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New Synthetic Strategies for Phosphorus-Containing Cryptands and the First Phosphorus Spherand Type Compound

Joëlle Mitjaville, Anne-Marie Caminade, René Mathieu, and Jean-Pierre Majoral*

Laboratoire de Chimie de Coordination du CNRS
205, route de Narbonne, 31077 Toulouse Cédex, France

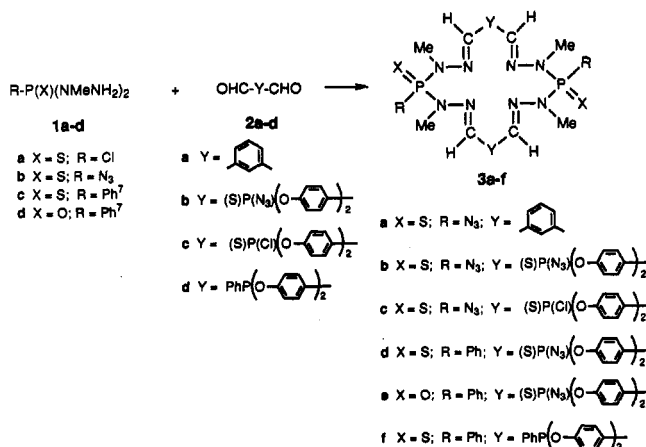
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Studies concerning phosphorus-containing macrocycles are now well documented¹ and offer a large choice of synthetic methods. On the other hand, only a few publications concerning phosphorus cryptands have appeared.² To our knowledge no phosphorus spherand has even been described. Experimental difficulties (multistep procedures, low yields) probably explain the lack of results in this field.

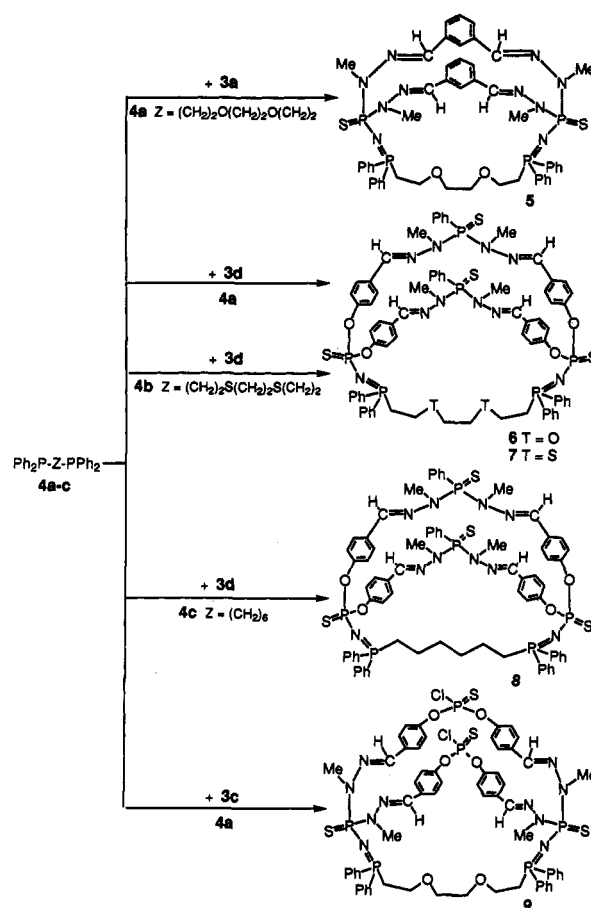
We report here the easy and high-yield preparation of a variety of so far unique, functionalized or not, phosphorus-containing cryptands and the synthesis of the first phosphorus spherand type compound.

The reaction of the previously unknown thioxobis(1-methyl-hydrazino)phosphoranyl azide (**1b**), prepared from **1a** and sodium azide in the presence of 18-dibenzo C-6 crown ether, with benzene-1,3-dicarboxaldehyde (**2a**) gives quantitatively the "[2 + 2] cycloadduct"³ **3a**⁴ (Scheme 1), and subsequent addition of the bis(phosphine) **4a**⁵ leads to the tetraphosphorus-containing cryptand **5** in 80% yield (Scheme 2). The ³¹P{¹H} NMR spectrum of **5** in dichloromethane shows two characteristic doublets at 56.2 (NP(S)N) and 14.0 (N=PC) ppm (²J_{PP} = 26 Hz). Mass

Scheme 1



Scheme 2



(1) Caminade, A.-M.; Majoral, J.-P. *Chem. Rev.*, in press.
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(3) The term cyclocondensation indicates the condensation between two functionalized species leading to a macrocycle. For example, a [2 + 2] cycloadduct is, here, a compound arising from the cyclocondensation of 2 equiv of each partner.

