# Synthesis, Structure, and Reactivity of Tetrakis(*O,O*-phosphorus)-Bridged Calix[4]resorcinols and Their Derivatives☆

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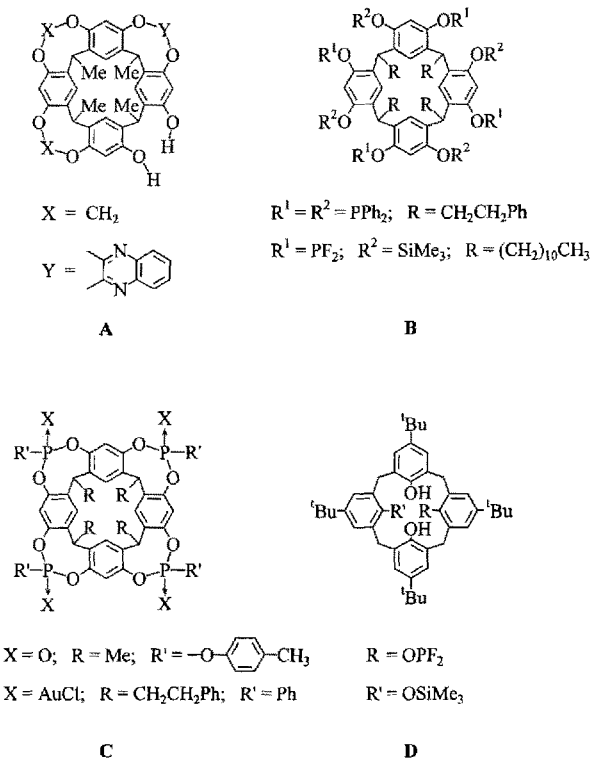
The synthesis and characterisation of the reactive tetrakis(*O,O*-phosphorus)-bridged calix[4]resorcinols **3** and **4** is described. Because of its poor solubility in common organic solvents, a solid-state NMR investigation of **3** ($^1$H, $^{13}$C, $^{31}$P) was conducted. Reaction of **3** with MeMgI, $Me_3SiNMe_2$, and $HNMe_2$ furnished the $\sigma^3\lambda^3$P-substituted cavitands **5** and **6**. Oxidative addition reactions of **6** with the $(H_2N)_2C(=O)/H_2O_2$ (1:1) adduct, tetrachloro-*o*-benzoquinone (TOB), and hexafluoroacetone (HFA) led to the $\sigma^4\lambda^5$P derivative **7**, and to the $\sigma^5\lambda^5$P derivatives **8** and **9**. An X-ray crystal-structure determination of the tetrakis(*O,O*-phosphorus)-bridged calix[4]resorcinol **4** has been conducted. The framework displays the cone conformation; the chlorine atoms are directed inwards.

## Introduction

Calix[4]arenes and calix[4]resorcinols are cavity-containing macrocyclic compounds, that attract considerable interest in the field of host-guest and supramolecular chemistry as three-dimensional "building blocks" for the design of selective cation receptors and carriers[1]. Calix[4]resorcinols can act, e.g. in phase-transfer processes[2][3] or as catalysts, e.g. for solvolysis reactions[4]. The use of calix[4]resorcinols for the chemo- and stereoselective recognition of carbohydrates is particularly important[5]. The introduction of different bridging groups X and Y between two neighbouring oxygen atoms (Scheme 1) into the latter furnished chiral cavitands of type **A**[6][7]. Phosphorus-containing calix[4]arenes and calix[4]resorcinols have been of increasing interest during the past few years, mainly because of their ability to act as unusual multidentate ligands. A number of phosphorus-containing calix[4]resorcinols of types **B** and **C** are known in which the phosphorus atom adopts various coordination numbers and oxidation states[8–13] (Scheme 1).

Derivatives of calix[4]resorcinols with $Ph_2P$, PhP, $(Et_2N)_2P(=O)$, and $(EtO)_2P(=O)$ units show strong coordinating ability, complexing transition metals such as Au, Pt, Ag, or Cu, to give transition-metal-rimmed bowl complexes, which have the potential to accept small guest molecules and ions[8][10][14][15].

