Synthesis and Binding Properties of *iiii (4i)* Stereoisomers of Phosphonato Cavitands − Cooperative Effects in Cation Complexation in Organic Solvents

Pascale Delangle,[a][‡] Jean-Christophe Mulatier,[a] Bernard Tinant,[b] Jean-Paul Declercq,[b] and Jean-Pierre Dutasta*[a]

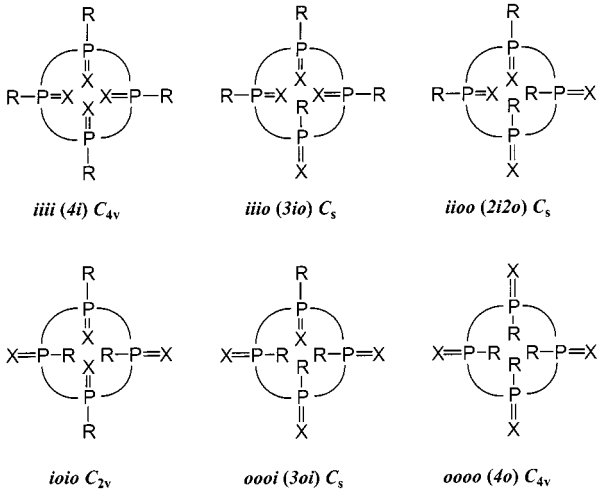
Dedicated to the memory of Prof. André Collet

Keywords: Cations / Cavitands / NMR spectroscopy / Supramolecular chemistry / X-ray diffraction

Syntheses and host-guest properties of tetrabridged phosphorylated cavitands in their *iiii* (*4i*) configurations are described. The tetraphosphonato cavitands **2** and **3**, with the four P=O bonds oriented inwards (*4i* stereoisomer) were prepared in 25% and 53% yields respectively, from the corresponding resorc[4]arenes, dichloro(phenyl)phosphane oxide and base. The formation of the *4i* stereoisomers is solvent-dependent and is attributable to the capability of an ammonium guest to form an inclusion complex. Only the *iiio (3io)* stereoisomer of **3** was isolated otherwise, in low yield. These phosphonato cavitands, in their *4i* configurations, are particularly efficient extractants for metal ions. The free energies of complexation of **3** with alkali metal and ammonium cations in chloroform solution are in the range from –43.3 (Li^+) to –52.4 kJ mol^{-1} ($CH_3NH_3^+$). High binding constants, ^1H, ^{31}P and ^{133}Cs NMR studies in solution and single-crystal X-ray analysis clearly demonstrated that the aromatic cavity of the host and the four hard donor P=O groups act cooperatively to ensure the encapsulation of the cationic guests. In the solid, the **2**·Cs^+ complex showed the Cs^+ ion inside the aromatic cavity, interacting strongly with the four phosphoryl groups. The **2**·$CH_3NH_3^+$ complex showed the methyl group of the guest oriented inside the cavity, with the stability of the complex supported by a complex H bond pattern involving H_2O molecules and the anion.

Introduction

Phosphorus groups play an important role in host-guest chemistry and the propensities of the phosphoryl (P=O) and thiophosphoryl (P=S) groups to bind cationic species have been investigated. The phosphoryl group binds alkali or alkaline earth metal ions through its oxygen atom, whereas the sulfur atom of the P=S thiophosphoryl group has more affinity for soft cations such as mercury or silver. Because of their high binding capabilities, these groups have been included in preorganized structures to increase the stability of the complexes thus formed. Many references in the literature are concerned with phosphorus macrocycles containing (thio)phosphorylated groups,[1−4] phosphorus cryptands[5−7] and phosphahemispherands.[8,9]

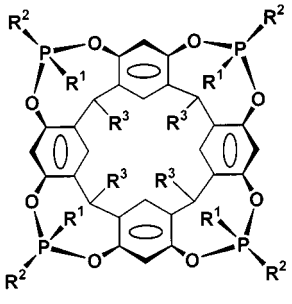


Much attention is currently being devoted to the cone-shaped cavitands derived from the resorc[4]arenes, which have opened the route to promising preorganized hosts.[10−12] Their phosphorus derivatives have received intensive study.[13−15] In the tetrabridged phosphocavitands, the inwards (*i*) and outwards (*o*) configurations are defined relative to the *endo* and *exo* orientations of the P=X bonds [X = O, S, lone pair (lp)]. The preorganized structure is imposed by the fixed boat-chair conformation of the four

[a] Stéréochimie et Interactions Moléculaires, UMR CNRS no. 5532, École Normale Supérieure de Lyon,
69364 Lyon cedex 07, France
Fax: (internat.) + 33-4/72728483
E-mail: dutasta@ens-lyon.fr
[b] Laboratoire de Chimie-physique et de Cristallographie, Université Catholique de Louvain,
Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium
[‡] Present address: C.E.A. Grenoble, DRFMC/SCIB/RI, 17, rue des Martyrs, 38054 Grenoble cedex 9, France

  1434−193X/01/1019−3695 $ 17.50+.50/0

fused eight-membered rings. Six different stereoisomers can result from the equatorial or axial orientations of the substituents on the phosphorus atoms, and the exclusive formation of one stereoisomer is a difficult and rather unpredictable task. To ensure strong binding, the cavity should contain binding sites preorganized for interaction with guests, and the *iiii* (*4i*) stereoisomer appears to be a prerequisite for good recognition properties for cationic species. In the *P*-phenylphosphonitocavitand **1a**, the free electron pairs of the four phosphorus atoms are oriented toward the macrocyclic cavity (*4i* stereoisomer), allowing complexation of four transition metal cations. The tetracopper and -silver complexes of **1a** have been shown to act as size-selective hosts for the inclusion of halide anions.[16−20] Puddephatt et al. have demonstrated, by molecular mechanics calculations for the six possible isomers, that the orientation of one phenyl group toward the macrocyclic cavity is probable [*iiio* (*3io*) isomer], but that two or more phenyl groups oriented inwards are highly unlikely.[19] The X-ray structure of the triply coordinated $P^{III}Cl$ compound **1b** possessed the *4o* configuration, with the four P−Cl bonds oriented inwards and the four lone pairs outwards,[21] whereas the *4i* stereoisomer was observed in the solid-state structure of the tetrakis(thiophosphoramidate) compound **1c**.[22,23] Recently, new cavitands with phosphate or phosphonate bridging units have been obtained as several stereoisomers.[24−28] In the synthesis of phosphate derivatives, the *iiio* (*3io*), *iioo* (*2i2o*), *ioio*, and *oooi* (*3oi*) isomers were obtained, but the *4i* and *4o* isomers were either not formed or produced only in trace amounts.[24−26] The structure of the *ioio* isomer of the tetraphosphate **1d** has been reported.[26] In the case of the phenylphosphonate derivatives, the presence of the four P(O)−phenyl groups should make the likelihood of more than one phenyl substituent being oriented inwards even more remote, but a synthetic pathway recently described afforded mainly the *3oi*, *2i2o* and *ioio* stereoisomers.[27] In earlier work, we have demonstrated that the tetraphosphonato cavitand **2** can be obtained exclusively as its *4i* stereoisomer in fairly good yields.[29]



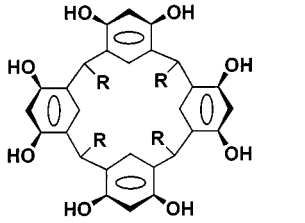
	R^1	R^2	R^3
1a	lp	C_6H_5	$CH_2CH_2C_6H_5$
1b	Cl	lp	CH_3
1c	S	$N(CH_2CH_3)_2$	CH_3
1d	O / O-*p*-Tolyl		CH_3

We wish to report here experimental evidence of the directed syntheses of the *4i* stereoisomers of the tetraphosphonato cavitands **2** and **3**, with the four P=O groups oriented inwards. Compounds **2** and **3** represent unique examples of phosphorylated cavitands, with *4i* stereochemistry favourable to intracavity complexation. The four convergent phosphoryl oxygen atoms and the aromatic cavities should indeed guarantee selective recognition of cationic guests. Compound **3**, like compound **2**, is a powerful complexing agent for hard metal cations and ammonium guests. The introduction of four CH_2CH_2Ph chains at the lower rim in **3**, in place of the methyl groups in **2**, increased the solubility of the receptor, permitting more detailed complexation studies in solution. Additionally, we wish to report the first single-crystal X-ray analysis molecular structures of the Cs^+ and $CH_3NH_3^+$ complexes of the tetraphosphonato cavitand **2**.

