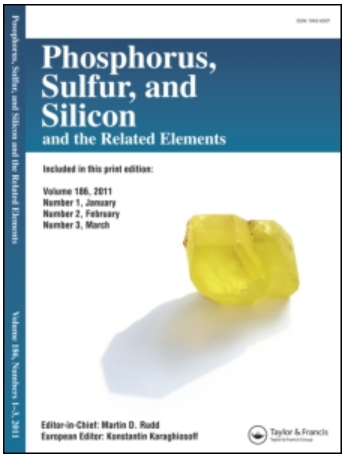


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# SINGLY, DOUBLY AND TRIPLY BRIDGED POLYAZAHETEROPHANES DERIVED FROM HEXACHLOROCYCLOTRIPHOSPHAZENE, $N_3P_3Cl_6$

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# SINGLY, DOUBLY AND TRIPLY BRIDGED POLYAZAHETEROPHANES DERIVED FROM HEXACHLOROCYCLOTRIPHOSPHAZENE, $N_3P_3Cl_6$

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Singly, doubly and triply bridged polyazaheterophanes (**1**, **2**, **3**) have been synthesized from hexachlorocyclotriphosphazene, $N_3P_3Cl_6$. $^{31}P$ NMR spectra indicate that the molecules **2** exist in a single conformation when there are three differently populated conformations A, B and C, in molecules **3** at ambient temperature, A and (B + C) being separated by a high interconversion barrier (about 22 Kcal $mole^{-1}$) whereas the barrier between B and C is much lower (about 4 Kcal $mol^{-1}$).



## INTRODUCTION

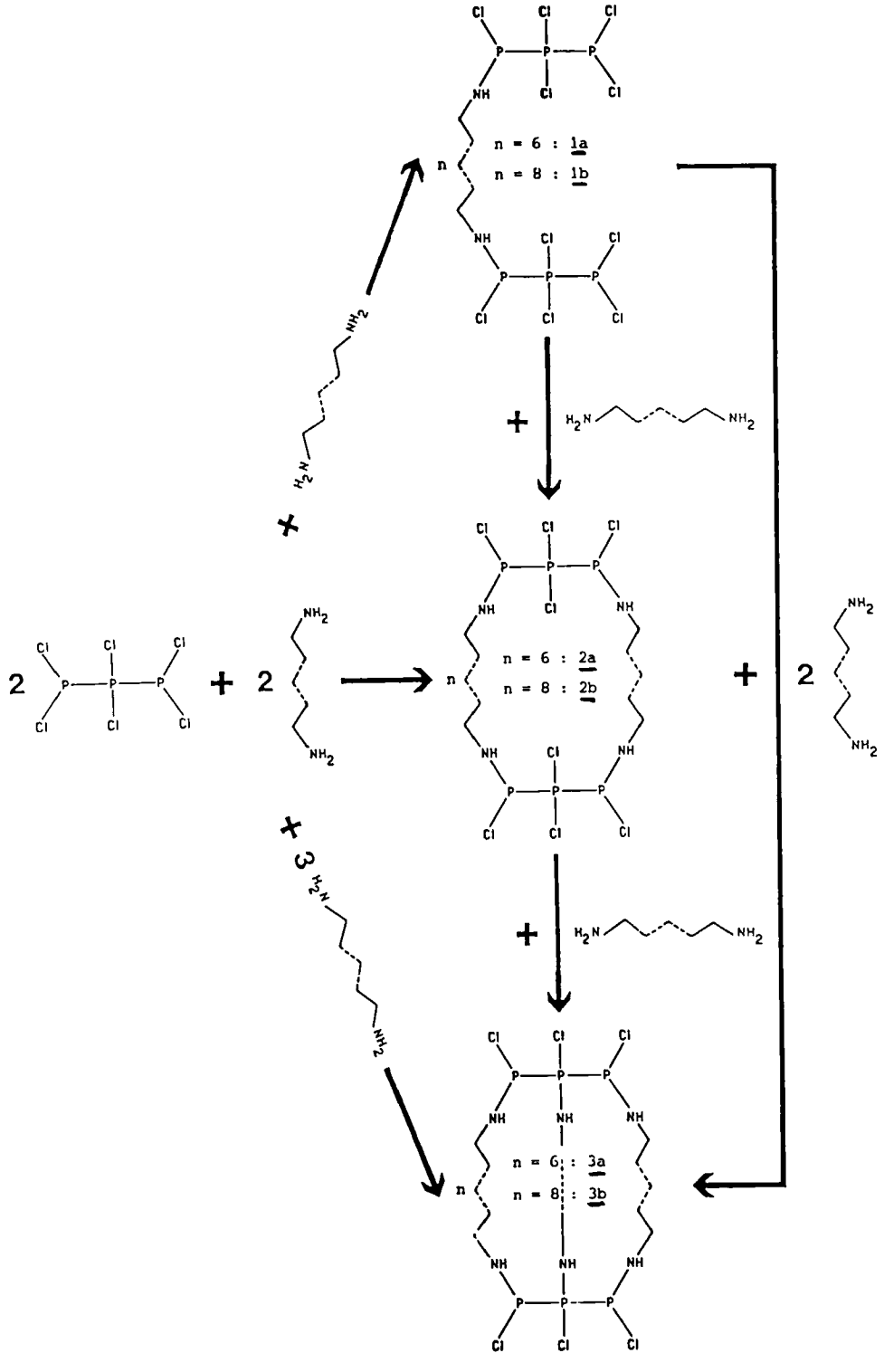
An exciting and rapidly growing development in the chemistry of host molecules capable of molecular recognition has occurred in the last few years: coronands, cryptands, podands,[1] cylindranes,[2–5] spherands[2] and, very recently, doubly and triply bridged polyoxapolyazaheterophanes derived from 2,4,6-trichloro-s-triazine (triazinophanes)[6] have been designed and synthesized. Numerous factors influence the selectivity of these compounds in binding host molecules or cations, among them are the cavity size, the conformational freedom, the lipophilicity, and the nature and the number of coordination sites.

