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Macrocycles Containing Bicyclophosphorane Moieties [1]

Douraid Houalla,* Zouhair Bounja, Saïd Skouta, and Robert Wolf

Laboratoire de Synthèse, Structure et Réactivité de Molécules Phosphorées, E.R. 76, Université Paul Sabatier, 31062 Toulouse Cedex, France

Joel Jaud

Centre d'Elaboration des Matériaux et d'Etudes Structurales du Centre National de la Recherche Scientifique, 31400 Toulouse, France

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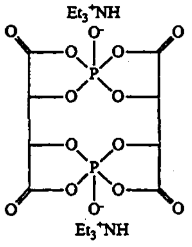
ABSTRACT

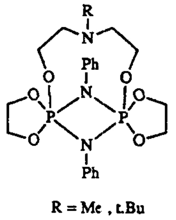
The first stable macrocycles, **12–15**, **16**, **18**, *and* **23**, *containing pentacovalent phosphorus have been obtained by an Atherton–Todd reaction between the bis(hydridobicyclophosphoranes)* **3–7** *and the corresponding binucleophile* $HO–(CH_2)_2–X–(CH_2)_2–OH$. *The tricyclic monophosphoranes* **8–11** *as well as the noncyclic derivative* **20** *have also been isolated. A pathway that accounts for the formation of all these compounds is proposed. The X-ray crystal study of two 16-membered rings,* **14**, **15**, *confirms the diequatorial placement of the macrocyclic frame on the trigonal bipyramidal phosphorus which retains the most favorable axial-equatorial-axial annelation of the bicyclic moiety. Comparison of these two molecular structures points out the effect of the nature of X on the conformation of the macrocycle.*

INTRODUCTION

Phosphorus-containing macrocycles, which are predominantly built with tetracoordinated phosphorus atoms, represent a minor part of macrocyclic compounds [2–5]. To the best of our knowledge, the few attempts to obtain pentacovalent phosphorus-containing macrocycles have been unsuccessful. They resulted in the formation of nonseparable oligomers [6] or in the production of mixtures of tri and penta [7], or tetra and penta, coordinated phosphorus species [8]. On the other hand, the 10-membered rings **A** [9] and **B** [10] described earlier should be considered as medium rings rather than macrocycles.*



A



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The synthesis of macrocycles containing pentacovalent phosphorus is interesting for at least two reasons: (1) they constitute a new class of phosphorus macrocycles; and (2) they are expected to possess some specific properties in the field of molecular recognition. Similarly to the recent results obtained in the reaction of potassium methoxide with some spirophosphoranes in the presence of crown ethers [11], the cation capture by the macrocyclic frame could be accompanied by a nucleophilic attack at the P^V electrophilic center by the corresponding anion. Such an approach has

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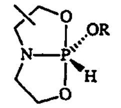
*To whom correspondence should be addressed.

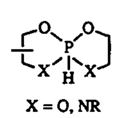
*After the submission of the manuscript, there was a publication dealing with a 12-membered ring containing 2 pentacoordinated phosphorus atoms [34].

been investigated recently with conventional macrocycles bearing an electrophilic center [12,13].

In the course of our study of hydridobicyclophosphoranes [14] (**I**), we have



(I)



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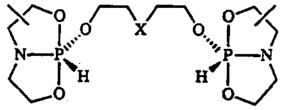
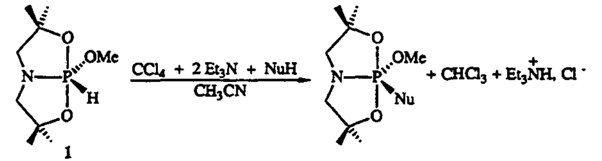


(II)

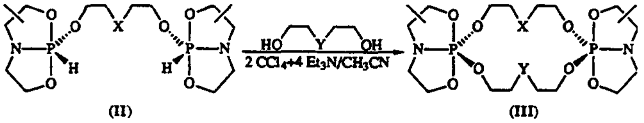
established that the nucleophilic substitution at the H–P bond in the presence of carbon tetrachloride and triethylamine (Atherton–Todd reaction [15]), which has recently been used with some hydridospirophosphoranes **C** [16,17], can also be extended to compound **1** [18].



1

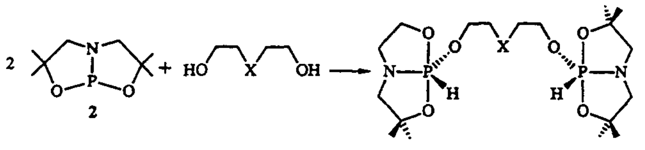
Nu = OR, NR2

Thus, it appears that the extension of this reaction to the *bis*(hydridobicyclophosphoranes) (**II**) could be a simple route to obtain the new bicyclophosphoranes containing macrocycles (**III**):



(II) (III)

For that purpose, we have synthesized the five precursors **3–7** using the oxidative addition of the corresponding diol **a–e** to the 3.3.7.7-tetramethyl 2.8-dioxa 5-aza-1λ^3-phosphabicyclo(3.3.0)octane **2** [19], i.e. the "bicyclophosphane."



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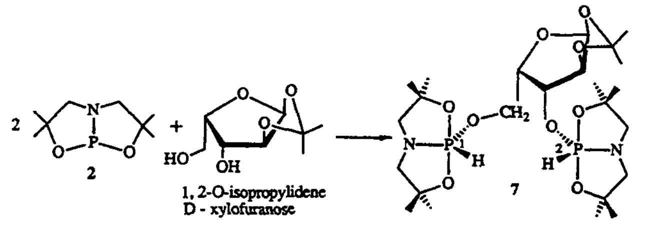
			δ^{31}P	$^1J_{HP}$ Hz
a	X = O	3	-36.4	800
b	X = N-Bu	4	-36.0	796.3
c	X = N-t.Bu	5	-36.3	796
d	X = N-Ph	6	-37.2	796



2 7

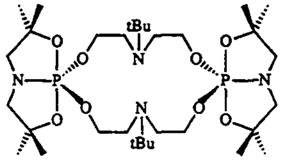
$\delta^{31}P = -37$ $^1J_{PH} = 800$ Hz

$\delta^{31}P = -41$ $^1J_{PH} = 807$ Hz

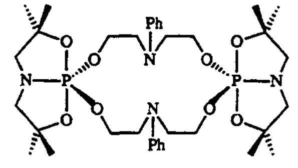
Compounds **3–7** which have been fully characterized by NMR spectroscopy (Tables 1 and 2) and elemental analyses, have served to carry out two types of macrocyclization:

1. "symmetric macrocyclizations" $X = Y$: **3** + **a**, **4** + **b**, **5** + **c**, **6** + **d**; and
2. "nonsymmetric macrocyclizations" restricted in this work to the condensation **7** + **a**.

In this article, we report the results obtained in this investigation, including the description of the X-ray molecular structures of the two 16-membered rings **14** and **15**.



14



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RESULTS AND DISCUSSION

All the macrocyclizations, monitored by ^{31}P NMR, were performed in acetonitrile as the solvent. The consumption of the starting materials required 2–4 days of heating at 40°C. Then the ^{31}P NMR spectra showed the formation of several new P^V peaks, accompanied by minor peaks corresponding to tetracoordinated phosphorus compounds ($\delta = -11$, 20). The use of the high dilution experimental conditions favored the formation of these side products. The separation of the resulting products was performed by column chromatography using ethyl acetate or 1/4 ethyl acetate/cyclohexane as an eluent. The isolated compounds were fully characterized by NMR (^{31}P, ^{1}H, ^{13}C) and mass spectroscopy.

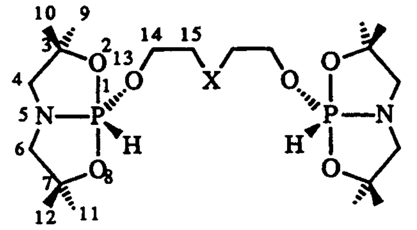
Symmetric Macrocyclizations

The four symmetric macrocyclizations **3** + **a**, **4** + **b**, **5** + **c**, and **6** + **d** gave similar results. They differed only by the number of eluted compounds. In the following paragraphs, we relate in detail the **3** + **a** condensation as an example of this reaction and indicate the difference with the other macrocyclizations.

The P^V part of the NMR spectrum of the final reaction mixture contained five peaks: $\delta = -42.9$ (5%); $\delta = -44.6$ (30%); $\delta = -45.1$ (11%); $\delta = -45.3$ (27%); and $\delta = -45.6$ (27%).