Results and Discussion

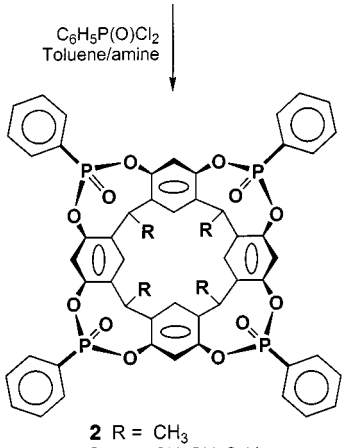
Synthesis of Host Molecules 2 and 3

The synthesis of the phosphonato cavitands **2** and **3** is fairly straightforward, and is achieved through the ring-closure reaction, with the aid of dichloro(phenyl)phosphane oxide, of the eight-membered rings delineated by the phenyl groups of the aromatic cavity of the resorc[4]arene molecule in its frozen cone conformation. The procedure used is outlined in Scheme 1 and consists of the reaction between the



4a R = CH_3
4b R = $CH_2CH_2C_6H_5$

$C_6H_5P(O)Cl_2$
Toluene/amine



2 R = CH_3
3 R = $CH_2CH_2C_6H_5$

Scheme 1

tetraresorcinol **4**[30−32] and dichloro(phenyl)phosphane oxide in the presence of an amine in refluxing toluene.

Our preliminary results showed that use of 1 equiv. of *N*-methylpyrrolidine resulted in exclusive production of the *4i* stereoisomer of **2**, in 25% isolated yield, from the reaction between $PhP(O)Cl_2$ and **4a** in toluene.[29] The same treatment of **4b** provided the *4i* and *3io* stereoisomers of **3** in 51% and 5% yields, respectively. It should be noted that a 51% yield of isolated **3** (*4i*) corresponds roughly to an 85% yield for each individual cyclization step. From this it may reasonably be inferred that the multiple ways by which the resorcinol moieties may ring-close, including intermolecular coupling, are essentially limited to the formation of **3** in its *4i* and *3io* configurations. The residual material was not identified, but may be attributable to oligomeric compounds and probably to some degradation products arising from hydrolysis. The ring-closure reactions with dichloro(phenyl)phosphane oxide thus mainly produce the expected *4i* stereoisomers of the phosphonato cavitands **2** and **3**. According to literature data, we might have expected a catalytic effect from the *N*-methylpyrrolidine.[33] An attempt to use a catalytic amount of this amine (0.2 equiv.) did not, however, produce any extractable compounds. Interestingly, the use of 8 equiv. of amine, to trap all of the HCl formed, did not dramatically change the yields and isomer ratios (Entries 2 and 3, Table 1). In a separate experiment, **4b** was allowed to react with $PhP(O)Cl_2$ in the presence of 8 equiv. of triethylamine, providing the *4i* and *3io* isomers in 28.5% and 7% yields, respectively. However, it is noteworthy that no other isomers were recovered, indicating a reaction pathway different to that developed by the Dalcanale group (compare Entries 4 and 6 in Table 1).[27] According to this latter literature procedure, we tried to perform the ring-closure reaction with **4a** in acetone instead of toluene (see Entry 7, Table 1). The findings were the same as the literature ones: No *4i* or *3io* isomers could be characterized, only a mixture consisting especially of the *ioio*, the *2i2o* and the *3oi* isomers.[34]

Table 1. Yields of isolated *4i* and *3io* isomers of hosts **2** and **3**

Entry	Octol	Amine	Amine [equiv.]	Solvent	*4i* (%)	*3io* (%)
1	**4b**	*N*-methylpyrrolidine	0.2	toluene	0	0
2	**4b**	*N*-methylpyrrolidine	1	toluene	51	5
3	**4b**	*N*-methylpyrrolidine	8	toluene	53	9
4	**4b**	triethylamine	8	toluene	28.5	7
5	**4a**	*N*-methylpyrrolidine	1	toluene	25	0
6[a]	**4a**	triethylamine	10	acetone	0	0
7	**4a**	*N*-methylpyrrolidine	10	acetone	0	0

[a] From ref.[27]

From the differences in the experimental procedures, it seems likely that the solvent/amine pair plays a crucial role in the formation of the *4i* stereoisomer, and this is supported by the following observations. Firstly, the procedure is highly solvent-dependent; the *4i* stereoisomer is the major product obtained in toluene, but other isomers (*ioio*, *2i2o*, *3oi*) are predominant and the *4i* stereoisomer is not observed when the reaction is run in acetone. Secondly, it is most noteworthy that the synthesis performed in toluene with *N*-methylpyrrolidine as base mainly produced crude **2** and **3** as their ammonium complexes, with the *4i* configurations. Light is shed on this on examination of the ^1H and ^{31}P spectra of the isolated compounds [^{31}P: δ = 10.8 (**2**, $C_2D_2Cl_4$), 10.9 (**3**, $CDCl_3$)]. The protons of the *N*-methyl group of the ammonium salt are strongly shifted to higher field (δ = 0.0 to −0.6), indicating the positioning of this group inside the aromatic cavity of the host molecule. Careful purification by silica gel column chromatography was needed to obtain the expected uncomplexed *4i* isomer [^{31}P: δ = 9.15 (**2**, $C_2D_2Cl_4$), 7.7 (**3**, $CDCl_3$)].

It has been shown that resorc[4]arenes are good binders for amine and ammonium salts,[35−37] and so it is tempting to suggest that a host-guest complex is formed between the resorc[4]arenes **4** and the *N*-methylpyrrolidinium salt produced in the first stage of the reaction. Consequently, the ammonium cation might act as an efficient templating agent under our experimental conditions. In the course of the reaction, the strong donor phosphoryl groups can displace residual solvating molecules from the encapsulated ammonium cation, and are therefore spontaneously directed inwards into the cavity, so that the *4i* stereoisomer is formed preferentially. The complexation of the polar ammonium guest by the phosphane oxide ligand strongly depends on the solvating character of the medium, as earlier works attest. The association constants K_a of the host-guest complexes decreased by a factor of 1000 on going from *o*-dichlorobenzene (poorly solvating solvent) to THF (strong solvating solvent), due to greater specific cation−solvent interaction in the latter.[38] At this point, it is interesting to note that syntheses of tetrabromo- and tetramethyl-substituted phosphonato cavitands, performed in THF solution, produced neither *4i* nor *3io* isomers.[27] In acetone, solvation of the ammonium cation results in significant inhibition of complexation compared to the situation in the weakly solvating toluene.

In conclusion, these results show that the presence of an ammonium guest bound to the preformed cavity of the host molecule is highly desirable for directing the formation of the *4i* stereoisomer of the tetraphosphonato cavitands. Apparently, this requirement is not met in the case of the much better cation-solvating solvent acetone. All the data presented here are consistent with a template effect induced by the solvent/amine pair, and further investigations on new phosphonato cavitands continue to support this conclusion, allowing the formation of highly efficient binders for cationic species.[39]

NMR Study of Host 3

The *4i* and *3io* isomers of **3** were characterized by ^1H, ^{13}C, ^{31}P, ^1H-^1H and ^{13}C-^1H correlation 2D NMR spectroscopy and mass spectrometry. The C_{4v} isomer *4i* was characterized by its unique ^{31}P NMR resonance at δ = 7.73 in $CDCl_3$ and by its ^1H and ^{13}C NMR spectra, which were unambiguously assigned by means of 2D correlation experiments (see Exp. Sect.).

