Synthesis and Configurational Analysis of a Novel Class of Cavitands Containing Four Dioxaphosphocin Moieties†

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Synthesis, separation, and configurational analysis of diastereomeric cavitands having general structure **I** are described. The cavitands are obtained by incorporation of four phosphate groups on the *all-cis*-resorcin[4]arene. Four dioxaphosphocin rings with four stereogenic centers on the phosphorus(V) atoms are formed by bridging the eight phenolic functions. The reaction leads to all the six possible diastereoisomers having different orientations of the P=O groups either outward (o) or inward (i) with respect to the cavity. The separation of the different diastereoisomers of cavitands **3–12** was achieved by chromatographic methods and the configuration of each one elucidated with ^{1}H, ^{13}C, and ^{31}P NMR. Variation of the R^2 substituents on the phosphorus atoms was studied with the aim of a stereoselective formation of the iiii and iiio isomers which possess the best qualifications for multiple hydrogen-bonding interactions.

Introduction

The design of preorganized receptors capable of multiple hydrogen-bonding interactions[1] is highly pursued nowadays. Resorcin[4]arenes are convenient molecular platforms for the construction of cavitands.[2] They can be easily prepared in high yield by the acid-catalyzed reaction between resorcinol and either aliphatic or aromatic aldehydes.[3] The flexible macrocycles formed can be rigidified by reacting its four couples of adjacent phenolic oxygens with different bridging groups. In this way several cavitands have been synthesized, presenting rigid bowl-shaped cavities of different shapes and dimensions according to the bridging group employed. The bridging groups used so far are one-, two- or three-methylene units,[4] quinoxaline,[5] pyrazine,[5] silanes,[6] phenylphosphine,[7] aryl phosphites,[8] phenylphosphine oxide,[9] aryl phosphates,[10] and ethoxycarbonyl methine groups.[11] Only in a few cases have stereogenic centers like phosphorus(III),[7,8] phosphorus(V),[9,10] and asymmetric carbon[11] been introduced as bridging groups on cavitands.

The aim of the present work is preparation and conformational study of cavitands of general structure **I** (Chart 1) with four dioxaphosphocin moieties obtained by incorporation of four phosphate groups in resorcin[4]-arenes. The presence of four stereogenic centers in the upper rim gives rise to six possible diastereoisomers which have been found and isolated.

Results and Discussion

Synthesis and Separation. Resorcin[4]arenes 1 and 2 served as molecular platforms for the preparation of the cavitands reported here. *all-cis*-Tetramethylresorcin-[4]arene (1) was easily prepared from resorcinol and acetaldehyde under acidic conditions.[3b] 1 was converted to the tetrabromo derivative 2 using *N*-bromosuccinimide.[4] Cavitand 3 (R^1 = H, R^2 = OC_2H_5) was prepared in 12% yield by treatment of 1 with ethyl dichlorophosphate in dry acetone, using triethylamine as base (Scheme 1). The product was a diastereoisomeric mixture in which three of the six possible isomers were dominant. The majority of the reaction product consists of polymers owing to intermolecular connection of resorcin[4]arene

† Dedicated to Prof. D. J. Cram on occasion of his 75th birthday.

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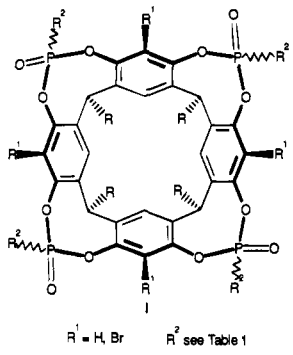
Chart 1



units. To reduce the extent of the intermolecular reaction, we used as bridging units aryl dichlorophosphates. Indeed 50–80% yields were reached in the case of cavitands **4–9** by reducing the oligomerization side reaction with the introduction of bulky aryl substituents on dichlorophosphates (Table 1). Analogous reaction of **2** with aryl dichlorophosphates led to the isolation of cavitands **10–12** (Scheme 1) in good yields. The presence of bromo substituents in the 2 position of the resorcinol moieties did not influence the outcome of the reaction.

HPLC analyses of the crude products allowed in each case for compounds **4–12** the determination of the number of the stereoisomers present (Table 2). The isolation of the different isomers was achieved either by column chromatography or by thick-layer chromatography (see Experimental Section).

Configurational Analysis. The six possible diastereoisomers in compounds of general structure I are shown in Figure 1. The various isomers have different orientations of the P=O groups, either inward (i) or outward (o) with respect to the cavity. The identification of these isomers was done by combination of ^{1}H, ^{13}C, and ^{31}P NMR. Owing to the symmetry of the different isomers, the signal patterns given in Table 3 are to be expected. The number of resonances of the phosphorus atoms and R^1 protons reflects the different symmetry of the six diastereoisomers. The combination of the two allowed the univocal identification of isomers **c** (iioo; C_s) and **d** (ioio; C_{2v}). To distinguish further between the two pairs of remaining diastereoisomers (**a/f** and **b/e**), chemical shift differences must be considered. As shown by Cram and co-workers on other bridged cavitands,[4,6b] the protons directed inward with respect to the cavity experience a strong high-field shift. Also in this case the ^{1}H NMR signals of the aryl hydrogens of R^2 in compounds **4–9** are shifted upfield when the substituents are directed inward with respect to the cavity. Thus comparison of the R^2 protons chemical shifts of isomers **b** and **e** leads to the attribution of the iiio configuration to the isomer **b** (predominantly low-field R^2 signals) and the iooo configuration to the isomer **e** (predominantly high-field R^2 signals).

In the absence of a crystal structure of any of the possible isomers,[12] useful information with regard to the configuration of these stereoisomers in solution has been obtained by comparison of the ^{13}C-NMR relaxation parameters of **4f** (oooo) and **4d** (ioio). The last one presents remarkable differences between the mobilities of the two R^2 groups pointing inward and the two pointing outward, which can be correlated to the proposed configuration. The R^2 groups pointing inward experience a reduced mobility due to the space constraint imposed by the cavity.

The ^{13}C-NMR spectrum of the C_{4v} symmetry isomer **4f** in $CDCl_3$ at 45 °C presents four aromatic methine signals (Table 4, Figure 2), together with one signal for the aliphatic methine and two for the methyl groups. In the corresponding spectrum of the C_{2v} symmetry isomer **4d**, all the aromatic methine signals are split with the exception of those belonging to the resorcin[4]arene (Table 4). The quaternary carbons are readily recognizable as they are suppressed in DEPT experiments, but a careful assignment of these signals has not been attempted.

^{13}C-NMR Relaxation Times. Under extreme narrowing condition ($\omega_o\tau_C \ll 1$), the ^{13}C relaxation times (T_1) for the protonated carbons can be expressed in the following way:[13]

$$\frac{1}{T_1} = N\frac{\gamma_H^2\gamma_C^2\hbar^2}{R_{CH}^6}\tau_C \qquad (1)$$

where N is the the number of attached protons, γ_H and γ_C are respectively the proton and carbon magnetogyric ratios, R_{CH} is the C–H bond distance, and τ_C is the correlation time for the C–H vector. Since the dominant dipolar relaxation for the protonated carbons involves only the directly attached protons, the fixed value of 1.084 Å can be assumed for R_{CH}. Equation 1 is valid for isotropic molecular motions; in our case this assumption is unlikely to be true. Therefore the τ_C values obtained through eq 1 should be considered "effective" correlation times and they have only a qualitative value.

For the isomer **4d** the τ_C values reported in Table 4 for the methine and methyl carbons ($CDCl_3$, 45 °C) are sensibly different in the same chemical structure, and they can be separated in three narrow ranges (the methyl groups require a further discussion): $(1.1–1.2) \times 10^{-11}$ s; $(3.8–4.0) \times 10^{-11}$ s; $(7.5–8.5) \times 10^{-11}$ s. The signals at 30.3 and 30.1 ppm are assigned to the methine carbons bonded to the methyl groups, and their correlation time is included in the third, longest, range, together with the only two not split aromatic methine carbons C_a and C_b. Therefore, this can be considered the effective correlation time for the overall tumbling of the whole structure, sufficiently fast to guarantee the extreme narrowing condition, despite the quite high molecular weight. Longer T_1 values and faster motions characterize the remaining aromatic methine carbons: that is, the additional rotational motion of the R^2 groups adds to the overall isotropic tumbling for these carbons.