The first eluted compound, $\delta^{31}P = -42.9$, was identified as the tricyclic monophosphorane **8** by mass spectroscopy: $m^+/z = 294$ (100 ($M_8^+ + 1$)). By comparison with the literature data [20,21], its eight-membered ring is very likely positioned at (*e-e*) sites of the trigonal bipyramid. The same be-

TABLE 1 ^1H and ^{13}C NMR Parameters (250.13 and 62.89 MHz, C_6D_6) δ, J(Hz) of Compounds **3–6**

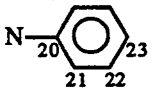


3 X = O

4 $X = N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
20 21 22 23

5 $X = N\text{-}C(CH_3)_3$
20 21

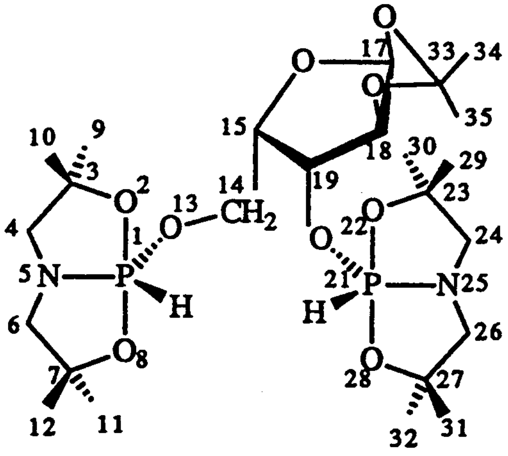
6 X = N–



	3		**4**		**5**		**6**	
Me(9, 11) or (10, 12)	s	1.21	s	1.18	s	1.21	s	1.20
Me(10, 12) or (9, 11)	s	1.30	s	1.27	s	1.33	s	1.27
H(41)		2.48		2.49		2.49		2.44
H(61)	$^2J_{HH}$	−7.9	$^2J_{HH}$	−8	$^2J_{HH}$	−7.8	$^2J_{HH}$	−7.9
	$^3J_{HP}$	12.7	$^3J_{HP}$	12	$^3J_{HP}$	12	$^3J_{HP}$	12.1
H(42)		2.54		2.54		2.57		2.50
H(62)	$^3J_{HP}$	14.6	$^3J_{HP}$	15.4	$^3J_{HP}$	15.1	$^3J_{HP}$	12.1
H(151)	td	3.53	t	2.69	t	2.78	t	3.52
H(152)	$^3J_{HH}$	5.4	$^3J_{HH}$	6.7	$^3J_{HH}$	7.8	$^3J_{HH}$	6.6
	$^3J_{HP}$	0.8						
H(141) + H(142)	td	4.06	td	3.96	td	4.0	td	4.06
	$^3J_{HP}$	9.9	$^3J_{HP}$	10	$^3J_{HP}$	10.6	$^3J_{HP}$	10.2
Me			t	0.81				
			$^3J_{HH}$	7.3	s	0.91		
CH_2–CH_2			m	1.05–1.4				
N–CH_2			t	2.42				
			$^3J_{HH}$	7.3				
N–C_6H_5							m	6.7–7.2
HP	d	7.18	d	7.02	d	7.13	d	7.15
	$^1J_{HP}$	799.7	$^1J_{HP}$	795.7	$^1J_{HP}$	794.4	$^1J_{HP}$	795.2
C(9, 11) or (10, 12)	s	29.1	s	29.2	s	29.3	s	29.1
C(10, 12) or (9, 11)	d	29.6	d	29.7	d	29.7	d	29.5
	$^3J_{CP}$	5.1	$^3J_{CP}$	5.3	$^3J_{CP}$	5.2	$^3J_{CP}$	5.1
C(4, 6)	d	55.4	d	29.7	d	29.7	d	55.3
	$J_{CP}{}^a$	18.9	$J_{CP}{}^a$	19	$J_{CP}{}^a$	18.9	$J_{CP}{}^a$	19
C(3, 7)	d	70.3	d	70.1	d	70.2	d	70.3
	$J_{CP}{}^b$	5.7	$J_{CP}{}^b$	5.6	$J_{CP}{}^b$	5.6	$J_{CP}{}^a$	5.5
C(15)	d	71.4	d	55.7	d	52.2	d	52.0
	$^3J_{CP}$	9.2	$^3J_{CP}$	10.7	$^3J_{CP}$	9.3	$^3J_{CP}$	9.1
C(20)			s	55.6	s	54.6	s	148.1
C(21)			s	30.4	s	27.3	s	129.6 or 122.2
C(22)			s	20.7			s	112.2 or 129.6
C(23)			s	14.3			s	116.3

[a] $J_{CP} = 1/2(^2J_{C\text{-}N\text{-}P} + {}^3J_{C\text{-}C\text{-}O\text{-}P})$.
[b] $J_{CP} = 1/2(^2J_{C\text{-}O\text{-}P} + {}^3J_{C\text{-}C\text{-}N\text{-}P})$.

TABLE 2 ^1H and ^{13}C NMR Parameters (250.13 and 62.89 MHz, C_6D_6), δ, J(Hz) of Compound **7**



Me[a](9,10,11,12,29,30,31,32,34,35)		1.0–1.36	10s					
N-CH$_2^a$ (4,6,24,26)		2.39–2.62 m corresponding to the AB parts of 4 ABX systems (X = P)						
H(141)[b]		4.48	$^2J_{H\text{-}H(142)}$ $^3J_{H\text{-}H(15)}$ $^3J_{H\text{-}P(1)}$	10.8 6.4				
H(142)[b]		4.56	$^3J_{H\text{-}H(15)}$	5.8			$^3J_{H\text{-}P(1)}$	0
H(15)		4.64	$^3J_{H\text{-}H(19)}$	3.0				
H(18)	d	4.65	$^3J_{H\text{-}H(17)}$	3.8				
H(19)	dd	5.14	$^3J_{H\text{-}H(18)}$	10.0				
H(17)	d	5.91	$^3J_{H\text{-}H(18)}$	3.8				
H–P(1)	d	7.15	$^1J_{H\text{-}P(1)}$	803				
H–P(21)	d	7.22	$^1J_{H\text{-}P(21)}$	808				
C(34) or C(35)	s	26.4						
C(35) or C(34)	s	26.5						
C(9,10,11,12,29,30,31,32)	4s	28.9 29.0 (×2) 29.2			4d	29.3 29.4 29.3 (× 2)	$^3J_{CP}$ $^3J_{CP}$ $^3J_{CP}$	4.8 4.1 4.8
C(4,6,24,26)	4d	54.9 55.0 55.2 (×2)	J_{CP}^c J_{CP}^c J_{CP}^c	18.9 19.1 18.9				
C(14)	d	64.2	$^2J_{CP}$	6.0				
C(3,7,23,27)	4d	70.4 70.5	J_{CP}^d J_{CP}^d	5.5 5.5		70.6 70.9	J_{CP}^d J_{CP}^d	5.2 5.2
C(19)	d	79.1	$^2J_{C\text{-}P(21)}$	7.8				
C(15)	dd	80.4	$^3J_{CP}$ $^3J_{CP}$	7.9 10.2				
C(18)	d	85.3	$^3J_{CP}$	2.6				
C(17)	s	105.5						
C(33)	s	111.6						

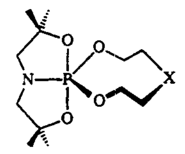
[a] Due to the chirality of the xylofyranosyl group, all the Me as well as the N-CH_2 become diastereotopes.

[b] H(141) and H(142) are the AB part of an ABXY system (X = H(15), Y = P).

[c] $J_{C\text{-}P} = 1/2(^2J_{C\text{-}N\text{-}P} + {}^3J_{C\text{-}C\text{-}O\text{-}P})$.

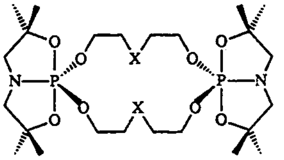
[d] $J_{C\text{-}P} = 1/2(^2J_{C\text{-}O\text{-}P} + {}^3J_{C\text{-}C\text{-}N\text{-}P})$.

havior was observed in the three other reactions, leading to similar compounds **9–11** (Table 3).



		$\delta^{31}P$
8	X = O	-42.9
9	X = N-Bu	-42.6
10	X = N-tBu	-42.1
11	X = N-Ph	-46.7

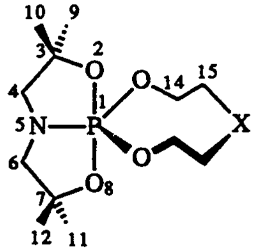
Mass spectroscopy as well as ^1H and ^{13}C NMR spectra (Table 4) show that the second eluted compound, $\delta^{31}P = -44.6$, was the bis-(bicyclophosphorane) containing macrocycle **12** $[m^+/z = 587(95\ (M_{12}^+ + 1))]$. The similar macrocycle **13** (condensation **4** + **b**) was also separated by chromatography, while **14** and **15** precipitated spontaneously from the reaction mixtures. Compounds **12–15** have been characterized by mass (see the Experimental section) and ^1H and ^{13}C NMR spectroscopy (Table 4).



		$\delta^{31}P$
12	X = O	-44.6
13	X = N-Bu	-44.6
14	X = N-tBu	-44.9
15	X = N-Ph	-44.4

The third eluted component, $\delta^{31}P = -45.1$, was identified as the 24-membered ring **16** $[m^+/z = 880\ (11.6\ (M_{16}^+ + 1))]$. The similar compound **18** $m^+/z = 1045\ (100\ (M_{18}^+ + 1))$ was also eluted, while the

TABLE 3 ^1H and ^{13}C NMR Parameters (250.13 and 62.89 MHz, C_6D_6) δ, J(Hz) of Compounds **8–11**

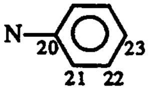


8 X = O

9 $X = N\text{-}\underset{20}{CH_2}\text{-}\underset{21}{CH_2}\text{-}\underset{22}{CH_2}\text{-}\underset{23}{CH_3}$