Scheme 1. Structures of calix[4]resorcinol and calix[4]arene derivatives **A**–**D**



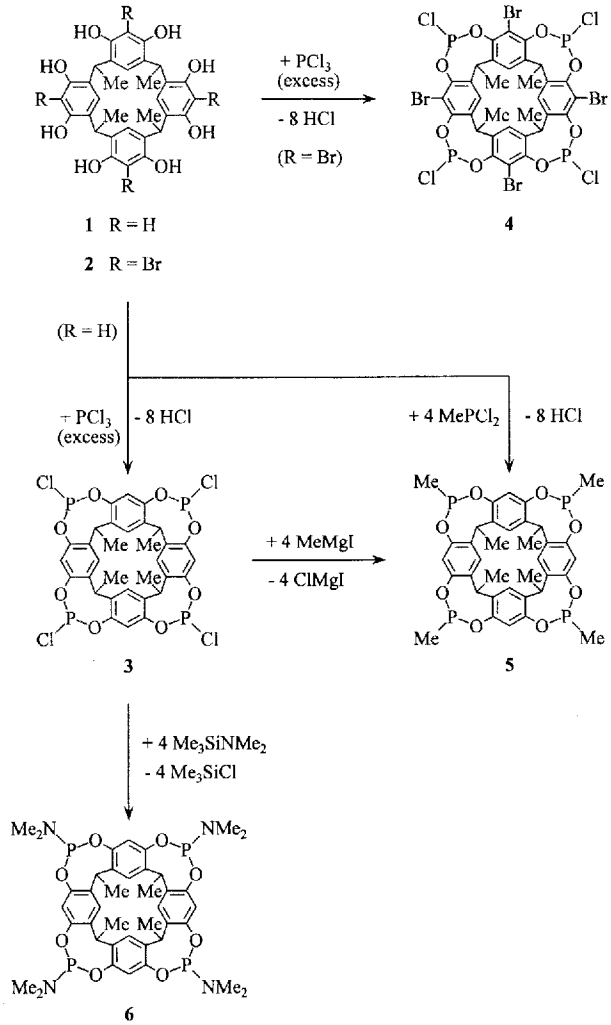

## Results and Discussion

The main problems in the chemistry of phosphorus-containing calix[4]resorcinols are: (i) separation of the six possible diastereoisomers (*iiii, iiio, iioo, ioio, iooo, oooo*)[9], [*i* (in) refers to the substituent at the phosphorus atom – directed towards the middle of the bowl, *o* (out) means that the substituent points in an outward direction], and preparation of suitable crystals for X-ray structure analysis; (ii) the lack of useful precursors that could give access to various $P^{III}$ derivatives. Previously, we reported a convenient method of

functionalizing the periphery of calix[4]resorcinols with $PF_2Cl$ via intermediates containing *O*-trimethylsilyl groups[13].

In this paper we describe a facile synthesis of tetrakis-(*O,O*-phosphorus)-bridged and other $P^{III}$-containing calix[4]resorcinols and their oxidation reactions with the $(H_2N)_2C(=O)/H_2O_2$ (1:1) adduct, tetrachloro-*o*-benzoquinone (TOB), and hexafluoroacetone (HFA). Thus far, $P^{III}$-containing calix[4]resorcinols have been prepared by the reaction of calix[4]resorcinols with the corresponding mono- or dichlorophosphanes. However, this method of preparation is of limited efficiency, as a result of the different reactivity of the phosphane and steric effects, and in some cases gives rise to low yields only. The reaction of an octakis(trimethylsiloxy)calix[4]resorcinol[13][16] with chlorodifluorophosphane and phosphorus trichloride led neither to the expected octakis[$P^{III}$]-substituted products[13][16], nor to tetrakis(*O,O*-phosphorus)-bridged calix[4]resorcinol derivatives. Because of steric effects and, due to the low reactivity, e.g. of octakis(trimethylsiloxy)calix[4]resorcinol[13] and, by comparison, of *p-tert*-butyldihydroxybis(trimethylsiloxy)calix[4]arene[17], only half of the trimethylsilyl groups were substituted and compounds **B** and **D** (Scheme 1) were obtained. Therefore, the P−Cl compounds **3** and **4** are useful starting materials for further substitution reactions. They represent new and important "building blocks" in supramolecular chemistry. The crystal structure of **4** is the first of a tetrakis(*O,O*-phosphorus)-bridged calix[4]resorcinol.

Scheme 2




### Preparation of 3 and 4

The reaction of **1** and **2** with $PCl_3$ did not yield the expected octakis(dichlorophosphites), and the conformationally frozen tetrakis(*O,O*-phosphorus)-bridged calix[4]resorcinol derivatives **3** and **4** as the cone conformers were formed instead, according to Scheme 2.