The rotational contribution is not equal for all four R^2 groups: on the basis of the τ_C values, it is evident that two of them are more freely rotating than the remaining two, these last ones being the more sterically hindered inward ones. The aromatic signals at 130.3 and 119.5 ppm are therefore assigned to the C_c and C_d carbons on the pointing outward R^2 groups and those at 130.6 and 119.2 ppm to C_c and C_d carbons on the pointing inward

(12) Suitable X-ray crystals of several isomers of **4** and **6** were grown, but any attempt to solve the crystal structures failed because of the low number of observed reflections at room temperature. In particular an unusual decrease of the diffracted intensities was observed even at intermediate values of sin θ/λ, probably due to severe static disorder which affects the conformationally mobile R^2 groups of the cavitands in the solid state.

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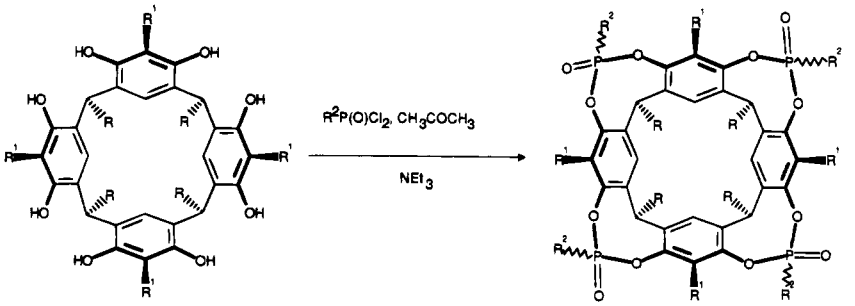
Scheme 1



1 R^1=H; R=CH_3
2 R^1=Br; R=CH_3

3-12 R^2 see Table 1

Table 1. Isomer Distribution of Cavitands 3–12, Obtained by HPLC Analyses

	R^2	R^1	a iiii	b iiio	c iioo	d ioio	e iooo	f oooo	overall isolated yield, %
3	ethoxy	H			33[a]	25[a]	42[a]		12
4	4-methylphenoxy	H	<1	17	18	18	38	8	80
5	4-*tert*-butylphenoxy	H		14	39	12	32	3	75
6	4-chlorophenoxy	H		22	27	18	33		80
7	2-phenylphenoxy	H	10	34	26	17	13		50
8	2,6-diisopropyl-phenoxy	H		52	22	13	13		55
9	2,4,6-trimethyl-phenoxy	H		50	20	18	12		58
10	4-methylphenoxy	Br		22	20	21	34	3	70
11	4-*tert*-butylphenoxy	Br		30	27	16	27		68
12	4-chlorophenoxy	Br		33	28	14	25		65

[a] Obtained by column chromatography separation.

Table 2. HPLC Retention Times and Eluants of Compounds 4–12

compound eluant	iiii t_R [min]	iiio t_R [min]	iioo t_R [min]	ioio t_R [min]	iooo t_R [min]	oooo t_R [min]
4 6/4 $CHCl_3$/*n*-hexane		8.31	8.31	5.84	13.99	29.48
5 6/4 $CHCl_3$/*n*-heptane		6.99	5.86	3.70	8.86	11.90
6 4/1 $CHCl_3$/*n*-hexane		5.95	4.26	3.13	6.76	
7 4/1 $CHCl_3$/*n*-hexane	12.39	9.85	8.64	6.38	8.64	
8 1/1 $CHCl_3$/*n*-hexane		8.59	4.96	3.19	7.57	
9 6/4 $CHCl_3$/*n*-hexane		10.98	8.58	5.36	9.17	
10 7/3 $CHCl_3$/*n*-hexane		7.05	7.05	4.62	4.62	25.66
11 7/3 $CHCl_3$/*n*-hexane		3.84	4.27	3.15	6.97	
12 7/3 $CHCl_3$/*n*-hexane		5.22	4.40	3.32	8.12	

ones. In the same way, also the methyl signals at 20.5 and 20.7 ppm are assigned to the methyl groups on the R^2 substituents. The other two at 17.0 and 16.6 ppm, more constrained according to the T_1 values, are assigned to the methyl groups bound to the aliphatic methines. It is not surprising that the T_1 values of the methyl groups are usually longer than those of the other carbons of the structure, as they benefit of a much higher rotational freedom.[14]

On the basis of the results of the T_1 analysis of **4d**, the univocal identification of the configuration of **4f** is possible. The R^2 methines in **4f** have values of T_1 equal to 1.1 and 1.0 s (Table 4), close to those of C_c and C_d of the R^2 substituents of **4d** pointing inward. Therefore the oooo configuration is attributed to the **4f** isomer.

The ^{31}P resonances in compounds **4–6** and **10–12** present diagnostic chemical shifts depending on the relative orientation of the R^2 substituents. Using as reference the ^{31}P resonance of the C_{4v} symmetry **4f** isomer, the ^{31}P resonances of the various isomers have been correlated with the inward–outward orientation (Table 5): phosphorus atoms bearing R^2 groups directed inward have resonances at higher field with respect to those with R^2 directed outward. In this way the **a, b, e,** and **f** diastereoisomers can be easily distinguished. In sterically overcrowded compounds **7**, **8**, and **9**, however, this attribution is not so clear, because of the small differences among the ^{31}P chemical shifts.

^{1}H NMR Relaxation Times. This investigation has been undertaken to verify the assumption that, in cavitands, the inward-facing protons experience an upfield shift with respect to the outward ones.

Also in the case of proton nuclei the dipole–dipole is the major relaxation mechanism. The theory governing the relationship between correlation times and T_1 (^{1}H) relaxation times is well known[15] and will not be reproduced here. The main difference with respect to the ^{13}C relaxation theory is that the calculation of the correlation times is limited to those systems where the H–H distances are fixed and well defined. In this contest, it is necessary to define which neighbor protons are more relevant in the dipolar relaxation mechanism and to know the corresponding interproton distances.

The proton relaxation times for the isomer **4d** obtained in $CDCl_3$ at 45 °C are reported in Table 6. Significant differences are observed among the T_1 values of the aromatic protons. The ^{1}H spectrum exhibits four signals in the low-field region, with intensity ratio of 4:8:8:4. Following the same approach used for the assignment of the carbon signals, the singlet at 7.13 ppm (which changes into an AB system in DMSO-d_6), having longer T_1 value and intensity 8, is assigned to the protons on the pointing outward R^2 groups, while the upfield AB system centered at 6.80 ppm (δ_A = 6.83 ppm and δ_B = 6.77 ppm) is attributed to the pointing inward ones. Between the two signals with intensity 4, the more slowly relaxing one at 6.62 ppm belongs to H_a, while the other at 7.44 ppm to H_b. The remarkable difference in the relaxation times of H_a and H_b is due to the through-space interaction of H_b with the protons of the methyl groups

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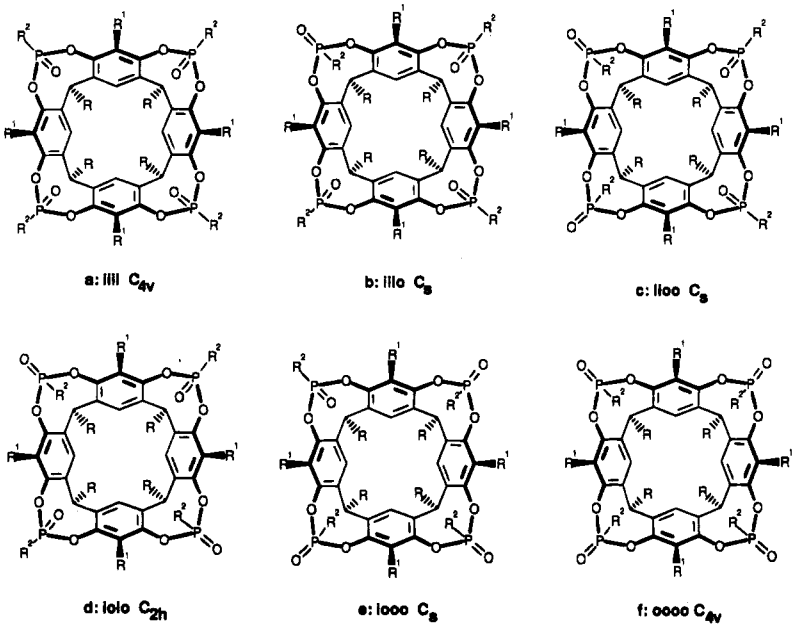

Figure 1. Top view of the six diastereoisomers of structure **I**.