In the present paper we describe the synthesis of dicyclotriphosphazenes (**1**, **2**, **3**) singly, doubly and triply bridged with diamino alkyl chains by using hexachlorocyclotriphosphazene (**4**) as the building block. Hexachlorocyclotriphosphazene shows indeed the feature of a stepwise replacement of the six halogens by nucleophiles, leading to well-defined architectures depending on the nature of the nucleophile.[7] We reported recently on the synthesis of singly bridged derivatives (code name: BINO*n* (**1**)) by the reaction of polyamines, $H_2N\text{-}(CH_2)_n\text{-}NH_2$ ($n = 6$ to 10)[8] with $N_3P_3Cl_6$ in suitable stoichiometric conditions and we could expect to synthesize macropolycyclic molecules by the stepwise connection of two cyclotriphosphazene rings with two or three diamino alkyl bridging chains.

## SYNTHESIS

The diamines used to bridge **4** leading to compounds **1**, **2** and **3** are 1,6-diaminohexane (DIAM6) and 1,8-diaminooctane (DIAM8).

Attack of the first chain on the cyclotriphosphazene rings was conducted at 0–5°C in anhydrous diethylether or acetonitrile as the solvent in the presence of



an amount of triethylamine just sufficient to pick up hydrogen chloride. Reactions were achieved after two days. The crude final products were submitted to $SiO_2$ column chromatography using $CCl_4CH_2Cl_2$ (3:7) as eluent to remove triethylammonium chloride and unreacted $N_3P_3Cl_6$ starting material. The yield of this column chromatographic method is good, i.e. about 85% (single flow): as an example, 8.2 g of crude final product for $n = 6$ leads to 2.1 g of $N_3P_3Cl_6$ and to 4.9 g of the expected BINO6 chemical (compound **1a**). However, 2 or 3 successive turns are needed for getting the final BINO6 (**1a**) and BINO8 (**1b**) derivatives in a state perfectly free from hydrochloride. Three successive turns have to be expressly performed if the samples of **1a** and **1b** are not used in sequence for further syntheses of compounds **2** and **3**: traces of hydrochloride induce indeed polymerization in time, i.e. after two or three weeks, even when samples are stored at low temperature. Such a polymerization proceeds through a proton-abstraction process from NH groups[9,10] which leads to cyclo-linear and/or cyclo-matrix polymers which are no more soluble in organic solvents. It must be emphasized that the formation of such non-crystalline white resins happens even in the bulk, that is in the solid state. The yield of pure **1a** and **1b** after 3 successive chromatographic runs is actually poor, about 40% maximum.

The second chain was inserted employing high dilution conditions in diethyl ether at 0°C, an appropriate excess of diamine was used to pick up hydrogen chloride. The third chain was inserted under high dilution conditions in acetonitrile at 0°C, again with a suitable excess of diamine (scheme). Yields of crude final products **2** and **3** are fair to good in the two latter steps but, again 2 to 3 successive chromatographic runs are required for obtaining samples free from hydrochloride which reduces the yields to about 40–50% maximum.



## NMR SPECTRA

Due to the complexity of the molecules investigated, $^{31}$PNMR spectroscopy is best suited to ascertain their structural and conformational properties. Compounds analogous to those reported here have been shown to exist at least in two conformations, with barriers high enough to be detectable by variable temperature NMR[6,11–15].

The room temperature $^{31}$P NMR spectra (36.43 MHz) of **1a** and **1b** in $CD_2Cl_2$ are complex multiplets circa. 20.89 ppm (Figure 1$\alpha$). Such multiplets give almost first-order $A_2B$ spectra when recorded at 101.27 MHz (Figure 1$\beta$) and pure $A_2B$ spectra at 162.08 MHz (Figure 1$\gamma$). The room temperature $^{13}$C (62.90 MHz) and the $^1$H (250 MHz) spectra of **1a** and **1b** (Figure 2) display the expected number of sharp lines for "chemically equivalent" carbons and hydrogens. No conformational pattern (splitting or broadening of lines) is then ever observed at room temperature. In other words, BINO6 and BINO8 are locked in a unique conformation at ambient temperature.

The room temperature $^{31}$P NMR spectrum (36.43 MHz) of doubly bridged derivatives, **2a** and **2b**, are "singlets" at 21.78 and 21.80 ppm respectively in $CDCl_3$ with $H_3PO_4$ 85% as a standard. Such false singlets prove that $\delta(PCl_2)$ and $\delta$(PClNH) chemical shifts in such doubly bridged derivatives are quite close

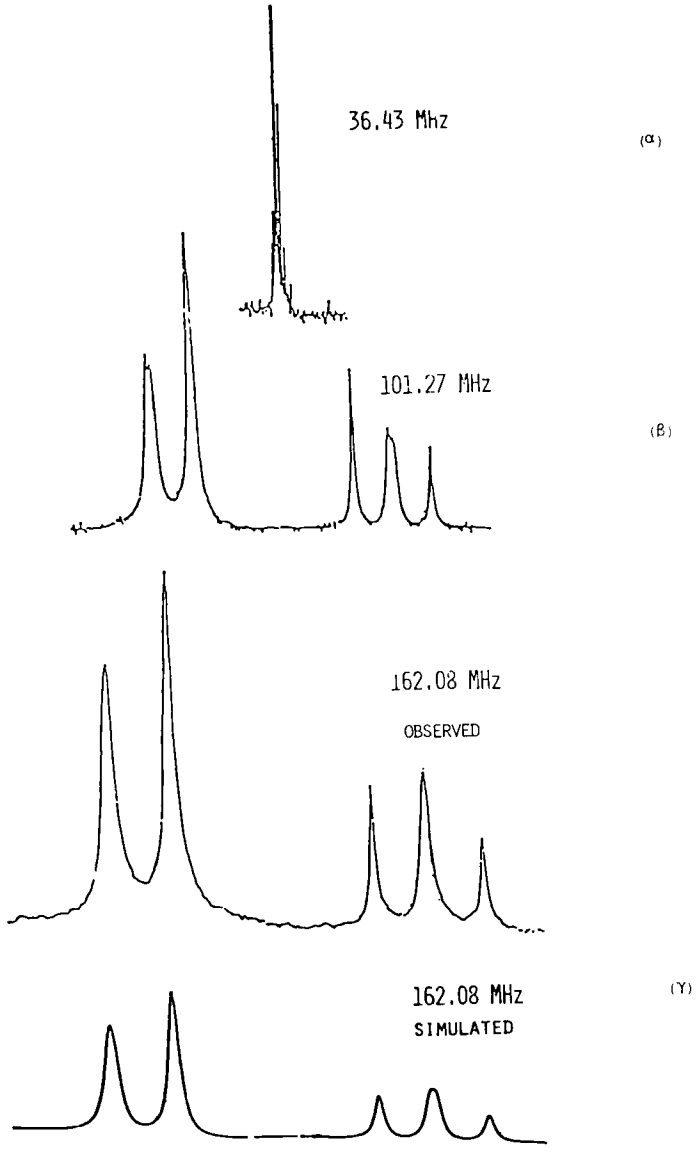



FIGURE 1 $^{31}P$ NMR spectra of **1a** and **1b** at 36.43 MHz ($\alpha$), at 101.27 MHz ($\beta$) and at 162.08 MHz ($\gamma$).

