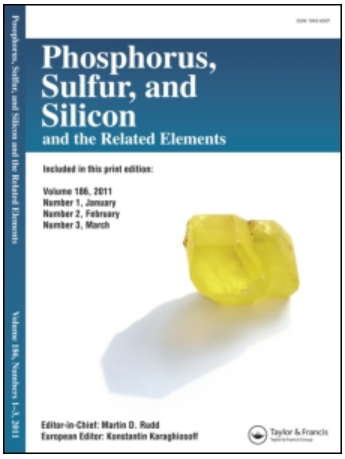



**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# ATTEMPTED SYNTHESIS OF PHOSPHORUS CRYPTANDS

Meryam Badri[a]; Anne-Marie Caminade[a]; Jean Pierre Majoral[a]; Alain Gorgues[b]
[a] Laboratoire de Chimie de Coordination du CNRS, UPR 8241 liée par conventions à, L'Université Paul Sabatier et à l'Institut Poly technique de Toulouse, Toulouse Cedex, France [b] Laboratoire de Synthèse Organique et d'Electrochimie, Université d Angers, Angers Cedex, France

**To cite this Article** Badri, Meryam , Caminade, Anne-Marie , Majoral, Jean Pierre and Gorgues, Alain(1991) 'ATTEMPTED SYNTHESIS OF PHOSPHORUS CRYPTANDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 56: 1, 123 — 127
**To link to this Article: DOI:** 10.1080/10426509108038074
**URL:** http://dx.doi.org/10.1080/10426509108038074

*Phosphorus, Sulfur, and Silicon*, 1991, Vol. 56, pp. 123–127
Reprints available directly from the publisher
Photocopying permitted by license only



# ATTEMPTED SYNTHESIS OF PHOSPHORUS CRYPTANDS

MERYAM BADRI, ANNE-MARIE CAMINADE and JEAN PIERRE MAJORAL*

*Laboratoire de Chimie de Coordination du CNRS, UPR 8241 liée par conventions à L'Université Paul Sabatier et à l'Institut Polytechnique de Toulouse, 205, route de Narbonne, 31077 Toulouse Cedex, France*

and

ALAIN GORGUES

*Laboratoire de Synthèse Organique et d'Electrochimie, Université d'Angers, 2, boulevard Lavoisier 49045 Angers Cedex, France*

*(Received April 10, 1990, in final form July 11, 1990)*

Reaction of the aldehyde monoacetal OHC—C≡C—CH(OEt)$_2$ **4** with the phosphorhydrazide (S)P[N(CH$_3$)NH$_2$]$_3$ **3** leads to the phosphorhydrazide (S)P[N(CH$_3$)N=CH—C≡C—CH(OEt)$_2$]$_3$ **5**. Formolysis of **5** yields the new multifunctionalized 1.11.11′ phosphotrihydrazide (S)P[N(CH$_3$)-N=CH—C≡C—CHO]$_3$ **6**. Treatment of **3** either with **6** or with various 1.3 or 1.4 dialdehydes does not afford phosphorus cryptands but leads to phosphorus polymers possessing macrocyclic phosphorus sequencies.

*Key words:* 1.2, 1.3, 1.4 Dialdehydes, Phosphotrihydrazides, Phosphotrialdehyde, Phosphorus Macrocycles, Phosphorus Cryptands, Polymers.



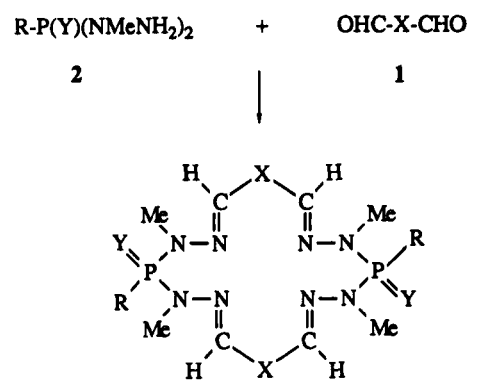
## INTRODUCTION

We recently reported a general method for the synthesis of polyazadiphosphorus macrocycles including 18, 20, 22, 26 and 30 membered rings.[1] These reactions involve the addition of various dialdehydes **1** to oxo- or thiophosphodihydrazides **2** and require very mild conditions (e.g., room temperature with stirring for several hours) (Scheme I). Most of the macrocycles are obtained in near quantitative yield and are easily isolated from the resulting mixture. Their ability to selectively bind certain cations[2] has prompted us to investigate other possibilities for the preparation of additional phosphorus macrocycles and thus to enhance the choice of complexing macrocyclic phosphorus species.