Reasonable quantities of the *3io* isomer were obtained from the chromatographic separation. In accordance with the C_s symmetry of the molecule, three signals with relative intensities 1:2:1 were observed in the ^{1}H-decoupled ^{31}P NMR spectrum at δ = 7.20, 9.70 and 11.45 ($CDCl_3$). Most of the proton resonances could be assigned from the ^{1}H-^{1}H COSY spectra (Figure 1). Three different sets of resonances in the 1:2:1 ratio were observed for the protons of the *P*-phenyl groups. Two of these sets correspond to the protons of the phenyl units located outside the molecular cavity, the other is associated with the protons of the phenyl unit residing inside the cavity. The eight aromatic protons (H_{a-d}) of the cavity gave four single resonances, which could be assigned unambiguously as they are not correlated to any other protons. The methine resonances also gave three triplets with relative intensities 1:2:1, with characteristic chemical shifts depending on the substituent orientation around the phosphorus atoms, at δ = 4.81, 4.84 and 5.09. Comparison of the proton NMR spectra (in $CDCl_3$) of the *4i* and *3io* isomers of **3** revealed significant differences. In the *3io* isomer the chemical shifts of the protons in the *ortho*- and *meta*-positions of the inward-oriented *P*-phenyl group (H_1 and H_2, Figure 1), are δ = 6.46 and 6.82, respectively. For the outward oriented *P*-phenyl groups of the *4i* isomer, these protons resonate at δ = 7.85 and 7.47. These upfield shifts observed with the *3io* isomer ($|\Delta\delta|$ = 1.4 and 0.65 ppm, respectively) are the result of the shielding effects exerted by the aromatic rings of the resorc[4]arene moiety on the *P*-phenyl group located inside the cavity.

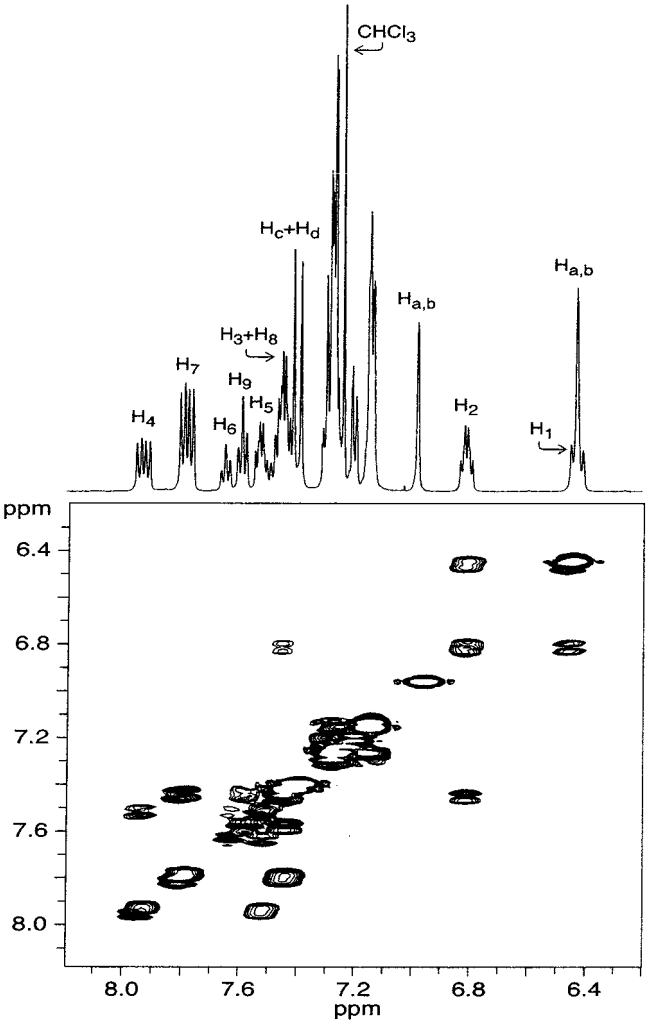
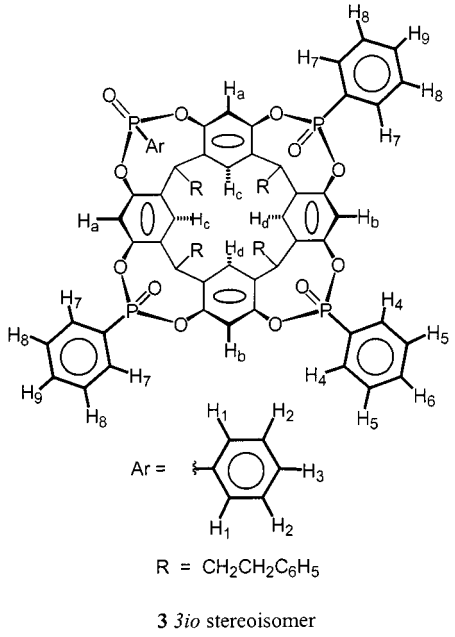


Figure 1. COSY spectrum of the aromatic region of the *3io* stereoisomer of **3**



3 *3io* stereoisomer

Cation Extraction Experiments with Phosphonato Cavitand 3

Dissolution of a normally insoluble picrate salt in an organic solution (usually chloroform) of the host molecule was the first evidence for complexation of cationic guests by the *4i* stereoisomers of the phosphonato cavitands **2** and **3**. In solution, the formation of the complexes induced downfield shifts in the ^{31}P NMR resonance of the hosts. The ionophoric properties of the phosphonato cavitand **3** towards metal cations were first determined by using the picrate extraction method.[40,41] According to this procedure, the percentage of picrate extracted was estimated by measurement of the distribution of picrate salts between chloroform and aqueous phases in the presence of the host molecule. The results presented in Figure 2 clearly show that the phosphonato cavitand **3** efficiently extracts these various hard metal cations, with maxima in the alkali and alkaline earth metal series for Cs^+ and Ba^{2+} cations, respectively. The values for alkaline earth cations are on the whole better than those with the alkali metal ions. Interestingly, the trivalent Eu^{3+} ion also exhibits a strong affinity for **3**. These results are attributable to the desolvation power of the phosphorylated cavitand and the encapsulation of the naked cation into the host cavity.

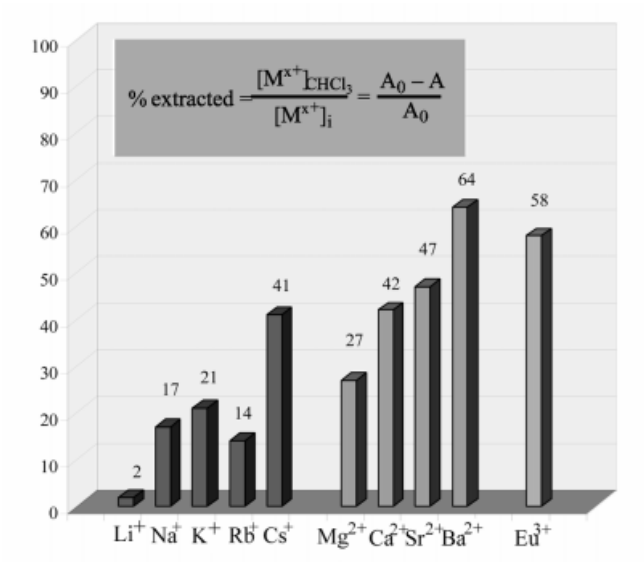


Figure 2. Percent extraction of alkali, alkaline earth and europium picrates into $CHCl_3$ at 298 K by host **3** (the initial concentrations of picrate salt in water, and of host in chloroform, are 10^{-3} mol L^{-1}; the volumes of both phases are 0.5 mL)