(4) Selected spectroscopic data are as follows. **3a**: ³¹P{¹H} NMR (CDCl₃) δ 66.9 ppm; ¹³C{¹H} NMR (CDCl₃) δ 138.7 (d, ³J_{CP} = 12 Hz, HC=N) ppm; IR (KBr) 2151 (ν_{N₃}) cm⁻¹; mass spectrum *m/z* 587 [M + 1]⁺. **3b**: ³¹P{¹H} NMR (CDCl₃) δ 67.2 (s, NP(S)N), 59.2 (s, OP(S)O) ppm; ¹³C{¹H} NMR (CDCl₃) δ 136.1 (d, ³J_{CP} = 12.7 Hz, HC=N) ppm; IR (KBr) 2150 and 2162 (ν_{N₃}) cm⁻¹; mass spectrum *m/z* 1013 [M + 1]⁺. **3c**: ³¹P{¹H} NMR (THF) δ 66.9 (s, NP(S)N), 57.3 (s, OP(S)O) ppm; ¹³C{¹H} NMR (CDCl₃) δ 137.8 (d, ³J_{CP} = 14 Hz, HC=N) ppm; IR (KBr) 2150 (ν_{N₃}) cm⁻¹; mass spectrum *m/z* = 999 [M + 1]⁺. **3d**: ³¹P{¹H} NMR (CDCl₃) δ 79.2 (s, NP(S)N), 58.7 (s, OP(S)O) ppm; ¹³C{¹H} NMR (CDCl₃) δ 135.9 (d, ³J_{CP} = 13 Hz, HC=N) ppm; IR (KBr) 2161 (ν_{N₃}) cm⁻¹; mass spectrum *m/z* 1083 [M + 1]⁺. **3e**: ³¹P{¹H} NMR (CDCl₃) δ 24.8 (s, NP(O)N) 58.7 (s, OP(S)O) ppm; ¹³C{¹H} NMR (CDCl₃) δ 135.7 (d, ³J_{CP} = 12 Hz, HC=N) ppm; IR (KBr) 2162 (ν_{N₃}) cm⁻¹; mass spectrum *m/z* 1051 [M + 1]⁺. **3f**: ³¹P{¹H} NMR (CDCl₃) δ 78.5 (s, NP(S)N), 158.5 (s, OPO) ppm; ¹³C{¹H} NMR (CDCl₃) δ 136.2 (d, ³J_{CP} = 13 Hz, HC=N) ppm; mass spectrum *m/z* 1090 [M + 1]⁺.

(5) Hill, W. E.; Taylor, J. G.; Mc Auliffe, C. A.; Muir, K. W.; Manojlovic-Muir, J. *J. Chem. Soc., Dalton Trans.* **1982**, 833.

spectrometry (*m/z* = 1017 [M + 1]⁺), analytical, and NMR spectrometry data confirm the formation of this cryptand.

The same assembling principle can be applied for the preparation of hexaphosphorus-containing cryptands. It necessitates the preliminary synthesis of the di- or tetrafunctionalized macrocycles **3b–e** arising from the [2 + 2] cyclocondensation between the original trifunctionalized thioxophosphoranes **2b,c** and phosphoranyldihydrazides **1b–d** (Scheme 1). These reactions proceed under mild conditions (room temperature, no high dilution required) and give macrocycles **3b–e** in high yield (>90%). The bis(azido) macrocycle **3d** is allowed to react in THF with an equimolecular amount of bis(phosphines) **4a**, **4b**,⁵ or **4c** during 3 h at room temperature (Scheme 2). The ³¹P NMR spectra of the resulting products clearly show the formation of the cryptands