The identity of compound **3** was established by IR spectroscopy, mass spectrometry, and elemental analysis. NMR data in solution could not be recorded because of the poor solubility of **3** in common organic solvents. Therefore, solid-state $^1H$-, $^{13}C$-, and $^{31}P$-NMR data were recorded. A broad $^1H$ peak (from simple MAS) at $\delta \approx 4.8$ was obtained, together with some broad spinning side bands, after a background spectrum of the empty rotor insert had been subtracted. No distinction between different chemical sites for hydrogen could be detected. In the present study the proton chemical shift is accurate to only ±0.5 ppm, as indirect referencing was used.

Both full and NQS (Non-Quaternary Suppression) CPMAS spectra were run, at a spin rate of 4.92 kHz for $^{13}C$, in order to assist assignment. The $\delta(^{13}C)$ values observed for **3** are listed in the Experimental Section. For the $^{31}P$-NMR spectrum, preliminary direct polarization experiments at a spin rate of 4.74 kHz indicated that a long relaxation delay of 30 s (implying long $T_1$) was necessary. However, for optimised cross polarization, with flip-back and decoupling during acquisition and with a contact time of 6 ms, a 2-s delay was sufficient. A different spin rate (of 3.98 kHz) was employed to identify the isotropic chemical shift of 122 ppm. The manifold of spinning sidebands was analysed to give the principal components of the $^{31}P$ shielding tensor[18]. A small impurity with an isotropic peak at $\delta = -1$ can also be seen.

From these results, there is nothing to suggest that there is any lack of fourfold symmetry within the molecule in the crystalline environment. The spectra are consistent with the structure proposed.

Consistent with previous observations[19b], the reaction of the tetrabromo-substituted compound **2** with $PCl_3$, furnishing the quadruply ClP-bridged derivative **4**, occurred more slowly than that of the unsubstituted compound **1**. Compound **4** was sufficiently soluble in $CH_2Cl_2$, $CHCl_3$, and THF and could, therefore, be characterized by solution NMR spectroscopy. The $^{31}P$-NMR-spectrum of the reaction mixture showed a sharp singlet at $\delta = 129.8$, indicating stereoselective formation of **4** in only one conformational isomer. The $^1H$-NMR spectrum, recorded at room temperature, proved the existence of **4** as the cone conformer. Single crystals of compound **4** suitable for an X-ray crystal-structure determination were obtained by overlayering a solution of $PCl_3$ in $CH_2Cl_2$ with **2** in THF. The X-ray structure de-

termination of **4** was conducted in order to determine the configuration at the phosphorus atoms. Compounds **3** and **4** were both used as precursors in various substitution reactions.

### Discussion of the X-ray Crystal Structure of 4[20]

Compound **4** crystallises as a dichloromethane solvate. The calix[4]resorcinol framework displays the cone conformation. The dihedral angles from the least-squares plane of the methylene bridge carbon atoms [plane 1: C17, C27, C37, and C47; mean deviation 4.9 pm] to the aromatic rings are 58° (plane 2: C11 to C16), 53° (plane 3: C21 to C26), 58° (plane 4: C31 to C36) and 56° (plane 5: C41 to C46). The distances between neighbouring phenyl group centres are 472 pm (plane 2−plane 5) to 481 pm (plane 2−plane 3); those between opposite phenyl groups are 666 pm (plane 2−plane 4) and 683 pm (plane 3−plane 5).

All phosphorus atoms display pyramidal coordination geometry. The largest angles at the phosphorus atoms in each case involve the two oxygen atoms [103.8(3)° (O4−P2−O3) to 104.8(2)° (O1−P1−O2 and O7−P4−O8)]. The remaining angles at the phosphorus atoms lie between 99.9(2)° (O2−P1−Cl1) to 101.4(2)° (O4−P2−Cl2). The four chlorine atoms are directed to the interior of the calix[4]resorcinol framework. The P−Cl bond lengths vary from 205.6(3) pm (P4−Cl4) to 206.8(3) pm (P3−Cl3). Intramolecular Cl···Cl contacts are observed: Cl1···Cl2 393 pm, Cl3···Cl4 403 pm, Cl2···Cl3 422 pm, Cl1···Cl4 436 pm, Cl1···Cl3 554 pm, and Cl2···Cl4 614 pm. The Br3 atom makes a short intermolecular contact of 360 pm to its counterpart at $0.67 - x$, $0.33 - y$, $1.33 - z$.