Binding Affinities and Thermodynamic Parameters of Host-Guest Complexation

Association constants (K_a) and free energies of complexation ($-\Delta G°$) of **3** with alkali metal and ammonium cations (Table 2) were calculated for 1:1 complexes at 294 K in $CHCl_3$ saturated with H_2O.[42−44] The K_a values range from 5×10^7 to 2×10^9, with maxima for the Cs^+ and $CH_3NH_3^+$ cations. These high association constants may be attributed to the cooperative effect of the four converging phosphoryl groups and favourable interactions with the aromatic cavity, suggesting that intracavity complexation occurs. The Cs^+ cation, which is better complexed than other alkali metal cations, fits perfectly into the macrocyclic cavity with maximized π-cation interactions, as shown in the solid-state structure described below. The stability constants with alkali metal cations are of the same order of magnitude as those obtained for the calix[4]arene crowns, which benefit from π-cation interactions with two of the aromatic rings in the 1,3-alternate conformation.[45,46]

Complexes with ammonium cations mainly involve NH···O=P hydrogen bonds. However, the stabilities of ammonium complexes of **3** are dependent on the size of the guest and particularly on the synergy of hydrogen bonding and encapsulation of the lipophilic part of the cation. The optimum point is reached with the $CH_3NH_3^+$ guest, as this combines CH_3 encapsulation (through favourable van der Waals interactions with the aromatic cavity of the host) and strong hydrogen bonding between NH and PO groups, as previously reported for **2**.[29] In chloroform solution, the large upfield-shifted resonance of the methyl protons of the guest at $\delta = -1$ ($|\Delta\delta| = 3.9$ ppm), is indeed due to the ring current effect of the phenyl groups of the host cavity. This result is consistent with the solid-state structure of the **2**·$CH_3NH_3^+Pic^-$ complex described below, and suggests that this structure of the complex persists in chloroform solution at room temperature. The bulky tBuNH$_3^+$ cation is too large to enter into the cavity of the phosphonato cavitand, as indicated by the chemical shift of the methyl protons in chloroform solution ($\delta = 1.1$, $|\Delta\delta| = 0.3$ ppm). In this case the host-guest complex is essentially stabilized by hydrogen bonds with the phosphoryl groups. The lack of structural data concerning the NH_4^+ cation does not permit precise determination of the location of the guest, which might be inside or outside the aromatic cavity.

As expected, the K_a values determined for **3** are close to those reported for **2**.[29] The increased rigidity of the phosphonato cavitands defines an optimal pocket suitable for hard cation encapsulation. The maximum $\Delta\Delta G°$ values of the free energy of binding are 5.9 and 3.5 kJ mol^{-1} in the alkali metal and the ammonium series, respectively. This results in a relatively small monotonic variation in the selectivity, which may be due to different factors including size and solvation of the guests. Further investigations, structural studies in particular, are called for to determine the factors that direct the selectivity of the phosphorylated hosts. However, a common feature is the dramatic effect of the stereochemistry of the tetraphosphonato cavitand. The *4i* stereochemistry is crucial for strong complex formation; a significantly lower value, for example, was reported for the complexation of the cyclohexylammonium cation by the *3io* isomer of a tetraphosphate cavitand ($K_a = 1.4\ 10^3$ M^{-1} vs. $8.5\ 10^8$ M^{-1} for **3**·tBuNH$_3^+$).[24]

^{133}Cs NMR Study of the 3·Cs^+ Complex

^{133}Cs NMR spectroscopy is an appropriate technique for the study of complexation of the Cs^+ ion. In spite of its quadrupole moment (spin 7/2), narrow NMR lines and large chemical shift differences between free and complexed cation are usually observed. The solvent dependence of the ^{133}Cs chemical shift in Cs^+ complexes is not straightforward and is largely due to solvation effects and the donating capability of the solvent. Complexation of $CsNO_3$ by **3** was studied by ^{133}Cs NMR spectroscopy in DMF solution, a highly competitive solvent for cation complexation. The

Table 2. Association constants (K_a, L mol^{-1}) and free energies of complexation ($-\Delta G°$, kJ mol^{-1}) for complexes of **3** with alkali metal and ammonium cations

	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	$CH_3NH_3^+$	tBuNH$_3^+$
K_a	$5.0\ 10^7$	$7.8\ 10^7$	$2.9\ 10^8$	$1.2\ 10^8$	$5.4\ 10^8$	$4.9\ 10^8$	$2.0\ 10^9$	$8.5\ 10^8$
$-\Delta G°$	43.3±0.5	44.4±0.1	47.6±0.3	45.4±0.8	49.2±0.2	48.9±0.4	52.4±0.1	50.2±0.4

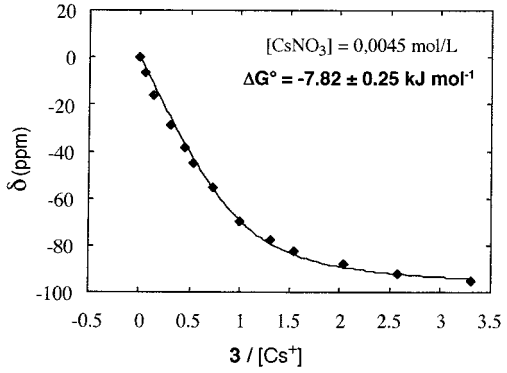


Figure 3. Plot of ^{133}Cs chemical shifts vs. [**3**]/[$CsNO_3$] mol ratio; concentration of $CsNO_3$ is 0.0045 M

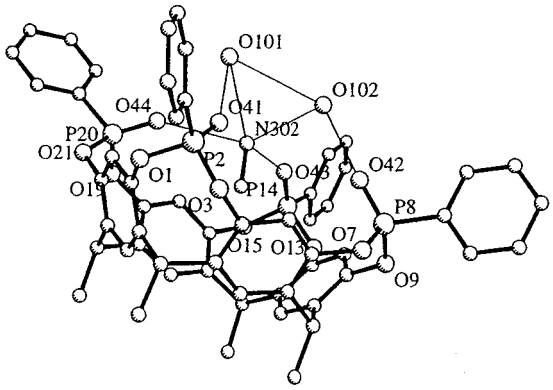


Figure 4. X-ray structure of the **2**·CH_3NH_3Pic complex

variation of ^{133}Cs chemical shift as a function of the [**3**]/[Cs^+] mol ratio is shown in Figure 3 and is consistent with the formation of a 1:1 complex. The binding constant K_a and the ^{133}Cs chemical shift of the **3**·Cs^+ complex were calculated by adjusting experimental chemical shifts to the equation corresponding to a 1:1 complex.[47] The ^{133}Cs resonance shifts upfield with increasing concentration of the cavitand. The chemical shift difference between the free and complexed Cs^+ ion is $|\Delta\delta| = 99$ ppm. It reflects significant changes around the cation during the complexation process, but it is dramatically different from the downfield shifts observed with the cryptand·Cs^+ complexes.[48−51] In calix[4]arene·Cs^+ complexes, a large ^{133}Cs upfield shift was attributed to polyhapto-aromatic binding in chloroform solution.[52,53] In the case of the **3**·Cs^+ complex, the large upfield shift observed might represent the influence of the encapsulation of the desolvated cation inside the aromatic cavity surrounded by the four P=O groups.

The stability constant of the phosphonato cavitand complex (log$K$ = 3.24) is of the same order of magnitude as that for the [2.2.1] cryptate (Table 3).[54] This result presents convincing evidence for the strong binding potential of the phosphonato cavitand **3** in DMF solution.