10 $X = N\text{-}\underset{20}{C}(\underset{21}{CH_3})_3$

11 X =

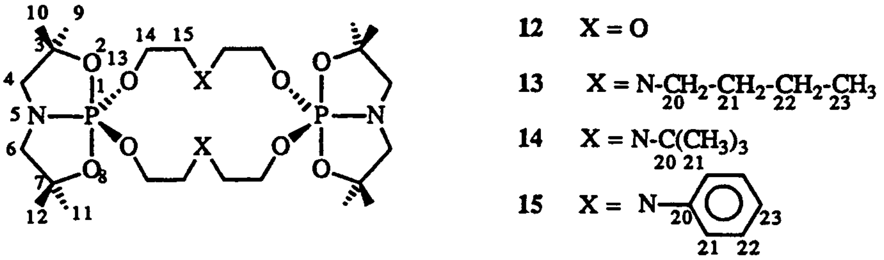


	8		**9**		**10**		**11**	
Me(9,10,11,12)	s	1.24	s	1.25	s	1.28	s	1.1
CH_2(4,6)	d	2.47	d	2.5	d	2.52	d	2.43
	$^3J_{HP}$	13.4	$^3J_{HP}$	13.4	$^3J_{HP}$	13.5	$^3J_{HP}$	13.3
CH_2(14) + CH_2(15)	m[a]	3.8–4	m[a]	2.9–4	m[a]	2.6–4.1	m[a]	3.3–4.1
Me			t	0.8	s	0.92		
			$^3J_{H\text{-}H}$	7.3				
CH-CH_2			m	1.2–1.3				
N-CH_2			t	2.52				
			$^3J_{H\text{-}H}$	6.9				
N-C_6H_5							m	6.3–7.2
C(9,10,11,12)	s	28.8	s	28.9	s	28.9	s	28.7
C(4,6)	d	55.0	d	55.1	d	55.1	d	55.2
	J_{CP}[b]	20.8	J_{CP}[b]	20.8	J_{CP}[b]	20.8	J_{CP}[b]	20.8
C(3,7)	s	69.3	s	69.1	s	69.1	s	69.5
C(15)	s	73.0	d	56.8	s	51.9	s	53.9
			$^3J_{CP}$	1.0				
C(20)			s	55.9	s	55.2	s	147.1
C(21)			s	30.7	s	26.9	s	129.4 or 111.9
C(22)			s	20.7			s	111.9 or 129.4
C(23)			s	14.3			s	115.7

[a] Nonresolved AA'XX'Y systems (Y=P).

[b] $J_{C\text{-}P} = 1/2(^2J_{C\text{-}N\text{-}P} + {}^3J_{C\text{-}C\text{-}O\text{-}P})$.

TABLE 4 ^{1}H and ^{13}C NMR Parameters (250.13 and 62.89 MHz, C_6D_6) δ, J(Hz) of Compounds **12–15**



12 X = O

13 X = N-CH_2-CH_2-CH_2-CH_3

14 X = N-$C(CH_3)_3$

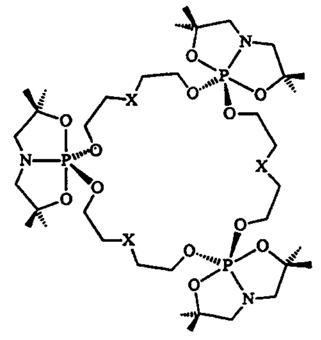
15 X = N-

	12		*13*		*14*		*15*	
Me(9,10,11,12)	s	1.23	s	1.31	s	1.35	s	1.23
CH_2(4,6)	d	2.46	d	2.52	d	2.54	d	2.45
	$^3J_{HP}$	13	$^3J_{HP}$	12.8	$^3J_{HP}$	12.9	$^3J_{HP}$	12.4
CH_2(15)	td	3.6	d	2.94	d	2.98	d	3.68
	$^3J_{HH}$	5.2	$^3J_{HH}$	6.8	$^3J_{HH}$	7.8	$^3J_{HH}$	6.8
	$^4J_{HP}$	2						
CH_2(14)	td	4.21	td	4.26	td	4.25	td	4.21
	$^3J_{HP}$	7.2	$^3J_{HP}$	6.8	$^3J_{HP}$	8.2	$^3J_{HP}$	9.2
Me			t	0.88	s	0.96		
CH_2–CH_2			m	1.1–1.43				
N–CH_2			t	2.57				
			$^3J_{HH}$	7				
N–C_6H_5							m	6.6–7.2
C(9,10,11,12)	d	28.8	d	29.0	d	29.1	d	28.9
	$^3J_{CP}$	3.7	$^3J_{CP}$	3.7	$^3J_{CP}$	4.0	$^3J_{CP}$	4.1
C(4,6)	d	55.2	d	55.3	d	55.4	d	55.1
	$J_{CP}{}^a$	20.8	$J_{CP}{}^a$	20.6	$J_{CP}{}^a$	20.6	$J_{CP}{}^a$	20.6
C(14)	d	67.1	d	66.3	d	68.4	d	64.5
	$^2J_{CP}$	9.3	$^2J_{CP}$	10.0	$^2J_{CP}$	10.0	$^2J_{CP}$	10.1
C(3,7)	s	69.5	s	69.4	s	69.4	s	69.6
C(15)	d	71.1	d	55.1	d	51.9	d	51.7
	$^3J_{CP}$	9.8	$^3J_{CP}$	9.8	$^3J_{CP}$	10.6	$^3J_{CP}$	8.9
C(20)			s	56.1	s	54.4	s	148.6
C(21)			s	30.4	s	27.4	s	129.6 or 111.9
C(22)			s	20.8			s	111.9 or 129.6
C(23)			s	14.4			s	116

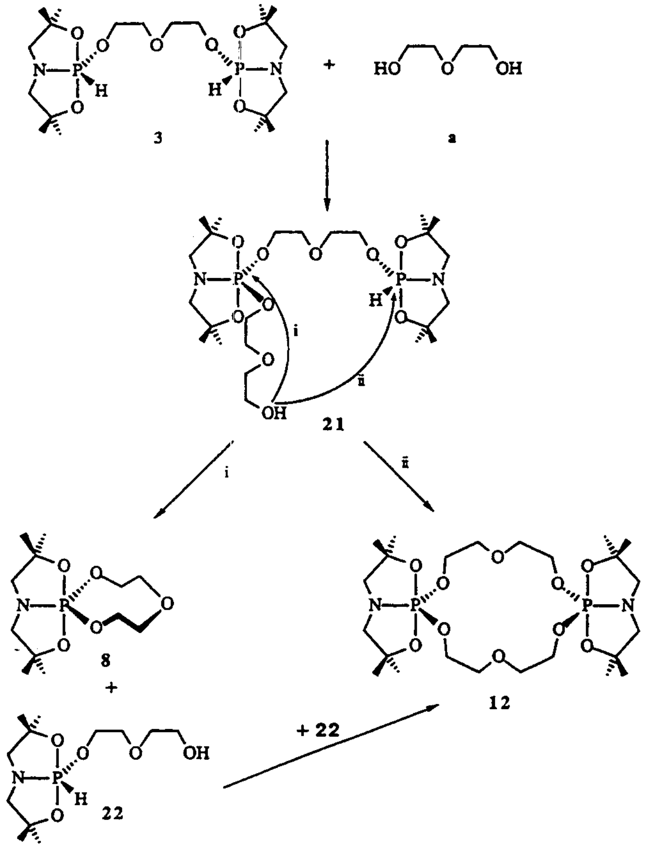
$^aJ_{C\text{-}P} = 1/2(^2J_{C\text{-}N\text{-}P} + {}^3J_{C\text{-}C\text{-}O\text{-}P})$.

expected macrocycles **17** and **19** were, very likely, retained on the silica gel column.

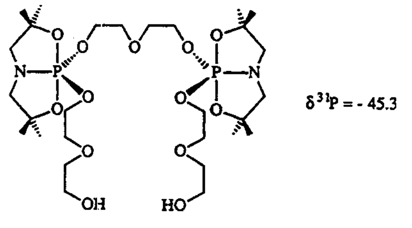
The noncyclic structure of the last eluted component **20**, δ^{31}P = −45.3, was confirmed by NMR spectroscopy (see the Experimental section). Although the similar compounds from the other reactions were not separated, their presence was evidenced by addition of **2**, which resulted in the formation in the ^{31}P NMR spectrum of new doublets at δ = −36, with $^1J_{PH}$ ~ 800 Hz, corresponding to the addition products of the OH functions to **2**.



		δ^{31}P
16	X = O	-45.1
17	X = N-Bu	
18	X = N-tBu	-45.4
19	X = N-Ph	



SCHEME 1

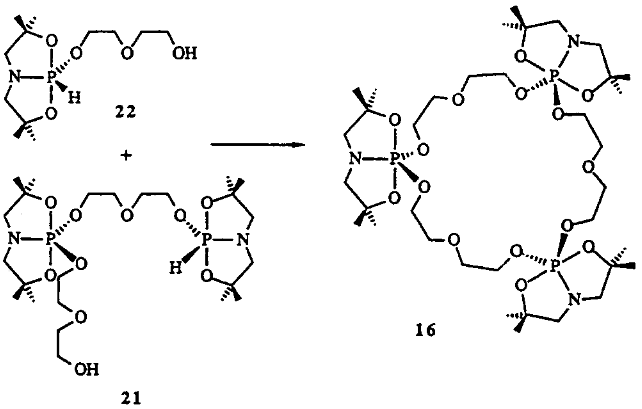


20

The last pentacovalent phosphorus compound present in the reaction mixture, δ^{31}P = −45.6, was not eluted even with acetonitrile as an eluent. It was transformed, as well as the retained compounds in the other reactions, into phosphate esters by using methanol as an eluent.

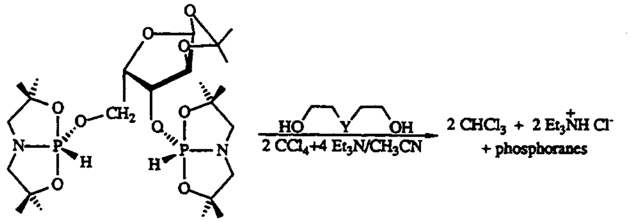
All these observations could be rationalized by the synthetic Scheme 1.

