

## Communications

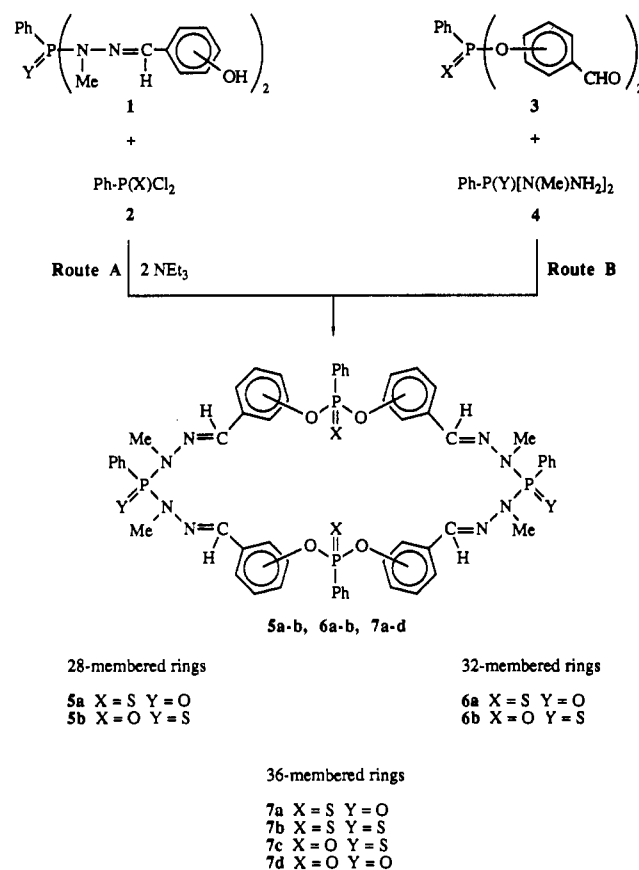
## Functionalized Macrocycles Incorporating P-N and P-O Bonds. Strategies of Synthesis

In recent years, phosphorus macrocyclic ligands have been prepared in an effort to find useful species capable of binding cations as well as neutral guest species of biological and industrial importance.<sup>1</sup>

The reaction of phosphodihydrazides  $RP(Y)(NCH_3NH_2)_2$  with dialdehydes proved to be a convenient route to various phosphorus macrocycles possessing a P-N-N<sup>2</sup> linkage or both P-N-N and P-C linkages.<sup>3</sup> We were particularly interested in showing the wide scope of this type of synthesis, whatever the phosphorus environment, since, up to now, no general method can be proposed for the preparation of macrocycles in which phosphorus atoms can be di-, tri-, tetra-, penta-, or hexacoordinated and linked either to nitrogen, carbon, or oxygen. Of additional interest is the possibility to obtain new ligands containing both "soft" donor atoms (i.e. sulfur, phosphorus, etc.) and "hard" ligating sites (i.e. imine nitrogen, aryloxy, etc.).

We now report the discovery (by two independent routes) of a new class of tetranucleating phosphorus macrocycles **5a,b**, **6a,b**, and **7a-d**, incorporating for the first time P-N-N and P-O bonds.

Scheme I



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Remarkably the reactions giving rise to these compounds allow also the formation of P-functionalized macrocycles **7e-h** as well as the generation of an unusual pentacoordinated phosphorus-containing macrocycle **9**, the first macrocycle possessing both tetra- and pentacoordinated phosphorus atoms.

Our approach to the synthesis of the 28-, 32-, and 36-membered rings **5a,b**, **6a,b**, and **7a-d** is based on two types of reactions (Scheme I). In the first procedure (route A) THF solutions of the new phosphodihydrazides **1** (Y = S or O, with OH in the ortho, meta, or para position)<sup>4</sup> and triethylamine are added slowly and simultaneously to a THF solution of thio- or oxophenyldichlorophosphorane **2a** or **2b** at 0 °C. The second protocol (route B) involves the treatment of a THF solution of the original 1-7, 1-9, or 1-11 phosphorus dialdehydes **3** (aldehyde groups in the ortho, meta, or para position)<sup>4</sup> with phosphodihydrazides  $C_6H_5-$