This paper reports attempts to prepare phosphorus cryptands from the reaction of phosphotrihydrazides (X)P[N(CH$_3$)NH$_2$]$_3$ **3** either with 1.2, 1.3, 1.4 dialdehydes or with a new functionalized 1.11.11′ phosphorus trialdehyde **6**.

## RESULTS AND DISCUSSION

Taking into account our previous results, two ways for the preparation of phosphorus cryptands were investigated. (A) the [1 + 1] cyclocondensation of a phos-




**Scheme I**

photrihydrazide such as **3a** with a phosphorus trialdehyde **6**. (B) the [2 + 3] cyclocondensation of 2 eq. of **3a** or **3b** with 3 eq. of non-phosphorylated dialdehydes (see Scheme II).

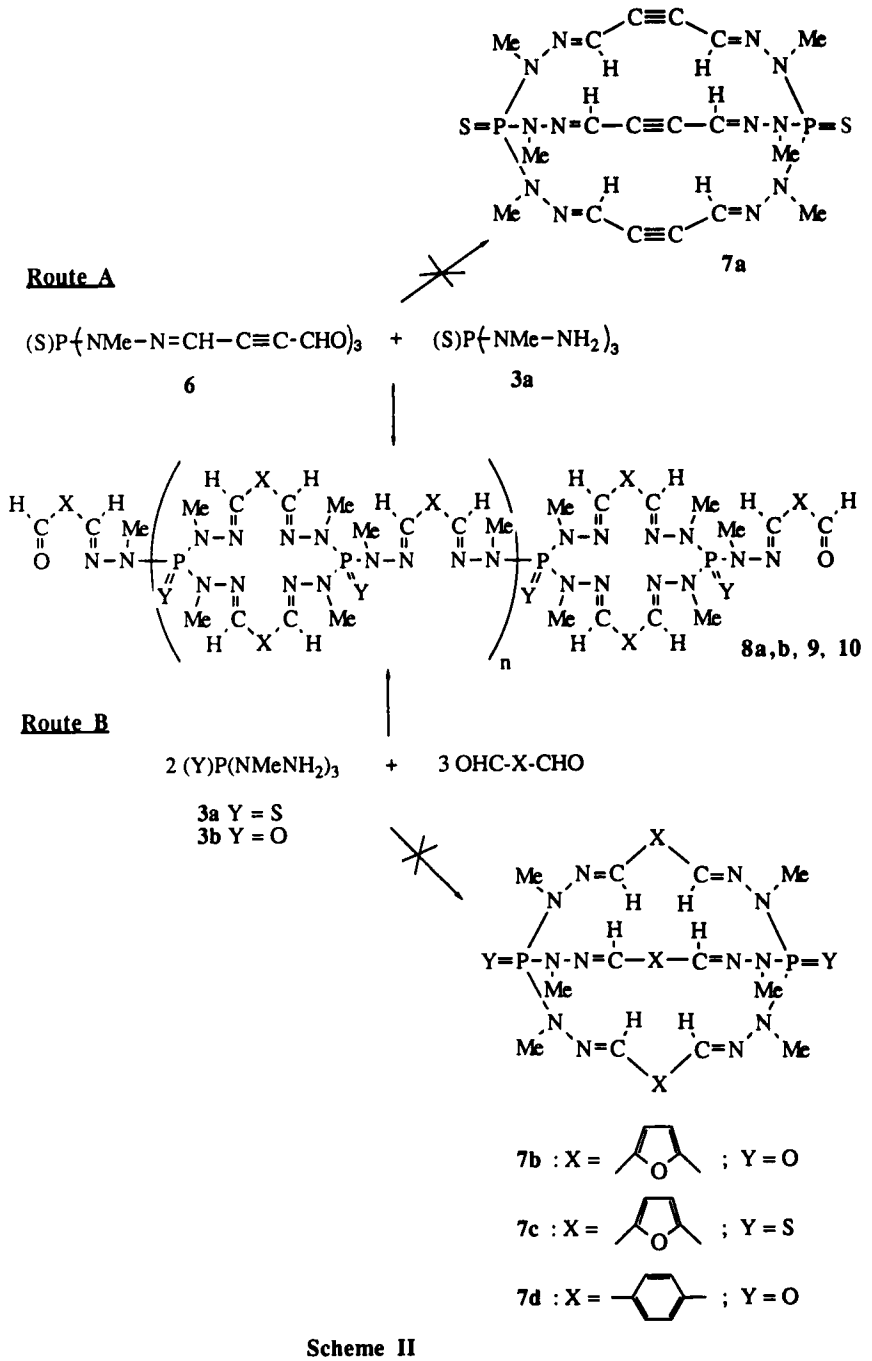
Route A necessitates the preliminary synthesis of a phosphorus trialdehyde. Up to now no phosphorus trialdehyde has been reported. The preparation of the first compound of this type is outlined in Scheme III. Addition of 3 eq. of monoacetal aldehyde **4**[3] to 1 eq. of thiophosphotrihydrazide **3a** leads to the phosphotrihydrazide **5** isolated as white crystals in 85% yield (see experimental section). Treatment of **5** with 6 eq. of formic acid leads to the new aldehyde **6** 15% yield. The structure of **6** is deduced from $^{31}P$, $^{1}H$, $^{13}C$ NMR, IR, mass spectrometry as well as microanalysis. $^{1}H$ NMR spectra show a characteristic resonance at 9.4 ppm for the aldehydic protons while $^{13}C$ NMR exhibits a signal at 176 ppm for the carbonyl groups. Furthermore IR spectroscopy (intense $\nu_{C=O}$ at 1685 $cm^{-1}$) and mass spectrometry (m/e: 390) are in agreement with the proposed structure.