together, closer yet than they are in singly bridged moieties. They are actually so close that the false singlets at 36.43 MHz cannot be resolved as previously when spectra are recorded at 101.27 MHz: Figure 3 shows the spectrum for **2a** in such conditions. Even very high-field $^{31}P$ NMR (202.458 MHz) does not reveal the expected $A_2B$ patterns (spectra not shown) for **2a** and **2b**. Anyhow, we may conclude that, when passing from singly to doubly bridged derivatives, $\delta(PCl_2)$ and $\delta$(PClNH) are at once becoming closer together and high-field shifted as a whole from 20.89 to 21.78 ppm.

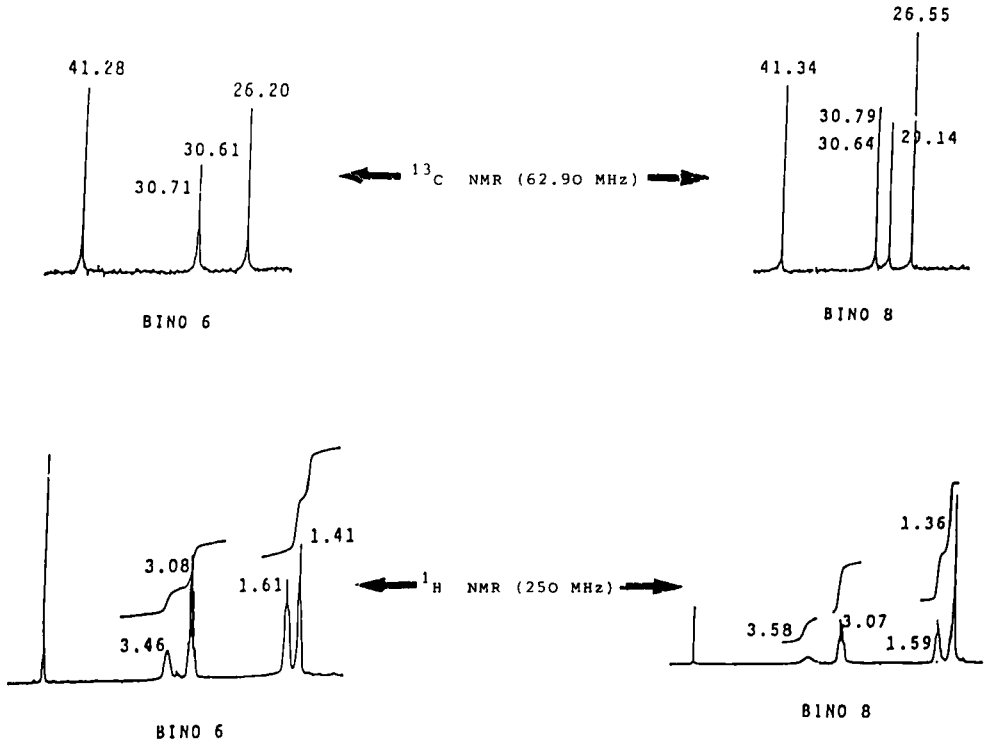



FIGURE 2 $^{13}C$ (62.90 MHz) and $^{1}H$ (250 MHz) NMR spectra of **1a** and **1b**.

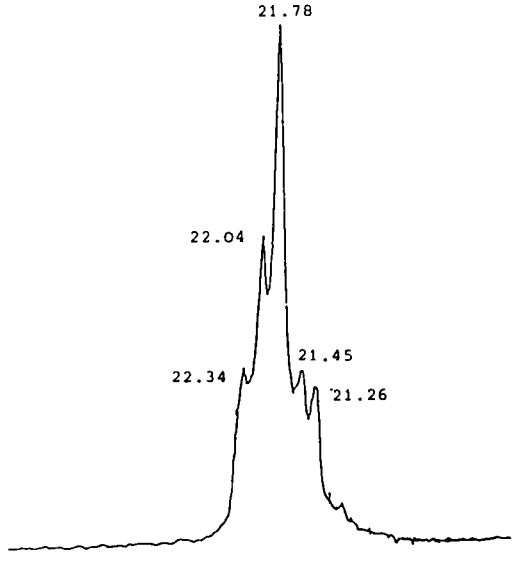



FIGURE 3 $^{31}P$ NMR spectrum of **2a** at 101.27 MHz.

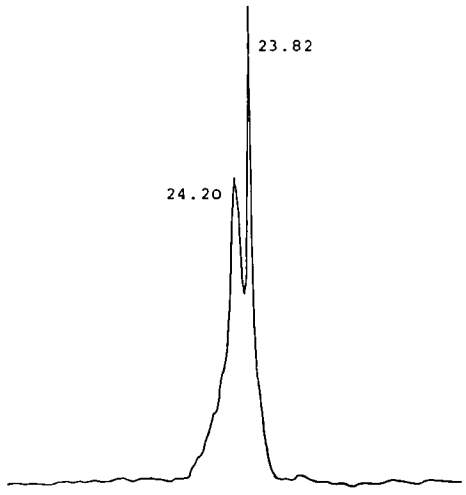



FIGURE 4 $^{31}$P NMR spectra of **3a** and **3b** at 101.27 MHz.