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Table I. Selected Spectral Data<sup>a</sup> for Macrocycles **5a**, **6a**, **7a**, and **7a-h**

compds	<sup>31</sup> P NMR (CDCl <sub>3</sub> )		<sup>13</sup> C NMR (CDCl <sub>3</sub> )		MS ([M + 1] <sup>+</sup> ), m/e	% yields (method)
	δ(P=X)	δ(P=O)	δ(C=N)	<sup>3</sup> J <sub>P-C</sub> , Hz		
<b>5a</b>	83.7	24.3	<i>b</i>		1121	69 (B)
<b>5b</b>	11.9	78.8	<i>b</i>		1121	38 (A)
<b>6a</b>	81.8	22.3	135.7 (d)	13.6	1121	47 (A) 75 (B)
<b>6b</b>	11.7	79.1	135.8 (d)	13.6	1121	68 (B)
<b>7a</b>	82.8	24.4	135.3 (d)	13.9	1121	72 (A)
<b>7b</b>	82.5	79.1	135.7 (d)	13.2	1153	45 (A) 71 (B)
<b>7c</b>	11.8	79	135.8 (d)	13.2	1121	78 (B)
<b>7d</b>	11.8	24.8	135.2 (d)	14	1089	51 (A) 78 (B)
<b>7e</b>	58.0	79.2	135.5 (d)	14	1069	81
<b>7f</b>	-5.8	78.9	135.4 (d)	13.8	1037	35
<b>7g</b>	67.3	79.0	135.6 (d)	13.3	1089	59
<b>7h</b>	51.1	78.6	135.5 (d)	13.9	1241	53

<sup>a</sup> <sup>1</sup>H NMR data are not given since imino protons signals are under aromatic protons signals. <sup>b</sup> Masked by aromatic carbon signals.

P(Y)[N(CH<sub>3</sub>)NH<sub>2</sub>]<sub>2</sub> (**4a**, Y = S; **4b**, Y = O) at room temperature.<sup>5</sup> The desired macrocycles, resulting from [2 + 2] condensation reactions in each case, are isolated with yields of 38–78% depending on the method used.

Initial evidence for the formation of these species is given by <sup>31</sup>P NMR. Monitoring the resultant solutions obtained via route A reveals the gradual disappearance of the signals attributable to thio- or oxophenyldichlorophosphorane with concomitant emergence of new signals at 82.7 or 11.8 ppm typical for C<sub>6</sub>-H<sub>5</sub>P(S)O<sub>2</sub> or C<sub>6</sub>H<sub>5</sub>P(O)O<sub>2</sub> linkages, respectively. Similarly <sup>31</sup>P chemical shifts observed for the resultant mixtures obtained from route B are distinguishable from those of the starting reactants (the <sup>31</sup>P values for the products being as for route A).

Corroborating evidence for the formation of macrocycles is gained by <sup>13</sup>C (imino carbons) NMR. Moreover mass spectrometry (field desorption or FAB) confirms the [2 + 2] condensation reaction in each case (see Table I).

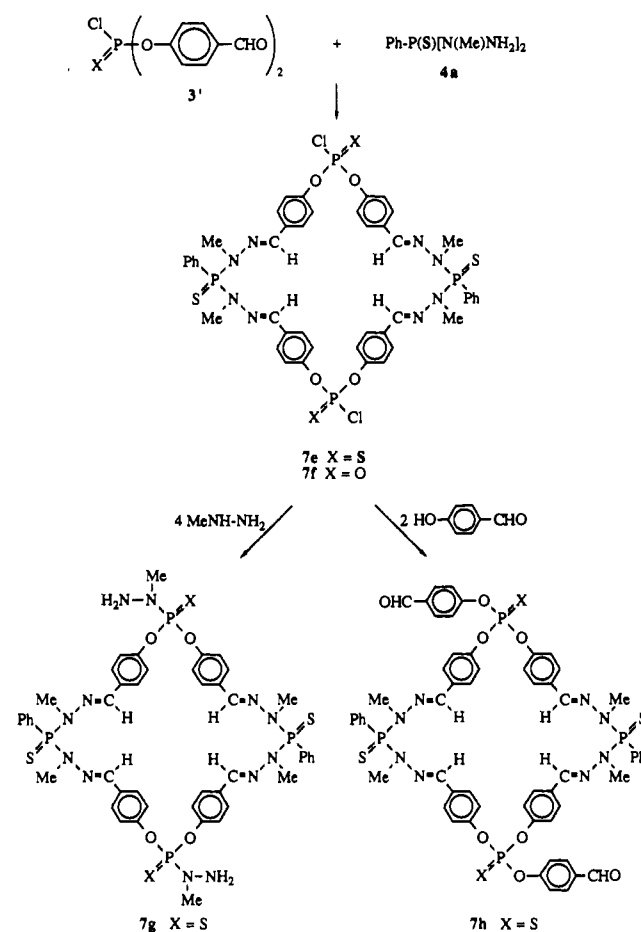
All of these new tetraphosphorus macrocycles are stable white or yellow powders easily dissolved in halogenated solvents, tetrahydrofuran, and acetonitrile.

Although the two methods lead to the same macrocycles, emphasis is placed on the advantages of route B: faster reactions<sup>5</sup> and higher yields (see Table I). Moreover, rigorous elimination of NEt<sub>3</sub>·HCl is difficult in route A due to its complexation by the macrocycles.