Use of this multifunctionalized phosphorus trialdehyde **6** should be of the greatest interest in organic and organometallic chemistry since three imino functions and three acetylenic functions are also present in the molecule.

Simultaneous addition of a methanolic solution of **6** to a methanolic solution of the phosphotrihydrazide **3a** (route A) or the addition of 3 eq. of 2,5 furandicarboxaldehyde or 1,4 benzene dicarboxaldehyde in methanol to a methanolic solution of phosphotrihydrazide **3a** or **3b** (2 eq.) (route B) does not lead to the desired macrobicyclic derivatives **7a–d**. In each case, polymeric species **8a, b, 9** or **10** are obtained as poorly soluble yellow orange or brown powders (Scheme II) in 60–80% yield.

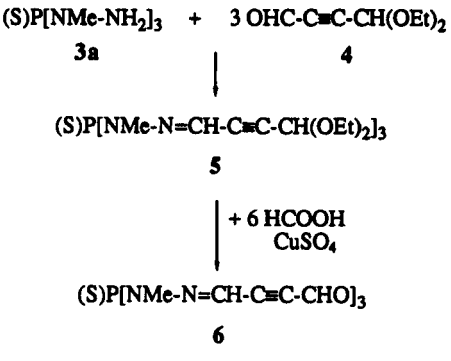
The most intense ions observed when the species were submitted to mass spectrometry correspond to macrocyclic fragments **11** possessing free hydrazino groups. In addition IR spectroscopy shows the presence of characteristic absorption bands of carbonyl functions ($\nu_{C=O}$: 1680 $cm^{-1}$ (w)) and imino functions ($\nu_{C=N}$: 1630 $cm^{-1}$ (w)). NMR data are consistent with the proposed polymeric structures; indeed the presence of terminal aldehydic functions are detected in $^{1}H$ NMR as well as $^{13}C$ NMR (see experimental section).

In conclusion attempts to obtain the first phosphorus nitrogen cryptands failed

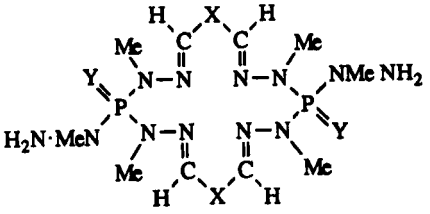



**Scheme II**

when phosphotrihydrazides were caused to react with various di- or trialdehydes. Nevertheless, our studies allowed us to prepare new polyfunctionalized phosphotrihydrazides which are useful in organic synthesis. Work is in progress to directly synthetize cryptands by using template reactions.




**Scheme III**



**11**



## EXPERIMENTAL

All manipulations were carried out using standard high vacuum or dry argon atmosphere techniques. $^1H$ and $^{13}C$ NMR spectra were recorded on a Brucker WM 250 or a Brucker AC 80 spectrometer. Chemical shifts are reported in ppm relative to $Me_4Si$ as internal standard. $^{31}P$ NMR spectra were obtained on a Brucker AC80 instrument and are reported in ppm. Standards for the shifts are 85% $H_3PO_4$. Infrared spectra were recorded on a Perkin-Elmer 225 instrument. Elemental analyses were performed by the Service Central d'Analyses CNRS. Mass spectra were obtained on a Varian MAT 311 A instrument.