Table 3. Expected NMR Signal Patterns of the Different Diastereoisomers of Compounds 3–9

isomer/symmetry	no. of P signals	no. of R′ = H signals
a (iiii)/C_{4v}	1	1
b (iiio)/C_s	3 (2:1:1)	2 (1:1)
c (iioo)/C_s	2 (1:1)	3 (2:1:1)
d (ioio)/C_{2v}	2 (1:1)	1
e (iooo)/C_s	3 (2:1:1)	2 (1:1)
f (oooo)/C_{4v}	1	1

Table 4. ^{13}C Chemical Shifts, Relaxation Times T_1, and Correlation Times τ_C for Isomers 4d and 4f in $CDCl_3$ at 45 °C

4d				4f			
carbon	δ (ppm)	T_1 (s)	τ_C (s)	carbon	δ (ppm)	T_1 (s)	τ_C (s)
quat	146.6	3.8		quat	146.3	3.2	
quat	146.5	3.8		quat	146.2	3.2	
quat	146.0	5.0		quat	135.6	2.3	
quat	135.6	3.7		quat	135.3	2.3	
quat	135.5	4.7					
quat	134.2	9.1					
C_c in	130.6	1.2	3.8×10^{-11}	C_c in	130.3	1.1	4.3×10^{-11}
C_c out	130.3	3.9	1.1×10^{-11}				
C_b	121.6	0.6	7.5×10^{-11}	C_b	121.7	0.3	1.1×10^{-10}
C_d out	119.5	4.0	1.1×10^{-11}				
C_d in	119.2	1.1	4.0×10^{-11}	C_d in	119.1	1.0	4.4×10^{-11}
C_a	116.9	0.5	8.2×10^{-11}	C_a	115.7	0.4	1.1×10^{-10}
CH	30.3	0.6	7.5×10^{-11}	CH	30.2	0.3	1.5×10^{-10}
CH	30.1	0.6					
CH_3-Ar out	20.7	2.6	5.7×10^{-11}	CH_3-Ar	20.4	2.2	7.0×10^{-12}
CH_3-Ar in	20.5	2.4	6.2×10^{-11}				
CH_3-CH	17.0	0.7	2.2×10^{-11}	CH_3-CH	16.4	0.3	4.0×10^{-11}
CH_3-CH	16.6	0.6					

of the macrocycle, also evidenced by an intense NOE cross-peak in the NOESY spectra.

Stereoselectivity of Cavitand Formation. The theoretical statistical distribution expected for the various isomers is: **a:b:c:d:e:f** = 1:4:4:2:4:1. For cavitands **4–6**, a slight preference for the outward orientation of at least three of the P=O moieties is observed (Table 1), in spite of the higher steric hindrance experienced by the R^2 groups placed inside the bowl. The presence of bromo substituents in R^1 position (cavitands **10–12**) does not significantly change the distribution. In all these cavitands, the iiii isomer is absent, indicating a strong preference of the molecules to fill the cavity with at least one R^2 group. The oxygen atom connecting the phosporus to the aryl group allows the R^2 groups to assume an upward orientation with respect to the bowl. The observed isomer distribution indicates that up to three R^2 groups can be easily accommodated above the bowl.

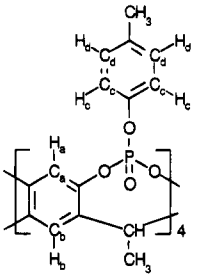

Figure 2. Atomic labeling scheme of diastereoisomers **4d** and **4f**.

Isomers iiii and iiio possess the best qualifications as receptor molecules via multiple hydrogen bonding interactions (vide infra), since they have respectively four and three P=O groups converging toward the center of the bowl. These isomers are formed in the bridging reaction with phosphate groups only in minor amounts (iiio) or they are absent (iiii). In order to change the isomer distribution in favor of iiii and iiio isomers, substituents in the ortho position of the R^2 moieties were introduced. The increased bulkiness of the R^2 groups in cavitands **7**, **8**, and **9** hinders the orientation of the P=O groups outward during the bridging reaction, shifting the isomer distribution toward the dominantly inward ones (Table 1). However only in the case of **7**, bearing bulky phenylphenoxy substituents, has the iiii isomer been obtained. For **8** and **9**, the diastereoselectivity of the reaction toward the formation of the iiio isomer is acceptable: in both cases the iiio isomer constitutes at least 50% of the isomeric mixture.

Complexation Properties. This novel family of diastereomeric cavitands is well suited for the evaluation of multiple hydrogen-bonding interactions in molecular recognition phenomena. Cyclohexylammonium chloride

Table 5. ^{31}P Chemical Shifts of Compounds 4, 5, 6, 10, 11, 12

	compound					
isomer	4	5	6	10	11	12
b (iiio)	−25.75 (1)	−25.56 (1)	−26.47 (1)	−25.41 (1)	−25.86 (1)	−26.26 (1)
	−18.72 (1)	−19.17 (3)	−18.65 (1)	−20.55 (1)	−20.26 (1)	−20.58 (1)
	−18.56 (2)		−18.48 (2)	−19.60 (2)	−19.90 (2)	−19.74 (2)
c (iioo)	−25.77 (2)	−26.21 (2)	−26.64 (2)	−25.57 (2)	−26.25 (2)	−26.51 (2)
	−17.57 (2)	−18.41 (2)	−17.90 (2)	−19.31 (2)	−19.58 (2)	−19.39 (2)
d (ioio)	−25.87 (2)	−25.72 (2)	−26.58 (2)	−25.68 (2)	−26.01 (2)	−26.15 (2)
	−17.79 (2)	−18.12 (2)	−17.39 (2)	−19.49 (2)	−19.67 (2)	−19.66 (2)
e (iooo)	−26.02 (1)	−26.51 (1)	−26.86 (1)	−26.71 (1)	−26.76 (1)	−27.24 (2)
	−25.45 (2)	−26.20 (2)	−26.54 (2)	−24.89 (2)	−25.85 (2)	−25.38 (1)
	−16.39 (1)	−18.01 (1)	−16.35 (1)	−17.16 (1)	−19.11 (1)	−16.40 (1)
f (oooo)	−25.62					

Table 6. ^{1}H NMR Chemical Shifts and T_1 Values for 4d in $CDCl_3$ at 45 °C

proton	δ (ppm)	T_1 (s)
H_b	7.44	0.16
$H_{c,d}$ out	7.13	2.91
$H_{c,d}$ in	6.83	1.10
$H_{c,d}$ in	6.77	0.63
H_a	6.62	2.10
CH	4.93	0.72
CH_3-Ar out	2.34	1.25
CH_3-Ar in	2.11	0.78
CH_3-CH	1.87	0.15

was chosen as guest for preliminary complexation experiments in solution, since it has three hydrogens in a tripodal arrangment available for a three-point interaction with the P=O groups.[16] As already reported,[10] the ^{31}P-NMR titration performed on cavitands **4b,c,d** in $CDCl_3$ solution led to significant complexation only in case of **4b** (K_a = 1370 M^{-1} for the 1:1 complex between **4b** and cyclohexylammonium chloride). In the other two cases, under the same conditions, either complexation was absent (**4d**) or negligible (**4c**). Gas phase complexation experiments are in progress to study the potential cooperative effect of multiple hydrogen-bonding patterns on molecular recognition phenomena, in the absence of interfering solvent effects.[17]