Until now no example of macrocycles possessing P–N bonds and functionalized phosphorus atoms has been reported. Synthesis of compounds with P–Cl bonds necessitates the preliminary formation of thio- or oxodichlorophosphoranes **3'a** or **3'b**, which are easily prepared by reacting (S)PCl<sub>3</sub> or (O)PCl<sub>3</sub> (1 equiv) with 2 equiv of 4-hydroxy benzaldehyde in presence of triethylamine (2 equiv).<sup>4</sup> Treatment of **3'a** or **3'b** with the phosphodihydrazide **4a** in THF results in the formation of macrocycles **7e** or **7f** (Scheme II) with yields of 81% or 35%, respectively. The [2 + 2] condensation reactions also take place in these cases, as clearly indicated by mass spectrometry (see Table I).

These macrocycles can react like common thio- or oxochlorophosphines. For example, addition of methylhydrazine (4 equiv) or addition of 4-hydroxybenzaldehyde (2 equiv) in the presence of triethylamine (2 equiv) lead to the formation of the new macrocyclic phosphodihydrazide **7g** or the new macrocyclic

Scheme II

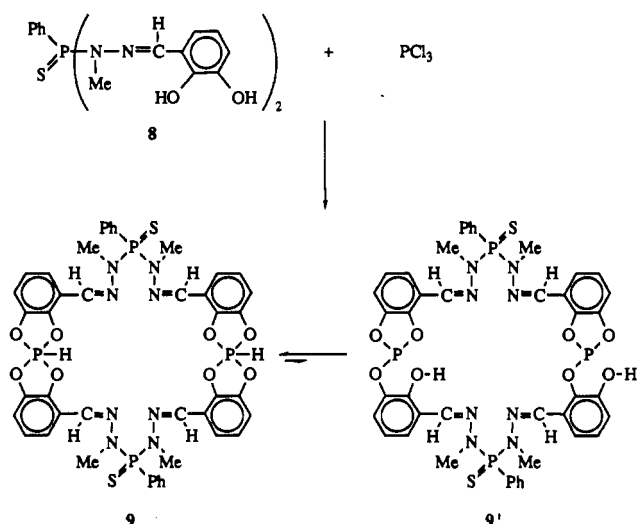


1-29 dialdehyde **7h**. Attempts to obtain macrotricyclic species by the reaction of **7g** with **7h** were unsuccessful. The simultaneous dropwise combination of THF solution of each into THF at 0 °C only resulted in the formation of apparently polymeric material.

Thus these reactions provide facile syntheses of macrocycles having halogen, hydrazine, or aldehyde functionalities. All attempts at growing X-ray quality crystals have, so far, been unsuccessful.

In the light of these results, it seemed plausible to prepare a macrocycle bearing phosphorus atoms in different coordination modes. For this purpose, the tetrahydroxyphosphodihydrazide **8<sup>4</sup>** (1 equiv) was reacted with PCl<sub>3</sub> (1 equiv) in THF. After workup, an air- and moisture-sensitive powder was isolated ( $\delta(^{31}\text{P}) = +132.9$  (s), +79 (s), -19 (d,  $J_{\text{PH}} = 924$  Hz) ppm). The upfield position of the <sup>31</sup>P chemical shift indicated a high-coordinate

(5) Route A: In a typical experiment a solution of thio- or oxophenyldichlorophosphorane ( $10^{-3}$  mol) in 5 mL of THF and a solution of triethylamine ( $2 \times 10^{-3}$  mol) in 5 mL of THF are simultaneously added dropwise to a solution of phosphodihydrazide **1** ( $10^{-3}$  mol) in 10 mL of THF at 0 °C. The mixture is stirred for 4 h, filtered, and evaporated to dryness. The resulting powder is washed with pentane ( $3 \times 20$  mL). Route B: In a typical experiment phosphodihydrazide **4a** or **4b** ( $10^{-3}$  mol) and phosphorus dialdehyde **3** ( $10^{-3}$  mol) are mixed together. Then, 10 mL of dichloromethane are added, and the resulting solution is stirred for 1 h at room temperature. Evaporation of the solvent gave the expected macrocycles as powders, which were purified by washing with pentane (10 mL).

Scheme III<sup>7</sup>

phosphorus, and the large coupling constant suggested a direct P-H bond.<sup>6</sup> Low-temperature spectra clearly confirmed the existence of a  $P_{III}$  ( $\delta = 132.9$ )  $\rightleftharpoons$   $P_V$  ( $\delta = -19$ ) equilibrium, the intensity of the signal at 132.9 ppm dramatically increased with the temperature, while the signal at -19 ppm decreased simultaneously in the same proportion. No change was observed for the signal due to the  $P_{IV}$  fragment ( $\delta = 79$ ). The above data are in agreement with the existence of an equilibrium between species 9 and 9' (Scheme III). Further support for these formulations was obtained from a molecular weight determination (mass spectrometry), indicating that a [2 + 2] condensation reaction had taken place (as described in Schemes I and II).