The formation of the intermediate **21** could be the first step. (1) An intramolecular transesterification affords the tricyclic monophosphorane **8** and the second intermediate **22**. (2) The expected macrocycle **12** (1 + 1 condensation) could be formed by an Atherton–Todd reaction between the remaining OH and PH bonds of **21** as well as by the same reaction between two molecules of **22** (3). The 24-membered ring **16** could be formed by an Atherton–Todd reaction between the two intermediates **21** and **22**. (4) Finally, the noncyclic derivative **20** could result from (a) an Atherton–Todd reaction between one molecule of **21** and one molecule of diethyleneglycol, (b) by a condensation of **3** with two molecules of diethyleneglycol, or (c) by a transesterification of **12** with diethyleneglycol.



Nonsymmetric Macrocyclization

As with the previous macrocyclizations, the condensation of *bis*(hydridobicyclophosphorane) **7** with diethyleneglycol **a** has led to a fairly rich reaction mixture: the ^{31}P NMR spectrum contained several pairs of singlets and some individual peaks between δ = −42 and −48 (Figure 1a).



7

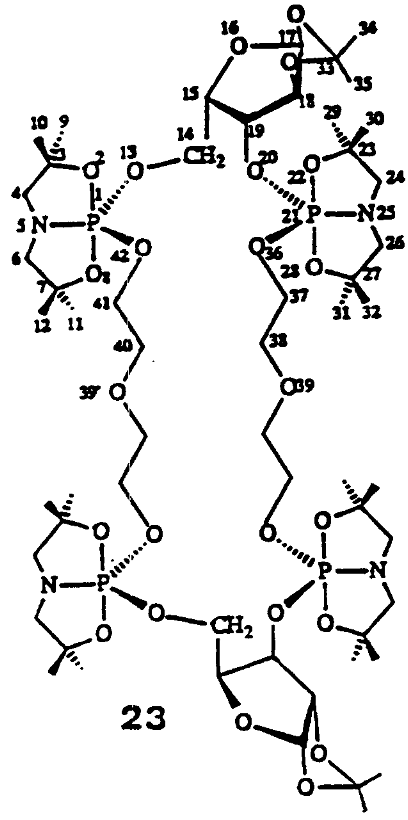
The chromatographic purification of this crude material (see the Experimental section) afforded two unequal fractions. The predominant one (Figure 1b) needed further purification. The final product (Figure 1c) was identified as a 95/5 mixture of the *tetrakis*(bicyclophosphorane)-containing macrocycle **23** [δ^{31}P = −42.9 and −47.1; m^+/z = 1341 (0.57 (M^+_{23} + 1))] a 28-membered ring formed by an unexpected 2 + 2 condensation, and the tricyclic monophosphorane **8** (δ^{31}P = −42.2). The characterization of **23** was achieved by the analysis of its ^{1}H and ^{13}C NMR spectra (Table 5). Compound **8** was also identified by its known ^{1}H NMR spectrum, which is quite different from that of **23**.

TABLE 5 ^{1}H and ^{13}C NMR Parameters (250.13 and 62.89 MHz, C_6D_6) δ, J(Hz) of Compound **23**[a]

Me	10 s between 1.1 and 1.5 ppm					
N–CH_2	m 2.3–2.7 corresponding to the eight expected AB subspectra					
H(381)	ddd	3.5	$^{2}J_{H\text{-}H(382)}$	−10		
			$^{3}J_{H\text{-}H(371)}$	2.8		
			$^{3}J_{H\text{-}H(372)}$	5.2		
H(401) H(402)	m	3.55				
H(382)	ddd	3.6	$^{3}J_{H\text{-}H(371)}$	2.6		
			$^{3}J_{H\text{-}H(372)}$	7		
H(371)	dddd	3.96	$^{2}J_{H\text{-}H(372)}$	−11.7		
			$^{3}J_{H\text{-}P(21)}$	13		
H(411)	dddd	4.12	$^{2}J_{H\text{-}H(412)}$	−12	$^{3}J_{H\text{-}H(402)}$	3
			$^{3}J_{H\text{-}H(401)}$	6	$^{3}J_{H\text{-}H(21)}$	7.5
H(412)	dddd	4.28	$^{3}J_{H\text{-}H(401)}$	2.6		
			$^{3}J_{H\text{-}H(402)}$	4.5	$^{3}J_{H\text{-}P(1)}$	9
H(372)	dddd	4.39	$^{3}J_{H\text{-}P(21)}$	14		
H(141)	ddd	4.65	$^{2}J_{H\text{-}H(142)}$	−12.1		
			$^{3}J_{H\text{-}H(15)}$	5.8	$^{3}J_{H\text{-}P(1)}$	6
H(18)	d	4.66	$^{3}J_{H\text{-}H(17)}$	3.8		
H(15)	ddd		$^{3}J_{H\text{-}H(19)}$	3.2		
			$^{4}J_{H\text{-}P(21)}$	3.2		
			$^{3}J_{H\text{-}H(142)}$	3.4		
H(142)	ddd	5.17	$^{3}J_{H\text{-}P(1)}$	6.0		
H(19)	dd	5.4	$^{3}J_{H\text{-}P(1)}$	9.8		
H(17)	d	6.14	$^{3}J_{H\text{-}H(18)}$	3.8		
C(34) or C(35)	s	26.6				
C(35) or C(34)	s	27.2				
C(9,10,11,12,29,30,31,32)	4d	28.5	$^{3}J_{C\text{-}P}$	2		28.7
		28.6	$^{3}J_{C\text{-}P}$	4.1	4s	29.0
		28.8	$^{3}J_{C\text{-}P}$	4.1		29.1
		28.9	$^{3}J_{C\text{-}P}$	4.1		29.2
C(4,6,24,26)	4d	55.0	$J_{CP}{}^{a}$	20.5		
		55.1 $(\chi 2)$	$J_{CP}{}^{a}$	20.5		
		55.2	$J_{CP}{}^{a}$	20.5		
C(14)	d	66.9	$^{2}J_{C\text{-}P}$	8.1		
C(37) or C(41)	d	67.8	$^{2}J_{CP}$	9.1		
C(41) or C(37)	d	68.5	$^{2}J_{CP}$	10.0		
C(3,7,23,27)	4s	69.4				
		69.6				
		69.7				
		70.2				
C(38) or C(40)	d	71.0	$^{3}J_{CP}$	10.0		
C(40) or C(38)	d	71.4	$^{3}J_{CP}$	7.6		
C(19)	d	80.7	$^{2}J_{CP}$	10.1		
C(15)	dd	82.2	$^{3}J_{CP}$	7.0	$^{3}J_{CP}$	12.2
C(18)	d	86.5	$^{3}J_{CP}$	3.1		
C(17)	s	105.5				
C(33)	s	111.3				

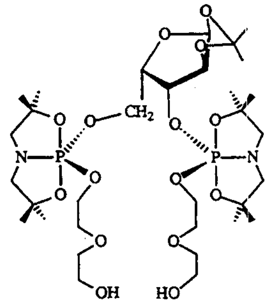
[a] For numbering, see drawing.

[b] $J_{CP} = 1/2(^{2}J_{C\text{-}N\text{-}P} + ^{3}J_{C\text{-}C\text{-}O\text{-}P})$.

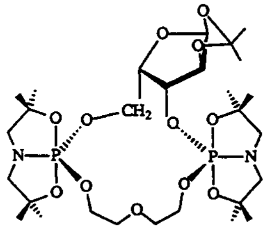


23

The second fraction was a 70/30 mixture of two components (Figure 1d) ($\delta^{31}P$ = −45.5 and −46.4; and $\delta^{31}P$ = −45.1 and −45.9). The ^1H NMR spectrum showed that the major compound was the noncyclic derivative **24** (the intensity ratio of the NCH_2 protons vs. the OCH_2 protons was 1/2), while mass spectroscopy revealed the presence of the *bis*(bicyclophosphorane)-containing macrocycle **25**, a 14-membered ring corresponding to the expected 1 + 1 condensation [m^+/z = 671 (0.57 (M_{25}^+ + 1))]



24

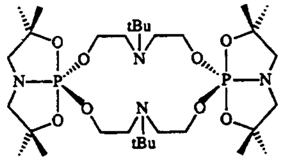


25

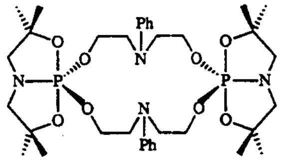
Thus, this nonsymmetric macrocyclization was preferentially oriented toward the 2 + 2 condensation [22], since the macrocycle needed for the 1 + 1 condensation is almost absent. The formation of the noncyclic compound **24** and the tricyclic monophosphorane **8** strongly supports the synthetic pathway proposed previously.

X-RAY MOLECULAR STRUCTURES OF 14 *AND* 15

In order to improve our knowledge of these new macrocycles, we have carried out an X-ray crystallographic study of **14** and **15** considered as representative examples of the *bis*(bicyclophosphorane)-containing macrocycles.