The room temperature $^{31}$P NMR spectrum (36.43 MHz and 101.27 MHz) of the triply bridged derivatives, **3a** and **3b**, in $CDCl_3$ reveal (Figure 4) two singlets, a sharp one at 23.82 ppm and a broader one at 24.20 ppm (relative intensity 1:1). These spectra suggest that the two molecules are locked at ambient temperature in at least two conformers of different stability, as described in ref[6] and.[11,12] In these conformers, the chains connecting the two rings are "frozen" (on the NMR time scale) in a definite spatial arrangement: as a consequence they can, in principle, give rise to a line for each of their phosphorus atoms, thus accounting for the two observed signals.

On warming **3a** to +150°C in N,N-dimethylacetamide, coalescence occurs (Figure 5), the single averaged signal being located at 23.82 MHz. A very rough estimate of the barrier required for this interconversion indicates a $\Delta G^{\#}$ value of about 22 Kcal. mol$^{-1}$. Most surprising is the irreversible character of this interconversion, the spectrum at 150°C (single at 23.82 ppm) remaining unchanged when the sample is recorded again at room temperature. In other words, the conformation(s) corresponding to the 24.20 ppm singlet are evoluting towards the one corresponding to the 23.82 ppm singlet when the temperature increases.

On cooling **3a** to −78°C in THF, the "24.2" ppm broad signal is split in at least two signals, when the "23.8" ppm singlet remains sharp and unaffected (Figure 6). This splitting is clearly revealed at −30°C, a rough estimation of the barrier required for interconversion being here about 4 Kcal. mole$^{1}$. This interconversion is reversible.

In other words, the VTP $^{31}$P NMR between −78°C to +150°C shows that the triply bridged compound **3a** does exist as a mixture of 3 conformers which could be the "eclipsed" D3h one and the two "folded" ones ($C_3^1$ and $C_3^{-1}$ symmetries operating on the D3h structure) (Figure 7).

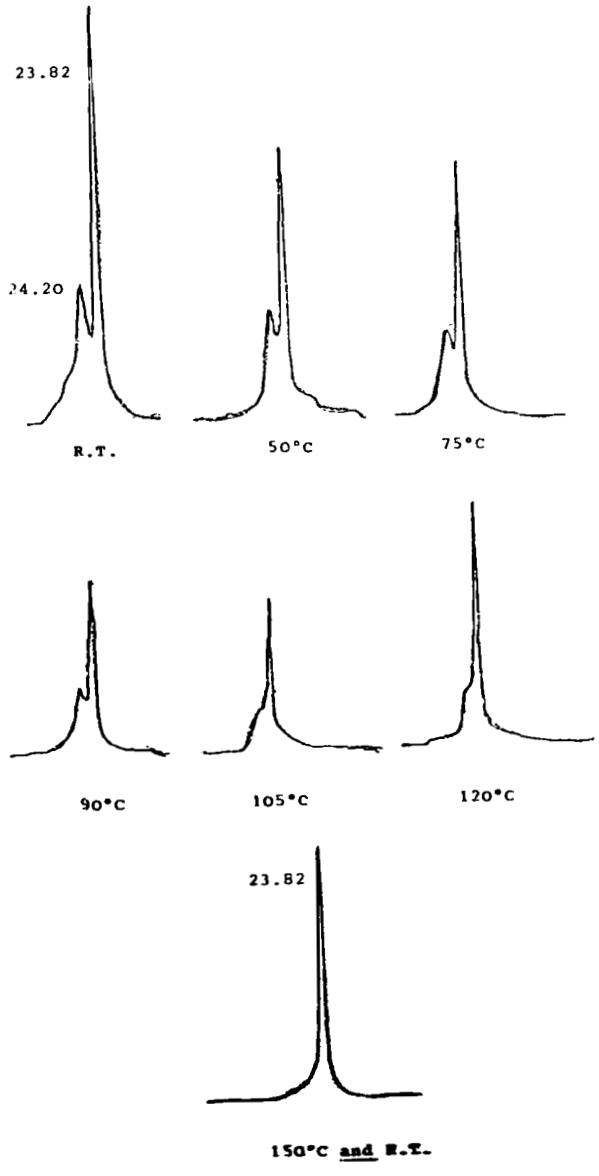



FIGURE 5 VTP $^{31}P$ NMR spectrum of **3a** (ambient to +150°C) in N,N-dimethyl-acetamide (36.43 MHz).

Incidentally, the "23.8" ppm conformation is less soluble in acetone than the "24.2" ppm ones. Washing of **3a** with acetone leads then to a white insoluble powder which is identified as the pure conformer at 23.8 ppm (sharp singlet, even at 121.496 and at 202.458 MHz) when the solution contains essentially the conformers giving the peak at 24.2 ppm. The former conformation will be coded below as **3aA**, the latter being labelled as **3aB**,**3aC**.

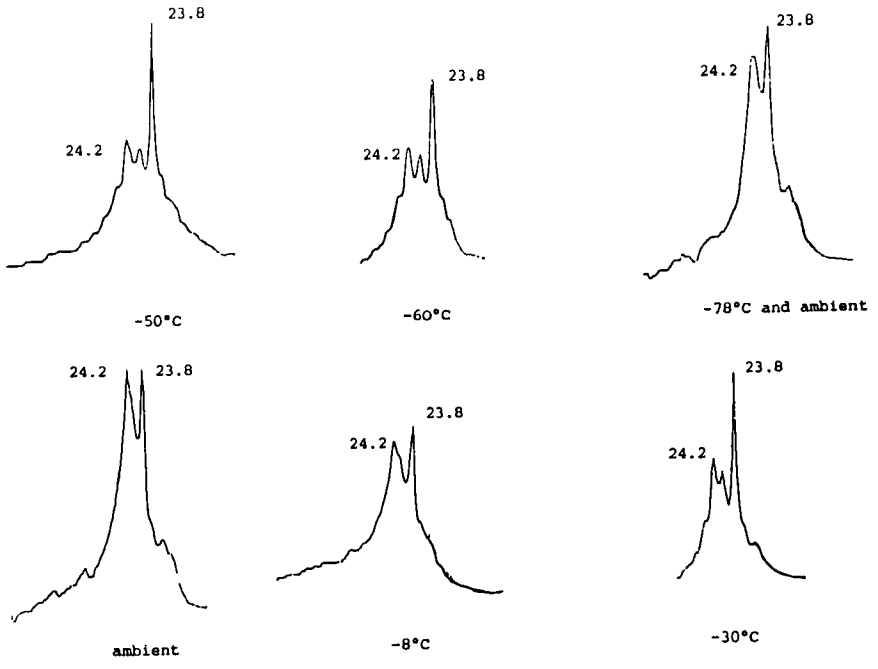



FIGURE 6 VTP $^{31}P$ NMR spectrum of **3a** (ambient to −78°C) in THF (36.43 MHz).