Table 3. Formation constants of Cs^+ ion complexes with **3** (293 K) and cryptands (298 K) in DMF solution

	Cryptands			Cavitand
	[2.1.1]	[2.2.1]	[2.2.2]	**3**
log$K$	1.23±0.07	3.33±0.04	2.16±0.03	3.24±0.08

X-ray Analysis of the 2·CH_3NH_3Pic Complex

The structure of the **2**·CH_3NH_3Pic complex confirms the *4i* configuration of the cavitand (Figure 4). The crystal contains two molecules of solvent tetrachloroethane and three molecules of water, two of them involved in hydrogen bonding. Host-guest stabilization is achieved through a combination of two P=O···H−N^+ hydrogen bonding interactions between the hydrogen atoms of the ammonium with the oxygen atoms of the phosphoryl groups (PO···N distances are 2.87 and 2.84 Å), and van der Waals stabilizing forces between the aromatic rings of the cavity and the CH_3N^+ group. The methyl carbon atom of the guest cation lies 1.16 Å below the plane defined by the oxygen atoms of the PO groups (the ammonium nitrogen atom being 0.16 Å above this plane), in agreement with deep encapsulation of the guest. The ammonium group is tilted from the C_4 axis of the ligand, with the nitrogen atom hydrogen-bonded to two adjacent PO groups, and the methyl group positioned roughly at the centre of the cavity. The methyl carbon atom lies at a distance of 3.79−3.86 Å from the centre of the aromatic rings of the molecular cavity, indicating a close contact between the CH_3 hydrogen atoms and the phenyl rings. Indeed, close van der Waals contacts account for attractive CH−π interactions. A complex hydrogen bond pattern involving the picrate anion completes the environment of the guest. The picrate ion is located above the macrocyclic cavity and is involved in hydrogen bonding with two water molecules through its phenolic oxygen atom and *ortho*-nitro groups, with [H_2O···O] distances in the 2.85−3.16 Å range. The water molecules are themselves hydrogen-bonded to the ammonium salt, with H_2O···N distances of 2.73 and 3.15 Å, and to the two PO oxygen atoms not involved in the ammonium coordination, with H_2O···OP distances of 2.62 and 2.72 Å (Figure 5). Thus, the improved stability of the **2**·CH_3NH_3Pic complex may be ascribed to a supramolecular assembly involving hydrogen bonding and CH−π interactions. This is consistent with the high binding constants measured in solution and with the NMR-spectroscopic data indicating that the complex structure persists in solution.

X-ray Analysis of the 2·CsPic Complex

The **2**·CsPic complex crystallizes with three molecules of solvent tetrachloroethane. As expected, cavitand **2** is in the *4i* configuration, with the four P−O bonds oriented inwards (Figure 6). The Cs^+ cation lies 0.57 Å below the average plane defined by the four PO oxygen atoms and is deeply "clamped" inside the cavitand by a combination of strong dipolar interactions with the four oxygen atoms of the phosphoryl groups supplemented by π−cation interactions. Average O···Cs distance is 3.29 Å, compared with

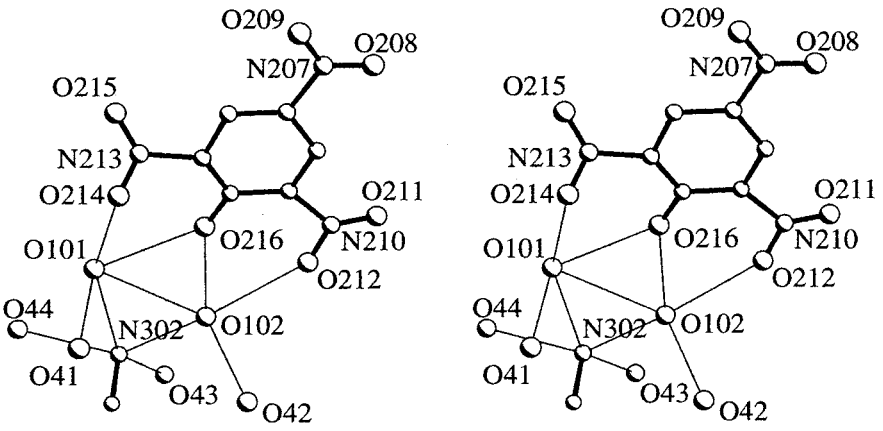


Figure 5. Partial view of the **2**·CH_3NH_3Pic complex showing the picrate anion coordination

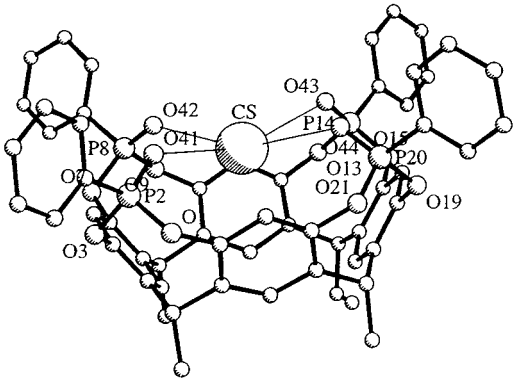


Figure 6. X-ray crystal structure of the **2**·CsPic complex

Table 4. Selected bond lengths [Å] and angles [°] involving the Cs^+ cation in **2**·CsPic with standard deviations in parentheses

Cs−O41	3.261(7)	Cs−O43	3.566(7)
Cs−O42	3.083(6)	Cs−O44	3.247(6)
O41−Cs−O42	83.3(2)	O42−Cs−O43	93.7(2)
O41−Cs−O43	161.3(2)	O42−Cs−O44	158.5(2)
O41−Cs−O44	97.4(2)	O43−Cs−O44	78.7(2)

O(ether)−Cs distances of 3.07−3.34 Å measured in crown ether derivatives (Table 4). The average distance from the Cs^+ ion to the mean plane of the aromatic rings is 4.09 Å, which roughly corresponds to the distance to the centroids of the phenyl rings. The Cs−C distances are about 0.5 Å greater than those reported for calix[4]arene·Cs^+ complexes, indicative of weak Cs^+−arene bonding with the aromatic rings of the cavity.[45,53,55] Therefore, dipolar interactions with the PO groups are predominant in the complex, and the stabilizing effect of the aromatic cavity favours the encapsulation of the cation. The encapsulated Cs^+ cation occupies the best centred position in the cavity, providing strong coordination with the four phosphoryl groups and with the four aromatic rings. Surprisingly, the picrate anion in this structure is located close to the lower rim of the ligand; in other words, there are no interactions or hydrogen bonds involving the picrate ion and the complexed cation. The *para*-nitro group of the anion is pointing toward the methyl groups of the ligand, with weak interactions with solvent molecules. This situation is dramatically different from that observed with the former ammonium complex, in which the phenolic oxygen atom and the nitro groups of the picrate anion are coordinated to water molecules close to the upper rim of the ligand. Within the crystal, the complex entities pack facing each other through their upper rims, to form rows separated by a layer of $C_2H_2Cl_4$ solvent molecules.

Conclusion

The results presented in this article represent a significant advance in the chemistry and binding properties of cavitands featuring the binding power of phosphorylated cavitands and the formation of *4i* stereoisomers. The highly preorganized phosphonato cavitands combine hard donor binding sites with an aromatic cavity. The phosphorylated upper rim of the host and the aromatic cavity act cooperatively, by means of ion−dipole, H-bonding and specific π-interactions for encapsulation of size-adapted species. The cooperative effect that results from this situation has been highlighted by the extracting properties of these hosts towards cationic species, and the high stability constants of the complexes. Indeed, the structures of the inclusion complexes analysed for two examples in the solid state are in accordance with the conclusions drawn from the solution NMR studies and the complexation experiments. The solid-state structures of the **2**·CsPic and **2**·CH_3NH_3Pic complexes showed the cationic guest embedded in the molecular cavity defined by the aromatic rings of the resorc[4]arene in its *4i* configuration. By means of extraction experiments and ^{133}Cs NMR spectroscopy, we were able to show that the phosphonato cavitands are very efficient receptors for the Cs^+ cation. Most of the alkaline earth metal cations are extracted well, as is europium ion. The strong affinity of these hosts for cationic species is quite remarkable and further developments are currently in progress.