14



15

The two unit cells are quite different: **15** crystallizes with two molecules of toluene; one mole-

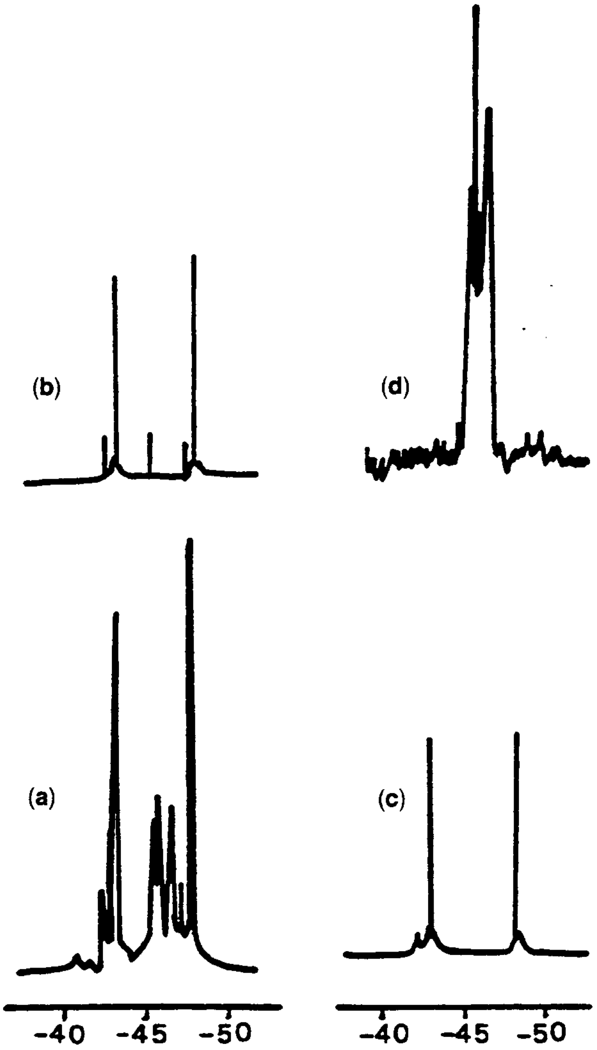


FIGURE 1 7 + **d** condensation. ^{31}P NMR spectra: (a) Reaction mixture, (b) first eluted fraction, (c) the same as (b) after further purification, and (d) second eluted fraction.

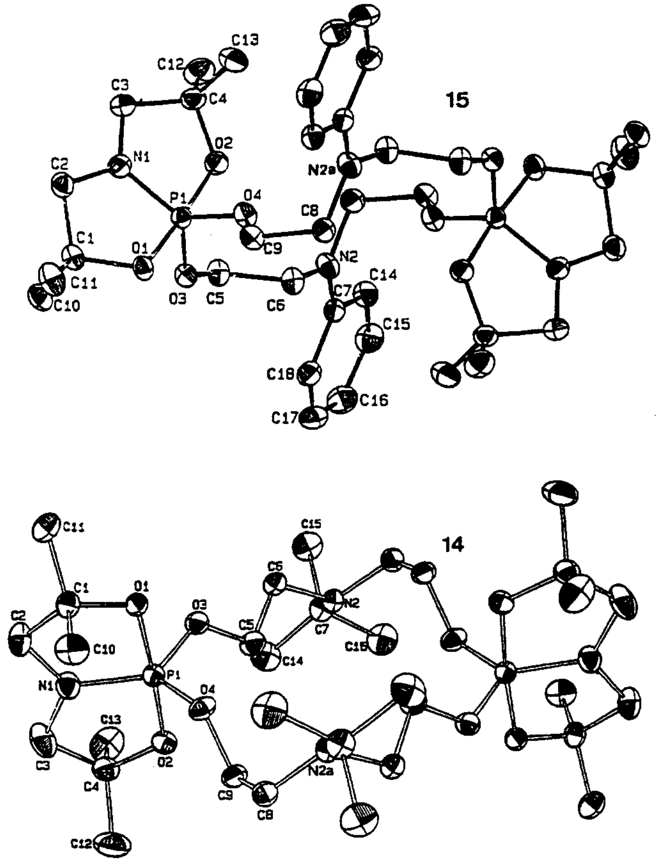


FIGURE 2 ORTEP plots of 14 and 15.

cule is in the neighbourhood of the N-phenyl group with a 80.9° angle between the two aromatic planes, and the second is in the neighborhood of a bicyclophosphorane group with a 78° angle between the apical plane and the plane of the toluene. Compound **14** is solvent-free.

Figure 2 depicts ORTEP views of **14** and **15**, the toluene and hydrogen atoms being omitted for clarity. We have reported in Tables 6–8 some selected parameters concerning either the bicyclophosphorane part or the 16-membered ring macrocyclic part of these molecules. A careful examination of Figure 2 and Tables 6–8 allows us to delineate the common features and the differences between these molecules.

1. Both molecules are centrosymmetric: the center of the 16-membered ring is the symmetry center.
2. The bicyclophosphorane moiety adopts a nearly perfect trigonal bipyramidal geometry (Table 6) with an axial-equatorial-axial annelation, as was the case with compound **D** [23].

TABLE 6 Selected Bond Distances (Å) and Bond Angles (deg) for **14** and **15**

			14	*15*
P(1)	O(1)		1.678(2)	1.672(2)
P(1)	O(2)		1.682(2)	1.677(2)
P(1)	O(3)		1.602(2)	1.598(2)
P(1)	O(4)		1.599(2)	1.593(2)
P(1)	N(1)		1.650(3)	1.663(2)
O(1)	C(1)		1.423(3)	1.433(3)
O(2)	C(4)		1.436(4)	1.424(3)
C(1)	C(2)		1.523(5)	1.526(4)
C(2)	N(1)		1.448(4)	1.431(4)
C(3)	C(4)		1.505(5)	1.532(5)
C(3)	N(1)		1.444(4)	1.436(4)
O(3)	C(5)		1.433(4)	1.437(2)
C(5)	C(6)		1.502(4)	1.520(4)
C(6)	N(2)		1.462(4)	1.451(4)
N(2)	C(8a)		1.455(4)	1.445(4)
O(4)	C(9)		1.429(3)	1.423(3)
C(9)	C(8)		1.504(4)	1.506(4)
O(1)	P(1)	O(2)	175.7(1)	176.4(1)
O(1)	P(1)	O(3)	87.3(1)	88.7(1)
O(1)	P(1)	O(4)	90.0(1)	93.0(1)
O(1)	P(1)	N(1)	87.7(1)	88.1(1)
O(2)	P(1)	O(3)	94.1(1)	93.3(1)
O(2)	P(1)	O(4)	93.3(1)	89.1(1)
O(2)	P(1)	N(1)	88.1(1)	88.3(1)
O(3)	P(1)	O(4)	110.1(1)	110.2(1)
O(3)	P(1)	N(1)	125.2(1)	124.5(1)
O(4)	P(1)	N(1)	124.4(1)	125.3(1)
P(1)	O(3)	C(5)	124.3(2)	126.0(2)
O(3)	C(5)	C(6)	108.6(2)	111.2(2)
C(5)	C(6)	N(2)	110.3(2)	111.7(2)
P(1)	O(4)	C(9)	126.6(2)	127.1(2)
O(4)	C(9)	C(8)	108.4(2)	106.8(2)
C(9)	C(8)	N(2a)	114.3(3)	113.9(2)

TABLE 7 Selected Torsion Angles (deg) for **14** and **15**

				14	*15*
P(1)	O(1)	C(1)	C(2)	−37.04	31.05
P(1)	N(1)	C(2)	C(1)	−16.78	10.60
P(1)	O(2)	C(4)	C(3)	−15.00	27.99
P(1)	N(1)	C(3)	C(4)	−8.14	13.18
P(1)	O(1)	C(1)	C(10)	83.32	88.09
P(1)	O(1)	C(1)	C(11)	−156.37	152.29
P(1)	O(2)	C(4)	C(12)	−137.87	147.65
P(1)	O(2)	C(4)	C(13)	104.12	−92.27
P(1)	O(3)	C(5)	C(6)	174.47	−79.45
O(3)	C(5)	C(6)	N(2)	173.80	168.11
C(5)	C(6)	N(2)	C(8)	−117.10	−93.7
C(6)	N(2)	C(8a)	C(9a)	69.57	−98.46
N(2)	C(8a)	C(9a)	O(4a)	68.20	17.91
C(8)	C(9)	O(4)	P(1)	−166.80	−174.89
O(4)	P(1)	O(3)	C(5)	63.78	82.84
O(3)	P(1)	O(4)	C(9)	−100.16	102.88

TABLE 8 Characteristic Parameters of the Five-Membered Rings

•Best plane P(1)–O(1)–N(1)–C(2)
•Best plane P(1)–O(2)–N(2)–C(3)

14: $0.41795x + 4.02352y - 11.84953z = -11.614$
$0.55008x + 3.89294y - 11.85665z = -11.623$
15: $0.7906x - 0.5504y - 0.2683z = 3.8204$
$0.8033x - 0.4909y - 0.3373z = 3.5582$

Distances of the five-membered ring atoms to the plane:

	14	**15**		**14**	**15**
P(1)	−0.014	0.038	P(1)	−0.000	−0.059
O(1)	0.009	−0.034	O(2)	0.000	0.142
N(1)	0.016	−0.015	N(1)	0.000	−0.028
C(2)	−0.012	0.028	C(3)	0.000	0.103
C(1)	−0.492	0.389	C(4)	0.204	−0.158

•Best apical plane P(1)–O(1)–O(2)–N(1)

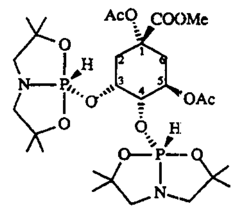
14: $-0.43695x - 3.94186y + 11.84245z = 11.619$
15: $0.8207x - 0.5247y - 0.2263z = 4.3889$