*Synthesis of the phosphorhydrazide* **5**. A methanolic solution of the monoacetal aldehyde **4** (0.3 mol.) maintained at 0°C is added dropwise to a methanolic solution of the phosphotrihydrazide **3a** (0.1 mol.). After stirring 4 hours the solvent is evaporated under reduced pressure, leading to a white powder which is recrystallized from a chloroform ether 1/1 solution.

**5** yield 85%. m.p. 83–84°C. $^{31}P$ NMR ($CDCl_3$) δ: 70.3 ppm. $^1H$ NMR ($CDCl_3$) δ 1.1 (*t*, $^3J_{HH}$ = 7 Hz, $OCH_2\underline{CH_3}$), 2.9 (*d*, $^3J_{PH}$ = 8.7 Hz, P—N—$\underline{CH_3}$), 3.5 (q. $^3J_{HH}$ = 7Hz, $O\underline{CH_2}$—$CH_3$), 5.25 (*s*, $\underline{HC}(OEt)_2$), 6.6 (*s*, $\underline{HC}$=N) ppm. $^{13}C$ NMR ($CDCl_3$) δ 15.3 (*s*, $OCH_2\underline{CH_3}$), 32.6 (*d*, $^2J_{PC}$ = 9 Hz, P—N—$\underline{CH_3}$), 61.4 (*s*, $O\underline{CH_2}CH_3$), 81.4 and 86.5 (*s*, —$\underline{C}$≡$\underline{C}$—), 91.9 (*s*, $\underline{CH}(OEt)_2$), 120.9 (*d*, $^3J_{PC}$ = 16.9 Hz, $\underline{HC}$=N) ppm. Mass spect. m/e: 612. Anal. Calcd. for $C_{27}H_{45}N_6O_6PS$: C 52.90, H 7.35, N 13.70; Found C 53.01, H 7.40, N 12.98.

*Synthesis of the phosphorhydrazide* **6**. To the phosphorhydrazide **5** ($2.4.10^{-3}$ mol. 1.46 g) in 3 ml of dichloromethane is added formic acid (1 mL) and anhydrous $Cu(SO_4)_2$ (2 g). The resulting red solution is stirred for one hour and 25 mL of dichloromethane are added. After filtration of $Cu(SO_4)_2$ on glass wool, the filtrate is slowly added to 20 mL of a dichloromethane suspension of $P_2O_5$ (4 g). The resulting mixture is filtrated and the solvent evaporated to yield **6** as an yellow oil. **6** is purified by several washings with chloroform ether 1-2 solution.

**6** orange oil yield 15%. $^{31}P$ NMR ($CDCl_3$) δ 71 ppm. $^1H$ NMR ($CDCl_3$) δ 3.01 (*d*, $^3J_{PH}$ = 8.9 Hz, PN$\underline{CH_3}$), 6.7 (*s*, $\underline{HC}$=N) 9.4 (*s*, $\underline{HC}$=O) ppm. $^{13}C$ NMR ($CDCl_3$) δ 32.4 (*d*, $^2J_{PC}$ = 9 Hz, PN$\underline{CH_3}$), 81.6 and 86.53 (*s*, $\underline{C}$≡$\underline{C}$), 120 (*d*, $^3J_{PC}$ = 16 Hz, P—N—N=$\underline{C}$), 177.4 (*s*, $\underline{HC}$=O) ppm. Mass spect. m/e: 390. Anal. Calcd. for $C_{15}H_{15}N_6O_3PS$. C: 46.15, H 3.84, N 21.53. Found: C 45.97, H 3.65, N 20.75.

*Synthesis of the polymeric species* **7a**. A solution of the trialdehyde **6** (3.31 $10^{-4}$ mol., 130 mg) in 5 mL of methanol and a solution of the phosphotrihydrazide **3a** (3.31 $10^{-4}$ mol, 66 mg) in 5 mL of methanol are simultaneously added to 5 mL of methanol at room temperature. The mixture is then stirred for one hour and filtered. The resulting precipitate is washed several times with methanol to give **7a** as a brown insoluble powder. **7a** IR (KBr): 1628 ($\nu_{C=N}$) $cm^{-1}$. Due to its insolubility further characterization of **7a** was not possible.

*Synthesis of polymers* **7b–d**. The procedure is the same than the one used for the preparation of **7a**.