As in phosphorus-containing calix[4]resorcinol compounds, the C−O−P angles [127.7(4)° (C26−O5−P3) to 130.0(4)° (C16−O1−P1)] are large because of the eight-membered rings. The P−O bond lengths differ insignificantly [161.3(5) pm to 163.3(5) pm].

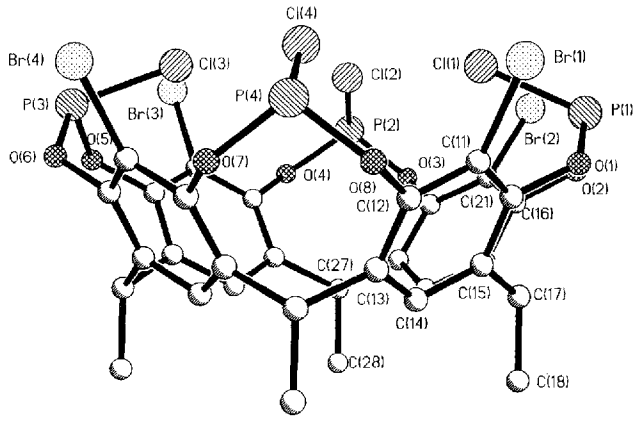
### Preparation of 5

The reaction of **3** with MeMgI furnished the tetramethyl-substituted compound **5** in good yield. The latter was identified by $^1$H- and $^{31}$P-NMR spectroscopy, mass spectrometry, and elemental analysis. Only one of six theoretically possible isomers[9] was formed, as indicated by a single resonance for the methyl protons in the $^1$H-NMR and a sharp singlet in the $^{31}$P-NMR spectrum. The data correspond to those of the product obtained by the reaction of **1** with $MePCl_2$ which, in the absence of an ancillary base, furnished **5** in comparable yield. From this reaction single crystals suitable for an X-ray crystal-structure determination were obtained, which, although imprecise, indicated the configuration of **5** with all methyl groups pointing in an outward direction from the bowl[21].

### Preparation of 6

According to Scheme 2, the reaction of **3** with $Me_3Si$-$NMe_2$ furnished the known compound **6**[10]. The driving force of the reaction is apparently the formation of $Me_3SiCl$ which can easily be removed in vacuo. Compound **6** was obtained almost quantitatively. Dimethylamine also reacted with **3** to give **6**. An excess of $HNMe_2$ was used in order to compensate for the consumption of amine by its reaction with HCl. The physical properties of **6** corresponded to those reported in the literature[10][11], the material was used in subsequent reactions without further purification.

Figure 1. Molecular structure of **4**[a]




[a] Hydrogen and solvent atoms have been omitted for clarity; selected bond lengths [pm] and angles [°]: P(1)−O(1) 161.8(5), P(1)−O(2) 163.3(5), P(1)−Cl(1) 206.3(2), P(2)−O(4) 161.5(4), P(2)−O(3) 161.8(5), P(2)−Cl(2) 206.7(2), P(3)−O(6) 161.8(5), P(3)−O(5) 162.9(4), P(3)−Cl(3) 206.8(3), P(4)−O(7) 161.3(5), P(4)−O(8) 161.8(5), P(4)−Cl(4) 205.6(3), O(1)−C(16) 140.6(7), O(2)−C(22) 138.3(7), O(3)−C(26) 139.8(7), O(4)−C(32) 140.9(7), O(5)−C(36) 138.9(7), O(6)−C(42) 140.0(7), O(7)−C(46) 139.9(7), O(8)−C(12) 140.0(7); O(1)−P(1)−O(2) 104.8(2); O(1)−P(1)−Cl(1) 100.7(2), O(2)−P(1)−Cl(1) 99.9(2), O(4)−P(2)−O(3) 103.8(2), O(4)−P(2)−Cl(2) 101.4(2), O(3)−P(2)−Cl(2) 100.4(2), O(6)−P(3)−O(5) 104.4(2), O(6)−P(3)−Cl(3) 100.5(2), O(5)−P(3)−Cl(3) 100.0(2), O(7)−P(4)−O(8) 104.8(2), O(7)−P(4)−Cl(4) 100.8(2), O(8)−P(4)−Cl(4) 100.3(2), C(16)−O(1)−P(1) 130.0(4), C(22)−O(2)−P(1) 128.4(4), C(26)−O(3)−P(2) 127.8(4), C(32)−O(4)−P(2) 129.7(4), C(36)−O(5)−P(3) 127.7(4), C(42)−O(6)−P(3) 127.9(4), C(46)−O(7)−P(4) 128.1(4), C(12)−O(8)−P(4) 129.3(4).