Experimental Section

General Methods. ACS grade reagents were used without further purification. Dry acetone was distilled from phosphorus pentoxide and stored over 3 Å molecular sieves. Aryl phosphate dichlorides were synthesized by conventional methods[18,19] and distilled before use. Analytical TLC was performed on Merck silica gel 60 F_{254} precoated plates. Preparative TLC employed glass-backed silica gel plates with a concentration zone (Merck, 60 F_{254}). Column chromatography was performed using silica gel (Merck, 70-230 mesh ASTM). Analyses of isomer distribution were carried out with an HPLC apparatus with UV-detection at 254 nm on a 250 × 4 mm LiChrospher Si 60 column. ^{1}H-NMR spectra were recorded at 400, 300, and 200 MHz. ^{31}P spectra were recorded at 161.9 and 81.0 MHz. Chemical shifts are given in part per million (δ_{TMS} = 0) using as internal reference the residual solvent resonances of deuteriated solvents (7.25 ppm for chloroform; 2.49 ppm for DMSO). ^{31}P-NMR chemical shifts were measured relative to H_3PO_4 (85%) as the external standard. ^{13}C- and ^{1}H-NMR relaxation experiments were performed respectively at 75.5 and 300 MHz. Spectra were recorded in $CDCl_3$ at 45 °C and DMSO-d_6 at 45 and 100 °C on sealed NMR tubes containing about 15 mg of sample dissolved in 0.6 mL of degassed deuteriated solvent. ^{13}C relaxation time measurements were carried out using the standard inversion−recovery technique with proton decoupling during acquisition. Six τ values were utilized, ranging from 0.1 to 10 s and 2048 scans for each τ value. The relaxation delay was 10 s. ^{1}H relaxation time measurements were carried out with the standard inversion−recovery pulse sequence. Twelve τ values were used, ranging from 0.05 to 10 s with a relaxation delay of 10 s. NOESY spectra were acquired in the phase-sensitive mode in both solvents. Mixing times were in the range of 0.2−0.8 s. Other parameters were sw = 2300 Hz, 256 increments, 32 scans for each increment, and a relaxation delay of 1.5 s. IR spectra were recorded with a FTIR instrument. Mass spectra were recorded on a single-stage quadrupole mass spectrometer using the DCI technique. Elemental analyses were performed by the Central service of Leipzig University.

Resorcin[4]arenes **1** and **2** were obtained following published procedures.[3b,4]

1,21,23,25-Tetramethyl-5,9,13,17-tetraethoxy-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]dioxaphosphocino-[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]benzodioxaphosphocin 3. To a stirred solution of 12.5 mmol of alkyl phosphate dichloride in 150 mL of dry acetone was added triethylamine (25 mmol) under nitrogen. To this solution was added 2.5 mmol of **1** dissolved in 80 mL of dry acetone over 10 h. After the solution was stirred for 10 h at room temperature, the solid triethylammonium chloride formed was filtered off and washed with 50 mL of acetone. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel with 20/1 chloroform/methanol as eluant to give three isomeric products in 12% overall yield: **3e (isomer iooo)** as white solid, mp > 360 °C; TLC R_f 0.52 plus another spot having R_f 0.41. This second spot turned out to be a mixture of two compounds by TLC (CH_2Cl_2/acetone 1/1), which were separated by silica gel column chromatography with the same eluant to give **3c (isomer iioo)** [white solid, mp > 360 °C; TLC R_f 0.65] and **3d (isomer ioio)** [white solid, mp > 360 °C; TLC R_f 0.32].

3c: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.75 (t, 6H), 1.48 (t, 6H), 1.82 (d, 6H), 1.86 (d, 6H), 4.03 (m, 4H), 4.42 (m, 4H), 4.86 (q, 4H), 6.69 (s, 1H), 6.73 (s, 2H), 6.82 (s, 1H), 7.40 (s, 4H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −14.83 (2P), −21.21 (2P); DCI MS *m/z* 904 (M^-, 100); IR (KBr pellet) br 1300 cm^{-1} ν(P=O). Anal. Calcd for $C_{40}H_{44}O_{16}P_4$: C, 53.11; H, 4.90; O, 28.30. Found: C, 53.47; H, 5.07; O, 28.65.

3d: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.64 (t, 6H), 1.50 (t, 6H), 1.82 (d, 6H), 1.86 (d, 6H), 3.97 (m, 4H), 4.44 (m, 4H), 4.86 (m, 4H), 6.74 (s, 4H), 7.38 (s, 4H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −13.37 (2P), −18.57 (2P); DCI MS *m/z* 904 (M^-, 100); IR (KBr pellet) br 1290 cm^{-1} ν(P=O). Anal. Calcd for $C_{40}H_{44}O_{16}P_4$: C, 53.11; H, 4.90; O, 28.30. Found: C, 53.35; H, 4.98; O, 28.50.

3e: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.79 (t, 6H), 0.98 (t, 3H), 1.49 (t, 3H), 1.85 (m, 12H), 4.00 (m, 4H), 4.44 (m, 2H), 4.86 (m, 4H), 6.68 (s, 2H), 6.71 (s, 2H), 7.43 (s, 2H), 7.44 (s, 2H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −13.28 (1P), −18.56 (2P), −19.01 (1P); DCI MS *m/z* 904 (M^-, 100); IR (KBr pellet) br

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1290 cm^{-1} ν(P=O). Anal. Calcd for $C_{40}H_{44}O_{16}P_4$: C, 53.11; H, 4.90; O, 28.30. Found: C, 53.33; H, 4.81; O, 28.55.

General Procedure for Synthesis of Aryl Phosphate Substituted Cavitands. To a stirred solution of **1** (2.9 mmol) and triethylamine (29 mmol) were added 150 mL of dry acetone and aryl phosphate dichloride (14.4 mmol) in dry acetone (50 mL) dropwise over 1 h. The reaction mixture was stirred for 5 h at room temperature. The solid triethylammonium chloride formed was filtered off and washed with 50 mL of acetone. The solvent was evaporated and the residue purified by column chromatography.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(4′-methylphenoxy)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]-benzodioxaphosphocin (4). The crude of the reaction was purified by column chromatography on silica gel with 40/1 CH_2Cl_2/acetone as eluant to give four fractions in 80% overall yield: **4d (isomer ioio),** white solid, mp > 360 °C, TLC R_f 0.65; **4b** + **4c**, TLC R_f 0.52; **4e (isomer iooo)**, white solid, mp > 360 °C, TLC R_f 0.32; and **4f (isomer oooo)**, white solid, mp > 360 °C, TLC R_f 0.23. **4b** and **4c** were separated (column chromatography; silica gel with 20/1 $CHCl_3$/acetone as eluant) to give **4c (isomer iioo)**, white solid, mp > 360 °C, TLC R_f 0.73; and **4b (isomer iiio),** white solid, mp > 360 °C, TLC R_f 0.43.

4b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.82 (d, 6H, J = 7.4 Hz), 1.84 (d, 6H, J = 7.4 Hz), 2.17 (s, 3H), 2.33 (s, 6H), 2.37 (s, 3H), 4.85 (q, 2H, J = 7.4 Hz), 4.90 (q, 1H, J = 7.4 Hz), 4.96 (q, 1H, J = 7.4 Hz), 6.57 (s, 2H), 6.86 (d, 2H), 6.88 (s, 2H), 6.97 (d, 2H), 7.13 (d, 4H), 7.16 (d, 4H), 7.17 (d, 2H), 7.23 (d, 2H), 7.37 (s, 2H), 7.38 (s, 2H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −18.56 (2P), −18.72 (1P), −25.75 (1P); DCI MS *m/z* 1153 (M^-, 100); FTIR (KBr pellet) 1299 cm^{-1}, 1313 ν(P=O). Anal. Calcd for $C_{60}H_{52}O_{16}P_4$: C, 62.50; H, 4.55, O; 22.02. Found: C, 62.37; H, 4.66; O; 22.40.