Distances of the two five-membered ring atoms to the plane:

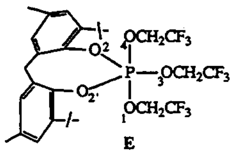
	14	**15**		**14**	**15**
P(1)	0.018	−0.002	C(1)	0.511	0.493
O(1)	0.000	−0.004	C(2)	0.036	0.136
O(2)	0.000	0.003	C(3)	0.020	−0.009
N(1)	0.000	0.014	C(4)	−0.223	−0.382

Distances of the 16-membered ring atoms to the plane:

	14	**15**		**14**	**15**
P(1)	0.012	−0.002	P(1a)	−0.002	−2.198
O(3)	−1.284	1.305	O(3a)	1.294	−3.505
C(5)	−1.641	1.968	C(5a)	1.651	−4.168
C(6)	−2.980	1.245	C(6a)	2.990	−3.445
N(2)	−3.316	1.730	N(2a)	3.326	−3.930
C(8a)	−3.439	−3.206	C(8)	3.449	1.006
C(9a)	−2.140	−3.108	C(9)	2.149	−2.210
O(4a)	−1.330	−3.810	O(4)	1.346	−1.310



D



E

Both angles between the equatorial bonds included in the 16-membered rings (110.1° for **14** and 110.2° for **15**) are smaller than the expected 120°. Surprisingly, they are also smaller than the corresponding angle of the diequatorial eight-membered ring of the pentaoxyphosphorane **E** [21] mentioned previously (O(2)–P–O(2′) = 116.8°). This pinching is compensated by an increase of the two other diequatorial angles: 125.2° and 124.4° for **14** and 124.5° and 125.3° for **15**.

3. Table 8 shows that, as observed in compound **D** [23], the five-membered rings of both compounds adopt an envelop conformation, the C(1) and C(4) carbon atoms being at the ends of the folds which are inversely oriented with respect to the apical plane.
4. Although both molecules are centrosymmetric, the conformations of the 16-membered rings are quite different. This difference, reflected by the torsion angles of Table 7, is very well illustrated by Figure 3, where P(1)–N(1) is taken as the x-axis and P(1)–O(1) as the y-axis. One can observe the zigzag form of the first macrocycle and the stair shape of the second one.
5. The relative positions of the macrocycles and the apical planes P(1)–O(1)–O(2)–N(1) are also quite different. In **14**, this plane contains the symmetry center of the molecule; the homologous atoms of the macrocycle are equidistant from that plane (Table 8). In **15**, the apical plane does not contain the symmetry center; the homologous atoms of the 16-membered ring are not equidistant from that plane. Very likely, this situation explains why the two bicyclophosphorane groups of **15** appear so unwedged.

   In our opinion, all of these differences are caused by the replacement of the N(2) *tert*-butyl substituent by the phenyl group on going from **14** to **15**. In the latter, the N(2) nitrogen atom is sp^2 hybridized (C(6)–N(2)–C(8a) = 116.57°, C(6)–N(2)–C(7) = 121.86°, and C(7)–N(2)–C(8a) = 121.5°). The interaction of its lone pair with the aromatic π electrons forces the C(6)–N(2) and C(8a)–N(2) bonds to lie in the aromatic plane, as confirmed by the following torsion angles: C(18)–C(7)–N(2)–C(8a) = 179.65°; C(18)–C(7)–N(2)–C(6) = 2.77°; C(14)–C(7)–N(2)–C(8a) = 1.41°; and C(14)–C(7)–N(2)–C(6) = −175.48°. Therefore, in **15**, the C(6)–N(2) and C(8a)–N(2) bonds are almost eclipsed (Figure 3); the macrocycle appears as almost a 12-membered ring instead of a 16-membered ring. Comparatively, the P–P lengths are 7.89 Å in **14** and 6.48 Å in **15**.
6. The crystal structure of **14** is stabilized by intramolecular and intermolecular hydrogen bonds involving the apical oxygen atom and a proximate (C)–H atom:

O(2)–H(52) = 2.297 Å; C(5)–H(52)–O(2) = 101.9°

C(4)–O(2)–H(52) = 117.26°

O(1)–H(121) = 2.558 Å; C(12)–H(121)–O(1) = 167.7

P(1)–O(1)–H(121) = 103.94°

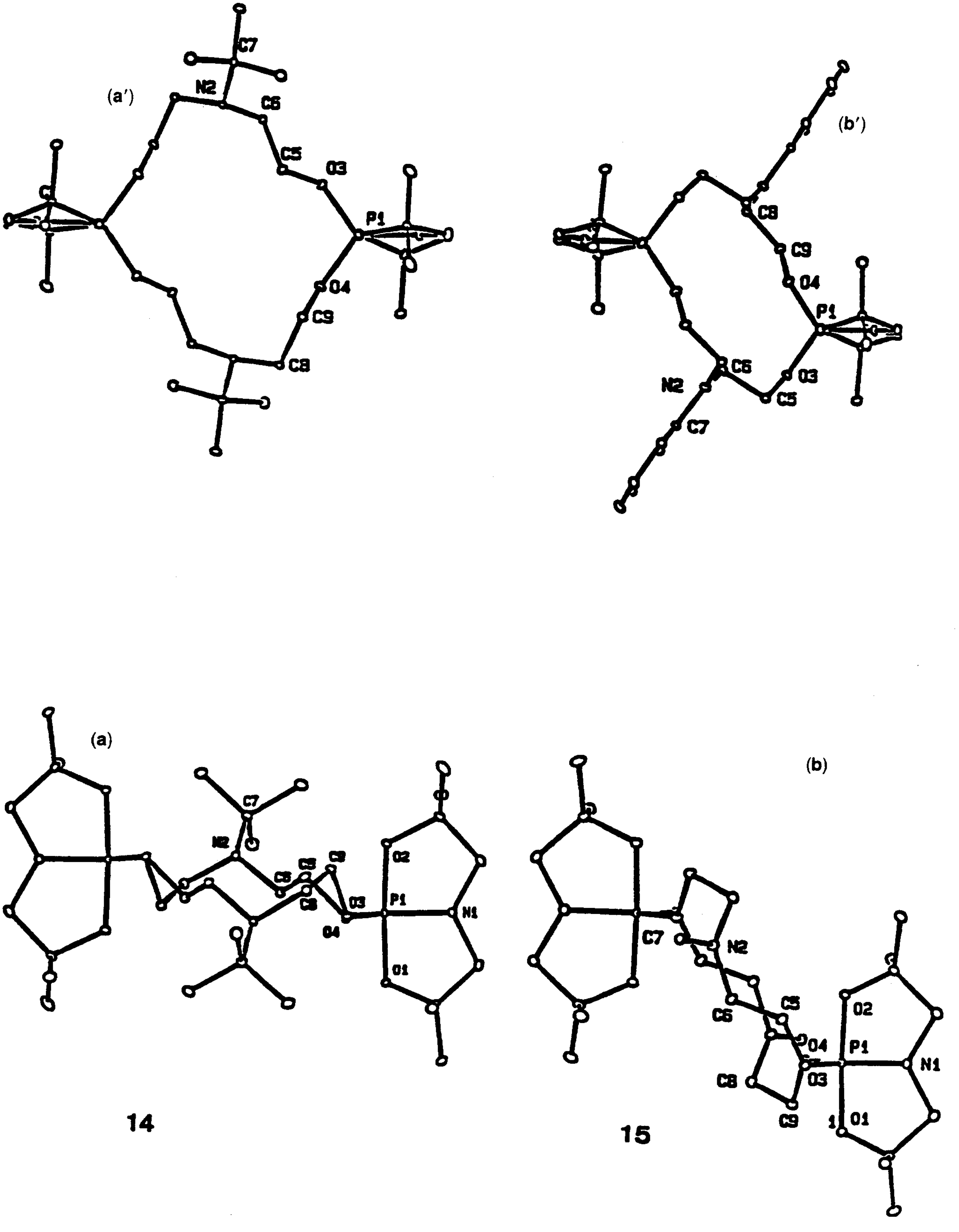


FIGURE 3 Perspective views of (a) **14** and (b) **15**: (a) and (b) after 90° rotation about P(1)–N(1). For clarity, the aromatic rings have been omitted in (b) and represented by C(7).

In compound **15**, there is only the intramolecular hydrogen bond involving the same oxygen atom: O(2)–H(52) = 2.191 Å, C(5)–H(52)–O(2) = 102.3°, and C(4)–O(2)–H(52) = 125.63°.

Such observations have been made previously with two compounds investigated in our laboratory [23,24]. They illustrate the new concept of hydrogen bonding involving hydrogen atoms linked to a carbon atom [25].

CONCLUSIONS

We have prepared the first stable pentacovalent phosphorus-containing macrocycles by an Atherton–Todd reaction between *bis*(hydridobicyclophosphoranes) and binucleophiles. The preliminary results obtained suggest that the symmetric macrocyclizations seem to favor the 1 + 1 condensation, while the nonsymmetric ones seem to favor the 2 + 2 condensation. This observation needs to be confirmed by further experiments. Nevertheless, the formation, in the former, of compounds, containing an odd number of phosphorus atoms **8–11**, **16**, and **18**, as well as the noncyclic derivative **20**, indicates that the synthetic pathway is more complicated than the simple 1 + 1 condensation.

