorgues, J. Jaud, *J. Am. Chem. Soc., 112*, 1990, 5618; (d) M. Badri, J. P. Majoral, F. Gonce, A. M. Caminade, M. Sallé, A. Gorgues, *Tetrahedron Lett., 31*, 1990, 6343; (e) J. P. Majoral, M. Badri, A. M. Caminade, M. Delmas, A. Gaset, *Inorg. Chem., 30*, 1991, 344; (f) J. P. Majoral, M. Badri, A. M. Caminade, *Heteroatom Chem., 2*, 1991, 45; (g) D. Colombo, A. M. Caminade, J. P. Majoral, *Inorg. Chem., 30*, 1991, 3365; (h) J. P. Majoral, A. M. Caminade: The Chemistry of Inorganic Ring Systems, in R. Steudel (ed): *Inorganic Chemistry*, Elsevier Science Publishers B. V., vol. 14, ch. 12, p. 209 (1992); (i) B. Oussaid, B. Garrigues, A. M. Caminade, J. P. Majoral, *Phosphorus, Sulfur and Silicon, 73*, 1992, 41; (j) A. M. Caminade, D. Colombo-Khater, J. Mitjaville, C. Galliot, P. Mas, J. P. Majoral, *Phosphorus, Sulfur and Silicon, 75*, 1993, 67; (k) D. Colombo-Khater, A. M. Caminade, B. Delavaux-Nicot, J. P. Majoral, *Organometallics, 12*, 1993, 2861; (l) B. Oussaid, B. Garrigues, J. Jaud, A. M. Caminade, J. P. Majoral, *J. Org. Chem., 58*, 1993, 4500; (m) J. P. Majoral, A. M. Caminade, A. Igau: in L. D. Quin, J. G. Verkade (eds): *Phosphorus-31 NMR Spectral Properties in Compounds Characterization and Structural Analysis*, VCH Publishers, Inc., New York, NY, Chap. 5, 57 (1994); (n) N. Launay, F. Denat, A. M. Caminade, J. P. Majoral, J. Dubac, *Bull. Soc. Chim. Fr., 131*, 1994, 758.

[4] J. Mitjaville, A. M. Caminade, J. P. Majoral, *Tetrahedron Lett., 35*, 1994, 6865.

[5] (a) J. Mitjaville, A. M. Caminade, R. Mathieu, J. P. Majoral, *J. Am. Chem. Soc., 116*, 1994, 5007; (b) J. Mitjaville, A. M. Caminade, J. P. Majoral, *J. Chem. Soc. Chem. Commun.*, 1994, 2161.

[6] N. Launay, A. M. Caminade, R. Lahana, J. P. Majoral, *Angew. Chem. Int. Ed. Engl., 33*, 1994, 1589.

[7] (a) C. Galliot, A. M. Caminade, F. Dahan, J. P. Majoral, *Angew. Chem. Int. Ed. Engl., 32*, 1993, 1477; (b) D. Colombo-Khater, Z. Hé, A. M. Caminade, F. Dahan, R. Kraemer, J. P. Majoral, *Synthesis*, 1993, 1145; (c) D. Colombo-Khater, A. M. Caminade, R. Kraemer, B. Raynaud, J. Jaud, J. P. Majoral, *Bull. Soc. Chim. Fr., 131*, 1994, 733; (d) C. Galliot, A. M. Caminade, F. Dahan, J. P. Majoral, W. Schoeller, *Inorg. Chem.*, in press.

[8] F. Gonce, A. M. Caminade, J. P. Majoral, *Tetrahedron Lett., 32*, 1991, 203.

[9] (a) F. Gonce, A. M. Caminade, J. Jaud, P. Vignaux, J. P. Majoral, *Bull. Soc. Chim. Fr., 129*, 1992, 237; (b) F. Gonce, A. M. Caminade, F. Boutonnet, J. P. Majoral, *J. Org. Chem., 57*, 1992, 970.

[10] R. Engel, *Organic Reactions, 36*, 1988, 173.

[11] J. P. Majoral, R. Kraemer, J. Navech, F. Mathis, *Tetrahedron, 32*, 1976, 2633.

[12] (a) J. P. Albrand, J. P. Dutasta, J. B. Robert, *J. Am. Chem. Soc., 96*, 1974, 4584; (b) J. P. Dutasta, A. C. Guimaraes, J. Martin, J. B. Robert, *Tetrahedron Lett.*, 1975, 1519; (c) J. P. Dutasta, A. C. Guimaraes, J. B. Robert, *Tetrahedron Lett.*, 1977, 801; (d) J. P. Dutasta, J. B. Robert, *J. Am. Chem. Soc., 100*, 1978, 1925; (e) J. P. Dutasta, A. Grand, A. C. Guimaraes, J. B. Robert, *Tetrahedron, 35*, 1979, 197; (f) J. P. Dutasta, J. Martin, J. B. Robert, *Heterocycles, 14*, 1980, 1631; (g) J. P. Dutasta, K. Jurkschat, J. B. Robert, *Tetrahedron Lett.*, 1981, 2549.

[13] (a) J. Omelanczuk, M. Mikolajczyk, *Tetrahedron Lett., 25*, 1984, 2493; (b) J. Omelanczuk, *J. Chem. Soc. Chem. Commun.*, 1992, 1718.