4c: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86 (d, 6H, J = 7.2 Hz), 1.87 (d, 6H, J = 7.2 Hz), 1.99 (s, 6H), 2.34 (s, 6H), 4.91 (m, 4H), 6.50 (s, 2H), 6.56 (s, 1H), 6.66 (d, 4H), 6.70 (d, 4H), 6.96 (s, 1H), 7.15 (d, 4H), 7.18 (d, 4H), 7.48 (s, 3H), 7.50 (s, 1H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −17.57 (2P), −25.77 (2P); DCI MS *m/z* 1153 (M^-, 100); FTIR (KBr pellet) 1299 cm^{-1}, 1313 ν(P=O). Anal. Calcd for $C_{60}H_{52}O_{16}P_4$: C, 62.50; H, 4.55; O, 22.02. Found: C, 62.82; H, 4.85, O; 22.39.

4d: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (d, 6H, J = 7.3 Hz), 1.87 (d, 6H, J = 7.3 Hz), 2.10 (s, 6H), 2.33 (s, 6H), 4.84 (q, 2H, J = 7.3 Hz), 4.97 (q, 2H, J = 7.3 Hz), 6.57 (s, 4H), 6.75 (d, 4H), 6.81 (d, 4H), 7.11 (s, 8H), 7.41 (s, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −17.79 (2P), −25.87 (2P); DCI MS *m/z* 1153 (M^-, 100); FTIR (KBr pellet) 1291 cm^{-1}, 1313 ν(P=O). Anal. Calcd for $C_{60}H_{52}O_{16}P_4$: C, 62.50; H, 4.55; O, 22.02. Found: C, 62.25; H, 4.72; O, 22.41.

4e: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.78 (s, 3H), 1.89 (m, 12H), 2.16 (s, 6H), 2.38 (s, 3H), 4.96 (m, 4H), 5.95 (d, 2H), 6.17 (d, 2H), 6.61 (s, 2H), 6.66 (s, 2H), 6.81 (d, 4H), 6.89 (d, 4H), 7.19 (d, 2H), 7.21 (d, 2H), 7.46 (bs, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −16.39 (1P), −25.45 (2P), −26.02 (1P); DCI MS *m/z* 1153 (M^-, 100); FTIR (KBr pellet) 1291 cm^{-1}, 1313 ν(P=O). Anal. Calcd for $C_{60}H_{52}O_{16}P_4$: C, 62.50; H, 4.55; O, 22.02. Found: C, 62.76; H, 4.79; O, 22.35.

4f: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.91 (d, 12H), 2.01 (s, 12H), 5.02 (q, 4H), 6.41 (d, 8H), 6.62 (s, 4H), 6.66 (d, 8H), 7.47 (s, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −25.62 (4P); DCI MS *m/z* 1153 (M^-, 100); FTIR (KBr pellet) 1301 cm^{-1}, 1322 ν(P=O). Anal. Calcd for $C_{60}H_{52}O_{16}P_4$: C, 62.50; H, 4.55; O, 22.02. Found: C, 62.42; H, 4.58, O, 22.37.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(4′-*tert*-butylphenoxy)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′] benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]benzodioxaphosphocin (5). The crude of the reaction was purified by column chromatography on silica gel with 40/1 CH_2Cl_2/acetone as eluant to give a mixture of **5b** and **5d**, TLC R_f 0.68 and 0.65; **5c (isomer iioo)**, white solid, mp > 360 °C, TLC R_f 0.47; and **5e (isomer iooo)**, white solid, mp > 360 °C, TLC R_f 0.30. **5b** and **5d** were separated by column chromatography with $CHCl_3$ as eluant; **5d (isomer ioio)**, white solid, mp > 360 °C, TLC R_f 0.58; **5b (isomer iiio)**, white solid, mp > 360 °C, TLC R_f 0.18. Overall yield of the four isomers: 75%.

5b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (s, 9H), 1.31 (s, 18H), 1.32 (s, 9H), 1.88 (m, 12H), 4.91 (m, 3H), 4.99 (q, 1H), 6.66 (s, 2H), 6.89 (s, 2H), 7.24 (m, 10H), 7.38 (m, 10H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −19.17 (3P), −25.56 (1P); DCI MS *m/z* 1320 (M^-, 100); IR (KBr pellet) br 1320 cm^{-1} ν(P=O). Anal. Calcd for $C_{72}H_{76}O_{16}P_4$: C, 65.45; H, 5.80; O, 19.37. Found: C, 65.71; H, 5.87; O, 19.47.

5c: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08 (s, 18H), 1.32 (s, 18H), 1.87 (d, 6H, J = 7.2 Hz), 1.88 (d, 6H, J = 7.2 Hz), 4.96 (m, 4H, J = 7.2 Hz), 6.52 (s, 2H), 6.71 (s, 1H), 6.83 (d, 4H), 6.93 (s, 1H), 7.02 (d, 4H), 7.22 (d, 4H), 7.37 (d, 4H), 7.43 (bs, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −18.41 (2P), −26.21 (2P); DCI MS *m/z* 1320 (M^-, 100); IR (KBr pellet) br 1310 cm^{-1} ν(P=O). Anal. Calcd for $C_{72}H_{76}O_{16}P_4$: C, 65.45; H, 5.80; O, 19.37. Found: C, 65.84; H, 5.99; O, 19.37.

5d: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.09 (s, 18H), 1.29 (s, 18H), 1.85 (d, 6H), 1.88 (d, 6H), 4.89 (q, 2H), 4.99 (q, 2H), 6.65 (s, 4H), 6.86 (d, 4H), 7.08 (d, 4H), 7.15 (d, 4H), 7.32 (d, 4H), 7.43 (s, 4H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −18.12 (2P), −25.72 (2P); DCI MS *m/z* 1320 (M^-, 100); IR (KBr pellet) 1290 cm^{-1}, 1310 ν(P=O). Anal. Calcd for $C_{72}H_{76}O_{16}P_4$: C, 65.45; H, 5.80; O, 19.37. Found: C, 65,83; H, 5.70; O, 19.21.

5e: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (s, 9H), 1.13 (s, 18H), 1.31 (s, 9H), 1.91 (m, 12H), 4.92 (q, 1H), 5.01 (m, 3H), 6.54 (s, 2H), 6.57 (m, 4H), 6.66 (s, 2H), 7.01 (d, 4H), 7.17 (d, 4H), 7.21 (d, 2H), 7.36 (d, 2H), 7.50 (bs, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −18.01 (1P), −26.20 (2P), −26.51 (1P); DCI MS *m/z* 1320 (M^-, 100); IR (KBr pellet) 1290 cm^{-1}, 1310 ν(P=O). Anal. Calcd for $C_{72}H_{76}O_{16}P_4$: C, 65.45; H, 5.80; O, 19.37. Found: C, 65.84; H, 6.20; O, 19.13.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(4′-chlorophenoxy)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]-benzodioxaphosphocin (6). The crude of the reaction was purified by column chromatography on silica gel with 30/1 CH_2Cl_2/acetone as eluant to give **6d (isomer ioio)**, white solid, mp > 360 °C, TLC R_f 0.70; **6b (isomer iiio)**, white solid, mp > 360 °C, TLC R_f 0.61; **6c (isomer iioo)**, white solid, mp > 360 °C, TLC R_f 0.52; and **6e (isomer iooo)**, white solid, mp > 360 °C, TLC R_f 0.35. Overall yield of the four isomers: 80%.

6b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86 (m, 12H), 4.96 (m, 4H), 6.53 (s, 2H), 6.86 (s, 2H), 6.88 (d, 2H), 7.17 (d, 2H), 7.24 (d, 4H), 7.31 (d, 2H), 7.35 (d, 4H),7.42 (d, 2H), 7.45 (s, 4H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −18.48 (2P), −18.65 (1P), −26.47 (1P); DCI MS *m/z* 1234 (M^-, 100); IR (KBr pellet) br 1300 cm^{-1} ν(P=O). Anal. Calcd for $C_{56}H_{40}Cl_4O_{16}P_4$: C, 54.48; H, 3.26; Cl, 11.49. Found: C, 54.17; H, 3.55; Cl, 11.62.