On the other hand, the X-ray crystal study of the *bis*(bicyclophosphorane)-containing macrocycles **14** and **15** confirms the structural features expected for these molecules: (1) the diequatorial placement of the 16-membered ring, which is consistent with the observation that, in some cyclic pentacoordinated phosphorus compounds rings larger than six-membered rings are diequatorially branched [20,21]; and (2) the correlative axial-equatorial-axial annelation of the bicyclophosphorane moiety which is, simultaneously, the only remaining possibility and the most favorable one in the absence of special constraints [26–28].

EXPERIMENTAL

Instrumentation

^1H and ^{13}C NMR spectra were recorded on several Bruker spectrometers: AC 200, AC 250 and WM 250, with TMS as the internal standard; and ^{31}P NMR spectra were recorded on a Bruker AC 80 instrument, with 85% H_3PO_4 as the standard. Calculation of NMR parameters was achieved using proton-proton, carbon-proton, and carbon-phosphore decoupling as well as by 2D H–H correlation (compound **23**). Chemical ionization (CI) mass spectra (NH_3) were obtained with a Nermag R10 10 instrument. X-ray diffraction studies were performed with an automatic ENRAF-NONIUS CAD 4 diffractometer.

Chemicals

Toluene was distilled from Na/benzophenone and stored over 4 Å MS. Acetonitrile was distilled from CaH_2 and stored over 3 Å MS. Triethylamine was distilled and stored over KOH. Ethyl acetate and cyclohexane were distilled and stored over 4 Å MS. Diethyleneglycol and N-butyldiethanolamine were used freshly distilled, while N-*tert*-butyldiethanolamine and N-phenyl-diethanolamine were recrystallized prior to use. All the experiments have been carried out under an argon atmosphere.

Synthesis

Bis(hydridobicyclophosphoranes) **3-7** These compounds have been obtained by the oxidative addition of the binucleophiles **a–e** to the bicyclophosphane **2** previously prepared [29]. The reactions were carried out in toluene at room temperature and monitored by ^{31}P NMR spectroscopy. They were almost instantaneous. Thus, the removal of the solvent afforded colorless oils which have been fully characterized by NMR ^1H and ^{13}C spectra (Tables 1 and 2) and by elemental analyses. These oils were used without further purification

3. *Bicyclophosphane* **2:** 1.141 g (6.04 mmol); diethyleneglycol **a**: 0.320 g (3.02 mmol); toluene: 5 mL. Anal. calcd for $C_{20}H_{42}N_2O_7P_2$: C, 49.57; H, 8.74; N, 5.78. Found: C, 48.4; H, 8.8; N, 5.7.

4. *Bicyclophosphane* **2:** 0.668 g (3.53 mmol); N-butyl-diethanolamine **b**: 0.284 g (1.76 mmol); toluene: 5 mL. Anal. calcd for $C_{24}H_{51}N_3O_6P_2$: C, 53.41; H, 9.52; N, 7.78. Found: C, 53.2; H, 9.7; N, 8.1.

5. *Bicyclophosphane* **2:** 1.335 g (7.06 mmol); N-*tert*-butyldiethanolamine **c**: 0.569 g (3.53 mmol); toluene: 5 mL. Anal. calcd for $C_{24}H_{51}N_3O_6P_2$: C, 53.41; H, 9.52; N, 7.78. Found: C, 53.4; H, 9.7; N, 7.6.

6. *Bicyclophosphane* **2:** 1.165 g (6.16 mmol); N-phenyl-diethanolamine **d**: 0.558 g (3.08 mmol); toluene: 5 mL. Anal. calcd for $C_{26}H_{47}N_3O_6P_2$: C, 55.79; H, 8.46; N, 7.51. Found: C, 55.2; H, 8.4; N, 7.8.

7. *Bicyclophosphane* **2:** 0.890 g (4.7 mmol); 1.2-O-isopropylidene-D-xylofuranose **e**: 0.448 g (2.35 mmol); toluene: 5 mL. Anal. calcd for $C_{24}H_{46}N_{23}O_9P_{23}$; C, 50.69; H, 8.15; N, 4.93. Found: C, 52.1; H, 8.2; N, 5.0.

Macrocyclizations—General Procedure

All the macrocyclizations, monitored by ^{31}P NMR spectroscopy have been carried out in acetonitrile as the solvent, with use of a 100% excess of triethylamine. The reaction mixtures were stirred at 40°C during 2–3 days. The amounts of triethylammonium chlorhydrate precipitated by addition of dry diethyl ether corresponded to those expected. The evaporation of the solvent afforded red-brown oils which have been purified mainly by liquid chromatography [1.2 × 20 cm silica gel (60 Acc, 70–230 mesh) column].

3 + **a** *Condensation*

Bis(hydridobicyclophosphorane) **3**. 1.141 g (3.02 mmol); CCl_4: 0.93 g (6.04 mmol); Et_3N: 1.22 g (12.1 mmol), diethyleneglycol **a**: 0.32 g (3.02 mmol); CH_3CN: 40 mL. The ^{31}P NMR spectrum of the final reaction mixture was described previously. All the attempts to precipitate the components have failed. The chromatographic separation was carried out with ethyl acetate as an eluent. It afforded, with poor yield [30], the compounds **8**, **12**, **16** and **20** which have been characterized by NMR and mass spectroscopy.

Tricyclic Monophosphorane **8**. White solid (neat) 0.007 g (10%), δ^{31} P (C_6D_6) = −42.9. ^1H and ^{13}C NMR spectra (Table 3). Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 294 (100, (M^+ + 1)).

Bis(bicyclophosphorane)-containing Macrocycle **12**. White solid nonrecrystallized, 0.020 g (5%) $\delta^{31}P$ (C_6D_6) = −44.6. ^1H and ^{13}C spectra (Table 4). Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 587 (95, (M^+_{12} + 1)), 294 (100, ($M^+/2$ + 1)).

Tris(bicyclophosphorane)-Containing Macrocycle **16**. White solid, traces. $\delta^{31}P$ (C_6D_6) = −45.1. ^1H NMR (250.13 MHz, C_6D_6) δ = 1.25 (s, 36H, CH_3), 2.47 (d, 12H, $^3J_{HP}$ = 12.8 Hz, N–CH_2), 3.75 (td, 12 H, $^3J_{HH}$ = 5.2 Hz, $^4J_{HP}$ = 1.5 Hz, OCH_2), 4.21 (td, 12 H, $^3J_{HP}$ = 8.0 Hz, P–O CH_2). ^{13}C NMR (62.89 MHz, C_6D_6) δ = 28.9 (d, $^3J_{CP}$ = 2.8 Hz, CH_3), 55.2 (d, J_{CP} = 1/2 ($^2J_{C\text{-}N\text{-}P}$ + $^3J_{C\text{-}C\text{-}O\text{-}P}$) = 20.6 Hz, NCH_2), 67.3 (d, $^2J_{CP}$ = 8.9 Hz, P–O CH_2), 69.5 (s, O–C(Me)$_2$), 71.5 (d, $^3J_{CP}$ = 9.6 Hz, OCH_2). Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 880 (11.6, (M^+ + 1)), 587 (34, ($2M^+/3$ + 1)), 294 (100, ($M^+/3$ + 1)).

Noncyclic Bis(bicyclophosphorane) **20**. A white solid, traces $\delta^{31}P$ = −45.1. ^1H NMR (250.13 MHz, C_6D_6) δ = 1.24 (s, 24 H, CH_3), 2.44 (d, 8 H, $^3J_{HP}$ = 13 Hz, NCH_2), 3.4 (m, 8H, CH_2 (21) + CH_2 (22) and their homologues) (see drawing in the text), 3.66 (m, 8H, CH_2 (15) + CH_2 (17) and their homologues), 4.14 (m, 8H, CH_2 (14) + CH_2 (18) and their homologues). ^{13}C NMR (62.89 MHz, C_6D_6) δ = 28.7 (d, $^3J_{CP}$ = 3.8 Hz, CH_3), 55.1 (d, 1/2 ($^2J_{C\text{-}N\text{-}P}$ + $^3J_{C\text{-}C\text{-}O\text{-}P}$) = 20.4 Hz, N–$CH_2$), 61.9 (s, C(21)), 67.4 (d, $^2J_{CP}$ = 9.7 Hz, C(14) + C(18)), 69.8 (s, C(3) + C(7)), 70.9 (d, $^3J_{CP}$ = 9.6 Hz, C(15) + C(17)), 72.8 (s, C(22)).

(4 + **b**) *Condensation*

Bis(hydridobicyclophosphorane) **4**. 0.954 g (1.76 mmol); CCl_4: 0.54 g (3.52 mmol); Et_3N: 0.712 g (7.04 mmol); N-butyl diethanolamine **b**: 0.284 g (1.76 mmol); CH_3CN: 40 mL. ^{31}P NMR spectrum (CH_3CN) of the reaction mixture: δ = −42.9 (29%); −45.0 (17%); −45.6 (16%); −45.7 (26%); and −46.0 (12%). Under the same experimental conditions as described earlier, the liquid chromatography separated only compounds **9** and **13**.

Tricyclic Monophosphorane **9**. White solid, 0.090 g (25%) recrystallized from toluene $\delta^{31}P$ (C_6D_6) = −42.6 ^1H and ^{13}C NMR (Table 3). Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 349 (100, (M^+ + 1)). Anal. calcd for $C_{13}H_{33}N_2O_4P$: C, 55.15; H, 9.54; N, 8.04. Found: C, 54.7; H, 9.5; N, 8.1.

Bis(bicyclophosphorane)-containing Macrocycle **13**. White solid, 0.200 g (95%), recrystallized from toluene $\delta^{31}P$ (C_6D_6) = −44.6 ^1H and ^{13}C NMR spectra (Table 4). Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 697 (100, (M^+ + 1)), 349 (9.2 ($M^+/2$ + 1)).