Experimental Section

General Remarks: All manipulations involving air-sensitive species were carried out under dry argon. Unless otherwise noted, all re-

agents were purchased from commercial suppliers and used without further purification. Toluene was distilled from Na. Triethylamine and *N*-methylpyrrolidine were distilled prior to use. Reactions were monitored by ^{31}P NMR and thin layer chromatography (Merck 60 Kieselgel, F254). Silica gel used for column chromatography was Merck 60 Kieselgel (0.040−0.063 mm). − Elemental analyses and electrospray mass spectra were performed by the Service Central d'Analyses, CNRS. − Melting points were measured with a Reichert melting point apparatus or with a DSC7 Perkin−Elmer calorimeter. − ^1H, ^{13}C and ^{31}P NMR spectra were recorded with Varian Unity 500 and Bruker AC 200 spectrometers. Chemical shifts are given as δ values from Me_4Si (^1H and ^{13}C) or H_3PO_4 85% (^{31}P). ^{13}C and ^{31}P NMR spectra are proton-decoupled. The aromatic protons were labelled as follows: calix-ArH, P-ArH and Ar-H, respectively for the protons attached to the resorc[4]arene, the *P*-phenyl and the CH_2CH_2Ph groups. Similar labelling was used for the carbon nuclei (Cq = quaternary carbon atom). The reported multiplicities of ^{13}C NMR spectra represent ^{31}P-^{13}C couplings. ^{13}C assignments were mainly based on DEPT, HMQC and HMBC 2D correlation spectra. − 2D NMR correlation experiments were run with a Varian Unity 500 spectrometer. For each 2D NMR experiment a total of 256 increments of 1 K or 2 K data points were collected. ^{133}Cs chemical shifts were measured with a Varian Unity 500 at 65.6 MHz. The measurements were made at 293 K on a series of solutions placed in a 10-mm (o.d.) NMR tube containing a constant amount of cesium salt (0.0045 M $CsNO_3$ in DMF), and a variable amount of cavitand **3**. Chemical shifts are given relative to the starting DMF solution of the pure salt (downfield shifts have positive values). − Binding constants K_a are listed in Table 2, and were determined using the picrate salt extraction technique from H_2O into $CHCl_3$ at 294 K, reported previously by Cram et al.[42−44] The percentage extraction of alkali, alkaline earth and europium picrate salts were determined according to the same procedure as for K_a measurements, by using 0.5 mL of 10^{-3} M initial solutions of host and picrate salts. For each salt, absorbance of the picrate salt in the aqueous layer was measured at 380 nm for the extracted phase (A) and the reference phase containing no host (A_o). The percentage extracted was given by $100[(A_o - A)/A_o]$; the results are presented in Figure 2. Picrate salts were already available or prepared according to known procedures.[56] Resorc[4]arenes **4a** and **4b** were synthesized according to literature procedures.[30−32]

5,9,13,17-Tetraphenyl-1,21,23,25-tetrakis(2-phenylethyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2]benzodioxaphosphocine 5,9,13,17-Tetraoxide (3): Azeotropic distillation, by means of a Dean−Stark apparatus, of a suspension of **4b** (1.52 g, 1.68 mmol) in toluene (200 mL) was performed overnight under dry argon to remove traces of water from the starting material. After this, *N*-methylpyrrolidine (0.16 g, 1.9 mmol), and dichloro(phenyl)phosphane oxide (1.38 g, 7.1 mmol) were added at room temperature. The resultant mixture was heated to reflux and vigorously stirred for 5 h. The reaction mixture was cooled to room temperature and concentrated under vacuum to 50 mL. The resulting dark precipitate was filtered and the filtrate was concentrated under vacuum. Silica gel column chromatography (acetone/dichloromethane, 1:9 and then 1:1, as eluent) of the residue afforded the *4i* stereoisomer of **3** (1.2 g, 0.86 mmol, 51%) as a white powder, m.p. 243 °C (dec.). − ^1H NMR

Table 5. Crystal data and refinement parameters for **2**·CH_3NH_3Pic and **2**·CsPic

	2·CH_3NH_3Pic	**2**·CsPic
Empirical formula	$C_{56}H_{44}O_{12}P{\cdot}C_6H_2N_3O_7{\cdot}CH_6N{\cdot}2C_2H_2Cl_4{\cdot}3H_2O$	$C_{56}H_{44}O_{12}P{\cdot}C_6H_2N_3O_7{\cdot}Cs{\cdot}3C_2H_2Cl_4$
Molecular mass	1672.61	1891.26
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a [Å]	20.904(6)	14.747(3)
b [Å]	20.971(3)	15.210(3)
c [Å]	17.274(3)	20.124(4)
α [°]	90	110.21(3)
β [°]	90	109.15(3)
γ [°]	90	94.42(3)
V [Å^3]	7573(3)	3908(1)
D_x [g cm^{-3}]	1.467	1.607
Z	4	2
F(000)	3416	1890
μ [mm^{-1}]	4.17	8.84
Crystal size [mm]	0.32 × 0.08 × 0.08	0.24 × 0.20 × 0.15
$2\theta_{max}$ [°]	95	135
Range of *hkl*	$-16 \le h \le 16$	$0 \le h \le 16$
	$0 \le k \le 20$	$-18 \le k \le 18$
	$0 \le l \le 16$	$-24 \le l \le 22$
No. of unique refl.	6575	14111
No. of observed refl. [$I \le 2\sigma(I)$]	3587	7348
No. of parameters	869	821
No. of restraints	272	77
R (*R* all data)	0.103 (0.159)	0.099 (0.148)
R_w $\{w = 1/[\sigma^2(F_o^2) + xP^2]$, $P = (F_o^2 + 2Fc^2)/3\}$	0.26	0.27
x	0.1839	0.1857
Goodness of fit	0.974	0.987
Flack parameter	0.09(6)	
Mean (Δ/σ)	0.017(1)	0.001(1)
Δρ(max/min) [e·Å^{-3}]	0.76/−0.53	1.05/−1.15