6c: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.81 (d, 12H), 4.85 (m, 4H), 6.39 (s, 2H), 6.51 (d, 4H), 6.66 (s, 1H), 6.86 (d, 4H), 6.87 (s, 1H), 7.19 (d, 4H), 7.30 (d, 4H), 7.36 (bs, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −17.90 (2P), −26.64 (2P); DCI MS *m/z* 1234 (M^-, 100); IR (KBr pellet) br 1310 cm^{-1} ν(P=O). Anal. Calcd for $C_{56}H_{40}Cl_4O_{16}P_4$: C, 54.48; H, 3.26; Cl, 11.49. Found: C, 54.58; H, 3.29; Cl, 11.32.

6d: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.86 (d, 6H), 1.89 (d, 6H), 4.87 (q, 2H), 4.98 (q, 2H), 6.60 (s, 4H), 6.77 (d, 4H), 7.01 (d, 4H), 7.20 (d, 4H), 7.36 (d, 4H), 7.42(s, 4H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −17.39 (2P), −26.58 (2P); DCI MS *m/z* 1234 (M^-, 100); IR (KBr pellet) 1295 cm^{-1}, 1310 ν(P=O). Anal. Calcd for $C_{56}H_{40}Cl_4O_{16}P_4$: C, 54.48; H, 3.26; Cl, 11.49. Found: C, 54.61; H, 3.30; Cl, 11.36.

6e: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.90 (m, 12H), 4.96 (m, 4H), 6.18 (s, 4H), 6.58 (s, 2H), 6.70 (s, 2H), 6.84 (d, 4H), 7.13 (d, 4H), 7.28 (d, 2H), 7.44 (d, 2H), 7.47 (bs, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −16.35 (1P), −26.54 (2P), −26.86 (1P); DCI MS *m/z* 1234 (M^-, 100); IR (KBr pellet) br 1300 cm^{-1} ν(P=O). Anal. Calcd for $C_{56}H_{40}Cl_4O_{16}P_4$: C, 54.48; H, 3.26; Cl, 11.49. Found: C, 54.48; H, 3.65; Cl, 11.88.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(2′-phenylphenoxy)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]-benzodioxaphosphocin (7). The crude of the reaction was purified by column chromatography on silica gel with 40/1 CH_2Cl_2/acetone as eluant to give **7d (isomer ioio)**, white solid,

mp > 360 °C, TLC R_f 0.67; **7c, 7b** and **7a**, TLC R_f 0.48; and **7e (isomer iooo)**, mp > 360 °C, TLC R_f 0.39. **7b** and **7c** were separated on silica gel thick-layer plates with preparative thin-layer with 20/1 $CHCl_3$/acetone as eluant to give **7c (isomer iioo)**, white solid, mp > 360 °C, TLC R_f 0.53; and **7b** + **7a** [**isomer iiio** (85%) + **iiii** (15%)], mp > 360 °C, TLC R_f 0.47. Overall yield of the five isomers: 55%.

7a + **7b** (the signals due to the iiii isomer **7a** are indicated by an asterisk): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.81 (d, *), 1.87 (m, 12H), 4.52 (q, 1H), 4.84 (q, 2H), 4.92 (m, 1H + *), 5.67 (s, *), 6.68 (s, 2H), 6.98 (s, 2H), 6.42–7.58 (m, 38H + *); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −20.70 (1P), −23.24 (2P), −24.55 (1P) and −20.44 (*); DCI MS *m/z* 1401 (M^-, 100); FTIR (KBr pellet) 1289 cm^{-1}, 1311 ν(P=O).

7c: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.81 (d, 6H), 1.93 (d, 6H), 4.24 (q, 2H), 4.67 (q, 2H), 5.58 (s, 2H), 5.82 (s, 1H), 6.01 (s, 1H), 6.79–7.37 (m, 36H), 8.05 (s, 2H), 8.06 (s, 2H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −20.68 (2P), −24.26 (2P); DCI MS *m/z* 1401 (M^-, 100); FTIR (KBr pellet) 1289 cm^{-1}, 1313 ν(P=O). Anal. Calcd for $C_{80}H_{60}O_{16}P_4$: C, 68.57; H, 4.32; O, 18.27. Found: C, 68.80; H, 4.61; O, 18.07.

7d: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.71 (d, 6H), 1.73 (d, 6H), 4.61 (q, 2H), 4.86 (q, 2H), 6.29 (s, 4H), 6.75 (d, 2H), 6.95 (m, 4H), 7.18 (m, 12H), 7.35–7.54 (m, 22H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −19.99 (2P), −24.15 (2P); DCI MS *m/z* 1401 (M^-, 100); FTIR 1289 cm^{-1}, 1313 ν(P=O). Anal. Calcd for $C_{80}H_{60}O_{16}P_4$: C, 68.57; H, 4.32; O, 18.27. Found: C, 68.43; H, 4.39; O, 18.39.

7e: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.68 (d, 9H), 1.74 (d, 3H), 4.52 (q, 3H), 4.91 (q, 1H), 6.24 (s, 2H), 6.53 (s, 2H), 6.62 (d, 1H), 6.79 (t, 1H), 7.08–7.60 (m, 38H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −20.45 (1P), −20.89 (2P), −24.26 (1P); DCI MS *m/z* 1401 (M^-, 100); FTIR (KBr pellet) br 1312 cm^{-1} ν(P=O). Anal. Calcd for $C_{80}H_{60}O_{16}P_4$: C, 68.57; H, 4.32; O, 18.27. Found: C, 68.80; H, 4.61; O, 18.53.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(2′,6′-diisopropylphenoxy)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]benzodioxaphosphocin (8). The mixture of isomers was separated by silica gel column chromatography with 50/1 CH_2Cl_2/acetone as eluant to give **8d (isomer ioio)**, white solid, mp > 360 °C, TLC R_f 0.89; **8b** and **8c**, TLC R_f 0.63 and 0.58; and **8e (isomer iooo)**, white solid, mp > 360 °C, TLC R_f 0.36. **8b** and **8c** were separated on silica gel thick-layer plates with 50/1 CH_2Cl_2/acetone as eluant to give **8b (isomer iiio)**, white solid, mp > 360 °C; and **8c (isomer iioo)**, white solid, mp > 360 °C. Overall yield of the four isomers: 55%.

8b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (d, 12H, J = 6.8 Hz), 1.27 (m, 36H), 1.81 (d, 3H), 1.85 (d, 9H), 3.29 (m, 2H, J = 6.8 Hz), 3.57 (m, 6H), 4.91 (q, 1H), 5.00 (q, 2H), 5.12 (q, 1H), 6.58 (s, 2H), 6.83 (s, 2H), 7.04–7.21 (m, 12H), 7.27 (s, 2H), 7.28 (s, 2H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −20.08 (1P), −20.94 (2P), −21.92 (1P); DCI MS *m/z* 1433 (M^-, 100); FTIR br 1316 cm^{-1} ν(P=O). Anal. Calcd for $C_{80}H_{92}O_{16}P_4$: C, 67.03; H, 6.47; O, 17.86. Found: C, 66.80; H, 6.41; O, 17.51.

8c: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (d, 12H, J = 6.8 Hz), 0.99 (d, 12H, J = 6.8 Hz), 1.29 (d, 24H, J = 6.8 Hz), 1.84 (d, 6H), 1.85 (d, 6H), 3.21 (m, 4H, J = 6.8 Hz), 3.57 (m, 4H, J = 6.8 Hz), 4.99 (q, 2H), 5.14 (q, 2H), 6.32 (s, 1H), 6.58 (s, 2H), 6.88 (s, 1 H), 7.03–7.29 (m, 12H), 7.30 (bs, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −20.19 (2P), −21.42 (2P); DCI MS *m/z* 1433 (M^-, 100); FTIR (KBr pellet) br 1314 cm^{-1} ν(P=O). Anal. Calcd for $C_{80}H_{92}O_{16}P_4$: C, 67.03; H, 6.47; O, 17.86. Found: C, 66.79; H, 6.60; O, 17.98.