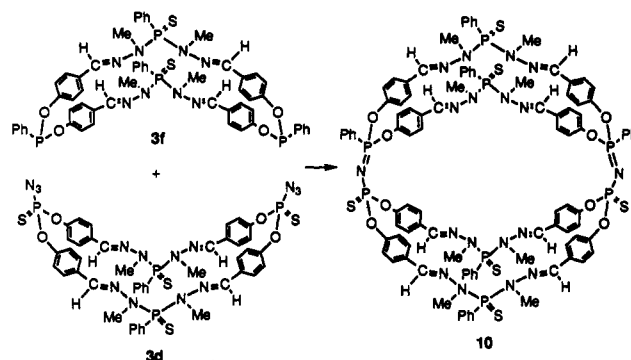
6, 7, and 8 (78, 88, and 85% yields, respectively): one singlet and two doublets are detected for each compound (6 δ = 79.3 (s, NP(S)N), 52.2 (d, OP(S)N), and 16.2 (d, CP=N) ppm ($^2J_{PP}$ = 30 Hz); 7 δ = 79.3 (s, NP(S)N), 52.2 (d, OP(S)N), and 17.1 (d, CP=N) ppm ($^2J_{PP}$ = 34 Hz); 8 δ = 79.0 (s, NP(S)N), 51.7 (d, OP(S)N), and 19.5 (d, CP=N) ppm ($^2J_{PP}$ = 29 Hz)). The structure of these three cryptands is confirmed by FAB and electron-spray spectrometry (6 m/z = 1514 [$M + 1$] $^+$; 7 m/z = 1545 [$M + 1$] $^+$; 8 m/z = 1503 [$M + Na$] $^+$). These cryptands are remarkably stable: no traces of hydrolysis products are detected when, for example, a 2/1 THF/water solution of 7 is stirred for 24 h at room temperature.

The use of 1,2-bis(phosphine) $Ph_2P(CH_2)_2PPh_2$ or 1,4-bis(phosphine) $Ph_2P(CH_2)_4PPh_2$ instead of bis(phosphines) 4a–c does not allow the isolation of the corresponding expected cryptands: only polymeric species are obtained in these cases. Indeed, the formation of cryptands strongly depends on the length of the chain of the considered bis(phosphines): at least seven bonds between the two phosphino groups are necessary in order to join properly the two wings of the butterfly structure of the [2 + 2] cycloadducts 3.⁶

An analogous procedure is employed for the preparation of a so far unique functionalized cryptand 9: the Staudinger reaction between the bis(azido) bis(chloro) macrocycle 3c and 4a leads to 9 in 86% yield (Scheme 2) (9 δ ^{31}P = 57.6 (s, OP(S)O), 55.8 (d, NP(S)N), and 13.0 (d, CP=N) ppm ($^2J_{PP}$ = 29.8 Hz); mass spectrum m/z = 1429 [$M + 1$] $^+$).

Lastly, such a methodology appears extremely useful for the preparation of the first phosphorus spherand type compound. It implies once again a Staudinger reaction but now between two macrocyclic species: the bis(azido) macrocycle 3d and the macrocycle 3f.⁴ The reaction proceeds smoothly at room temperature and gives the octaphosphorus-containing spherand 10 in 75% yield (Scheme 3). The expected butterfly type structure of the two starting macrocycles might explain why the spherand

Scheme 3



10 is so easily formed. This derivative was fully characterized by NMR, IR spectroscopy, elemental analysis, and electron-spray mass spectrometry (m/z = 2116 [$M + 1$] $^+$). The $^{31}P\{^1H\}$ NMR spectrum, for example, reveals the presence of one singlet (δ = 78.5 ppm, NP(S)N) and two doublets (δ = 45.5 (OP(S)N) and 4.6 (OP=N) ppm, $^2J_{PP}$ = 49 Hz).

All the macrocycles 3, cryptands 5–9, and spherand-like 10 can be isolated pure in the form of colorless to yellow stable solids. All attempts to obtain crystals for an X-ray structure determination have been unsuccessful. The possibility of obtaining all these multimacrocyclic species in high yield and in large quantities from easily available precursors opens new perspectives in phosphorus-containing macrocyclic chemistry.

Studies on the synthetic potential of these quite unusual macrocyclic and multimacrocyclic species as well as their complexation properties toward cations, anions, or neutral molecules are underway.

Acknowledgment. Thanks are due to the CNRS for financial support of this work.

Supplementary Material Available: Full experimental details, listing of spectral data, and elemental analysis for products 1a,b, 2b–d, 3a–f, and 5–10 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(6) We have already demonstrated that macrocyclic [2 + 2] adducts analogous to compounds 3a–e possess a butterfly type structure: (a) Badri, M.; Majoral, J.-P.; Caminade, A.-M.; Delmas, M.; Gaset, A.; Gorgues, A.; Jaud, J. *J. Am. Chem. Soc.* **1990**, *112*, 5618. (b) Oussaid, B.; Garrigues, B.; Jaud, J.; Caminade, A.-M.; Majoral, J.-P. *J. Org. Chem.* **1993**, *58*, 4500.

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