(499.83 MHz, 293 K, $CDCl_3$): δ = 2.71 (m, 8 H, CH_2CH_2Ph), 2.79 (m, 8 H, CH_2CH_2Ph), 4.83 (t, ^3J = 7.5 Hz, 4 H, C*H*), 6.98 (s, 4 H, calix-ArH), 7.16 (dd, 8 H, ^3J = 7.0, ^4J = 2.0 Hz, ArH), 7.30 (m, 12 H, ArH), 7.34 (s, 4 H, calix-ArH), 7.47 (m, 8 H, P-ArH), 7.60 (t, ^3J = 7.5 Hz, 4 H, P-ArH), 7.84 (dd, 8 H, ^3J = 7.5 Hz, $^3J_{PH}$ = 14.0 Hz, P-ArH). − ^{13}C NMR (50.32 MHz, 300 K, $CDCl_3$): δ = 32.59 (CH_2CH_2Ph), 33.75 (CH_2CH_2Ph), 34.95 (*C*H), 117.8 (calix-ArCH), 121.77 (calix-ArCH), 126.27 (ArCH), 126.54 (^1J = 205.5 Hz, P-ArC), 128.36 (^3J = 16.2 Hz, P-ArCH), 128.69 (ArCH), 128.76 (ArCH), 131.85 (^2J = 10.6 Hz, P-ArCH), 133.07 (P-ArCH), 134.42 (calix-ArCq), 140.83 (ArCq), 146.87 (^2J = 12.9 Hz, calix-ArCq). − ^{31}P NMR (81.02 MHz, 300 K, $CDCl_3$): δ = 7.73. − Electrospray MS: *m*/*z* = 1393.4 $[M + H]^+$, 1415.7 $[M + Na]^+$. − $C_{84}H_{68}O_{12}P_4{\cdot}2H_2O$: calcd. C 70.58, H 5.08, P 8.67; found C 70.38, H 5.04, P, 8.35. − The *N*-methylpyrrolidinium 1:1 complex of **3** was observed in the crude reaction mixture and had the following NMR spectroscopic data. ^{1}H NMR (499.83 MHz, 293 K, $CDCl_3$): δ = −0.5 (br. s, 3 H, NCH_3), 1.6 (br, 2 H, CH_2), 1.9 (br, 2 H, CH_2), 2.4 (br, 2 H, NCH_2), 2.9 (m, 8 H, CH_2CH_2Ph), 3.2 (br, 2 H, NCH_2), 3.5 (m, 8 H, CH_2 CH_2Ph), 4.7 (t, ^3J = 8.0 Hz, 4 H, C*H*), 6.75 (s, 4 H, calix-ArH), 7.1−7.3 (m, 28 H, P-ArH and ArH), 7.5 (m, 4 H, P-ArH), 7.4 (identified from the g-cosy spectrum, NH_3), 7.7 (m, 8 H, P-ArH), 9.15 (s, 4 H, calix-ArH); ^{31}P NMR (81.02 MHz, 300 K, $CDCl_3$): δ = 10.9. − The *3io* stereoisomer of **3** was obtained as the second isolated product from the column chromatography and recrystallized from a toluene/CH_2Cl_2 mixture (0.11 g, 0.08 mmol, 5%), m.p. 232 °C (dec.). − ^{1}H NMR (499.83 MHz, 293 K, $CDCl_3$): δ = 2.65−2.81 (m, 16 H, CH_2CH_2Ph), 4.81 (t, ^3J = 7.0 Hz, 1 H, C*H*), 4.84 (t, ^3J = 7.3 Hz, 2 H, C*H*), 5.09 (t, ^3J = 6.7 Hz, 1 H, C*H*), 6.45 (s, 2 H, calix-ArH), 6.46 (m, 2 H, P-ArH), 6.82 (m, 2 H, P-ArH), 6.96 (s, 2 H, calix-ArH), 7.12−7.32 (m, 20 H, ArH), 7.40 (s, 2 H, calix-ArH), 7.42 (s, 2 H, calix-ArH), 7.44 (m, 4 H, P-ArH), 7.45 (m, 1 H, P-ArH), 7.52 (m, 2 H, P-ArH), 7.58 (t, ^3J = 7.0 Hz, 2 H, P-ArH), 7.64 (t, ^3J = 6.9 Hz, 1 H, P-ArH), 7.80 (dd, 4 H, ^3J = 7.2 Hz, $^3J_{PH}$ = 14.2 Hz, P-ArH), 7.94 (dd, 2 H, ^3J = 7.3 Hz, $^3J_{PH}$ = 14.2 Hz, P-ArH). − ^{13}C NMR (125.68 MHz, 293 K, $CDCl_3$): δ = 32.51, 33.22, 33.84, 33.84, 33.92, 34.38 (CH_2CH_2Ph), 35.32, 35.46, 36.12 (*C*H), 117.66, 118.15 (calix-ArCH), 120.87 (^1J = 177.0 Hz, P-ArC), 122.41 (two types of carbon, calix-ArCH), 124.61 (two types of C, ^1J = 203.3 Hz, P-ArC), 126.31 (two types of C, ArCH), 126.39 (ArCH), 128.65 (^3J = 19.8 Hz, P-ArCH), 128.68 (^3J = 17.6 Hz, P-ArCH), 128.69 (^3J = 20.2 Hz, P-ArCH), 128.8−128.4 (overlapping signals, ArCH), 131.65 (^2J = 10.1 Hz, P-ArCH), 131.73 (^2J = 10.4 Hz, P-ArCH), 131.79 (^2J = 10.4 Hz, P-ArCH), 133.62, 133.72, 134.44 (P-ArCH), 133.96, 134.74, 134.93, 135.31 (calix-ArCq), 140.65, 140.72, 141.11 (ArCq), 146.20 (^2J = 9.8 Hz, calix-ArCq), 146.28 (two types of C, ^2J = 9.8 Hz, calix-ArCq), 147.70 (^2J = 9.8 Hz, calix-ArCq). − ^{31}P NMR (81.02 MHz, 300 K, $CDCl_3$): δ = 7.20, 9.70, 11.45. − Electrospray MS: *m*/*z* = 1393.3 $[M + H]^+$, 1415.6 $[M + Na]^+$, 1427.5 $[M + Cl]^-$.

Compound 3: This was prepared similarly, with use of 8 equiv. of triethylamine instead of *N*-methylpyrrolidine as base, to give the *4i* and *3io* isomers in 28.5% and 7% yields, respectively (see text). Reactions performed in the presence of 8 equiv. of base were run according to the general procedure described above, but the reagents were added to the octol solution in the sequence 1 equiv. of base (*N*-methylpyrrolidine or triethylamine), 4.2 equiv. of dichloro(phenyl)phosphane oxide, and − after 1 h at reflux temperature − 7 equiv. of base dissolved in toluene (yields are reported in Table 1). The addition of 8 equiv. of base all at once mainly resulted in non-isolable compounds and very low yields.

1,21,23,25-Tetramethyl-5,9,13,17-tetraphenyl-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo-[1,2-*d*:5,4-*d*′]bis[1,3,2]benzodioxaphosphocine 5,9,13,17-Tetraoxide (2): Compound **2** was obtained from resorc[4]arene **4a** and $PhP(O)Cl_2$ in the presence of 1 equiv. of *N*-methylpyrrolidine in toluene, according to the above procedure. Only the *4i* stereoisomer was isolated in 25% yield. The lower yield was attributable to the low solubility of **2** and the difficulties encountered in recovering the pure compound. ^{1}H NMR and MS data have been reported previously.[29]

X-ray Crystallographic Study: Crystals of the **2**·CsPic and **2**·CH_3NH_3Pic complexes of X-ray quality were obtained by slow concentration of a 1:1 solution of host and picrate salt guest in 1,1,2,2-tetrachloroethane. X-ray diffraction measurements were made at 293 K with a Huber four-circle diffractometer and Rigaku RU200 rotating anode generator with graphite-monochromatized Cu-K_α radiation (λ = 1.54178 Å). Table 5 provides a summary of the crystal data, data collection and refinement parameters for the [**2**·Cs][picrate] and [**2**·CH_3NH_3][picrate] complexes. The lattice parameters were refined using 30 reflections in the range 5° ≤ 2θ ≤ 40°. Intensities were measured with ω−θ scans. One standard reflection was checked every 50 reflections and no significant deviation was observed. The intensity data were corrected for Lorentz polarization. An empirical absorption correction (Ψ scans) was applied for the [**2**·Cs][picrate] structure. Both structures were solved by direct methods using the program SHELXS-86.[57] They were refined by full-matrix least squares on F^2 with anisotropic temperature factors for all non-hydrogen atoms with SHELXL-93.[58] Because of the low reflection to parameter ratios, restraints on similar bond lengths were applied. In each structure, one $C_2H_2Cl_4$ molecule was disordered. All the hydrogen atom positions were calculated; the hydrogen atoms of the water molecules were not included. The positions of the H atoms were refined with a common isotropic temperature factor. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-154493 (**2·CH_3NH_3Pic**) and -154494 (**2·CsPic**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The National Fund for Scientific Research, Belgium, is gratefully acknowledged for financial support. Thanks are due to Dr. B. Bibal for stimulating discussions and to Dr. A. Lesage for helpful contributions in NMR work.

[1] E. N. Tsvetkov, A. N. Bovin, V. Kh. Syundyukova, *Russ. Chem. Rev.* **1988**, *57*, 776−800.
[2] A.-M. Caminade, J.-P. Majoral, *Chem. Rev.* **1994**, *94*, 1183−1213.
[3] L. Van Oostenryck, B. Tinant, J.-P. Declercq, J.-P. Dutasta, P. Simon, *J. Incl. Phenom.* **1993**, *16*, 383−402.
[4] J.-P. Declercq, P. Delangle, J.-P. Dutasta, L. Van Oostenryck, P. Simon, B. Tinant, *J. Chem. Soc., Perkin Trans. 2* **1996**, 2471−2478.
[5] J. Mitjaville, A.-M. Caminade, R. Mathieu, J.-P. Majoral, *J. Am. Chem. Soc.* **1994**, *116*, 5007−5008.
[6] C. B. Allan, L. O. Spreer, *J. Org. Chem.* **1994**, *59*, 7695−7700.
[7] A.-M. Caminade, R. Kraemer, J.-P. Majoral, *New J. Chem.* **1997**, *21*, 627−632.
[8] P. Delangle, J.-P. Dutasta, L. Van Oostenryck, B. Tinant, J.-P. Declercq, *J. Org. Chem.* **1996**, *61*, 8904−8914.
[9] P. Delangle, J.-P. Dutasta, J.-P. Declercq, B. Tinant, *Chem. Eur. J.* **1998**, *4*, 100−106.