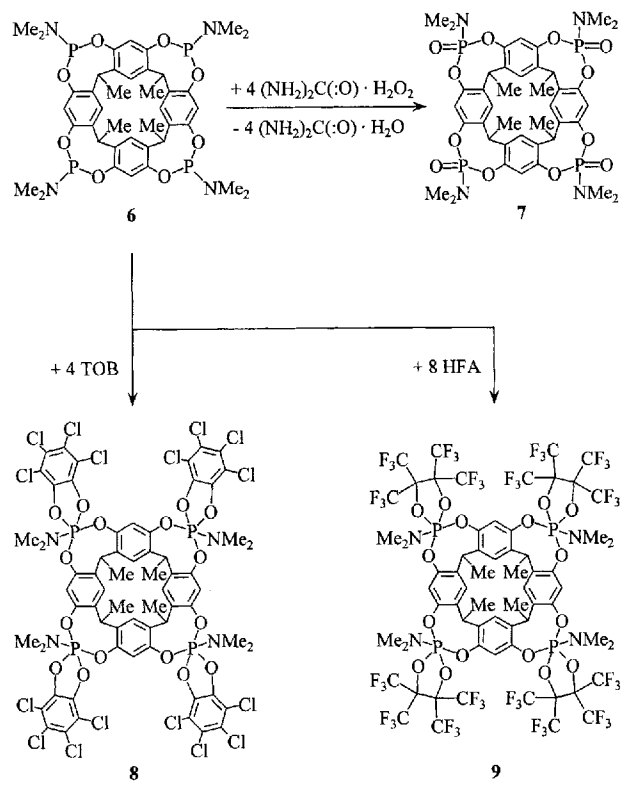
### Oxidation Reactions of 6

#### Preparation of the Phosphoryl Compound 7, and of the Phosphoranes 8 and 9

When **6** was treated with the $(H_2N)_2C(=O)/H_2O_2$ (1:1) adduct, the corresponding tetrakis($\sigma^4\lambda^5$-phosphoryl)-bridged calix[4]resorcinol **7** was formed stereoselectively. We assume the phosphoryl groups to be axial with respect to the plane of the bowl, as was observed for the thiophosphoryl compound by Nifantyev et al.[11]. The IR spectrum of **7** in nujol is characterized by an intense P=O stretching frequency at 1320 cm$^{-1}$. Additionally, $^1$H- and $^{31}$P-NMR-spectroscopic and mass-spectrometric investigations, and elemental analyses confirm the identity of **7** (Scheme 3).

Compound **8**, involving four $\sigma^5\lambda^5$-P atoms, was prepared by the oxidative addition of TOB to **6**. It was important to add the TOB solution slowly in order to avoid side reactions. The $^{31}$P-NMR spectrum showed a broad group of signals with four resonances ($\delta$ = −44.03, −44.73, −45.17, and −45.27) resulting from the presence of various con-

Scheme 3




formers of **8**. Several signals for the $N(CH_3)_2$ protons [$\delta$ = 2.80, 2.96 (2d)] are in agreement with this.

The reaction of **6** with HFA furnished the tetrakis(spirophosphorane) derivative **9**. Several conformers were again observed. The $^{31}$P-NMR spectrum showed two signals at $\delta = -42.37$ and $-45.83$. The signals for the $N(CH_3)_2$ protons in the $^1$H-NMR spectra were broad and not resolved. For **8** and **9**, the addition of the oxidizing agent (TOB, HFA) to the phosphorus atoms in a different mode is also conceivable: Detailed force-field calculations[22] (SYBYL) excluded structures **8a** and **9a** because of steric overload, whereas energy minimizations for structures **8** and **9** resulted in geometries with a minimum of strain energy. As a starting point for the calculations the coordinates of the X-ray structure of **4** were used. All computations were performed with the SPARTAN 4.0 software on an SGI (R4400) workstation (Scheme 4).