(5 + **c**) *Condensation*

Bis(hydridobicyclophosphorane) **5**. 1.904 g (3.53 mmol); CCl_4: 1.086 g (7.06 mmol); Et_3N: 1.43 g (14.1 mmol); N-*tert*-butyldiethanolamine **e**: 0.569 g (3.53 mmol); CH_3CN: 60 mL. ^{31}P NMR spectrum (CH_3CN) of the reaction mixture: δ = −42.1 (10%); −44.9 (40%); −45.4 (17%); −45.6 (33%). A spontaneous precipitation is observed during the concentration of the reaction mixture, and it is completed by addition of a mixture of 1/1 toluene/diethyl ether. This fraction was identified as the *bis*(bicyclophosphorane)-containing macrocycle **14**, while the chromatographic purification of the remaining material afforded compounds **10** and **18**.

Tricyclic Monophosphorane **10**. White solid, nonrecrystallized, 50 mg (20%) $\delta^{31}P$ (C_6D_6) = −42.1 ^1H and ^{13}C NMR spectra (Table 3). Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 349 (100, (M^+ + 1)).

Bis(bicyclophosphorane)-Containing Macrocycle **14**. Thin transparent plates, 0.570 g (57%) $\delta^{31}P$ (C_6D_6) = −44.9 ^1H and ^{13}C NMR spectra (Table 4). Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 697 (100, (M^+ + 1)), 349 (8.1, ($M^+/2$ + 1)). Anal. calcd for $C_{32}H_{66}N_4O_8P_2$: C, 55.15; H, 9.54; N, 8.04. Found: C, 55.4; H, 9.6; N, 7.7. Suitable crystals for X-ray study have been obtained by slow recrystallization in toluene.

Tris(bicyclophosphorane)-Containing Macrocycle **18**. White solid, traces. $\delta^{31}P$ (C_6D_6) = −45.6 ^1H

NMR (250.13 MHz, C_6D_6) δ = 1.14 (s, 27H $(CH_3)_3$–C); 1.34 (s, 36H, CH_3), 2.55 (d, 12 H, $^3J_{HP}$ = 12.9 Hz, N–CH_2), 3.05 (t, 12 H, $^3J_{HH}$ = 7.6 Hz, CH_2–N–*t*Bu), 4.23 (td, 12 H, $^3J_{HP}$ = 8.8 Hz, CH_2–O–P) ^{13}C NMR (62.89 MHz, C_6D_6) δ = 27.6 (s, $(CH_3)_3$ C), 29.1 (d, $^3J_{CP}$ = 4.0 Hz, CH_3), 52.6 (d, $^3J_{CP}$ = 8.5 Hz CH_2–N–*t*Bu), 54.8 (s, $C(CH_3)_3$), 55.5 (d, J_{CP} = 1/2 ($^2J_{C\text{-}N\text{-}P}$ + $^3J_{C\text{-}C\text{-}O\text{-}P}$) = 20.4 Hz, CH_2–N), 68.5 (d, $^2J_{CP}$ = 10.2 Hz, CH_2–O–P), 69.4 (s, O $C(Me)_2$).

(**6** + **d**) *Condensation*

Bis(hydridobicyclophosphorane) **6**: 1.723 g (3.08 mmol); CCl_4: 0.948 g (6.16 mmol); Et_3N: 1.247 g (12.32 mmol) N-phenyldiethanolamine **d**: 0.558 g (3.08 mmol); CH_3CN: 50 mL.

^{31}P NMR spectrum (CH_3CN) of the reaction mixture: δ = −44.4 (38%), −44.6 (26%); −45.0 (31%), −46.7 (5%).

A similar behavior to that described here was observed: the *bis*(bicyclophosphorane)-containing macrocycle **15** precipitated spontaneously from the reaction mixture. The chromatographic purification of the residue afforded two fractions. The NMR spectra of the first one revealed that it was a 40/60 mixture of **15** and noncyclic compounds ($\delta^{31}P$ = −45.0) similar to **20**. These two components have not been separated. The NMR analysis (Table 3) and mass spectroscopy of the second fraction showed that it was a 10/90 mixture of **15** and the tricyclic monophosphorane **11**. Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 737 (0.7, $(M^+_{15} + 1)$), 369 (100, $(M^+_{11} + 1)$).

Bis(bicyclophosphorane)-Containing Macrocycle **15**. Thin transparent plates, 0.500 g (57%) $\delta^{31}P$ (C_6D_6) = −44.4 ^1H and ^{13}C NMR spectral data (Table 4). Mass spectrum (C.I. NH_3), m^+/z (relative abundance, assignment) 737 (100, (M^+ + 1)), 349 (54, ($M^+/2$ + 1)). Anal. calcd for $C_{36}H_{58}N_4O_8P_2$; C, 58.68; H, 7.93; N, 7.6.[1] Found: C, 58.5; H, 8.2; N, 7.3. A slow recrystallization from toluene gave suitable crystals for X-ray study.

(**7** + **a**) *Condensation*

Bis(hydridobicyclophosphorane) **7**. 1.146 g (2.02 mmol); CCl_4: 0.620 g (4.04 mmol); Et_3N: 0.816 g (8.08 mmol); diethyleneglycol **a**: 0.214 g (2.02 mmol); CH_3CN: $\delta^{31}P$ = −42.2 (4.6%), −43.0 (21.7%), −45.0 (4%), −45.2 (7.9%), −45.5 (15.8%), −46.4 (19.2%), −47.1 (5.1%), and −47.7 (21.7%) (Figure 1a). This multiplicity is due to the presence of two different phosphorus atoms.

The chromatographic purification was slightly different from the others previously described. In a first step, the use of 1/1 ethyl acetate/cyclohexane as an eluent afforded only one fraction whose ^{31}P NMR spectrum contained two equal singlets at δ = −42.9 and −47.7, which represented 92% of the total intensity, and three minor peaks at −42.2, −45.0, and −47.1 (Figure 1b). Elution with pure ethyl acetate gave a second fraction, much less abundant than the first one, whose ^{31}P NMR spectrum contained two pairs of singlets at δ = −45.5 and −46.4 (67%) and −45.1 and −45.9 (33%) (Figure 1d). The presence in this fraction of the noncyclic compound **24** and the 14-membered ring macrocycle **25** is exemplified in the Discussion section.

TABLE 9 Summary of the Crystal Structure Data for **14** and **15**

	14	**15**
Formula	$C_{32}H_{66}N_4O_8P_2$	$C_{36}H_{58}N_4O_8P_22C_7H_8$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	7.892(8)	10.151(6)
b, Å	11.639(9)	12.031(7)
c, Å	12.008(9)	10.718(8)
α, deg	115.7(1)	98.13(9)
β, deg	99.5(1)	90.93(9)
γ, deg	96.3(2)	85.48(9)
V, Å^3	959()	1291()
Z	1	1
F(000)	380	496
d calcd, g/cm^3	1.206	1.18
Temperature, K	300	300
Radiation	graphite monochromator Cu$K\bar{\alpha}$ γ = 1.54051	graphite monochromator Mo$K\bar{\alpha}$ γ = 0.71069
μ, cm^{-1}	14.28	1.32
Scan type	$\theta/2\theta$	$\theta/2\theta$
Scan width, deg	(0.9 + 0.147 $tg\theta$)	(0.8 + 0.35 $tg\theta$)
Intensities (unique, Ri)	3120	4516
Intensities	$>\sigma(I)$ 2968	$>3\sigma(I)$ 4369
No. of parameters	209	255
R	0.05667	0.0814
R_w	0.057	0.084

A second chromatographic separation of the first fraction has been performed using 1/4 ethyl acetate/cyclohexane as an eluent. It afforded another fraction whose ^{31}P NMR spectrum contained the pair of singlets (>95%) and the minor peak at δ = −42.3 depicted previously (Figure 1c). After evaporation of the solvent, nearly pure **23** (0.500 g, 80%), admixed with traces of **8**, was obtained.

X-ray Crystallographic Studies of **14** *and* **15**

For both compounds, single crystals were obtained by slow recrystallization from toluene solution. The crystals were air sensitive. They were mounted in 0.3 mm Lindeman tubes.

Crystal data collection parameters are listed in Table 9 (Atomic coordinates and structural parameters have been submitted as supplementary material and are deposited in the Cambridge Crystallographic Database.). Lattice parameters were determined from 25 high-angle reflections. Intensities of three standard reflections were measured every 1 hour of X-ray exposure and showed no significant variation. An empirical absorption correction was also applied with minimum and maximum transmission factors of 1.07 and 1.18 for **14** and 1.02 and 1.04 for **15**. Intensity data were corrected for Lorentz and polarization effects.

The structures were solved using direct methods (SHELX programme) [31] and refined by full matrix least-squares refinement (CRYSTALS) [32] with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms attached to carbon atoms were given "idealized" positions and treated as fixed contributions with an isotropic thermal parameter of 1.1 equivalent of the isotropic thermal parameter of the attached carbon. A final difference Fourier synthesis map showed several peaks less than 0.8 e/Å^3 scattered about the unit cell without a significant feature. The discrepancy indices $R = \Sigma||F_0|| - |F_0|/\Sigma|F_0|$ and $R_w = [\Sigma_w(|F_0| - k|F_0|)^2/[\Sigma_w(|F_0|^2]^{1/2}$ were presented previously. All crystallographic computing was done on an ALLIANT VF × 80 computer. The representations of both molecules were carried out using the ORTEP programme [33].

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