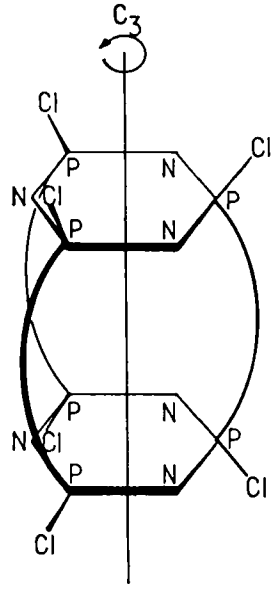



FIGURE 7 Disrotation around the $C_3$ vertical axis of **3a** and **3b** leading to folded conformations.

## MASS SPECTROMETRY

### *Compound* **3aA**

The spectrum was recorded (Figure 8) on a R1010 Ribermag Quadrupole Mass spectrometer using a direct inlet system. The source temperature was 150°C, electron energy 70 eV. The direct E.I. technique did not reveal the molecular ion $M^+$ when the electron multiplier and the amplifier were working in normal conditions, i.e. in non-saturated conditions. Thus, we used a compromise of E.I. (electron impact) and D.C.I. (direct chemical ionization) techniques, a very small amount of $NH_3$ being used during the E.I. process. In such conditions, it became possible both (i) to reveal the molecular ion $M^+$ and (ii) to analyze its fragmentation pathways.

The spectrum was analyzed by means of a DEC PDP 8/M computer and stored on disk. A small sample (~1 μg) was introduced into the probe and ammonia was added at a pressure of 0.5 torr. The areas under the curves corresponding to the current carried by the various ions were calculated by computer.

The molecular ion was observed at $m/z$ 825. The molecular weight of **3a** being 822.48, the maximum at 825 corresponds to the $MH^+$ peak of the M + 2 satellite of the real $M^+$, according to the fact that such a satellite has to be the major component of the $^{35}Cl/^{37}Cl$ isotopic distribution for a molecule containing 6 chlorine atoms.

The main fragmentation route proceeds through the loss of $N_3P_3$ $Cl_3$ as a whole, leading to the fragment $M_1NH_4^+$ $m/z$ 603 (100%) in which 3 [HN-$(CH_2)_6$-NH] pendants stay linked to the other $N_3P_3Cl_3$ moiety. The successive loss from $M_1NH_4^+$ of NH and $CH_2$ groups occurs step by step giving maximal peaks at $m/z$ 588 (58.0%), 574 (11.2%), 560 (4.5%), 546 (3.5%), 532 (12.3%), 518 (6.9%), 504 (3.7%), 490 (49.8%), 476 (33.3%), 462 (6.7%), 448 (2.5%), 434

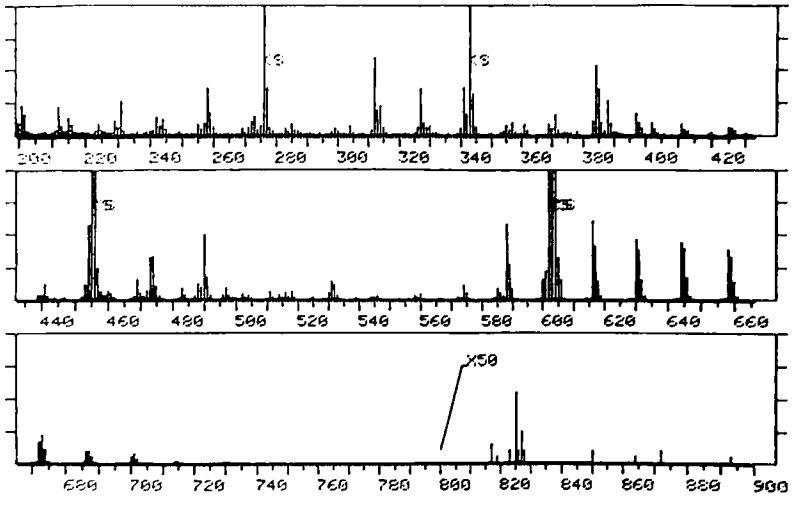



FIGURE 8 DCI-EI (70 eV) mass spectrum of conformer **A** of **3a** (**3aA**).

(1.4%), 420 (2.9%), 406 (2.5%), 392 (3.0%), 378 (3.3%), 364 (3.9%), 350 (1.8%), 336 (1.7%), 322 (2.1%), 308 (1.7%), 294 (2.4%), 280 (6.2%) and 266 (1.7%). Every peak of the series is accompanied by a second peak located 35 mass units lower which corresponds to the loss of one Cl atom from fragments of $M_1NH_4^+$. Actually, the base peak within both series are $m/z$ 455 and $m/z$ 343 respectively, which correspond to $[M_1NH_4^+ - (1\text{ pendant}) - 1Cl]$ and $[M_1NH_4^+ - (2\text{ pendants})]$ fragments.

A second fragmentation route occurs through the loss as a whole of one pendant [HN-$(CH_2)_6$-NH] from the $MH^+$ molecular peak, giving the $M_2NH_4^+$ peak at $m/z$ 730 (1.6%). The $M_2$ fragment contains two $N_3P_3Cl_3H$ moieties bridged by two [HN-$(CH_2)_6$-NH] entities. The loss of the second pendant (or bridge) from $M_2NH_4^+$ occurs step by step once more, giving maximal peaks at $m/z$ 715 (1.8%), 701 (8.0%), 687 (10.2%), 673 (22.5%), 659 (33.1%), 645 (39.4%), 631 (38.2%) and 616 (60.2%).

Incidentally, the $m/z$ 412 peak, which corresponds to half of the molecule, is observed but of rather poor intensity (5.2%).