[10] D. J. Cram, J. M. Cram, *Container Molecules and their Guests*, Royal Society of Chemistry, Cambridge, **1994**.
[11] P. Timmerman, W. Verboom, D. N. Reinhoudt, *Tetrahedron* **1996**, *52*, 2663−2704.
[12] D. M. Rudkevich, J. Rebek, Jr., *Eur. J. Org. Chem.* **1999**, 1991−2005.
[13] I. Neda, T. Kaukorat, R. Schmutzler, *Main Group Chem. News* **1998**, *6*, 4−29.
[14] J. Gloede, *Phosphorus Sulfur Silicon* **1997**, *127*, 97−111.
[15] C. Wieser, C. B. Dieleman, D. Matt, *Coordination Chem. Rev.* **1997**, *165*, 93−161.
[16] W. Xu, J. J. Vittal, R. J. Puddephatt, *J. Am. Chem. Soc.* **1993**, *115*, 6456−6457.
[17] W. Xu, J. P. Rourke, J. J. Vittal, R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.* **1993**, 145−147.
[18] W. Xu, J. J. Vittal, R. J. Puddephatt, *J. Am. Chem. Soc.* **1995**, *117*, 8362−8371.
[19] W. Xu, J. P. Rourke, J. J. Vittal, R. J. Puddephatt, *Inorg. Chem.* **1995**, *34*, 323−329.
[20] W. Xu, J. J. Vittal, R. J. Puddephatt, *Inorg. Chem.* **1997**, *36*, 86−94.
[21] A. Vollbrecht, I. Neda, H. Thönnessen, P. G. Jones, R. K. Harris, L. A. Crowe, R. Schmutzler, *Chem. Ber./Recueil* **1997**, *130*, 1715−1720.
[22] V. I. Maslennikova, E. V. Panina, A. R. Bekker, L. K. Vasyanina, E. E. Nifant'ev, *Phosphorus Sulfur Silicon* **1996**, *113*, 219−223.
[23] E. E. Nifant'ev, V. I. Maslennikova, E. V. Panina, A. R. Bekker, L. K. Vasyanina, K. A. Lysenko, M. Y. Antipin, Y. T. Struchkov, *Mendeleev Commun.* **1995**, 131−133.
[24] T. Lipmann, E. Dalcanale, G. Mann, *Tetrahedron Lett.* **1994**, *35*, 1685−1688.
[25] T. Lipmann, H. Wilde, E. Dalcanale, L. Mavilla, G. Mann, U. Heyer, S. Spera, *J. Org. Chem.* **1995**, *60*, 235−242.
[26] E. Dalcanale, P. Jacopozzi, F. Ugozzoli, G. Mann, *Supramol. Chem.* **1998**, *9*, 305−316.
[27] P. Jacopozzi, E. Dalcanale, S. Spera, L. A. J. Chrisstoffels, D. N. Reinhoudt, T. Lippmann, G. Mann, *J. Chem. Soc., Perkin Trans. 2* **1998**, 671−677.
[28] J. M. J. Nuutinen, A. Irico, M. Vincenti, E. Dalcanale, J. M. H. Pakarinen, P. Vainiotalo, *J. Am. Chem. Soc.* **2000**, *120*, 10090−10100.
[29] P. Delangle, J.-P. Dutasta, *Tetrahedron Lett* **1995**, *36*, 9325−9328.
[30] L. M. Tunstad, J. A. Tucker, E. Dalcanale, J. Weiser, J. A. Bryant, J. C. Sherman, R. C. Helgeson, C. B. Knobler, D. J. Cram, *J. Org. Chem.* **1989**, *54*, 1305−1312.
[31] A. G. S. Högberg, *J. Org. Chem.* **1980**, *45*, 4498−4500.
[32] A. G. S. Högberg, *J. Am. Chem. Soc.* **1980**, *102*, 6046−6050.
[33] R. M. Ismail, *Z. Anorg. Chem.* **1970**, *372*, 252−262.
[34] The reaction was run as described in ref.[27], using 10 equiv. of *N*-methylpyrrolidine in acetone.
[35] K. Murayama, K. Aoki, *Chem. Commun.* **1997**, 119−120.
[36] W. Iwanek, R. Fröhlich, M. Urbaniak, C. Näther, J. Mattay, *Tetrahedron* **1998**, *54*, 14031−14040.
[37] T. Lippmann, H. Wilde, M. Pink, A. Schäfer, M. Hesse, G. Mann, *Ang. Chem. Int. Ed. Engl.* **1993**, *32*, 1195−1197.
[38] J. B. Ezell, W. R. Gilkerson, *J. Am. Chem. Soc.* **1966**, *88*, 3486−3490.
[39] B. Bibal, J.-P. Dutasta, unpublished results.
[40] F. Arnaud-Neu, S. Cremin, D. Cunningham, S. J. Harris, P. McArdle, M. A. McKervey, M. McManus, M.-J. Schwing-Weil, K. Ziat, *J. Incl. Phenom.* **1991**, *10*, 329−339.
[41] F. Arnaud-Neu, M.-J. Schwing-Weil, K. Ziat, S. Cremin, S. J. Harris, M. A. McKervey, *New J. Chem.* **1991**, *15*, 33−37.
[42] E. P. Kyba, R. C. Helgeson, K. Madan, G. W. Gokel, T. L. Tarnowski, S. S. Moore, D. J. Cram, *J. Am. Chem. Soc.* **1977**, *99*, 2564−2571.
[43] S. S. Moore, T. L. Tarnowski, M. Newcomb, D. J. Cram, *J. Am. Chem. Soc.* **1977**, *99*, 6398−6405.
[44] K. E. Koenig, G. M. Lein, P. Stuckler, T. Kaneda, D. J. Cram, *J. Am. Chem. Soc.* **1979**, *101*, 3553−3566.
[45] A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud-Neu, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. de Jong, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1995**, *117*, 2767−2777.
[46] A. Casnati, A. Pochini, R. Ungaro, C. Bocchi, F. Ugozzoli, R. J. M. Egberink, H. Stuijk, R. Lugtenberg, F. de Jong, D. N. Reinhoudt, *Chem. Eur. J.* **1996**, *2*, 436−445.
[47] E. T. Roach, P. R. Handy, A. I. Popov, *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 359−363.
[48] E. Mei, A. I. Popov, J. L. Dye, *J. Am. Chem. Soc.* **1977**, *99*, 6532−6536.
[49] E. Mei, J. L. Dye, A. I. Popov, *J. Am. Chem. Soc.* **1976**, *98*, 1619−1620.
[50] E. Mei, A. I. Popov, J. L. Dye, *J. Phys. Chem.* **1977**, *81*, 1677−1681.
[51] E. Kauffmann, J. L. Dye, J.-M. Lehn, A. I. Popov, *J. Am. Chem. Soc.* **1980**, *102*, 2274−2278.
[52] R. Assmus, V. Böhmer, J. M. Harrowfield, M. I. Ogden, W. R. Richmond, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1993**, 2427−2433.
[53] J. M. Harrowfield, M. I. Ogden, W. R. Richmond, A. H. White, *J. Chem. Soc., Chem. Commun.* **1991**, 1159−1161.
[54] L.-L. Soong, G. E. Leroi, A. I. Popov, *J. Incl. Phenom.* **1992**, *12*, 253−262.
[55] R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill, H. Rouquette, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1506−1509.
[56] O. Silberrad, H. A. Phillips, *J. Chem. Soc.* **1908**, *93*, 474−489.
[57] G. M. Sheldrick, *Crystallographic Computing 3* (Eds.: G. M. Sheldrick, C. Krüger, R. Goddard), Oxford University Press, **1985**, pp. 175−189.
[58] G. M. Sheldrick, *SHELXL93*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1993**.

Received March 9, 2001
[O01119]