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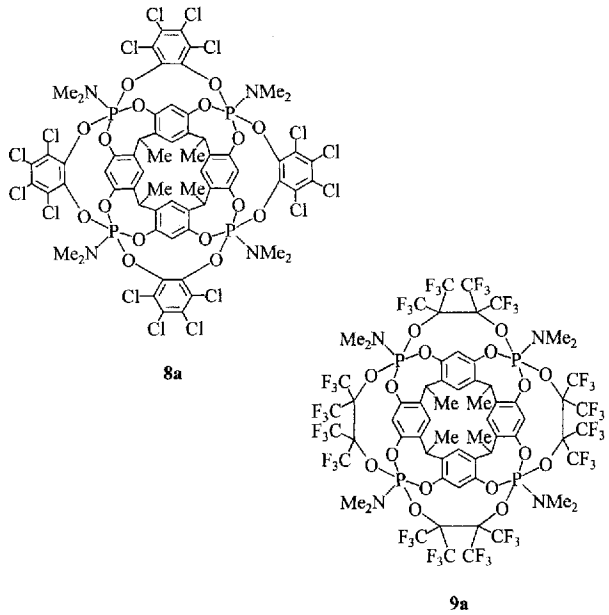
Scheme 4. Isomers of **8a** and **9a**



## Experimental Section

All experiments were carried out with exclusion of air and moisture; solvents were purified and dried according to the usual methods[23]. "In vacuo" (i.v.) refers to a pressure of 0.1 Torr at 25°C. – NMR spectra in solution were recorded with a Bruker AC 200 spectrometer at 200.1 MHz ($^1$H), 50.3 MHz ($^{13}$C) and 81.0 MHz ($^{31}$P). Low-frequency shifts were given negative, high-frequency shifts positive signs. Solid-state NMR spectra ($^1$H, $^{13}$C, $^{31}$P) were obtained using a Varian Unity Plus 300 spectrometer, operating at 75.43, 121.42, and 299.95 MHz for $^{13}$C, $^{31}$P, and $^1$H, respectively. Cross polarization from the proton spin bath was used in recording both $^{13}$C and $^{31}$P spectra. Magic-angle spinning was employed for all three nuclei, with spin rates in the range of 3.9 to 5.0 kHz. The sample was packed into a 7-mm o. d. rotor and then placed in a Doty MAS probe. Contact times were 6.0 ms. Recycle delays were 2.0 s. For the $^1$H spectrum, the pulse angle was set to 90°. The number of transients acquired was 100 for the $^1$H spectrum, 300–500 for $^{31}$P, and 1800 for $^{13}$C. The chemical shifts were referenced by replacement to the signals of tetramethylsilane for $^1$H and $^{13}$C (via the resonance of adamantane in the latter case), and of 85% $H_3PO_4$ for $^{31}$P. – IR spectra were recorded with an FT-IR spectrometer FTS 165, Bio-Rad Laboratories GmbH (Krefeld). – MS: Finnigan MAT 8430 and KRATOS MS 50 RF (GBF). – Elemental analyses: Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig. – Melting points were determined with a capillary melting-point apparatus MEL-TEMP®. – Starting materials: Compounds **1** and **2**[19a][19b]. All further compounds were commercially available.

*Preparation of* **3** *and* **4**: To a stirred solution of 5.44 g (10 mmol) of **1** or 1.72 g (2 mmol) of **2** in 100 ml of THF, respectively, was added 11.0 g (80 mmol) of phosphorus trichloride. The reaction mixture was stirred under reflux for 5 h. After 1.5 h, the product started to crystallize. The product was collected, washed with 20 ml of $CH_2Cl_2$ and dried i.v. at 120°C for 1 d. Because of the poor solubility of **3** in common organic solvents, no solution NMR data could be obtained.

**3:** Yield 8.02 g (quantitative), m.p. 475–477°C (dec). – IR (Nujol): $\tilde{\nu}$ = 1610 $cm^{-1}$ (w), 1586.85 (w), 1338.85 (vw), 1268.77 (st), 1177.23 (st), 1150.95 (st), 1089.55 (st), 1029.90 (st), 1003.76 (st), 898.54 (st), 888.08 (st), 862.41 (st), 746.41 (w), 689.06 (w), 600.80 (vw), 568.35 (w), 482.05 (st), 450.27 (w). – $^1H$, $^{13}C$, and $^{31}P$ solid-state NMR: $^1H$ NMR (from simple MAS): δ = 4.8 (br. s). – $^{13}C$ NMR (full and NQS spectra): δ = 16.6 (br. s, 4 C, $CH_3CH$), 31.7 (br. s, 4 C, $CH_3CH$), 117.7 and 121.2 (2 br. s, 8 C, CH aromatic), 136.7 (br. s, 8 C, $C_6H_2$ quaternary, bonded to C), 147.2 (br. s, 8 C, $C_6H_2$ quaternary, bonded to O). – $^{31}P$ NMR: δ = 122 (s). – EI-MS (70 eV); *m/z* (%): 802 (50) [$M^+$]. – $C_{32}H_{24}Cl_4O_8P_4$ (802.24): calcd. C 48.00, H 3.02; found: C 48.14, H 3.24.