Thus, mass spectrometry provides some indications about the relative weakness of chemical bonds in a triply bridged structure such as **3a**. (i) the staves are broken preferentially to the P—Cl bonds, the first stave leaving as a whole when the second is leaving more gently, that is through successive losses of NH and $CH_2$ components: in that case, indeed, the NH and $CH_2$ groups leave as the pearls of a pendant. (ii) in contrast, as soon as the first stave left, the picking-off of the second stave (or pendant) happens simultaneously with the loss of Cl atoms. In other words, the first leaving stave of the triply bridged structure is much more fragile than the P—Cl bonds but there exists a sort of competition between the fragilities of the remaining staves and P—Cl bonds within the fragment which has lost one stave, i.e. the $M_2NH_4^+$ fragment $m/z$ 730 (see above). The remarkable weakness of the first leaving stave in a triple bridged structure can be related to the kinetics of the reaction of an excess of 1,6-diaminohexane with $N_3P_3Cl_6$: when the synthesis of the doubly bridged molecule occurs rather rapidly, the formation of the triply bridged structure takes a much longer time (about 4–5 days versus 2–3 days at ambient temperature).



### *Compounds* **3aB, 3aC**

The DCI mass spectrum (Figure 9) shows that the $MH^+$ molecular ion is observed at $m/z$ 825, which confirms that **3aB** and **3aC** are really two conformers of **3aA**.

### *Compounds* **2a** *and* **2b**

The DCI mass spectra of **2a** (mw = 778) and **2b** (mw = 834) are reported on Figures 10 and 11. The molecular ion of the former is located as expected at the $MH^+$ position but the molecular ion of the latter is surprisingly situated at the $(M + 2NH_4^+)$ position, the $MH^+$ ($m/z$ 837) and $(M + NH_4^+)$ ($m/z$ 854) multiplets being noticeably less intense. There is no clear explanation for such a discrepancy about the behavior versus DCI mass spectrometry of parent molecules as **2a** and **2b**.

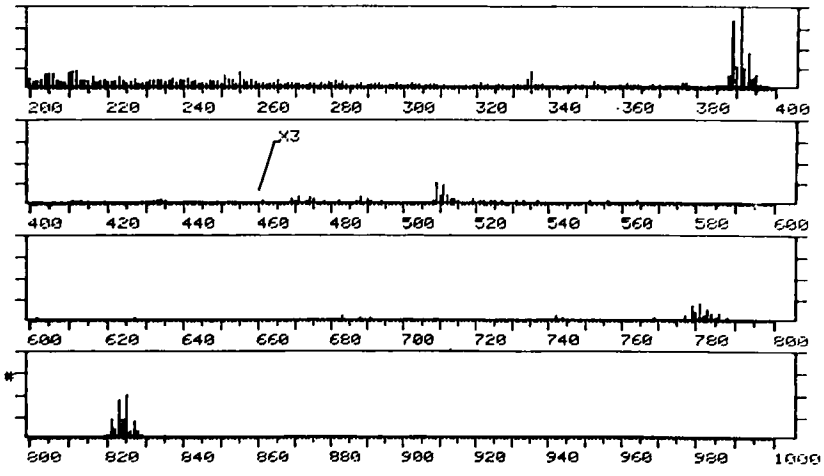



FIGURE 9 DCI mass spectrum of **3aB**, **3aC**.

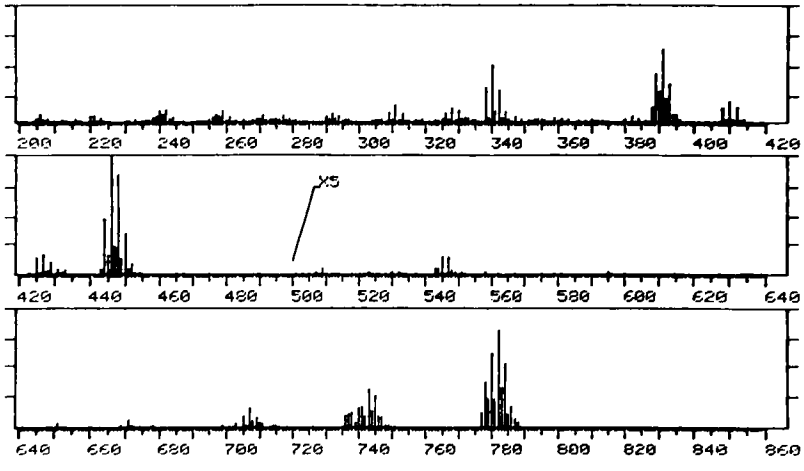



FIGURE 10 DCI mass spectrum of **2a**.

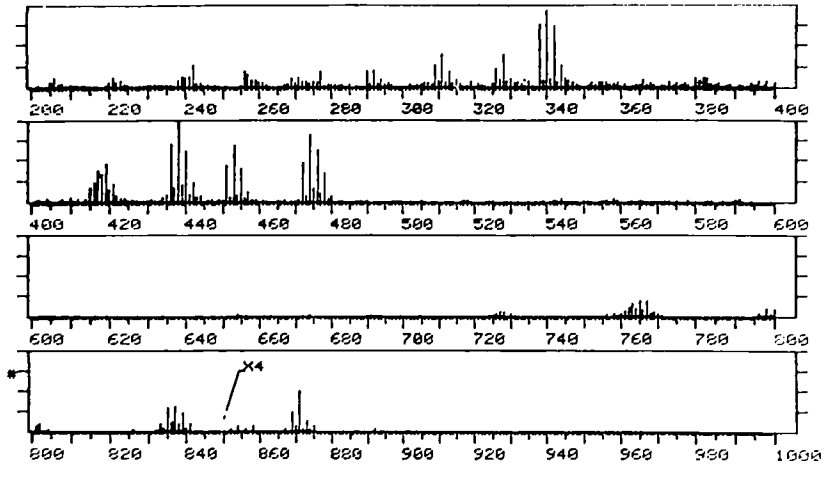



FIGURE 11 DCI mass spectrum of **2b**.