8d: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (d, 24H, J = 6.8 Hz), 1.31 (d, 24H, J = 6.8 Hz), 1.84 (d, 6H), 1.85 (d, 6H), 3.44 (m, 4H, J = 6.8 Hz), 3.62 (m, 4H, J = 6.8 Hz), 5.05 (q, 2H), 5.13 (q, 2H), 6.76 (s, 4H), 7.12–7.21 (m, 12H), 7.22 (s, 4H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −17.98 (2P), −19.86 (2P); DCI MS *m/z* 1433 (M^-, 100); FTIR (KBr pellet) br 1311 cm^{-1} ν(P=O). Anal. Calcd for $C_{80}H_{92}O_{16}P_4$: C, 67.03; H, 6.47; O, 17.86. Found: C, 67.19; H, 6.53; O, 17.56.

8e: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04 (d, 12H, J = 6.8 Hz), 1.14 (d, 12H, J = 6.8 Hz), 1.20 (d, 12H, J = 6.8 Hz), 1.30 (d, 12H, J = 6.8 Hz), 1.81 (d, 6H), 1.84 (d, 6H), 3.26 (m, 2H, J = 6.8 Hz), 3.41 (m, 4H, J = 6.8 Hz), 3.58 (m, 2H), 5.00 (q, 1H), 5.06 (q, 1H), 5.11 (q, 2H), 6.20 (s, 2H), 6.59 (s, 2H), 7.08–7.26 (m, 16H); ^{31}P NMR ($CDCl_3$, 81 MHz) δ −17.97 (2P), −19.17 (1P), −19.25 (1P); DCI MS *m/z* 1433 (M^-, 100); FTIR (KBr pellet) 1313 cm^{-1} ν(P=O). Anal. Calcd for $C_{80}H_{92}O_{16}P_4$: C, 67.03; H, 6.47; O, 17.86. Found: C, 66.92; H, 6.57; O, 18.02.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(2′,4′,6′-trimethylphenoxy)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]benzodioxaphosphocin (9). The mixture of isomers was separated by silica gel column chromatography with 40/1 CH_2Cl_2/acetone as eluant to give **9d (isomer ioio)**, white solid, mp > 360 °C, TLC R_f 0.73; **9b (isomer iiio)**, white solid, mp > 360 °C, TLC R_f 0.55; and **9c (isomer iioo)** and **9e (isomer iooo)**, R_f 0.42. Isomers **9c** and **9e** could not be separated by preparative column chromatography. Overall yield of the four isomers: 58%.

9b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (d, 6H, J = 6.8 Hz), 1.88 (d, 6H, J = 6.8Hz), 1.91 (s, 3H), 2.24 (s, 6H), 2.26 (s, 3H), 2.33 (s, 12H), 2.43 (s, 6H), 4.87 (q, 1H, J = 6.8 Hz), 4.93 (m, 3H), 6.43 (s, 2H), 6.45 (s, 2H), 6.84 (s, 4H), 6.86 (s, 2H), 6.88 (s, 2H), 7.36 (s, 2H), 7.38 (s, 2H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −18.42 (1P), −19.78 (2P), −28.75 (1P); DCI MS *m/z* 1265 (M^-, 100); FTIR (KBr pellet) 1317 cm^{-1} ν(P=O). Anal. Calcd for $C_{68}H_{68}O_{16}P_4$: C, 64.56; H, 5.42; O, 20.23. Found: C, 64.79; H, 5.33; O, 20.11.

9d: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.58 (s, 12H), 1.75 (d, 6H), 1.79 (s, 6H), 1.80 (d, 6H), 2.18 (s, 6H), 2.26 (s, 12H), 4.89 (m, 4H), 6.37 (s, 4H), 6.55 (s, 4H), 6.79 (s, 4H), 7.28 (s, 4H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −19.07 (2P), −25.22 (2P); DCI MS *m/z* 1265 (M^-, 100); FTIR (KBr pellet) 1317 cm^{-1} ν(P=O). Anal. Calcd for $C_{68}H_{68}O_{16}P_4$: C, 64.56; H, 5.42; O, 20.23. Found: C, 64.19; H, 5.22; O, 20.01.

Compounds **10**–**12** were obtained following the same general procedure as for **4**–**9**, using in each case as substrate resorcin[4]arene **2**.

7,11,15,28-Tetrabromo-1,21,23,25-tetramethyl-5,9,13,17-tetrakis(4′-methylphenoxy)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]benzodioxaphosphocin (10). The crude of the reaction was purified by column chromatography on silica gel with 30/1 CH_2Cl_2/acetone as eluant to give **10d (isomer ioio)**, white solid, mp > 360 °C, TLC R_f 0.78; **10b** and **10c**, TLC R_f 0.51 and 0.53; and **10e (isomer iooo)**, white solid, mp > 360 °C, TLC R_f 0.34. **10b** and **10c** were separated by column chromatography on silica gel with 30/1 $CHCl_3$/acetone as eluant to give **10c (isomer iioo)**, white solid, mp > 360 °C, TLC R_f 0.58; and **10b (isomer iiio)**, white solid, mp > 360 °C, TLC R_f 0.13. Overall yield of the four isomers: 70%.

10b: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.92 (m, 12H), 2.16 (s, 3H), 2.29 (s, 6H), 2.31 (s, 3H), 4.82 (m, 4H), 6.75 (bs, 2H), 6.90 (bs, 2H), 7.25 (d, 2H), 7.27 (d, 4H), 7.30 (d, 4H), 7.33 (d, 2H), 7.95 (s, 2H), 7.98 (s, 2H); ^{31}P NMR (DMSO-d_6, 161.9 MHz) δ −19.60 (2P), −20.55 (1P), −25.41 (1P); DCI MS *m/z* 1468 (M^-, 100); FTIR (KBr pellet) 1297 cm^{-1}, 1325 ν(P=O). Anal. Calcd for $C_{60}H_{48}Br_4O_{16}P_4$: C, 49.07; H, 3.29; O, 17.43. Found: C, 49.14; H, 3.34; O, 17.54.

10c: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.93 (d, 6H), 1.95 (d, 6H), 2.07 (s, 6H), 2.30 (s, 6H), 4.81 (q, 2H), 4.86 (q, 2H), 6.40 (bs, 4H), 6.51 (bs, 4H), 7.26 (d, 4H), 7.32 (d, 4H), 8.00 (bs, 4H); ^{31}P NMR (DMSO-d_6, 161.9 MHz) δ −19.31 (2P), −25.57 (2P); DCI MS *m/z* 1468 (M^-, 100); FTIR (KBr pellet) 1296 cm^{-1}, 1322 ν(P=O). Anal. Calcd for $C_{60}H_{48}Br_4O_{16}P_4$: C, 49.07; H, 3.29; O, 17.43. Found: C, 49.27; H, 3.52; O, 17.80.

10d: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.93 (d, 6H), 1.95 (d, 6H), 2.10 (s, 6H), 2.29 (s, 6H), 4.77 (q, 2H), 4.88 (q, 2H), 6.59 (bd, 4H), 6.69 (bd, 4H), 7.23 (d, 4H), 7.26 (d, 4H), 8.02 (s, 4H); ^{31}P NMR (DMSO-d_6, 161.9 MHz) δ −19.49 (2P), −25.68 (2P); DCI MS *m/z* 1468 (M^-, 100); FTIR (KBr pellet) 1295 cm^{-1}, 1323 ν(P=O). Anal. Calcd for $C_{60}H_{48}Br_4O_{16}P_4$: C, 49.07; H, 3.29; O, 17.43. Found: C,49.20; H, 3.52; O, 17.81.

10e: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.82 (s, 3H), 1.97 (m, 12H), 2.22 (s, 6H), 2.34 (s, 3H), 4.89 (m, 4H), 5.61 (bs, 2H), 5.91 (bs, 2H), 6.65 (bs, 4H), 6.81 (bs, 4H), 7.31 (d, 2H), 7.41 (d, 2H), 8.04 (s, 2H), 8.06 (s, 2H); ^{31}P NMR (DMSO-d_6, 161.9 MHz) δ −17.16 (1P), −24.89 (2P), −26.71 (1P); DCI MS *m/z* 1468

(M^-, 100); FTIR (KBr pellet) 1298 cm^{-1}, 1326 ν(P=O). Anal. Calcd for $C_{60}H_{48}Br_4O_{16}P_4$: C, 49.07; H, 3.29; O, 17.43. Found: C, 49.43; H, 3.41; O, 17.21.