**4:** Yield 1.56 g (69%), m.p. 394°C (dec.). – $^1H$ NMR ([D$_8$]THF): δ = 1.89 (d, *J* = 6.2 Hz, 12 H, $CHCH_3$), 4.34 (q, *J* = 6.2 Hz, 4 H, $CHCH_3$), 6.62 (s, 4 H, $C_6H_1$). – $^{31}P$ NMR ([D$_8$]THF): δ = 129.8 (s). – EI-MS (70 eV); *m/z* (%): 1118 (54) [$M^+$]. – $C_{32}H_{20}Br_4Cl_4O_8P_4$ (1117.83): calcd. C 34.55, H 1.81; found C 34.53, H 1.98.

*Preparation of* **5**: A Grignard reagent was prepared from 0.5 g of magnesium and 2.12 g (14.9 mmol) of methyl iodide in 30 ml of diethyl ether (30 min). The solution was filtered and added to a suspension of 3.0 g (3.7 mmol) of **3** in 30 ml of THF. Due to the poor solubility of **3** in organic solvents, it was employed in suspension here and during the following reaction. The reaction mixture was stirred overnight. The colourless solid product was collected, washed with 30 ml of $CH_2Cl_2$ and dried i.v. at 120°C for 1d. Yield 2.38 g (88%), m.p. 379°C (dec.). – $^1H$ NMR ([D$_8$]THF): δ = 1.45 (d, *J* = 9.4 Hz, 12 H, $PCH_3$), 1.69 (d, *J* = 7.5 Hz, 12 H, $CH_3CH$), 4.71 (q, *J* = 7.6 Hz, 4 H, $CH_3CH$), 6.34 and 7.45 (2 s, 8 H, $C_6H_2$). – $^{31}P$ NMR ([D$_8$]THF): δ = 192.83 (s). – EI-MS (70 eV); *m/z* (%): 720 (44) [$M^+$], 705 (100) [$M^+ - CH_3$], 690 (8) [$M^+ - 2\ CH_3$], 675 (15) [$M^+ - 3\ CH_3$]. – $C_{36}H_{36}O_8P_4$ (720.57): calcd. C 59.99, H 5.04; found C 59.83, H 5.03.

*Preparation of* **6**: To a suspension of 4.5 g (5.6 mmol) of **3** in 50 ml of THF was added 2.76 g (23.5 mmol) of $Me_2NSiMe_3$. The reaction mixture was refluxed with stirring for 5 h. The solid product was collected, washed with 30 ml of $CH_2Cl_2$ and dried i.v. at 120°C for 1 d. The NMR data of **6** corresponded to those reported[10]; the material was suitable for subsequent reactions. Yield 3.6 g (77%). – EI-MS (70 eV); *m/z* (%): 836 (38) [$M^+$], 792 (60) [$M^+ - NMe_2$], 748 (22) [$M^+ - 2\ NMe_2$].

*Preparation of* **7**: To a solution of 0.370 g (0.44 mmol) of **6** in 10 ml of $CH_2Cl_2$ was added 0.166 g (1.77 mmol) of $(H_2N)_2C(:O)/H_2O_2$ (1:1) adduct. The reaction mixture was stirred overnight. Subsequently, the solid product was filtered and the solvent was evaporated i.v. to give **7** as a colourless solid. The product was dried i.v. at 60°C for 3 d. Yield 0.43 g (quantitative), m.p. 311°C.– IR (Nujol): $\tilde{\nu}$ = 1320 $cm^{-1}$ (m) [P=O]. – $^1H$ NMR ($CDCl_3$): δ = 1.72 (d, *J* = 7.2 Hz, 12 H, $CH_3CH$), 2.78 [d, *J* = 10.5 Hz, 24 H, $N(CH_3)_2$], 4.75 (q, *J* = 7.2 Hz, 4 H, $CH_3CH$), 5.43 (s, 2 H, $CH_2Cl_2$), 6.34 and 7.48 (2 s, 8 H, $C_6H_2$). – $^{31}P$ NMR ($CDCl_3$): δ = 1.45 (s). – EI-MS (70 eV); *m/z* (%): 900 (30) [$M^+$], 856 (60) [$M^+ - NMe_2$], 812 (22) [$M^+ - 2\ NMe_2$], 44 (100) [$NMe_2^+$]. – $C_{40}H_{48}N_4O_{12}P_4 \cdot CH_2Cl_2$ (985.67): calcd. C 49.96, H 5.11; found C 49.89, H 5.12.