**7b** yellow powder m.p. decomp. >250°C. Yield 60%. $^{31}P$ NMR ($CDCl_3$): δ 11.5 ppm. $^1H$ NMR ($CDCl_3$): δ 3.19 (broad *s*. PN$\underline{CH_3}$), 6.42 (*s*. $C_4H_2O$) 7.41 (broad *s*. $\underline{H}C{=}N$), 9.47 (*s*. $\underline{H}C{=}O$) ppm. $^{13}C$ NMR ($CDCl_3$) δ 32.55 (broad *s*, PN$\underline{C}H_3$), 110.8 (broad *s*. $\underline{C}{-}C{-}O$), 122.9 (broad *s*, C—$\underline{C}$—O), 151.1 (*s*. H$\underline{C}{=}N$); 178.8 (*s*, H$\underline{C}{=}O$) ppm. IR (KBr): 1680 ($\nu_{C=O}$) 1645 ($\nu_{C=N}$) 1230 ($\nu_{P=O}$) $cm^{-1}$. Mass spect.: $M^+$: 540 ($H_2N{-}\underline{N}(CH_3)P(O)[N(CH_3)N{=}CH{-}X{-}CH{=}N{-}N(CH_3)]_2P(O)N(CH_3)NH_2$ fragment).

**7c** orange powder m.p. decomp. >200°C Yield 80%. $^{31}P$ NMR ($CDCl_3$): δ 72.3 ppm. $^1H$ NMR ($CDCl_3$): δ 3.08 (broad *s*. P—N—$\underline{CH_3}$), 6.3 (*s* $C_4H_2O$), 7.4 (broad *s*, $\underline{H}C{=}N$). $^{13}C$ NMR ($CDCl_3$): δ 31.08 (broad *s*., P—N—$\underline{C}H_3$), 111.2 (broad *s*. $\underline{C}{-}C{-}O$), 121.3 (broad *s*, C—$\underline{C}$—O), 151.6 (*s*. H$\underline{C}{=}N$), 178.4 (*s*. H$\underline{C}{=}O$) ppm. IR (KBr): 1685 ($\nu_{C=O}$), 1665 ($\nu_{C=N}$), 945 ($\nu_{P-N}$) 750 ($\nu_{P=S}$) $cm^{-1}$. Mass spect.: $M^+$: 572 ($H_2N{-}N(CH_3)P(S)[N(CH_3)N{=}CH{-}X{-}CH{=}N{-}N(CH_3)]_2P(S)N(CH_3)NH_2$ fragment).

**7d** yellow powder. m.p. decomp. >200°C. 80% yield. $^{31}P$ NMR ($CDCl_3$) δ 12.7 ppm. $^1H$ NMR ($CDCl_3$) δ 3.2 (broad *s*. P—N—$\underline{CH_3}$), 7.03–7.56 (m. $C_6\underline{H}_4$, $\underline{H}C{=}N$) 9.8 (*s*, $\underline{H}C{=}O$) ppm. $^{13}C$ NMR ($CDCl_3$) δ 32.55 (broad *s*, P—N—$\underline{C}H_3$), 130.7 (*s*,  ) 136.1 (*s*. H$\underline{C}{=}N$) 138.8 (*s*,  ), 191.82 (*s*, H$\underline{C}{=}O$) ppm. IR (KBr): 1687 ($\nu_{C=O}$) 1637 ($\nu_{C=N}$) 1258 ($\nu_{P=O}$) 964 ($\nu_{P-N}$) $cm^{-1}$. Mass spect.; $M^+$: 560 ($H_2N{-}N(CH_3)P(O){-}[N(CH_3)N{=}CH{-}X{-}CH{=}N{-}N(CH_3)]_2{-}P(O)N(CH_3)NH_2$).

## REFERENCES


1. J. P. Majoral, M. Badri, A. M. Caminade, M. Delmas and A. Gaset, *Inorg. Chem.*, **27**, 3873 (1988); M. Badri, J. P. Majoral, A. M. Caminade, A. Gorgues, M. Delmas, A. Gaset, J. Jaud, *J. Am. Chem. Soc.*, **112**, 5618 (1990); J. P. Majoral, M. Badri, A. M. Caminade, M. Delmas, A. Gaset; submitted for publication; J. P. Majoral, M. Badri, A. M. Caminade, A. Gorgues, M. Delmas, A. Gaset, *Phosphorus, Sulfur and Silicon*, **49–50**, 413 (1990).
2. M. Badri, A. M. Caminade, J. P. Majoral, M. Delmas and A. Gaset, unpublished results.
3. A. Gorgues, *Janssen Chim. Acta*, **4**, 21 (1986); A. Gorgues, A. Simon, A. Le Coq, A. Hercouet, F. Corre, *Tetrahedron*, **42**, 351 (1986); D. Stephan, A. Gorgues, A. Belyasmine, A. Le Coq; *J. Chem. Soc. Chem. Commun.*, 263 (1988).