## RESULTS AND DISCUSSION: $^{31}P$ NMR AND GEOMETRY

Let us consider firstly variations of $\delta(PCl_2)$ and of $\delta(PClNH)$ within the series **4**, **1**, **2** and **3**. The former chemical shift (36.43 MHz data) varies from 20.2 ppm in **4** to 21.78 ppm in **2** when the latter varies from 20.89 ppm in **1** to 23.82–24.20 ppm in **3**. In other words, both increase and move close together when the number of diamino bridges (i.e. staves) passes from 0 to 3. These features can be related to the geometrical neighbourhood of bridgehead phosphorus atoms. We have indeed demonstrated recently[16] that closer to a Td-like environment for the phosphorus atom, lower the corresponding chemical shift. For the series reported here, the smaller value for a $\delta(PCl_2)$ (20.2 ppm) is observed for **4** where endocyclic NPN and exocyclic ClPCl angles are 118.4 and 101.4° respectively. Concerning singly bridged derivatives of type **1**, the only X-Ray structure known is that of BINO4[17] where two kinds of P environments do exist: for the $PCl_2$ moieties, the endocyclic NPN and exocyclic ClPCl angles are 119.1 and 100.2°, respectively while for PClNH entities the endocyclic NPN and exocyclic ClNPH angles are 117.2 and 107.6°, respectively. Thus, the environment of the former P atoms is farer from the Td situation than in **4** and, consequently, their $\delta(PCl_2)$ chemical shifts are higher than in **4** (20.89 ppm vs. 20.2 ppm). X-Ray structures of doubly and triply bridged derivatives of types **2** and **3** are not available yet, but we may offer some predictions about the geometries around the P atoms of these molecules. For example, the 21.78 ppm value for $\delta(PCl_2)$ in **2** means that the corresponding endocyclic NPN and exocyclic ClPCl angles are higher than 119.1 and lower than 100.2° respectively, tending so to some limiting values which may be estimated around 121° and 99.5°, respectively. Indeed, the highest $\delta(PCl_2)$ value observed so far at 36.43 MHz is 25.1 ppm in the gem-$N_3P_3Az_4Cl_2$ ($Az = NC_2H_4$) derivative[18] where the endocyclic NPN and exocyclic ClPCl angles are 120.9 and 99.7°, respectively.[19]

Concerning the $\delta$ values for the groups (PClNH), the same reasoning can be applied. According to the evolution of this chemical shift within the **1**, **2** and **3** series, endocyclic NPN and exocyclic ClPNH angles would move from 117.2 and 107.6° in **1** to limiting values which can be estimated to about 121° (as for $\delta(PCl_2)$) and about 105°, respectively. The latter limit will have to be ascertained by X-Ray investigations of triply bridged derivatives as soon as single crystals have been obtained.

Then, when passing from **1** to **3**, the exocyclic ClPNH angle(s) decreases as well as, consequently, the distance between the two cyclophosphazene rings. In other words, the "push-pull" effect on the rings of the diamino "spring" is most pronounced in singly bridged derivatives and decreases step by step when the number of springs increases. Such a mechanical interpretation of chemical shift variations as a function of bond angles is quite similar to the one we proposed recently within the series of MONOSPIRO, DISPIRO and TRISPIRO cyclotriphosphazenes.[10,16]

It may be predicted, from the "springs and rings" mechanical model we mentioned above, that the distance between rings, i.e., the effective volume of the cage (or "barrel") for recognition of host molecules, is smaller in folded conformers than in the non-folded ones. Thus, the latter will complex smaller

host molecules than the former. Attempts at the use of **3a** and **3b** (coded as BARRELANES from now on) as macrocyclic ligands for several transition metal clusters having catalytic activity are currently under investigation.

ACKNOWLEDGEMENTS

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## EXPERIMENTAL SECTION

$^{31}$PNMR spectra were recorded on BRUKER WH 90, WM 250, WM 300, WM 400 and WM 500 instruments, in $CD_2Cl_2$ and/or $CDCl_3$ with $H_3PO_4$ 85% as a standard. $^{13}$C NMR spectra were recorded at 62.90 MHz on a BRUKER WM 250 instrument in $CD_2Cl_2$. $^1$H NMR spectra were recorded at 250 MHz with TMS as an internal standard. Infrared spectra were obtained on a Perkin Elmer 683 spectrometer. Melting points were measured on a Büchi 510 apparatus and are uncorrected. Satisfactory combustion analyses were obtained (C = ±0.40, H = ±0.20, N = ±0.40) for all compounds. Organic solvents, ACS grade, were used without further purification. Hexachlorocyclotriphosphazene, **4**, 99.5% grade, was kindly provided by Shin Nisso Kako, Tokyo, Japan. Mass spectra were recorded on a R1010 RIBERMAG Quadrupole Mass Spectrometer.



*Singly bridged BINO6* (**1a**) *and BINO8* (**1b**) *derivatives*

A solution of 29 mmol of 1,6-diaminohexane (DIAM**6**) in 150 ml of anhydrous ethyl ether was added dropwise to a solution of 58 mmol of **4** and 64 mmol of $Et_3N$ in 650 ml of diethyl ether. The mixture was stirred in an argon atmosphere for 48 h at 0°C and then filtered. Evaporation of the solvent afforded 15.5 g (73%) of an oily colourless crude product. The final product was washed three times with n-hexane to remove unreacted **4** (7.5 g). The remaining product (9 g) was dissolved in 400 ml of n-hexane. Traces of resins (white or light yellow) stick to the vessel. The n-hexane solution is poured off and stirred for 48 h at room temperature breaking down the $Et_2O$ clathrate which is responsible for the oily aspect mentioned above. 7 g of a white micro-crystalline powder (**1a**) is then obtained: m.p. 98°C, t.l.c. $R_f = 0.51$ with $Et_2O$ 10%-$CCl_4$ 90% as eluent. Anal.: found: C% 9.88, H% 2.00, N% 15.08, Cl% 47.84, calc. for the expected BINO structure: C% 9.76, H% 1.91, N% 15.17 and Cl% 48.01. Mass spectrum: $M^+$, $m/z$ 738, base peak (I = 100%), $m/z$ 312; $^{31}$P NMR ($CD_2Cl_2$) 22.27, 21.71, 20.74, 19.69 and 18.80 ppm; IR (KBr disks) 3240, 1220, 580 and 520 cm$^{-1}$. The same procedure was applied in the synthesis of **1b**, white crystalline powder, m.p. 80°C, t.l.c. $R_f = 0.78$ with $Et_2O$ 10%-$CCl_4$ 90% as eluent. NMR, IR and mass spectroscopic data very similar to those of **1a**.