7,11,15,28-Tetrabromo-1,21,23,25-tetramethyl-5,9,13,17-tetrakis(4′-*tert*-butylphenoxy)-2,20:3,19-dimetheno-1*H*,-21*H*,23*H*,25-bis[1,3,2λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]benzodioxaphosphocin (11). The mixture of isomers was separated by silica gel column chromatography with 40/1 CH_2Cl_2/acetone as eluant to give a mixture of **11d** and **11b**, TLC R_f 0.69 and 0.60; **11c (isomer iioo)**, white solid, mp > 360 °C, TLC R_f 0.50; and **11e (isomer iooo)**, white solid, mp > 360 °C, TLC R_f 0.37. Separation of **11d** and **11b** on silica gel column with $CHCl_3$ as eluant gave pure **11d (isomer ioio)**, white solid, mp > 360 °C, TLC R_f 0.51; and **11b (isomer iiio)**, white solid, mp > 360 °C, TLC R_f 0.26. Overall yield of the four isomers: 68%.

11b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18 (s, 9H), 1.27 (s, 18H), 1.29 (s, 9H), 1.88 (m, 12H), 4.91 (m, 3H), 5.03 (q, 1H), 6.92–7.48 (m, 20H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −19.90 (2P), −20.26 (1P), −25.86 (1P); DCI MS *m/z* 1637 (M^-, 100); IR (KBr pellet) 1300 cm^{-1}, 1320 ν(P=O). Anal. Calcd for $C_{72}H_{72}Br_4O_{16}P_4$: C, 52.83; H, 4.43; O, 15.64. Found: C, 52.90; H, 4.59; O, 15.79.

11c: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.13 (s, 18H), 1.30 (s, 18H), 1.96 (d, 6H), 2.00 (d, 6H), 5.02 (m, 4H), 6.81 (d, 4H), 6.94 (d, 4H), 7.35 (bs, 8H), 7.74 (s, 3H), 7.79 (s, 1H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −19.58 (2P), −26.25 (2P); DCI MS *m/z* 1637 (M^-, 100); IR (KBr pellet) 1290 cm^{-1}, 1310 ν(P=O). Anal. Calcd for $C_{72}H_{72}Br_4O_{16}P_4$: C, 52.83; H, 4.43; O, 15.64. Found: C, 52.72; H, 4.39; O, 15.50.

11d: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.13 (s, 18H), 1.27 (s, 18H), 1.89 (d, 6H), 1.93 (d, 6H), 4.95 (q, 2H), 5.08 (q, 2H), 6.83 (d, 4H), 7.03 (d, 4H), 7.25 (d, 4H), 7.30 (d, 4H), 7.51 (s, 4H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −19.67 (2P), −26.01 (2P); DCI MS *m/z* 1636 (M^-, 100); IR (KBr pellet) 1290 cm^{-1}, 1310 ν(P=O). Anal. Calcd for $C_{72}H_{72}Br_4O_{16}P_4$: C, 52.83; H, 4.43; O, 15.64. Found: C, 52.67; H, 4.51; O, 15.52.

11e: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.93 (s, 9H), 1.15 (s, 18H), 1.30 (s, 9H), 1.97 (m, 12H), 5.09 (m, 4H), 6.36 (d, 2H), 6.62 (d, 2H), 6.96 (d, 4H), 7.09 (d, 4H), 7.34 (s, 4H), 7.70 (s, 2H), 7.71 (s, 2H); ^{31}P NMR ($CDCl_3$, 161.9 MHz) δ −19.11 (1P), −25.85 (2P), −26.76 (1P); DCI MS *m/z* 1637 (M^-, 100); IR (KBr pellet) 1300 cm^{-1}, 1320 ν(P=O). Anal. Calcd for $C_{72}H_{72}Br_4O_{16}P_4$: C, 52.83; H, 4.43; O, 15.64. Found: C, 52.50; H, 4.50; O, 15.29.

7,11,15,28-Tetrabromo-1,21,23,25-tetramethyl-5,9,13,17-tetrakis(4′-chlorophenoxy)-2,20:3,19-dimetheno-1*H*,21*H*,-23*H*,25*H*-bis[1,3,2λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]benzodioxaphosphocin (12). The crude of the reaction was purified by column chromatography on silica gel with 30/1 CH_2Cl_2/acetone as eluant to give three fractions in 65% overall yield: **12d** and **12b**, TLC R_f 0.73 and 0.65; **12c (isomer iioo)**, mp > 360 °C, TLC R_f 0.56; and **12e (isomer iooo)**, mp > 360 °C, TLC R_f 0.47. **12d** and **12b** were chromatographed on silica gel with 40/1 $CHCl_3$/acetone as eluant to give **12d (isomer ioio)**, mp > 360 °C, TLC R_f 0.44; and **12b (isomer iiio)**, mp > 360 °C, TLC R_f 0.19.

12b: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.94 (m, 12H), 4.85 (m, 4H), 6.71 (bs, 2H), 7.12 (bs, 2H), 7.46 (d, 4H), 7.50 (d, 2H), 7.54 (d, 4H), 7.57 (d, 2H), 8.00 (s, 2H), 8.04 (s, 2H); ^{31}P NMR (DMSO-d_6, 161.9 MHz) δ −19.74 (2P), −20.58 (1P), −26.26 (1P); DCI MS *m/z* 1550 (M^-, 100); FTIR (KBr pellet) 1315 cm^{-1}, 1324 ν(P=O). Anal. Calcd for $C_{56}H_{36}Br_4Cl_4O_{16}P_4$: C, 43.39; H, 2.34; O, 16.51. Found: C, 43.21; H, 2.20; O, 16.40.

12c: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.95 (d, 12H), 4.85 (m, 4H), 6.29 (d, 4H), 6.76 (d, 4H), 7.48 (d, 4H), 7.55 (d, 4H), 8.04 (s, 3H), 8.06 (s, 1H); ^{31}P NMR (DMSO-d_6, 161.9 MHz) δ −19.39 (2P), −26.51 (2P); DCI MS *m/z* 1550 (M^-, 100); FTIR (KBr pellet) 1294 cm^{-1}, 1306, 1325 ν(P=O). Anal. Calcd for $C_{56}H_{36}Br_4Cl_4O_{16}P_4$: C, 43.39; H, 2.34; O, 16.51. Found: C, 43.60; H, 2.46; O, 16.70.

12d: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.94 (d, 12H), 4.81 (q, 2H), 4.88 (q, 2H), 6.51 (d, 4H), 6.77 (d, 4H), 7.42 (d, 4H), 7.52 (d, 4H), 8.04 (s, 4H); ^{31}P NMR (DMSO-d_6, 161.9 MHz) δ −19.66 (2P), −26.15 (2P); DCI MS *m/z* 1550 (M^-, 100); FTIR (KBr pellet) 1322 cm^{-1} ν(P=O). Anal. Calcd for $C_{56}H_{36}Br_4Cl_4O_{16}P_4$: C, 43.39; H, 2.34; O, 16.51. Found: C, 43.04; H, 2.35; O, 16.59.

12e: ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.97 (m, 12H), 4.91 (m, 4H), 5.93 (bs, 4H), 6.75 (bs, 4H), 7.06 (bs, 4H), 7.58 (d, 2H), 7.61 (d, 2H), 8.06 (s, 2H), 8.08 (s, 2H); ^{31}P NMR (DMSO-d_6, 161.9 MHz) δ −16.40 (1P), −25.38 (1P), −27.24 (2P); DCI MS *m/z* 1550 (M^-, 100); FTIR (KBr pellet) 1305 cm^{-1}, 1327 ν(P=O). Anal. Calcd for $C_{56}H_{36}Br_4Cl_4O_{16}P_4$: C, 43.39; H, 2.34; O, 16.51. Found: C, 43.48; H, 2.35; O, 16.78.

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