Studies of the chemical properties of these macrocycles are underway.

**Supplementary Material Available:** A table of CHN analyses of compounds 5a,b, 6a,b, 7a-h, and 9 (1 page). Ordering information is given on any current masthead page.

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 (7) 9' is one of the possible isomers arising from the migration of the proton from phosphorus to oxygen.

Laboratoire de Chimie de Coordination  
du CNRS

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l'Université Paul Sabatier et à  
l'Institut National Polytechnique de  
Toulouse

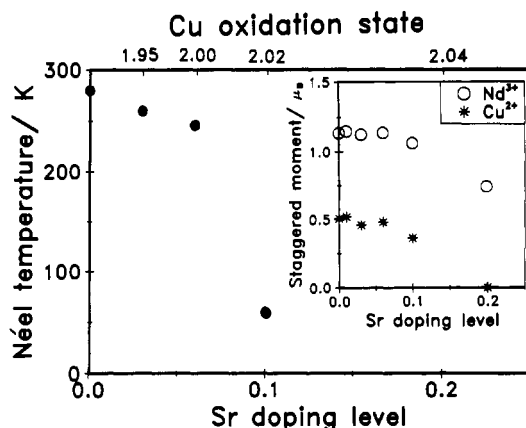
205 route de Narbonne  
31077 Toulouse Cedex, France

Dominique Colombo  
Anne-Marie Caminade  
Jean Pierre Majoral\*

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### Magnetic Phase Diagram of the Hole-Doped T' Phases $Nd_{2-x}Sr_xCuO_{4-\delta}$

The contrast in magnetic behavior with increasing dopant concentration between the hole carrier  $La_{2-x}Sr_xCuO_{4-\delta}$ <sup>1</sup> and the electron carrier  $Nd_{2-x}Ce_xCuO_{4-\delta}$ <sup>2</sup> systems illustrates the complex interplay between magnetism and superconductivity in the cuprate high  $T_c$  materials.<sup>3</sup> Electron doping in  $Nd_{2-x}Ce_xCuO_{4-\delta}$  has a much less marked effect on  $T_N$  and the staggered moment on the Cu(II) sublattice than hole doping in  $La_{2-x}Sr_xCuO_{4-\delta}$ , which rapidly destroys the Néel state.<sup>4,5</sup> This is due to the less pro-



**Figure 1.** Néel temperature (K) for LR Cu antiferromagnetic order as a function of dopant concentration in  $Nd_{2-x}Sr_xCuO_{4-\delta}$ , determined by the  $\mu$ SR experiments. The  $x = 0.2$  composition shows no evidence for an oscillation signal. Inset: Composition dependence of the staggered moments ( $\mu_B$ ) on the Cu and Nd sublattices at 1.5 K, determined by powder neutron diffraction.

**Table I.** Oxygen Concentration, Formal Cu Oxidation State, and Cu Moment (at 1.5 K) in  $Nd_{2-x}Sr_xCuO_{4-\delta}$

$x$	$\delta$	Cu oxidn state	$\mu_{Cu}/\mu_B$
0.03	0.04	+1.95	0.46 (2)
0.06	0.03	+2.00	0.48 (1)
0.10	0.04	+2.02	0.36 (8)
0.20	0.08	+2.04	0.0

nounced effect on magnetic long-range order (LRO) of dilution<sup>6-9</sup> by nonmagnetic  $Cu^I$  states compared to frustration arising from competing superexchange interactions from  $4^-$  or  $5^-$   $Cu^{III}$  states formed on hole doping. In both systems, the antiferromagnetic instability is removed before the onset of superconductivity.

In view of the differing magnetic behavior on hole and electron doping, it is important to note that, thus far, successful hole and electron doping of the same parent material, leading to superconductivity, has yet to be achieved. In the case of the  $K_2NiF_4$  (O) and T' structures, the tolerance factors<sup>10,11</sup> control the range of formal Cu oxidation states that the structures are compatible with. In this communication, we report on our attempts to achieve hole doping of the T' phase and the magnetic properties of the  $Nd_{2-x}Sr_xCuO_{4-\delta}$  ( $x = 0.00-0.20$ ) system, studied by zero-field longitudinal-geometry muon spin relaxation and powder neutron diffraction.

$Nd_{2-x}Sr_xCuO_{4-\delta}$  compositions ( $x = 0.03, 0.06, 0.10$ ) were synthesized by the citrate sol-gel technique;<sup>10,12</sup>  $Nd_{1.9}Sr_{0.1}CuO_{4-\delta}$

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