*Doubly bridged* (**2a**) *and* (**2b**) *derivatives*

A solution of 64 mmol of DIAM**6** in 500 ml of anhydrous diethyl ether was added dropwise to a solution of 29 mmol of **4** in 1500 ml of the same solvent. The mixture was stirred in an argon atmosphere for 72 h at 0°C and was then filtered. Evaporation of the solvent afforded 4.5 g of a waxy light yellow crude product. This crude product was dissolved in 400 ml of pentane and an addition of 100 ml of ethyl ether makes the light yellow polymeric resins sticking to the vessel. The solution is then poured off and evaporated. 4.2 g of a white powder is obtained (after 2 column chromatographic turns): m.p. 95°C, t.l.c. $R_f = 0.50$ with $CH_2Cl_2$-$CH_3OH$ (1:1) as eluent. Mass spectrometry: $MH^+$, $m/z$ 779 (see above); IR (KBr disk) 3390, 3240, 1190, 1090, 730, 640, 570 and 510 cm$^{-1}$. The same procedure was applied in the synthesis of **2b**, white powder, m.p. 55–57°C, t.l.c. $R_f = 0.52$ with $CH_2Cl_2$-$CH_3OH$ (1:1) as eluent. Mass spectrum: M, $2NH_4^+$, $m/z$ 873 (see above). NMR and IR data very similar to **2a**.

*Triply bridged* (**3a**) *and* (**3b**) *derivatives*

A solution of 95 mmol of DIAM**6** in 500 ml of anhydrous acetonitrile was added dropwise to a solution of 29 mmol of **4** in 1500 ml of the same solvent. The mixture was stirred in an argon atmosphere for 120h at 0°C and was then filtered. Evaporation of the solvent (and 2 column

chromatographic turns) afforded 4.8 g (40%) of a white cristalline powder: m.p. > 340°C (no decomposition). Mass spectrum: $MH^+$, $m/z$ 825 (see above). IR (KBr disk) 3390, 3200, 1185, 1095, 720, 610, 550 and 505. The same procedure was applied in the synthesis of **2b**, white crystalline powder, m.p. > 340°C (no decomposition). NMR, IR and mass spectroscopic data very similar to those of **3b**.

## REFERENCES


1. (a) R. M. Izatt and J. J. Christensen, "Synthetic Multidentate Macrocyclic Compounds"; Academic Press: New York, 1978. (b) E. Weber, F. Vögtle, "Host Guest Complex Chemistry I"; F. Vögtle, Ed.; Springer-Verlag: Berlin, 1981; *Top. Curr. Chem.*, 1981, 98, 1. (c) G. W. Gökel, S. H. Korzeniowski, "Macrocyclic Polyether Syntheses"; Springer-Verlag: Berlin, 1982.
2. (a) J. M. Lehn, *Struct. Bonding* (Berlin) 1973, 16, 1. (b) J. M. Lehn, *Acc. Chem. Res.*, 1978, 11, 49. (c) J. M. Lehn, *Pure Appl. Chem.*, 1978, 50, 871. (d) J. M. Lehn, *Ibid* 1980, 52, 2303. (e) J. M. Lehn, *Ibid* 1980, 52, 2441.
3. (a) J. P. Kintzinger, F. Kotzyba-Hibert, J. M. Lehn, A. Pagelot and K. Saigo, *J. Chem. Soc., Chem. Commun.* 1981, 833. (b) F. Kotzyba-Hibert, J. M. Lehn, K. Saigo, *J. Am. Chem. Soc.* 1981, 103, 4266. (c) C. Pascard, C. Riche, M. Cesario, F. Kotzyba-Hibert, J. M. Lehn, *J. Chem. Soc., Chem. Commun.* 1982, 557.
4. D. M. Walba, R. M. Richards, S. P. Sherwood and R. C. Haltiwanger, *J. Am. Chem. Soc.* 1981, 103, 6213.
5. (a) R. Mageswaran, S. Mageswaran and I. O. Sutherland, *J. Chem. Soc., Chem. Commun.* 1979, 722. (b) N. F. Jones, A. Kumar, I. O. Sutherland, *Ibid* 1981, 990.
6. P. L. Anelli, L. Lunazzi, F. Montanari and S. Quici, *J. Org. Chem.* 1984, 49, 4197.
7. J.-F. Labarre, *Top. Curr. Chem.* 1985, 129, 173.
8. P. Castera, J.-P. Faucher, G. Guerch, R. Lahana, A. Mahmoun, F. Sournies and J.-F. Labarre, *Inorg. Chim. Acta* 1985, 108, 29.
9. S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. Keat, R. A. Shaw and M. Woods, *J. Chem. Soc.*, Dalton Trans. 1976, 1405 and 1977, 1980.
10. N. El Murr, R. Lahana, J.-F. Labarre and J.-P. Declercq, *J. Mol. Struct.* 1984, 117, 73.
11. G. R. Newkome and T. Kawato, *J. Am. Chem. Soc.* 1979, 101, 7088.
12. T. Sato, M. Wakabayashi, K. Hata and M. Kainosho, *Tetrahedron* 1971, 27, 2737.
13. E. Graf, J. P. Kintzinger, J. M. Lehn and J. Le Moigne, *J. Am. Chem. Soc.* 1982, 104, 1672.
14. S. H. Mashraqui and P. M. Kuhn, *J. Org. Chem.* 1983, 48, 1341.
15. S. P. Adams and H. W. Whitlock, *J. Am. Chem. Soc.* 1982, 104, 1602.
16. M. Willson, L. Lafaille, G. Commenges and J.-F. Labarre, *Phosphorus and Sulfur*, 1985, 25, 273.
17. G. Guerch, J.-F. Labarre, R. Lahana, R. Roques and F. Sournies, *J. Mol. Struct.*, 1983, 99, 275.
18. G. Guerch, F. Sournies, J.-F. Labarre, M. Manfait, F. Spreafico and S. Fillipeschi, *Bioinorg. Chim. Acta*, 1982, 66, 175.
19. R. Enjalbert, G. Guerch, F. Sournies, J.-F. Labarre and J. Galy, *Zeitschrift für Kristallographie*, 1983, 164, 1.