*Preparation of* **8**: To a solution of 0.5 g (0.6 mmol) of **6** in 15 ml of $CH_2Cl_2$ was added slowly (2 h) a solution of 0.588 g (2.39 mmol) of TOB in 10 ml of diethyl ether. The reaction mixture was stirred overnight at room temperature. 15 ml of *n*-hexane was added to the solution. The solid was collected, washed with 10 ml of diethyl ether and dried i.v. at 60°C for 1 d. Yield 0.58 g (54%), dec. 147°C. – $^1H$ NMR ($CDCl_3$): δ = 1.78 (d, *J* = 7.2 Hz, 12 H, $CH_3CH$), 2.80 and 2.96 [2 d, *J* = 10.5 Hz, 24 H, $N(CH_3)_2$], 4.82 (q, *J* = 7.2 Hz, 4 H, $CH_3CH$), 5.44 (s, 2 H, $CH_2Cl_2$), 6.30 and 7.28 (2 s, 8 H, $C_6H_2$). – $^{31}P$ NMR ($CDCl_3$): δ = – 45.27, –45.17, –44.73, and –44.03, (4 s).– FAB-MS (NBA); *m/z* (%): 1813 (0.2) [M + $H^+$], 1768 (0.2) [M + $H^+$ – $HNMe_2$], 46 (100) [$H_2NMe_2^+$]. – $C_{64}H_{48}Cl_{16}N_4O_{16}P_4 \cdot CH_2Cl_2$ (1905.17): calcd. C 40.98, H 2.65; found C 40.45, H 2.68.

*Preparation of* **9**: A solution of 0.68 g (0.81 mmol) of **6** in 25 ml of $CH_2Cl_2$ was placed into a heavy-walled glass tube, fitted with a TEFLON® stopcock, and cooled to –196°C. HFA (1.56 g, 9.4 mmol) was condensed onto this solution. The tube was left at room temperature for 3 d. After 1 d, a colourless solid started to precipitate. The product was filtered, washed with 20 ml of $CH_2Cl_2$, and dried i.v. at 60°C for 1 d. Yield 0.92 g (52%), m.p. 224°C (dec).–$^1H$ NMR ($CDCl_3$): δ = 1.80 (d, *J* = 7.1 Hz, 12 H, $CH_3CH$), 2.89 [br. s, 24 H, $N(CH_3)_2$], 4.82 (q, *J* = 7.2 Hz, 4 H, $CH_3CH$), 6.34 and 7.30 (2 s, 8 H, $C_6H_2$).–$^{31}P$ NMR ($CDCl_3$): δ = –45.83, –42.37 (2 s). – FAB-MS (NBA); *m/z* (%): 2165 (33) [M + $H^+$], 2120 (100) [M – $NMe_2^+$], 2076 (40) [M – 2 $NMe_2^+$].– $C_{64}H_{48}F_{48}N_4O_{16}P_4$ (2164.92): calcd. C 35.51, H 2.23; found C 35.48, H 2.43.

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☆ Dedicated to Professor *Alfred Kolbe* on the occasion of his 65th birthday.


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[18] Sideband fitting using peak heights was carried out for spectra obtained at the two spin rates, in order to derive values for the $^{31}P$-shielding tensor parameters. An in-house Durham computer program (J. R. Ascenso, L. H. Merwin, H.-P. Bai, J. C. Cherryman, unpublished) was used. This was based on the equations of M. M. Maricq, J. S. Waugh, *J. Chem. Phys.* **1979**, *70*, 3300–3316, and incorporated the error analysis of A. C. Olivieri, *J. Magn. Reson. A*, **1996**, *123*, 207–210. The average value for the two spin rates for the shielding anisotropy, $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{11}+\sigma_{22})$, is 204 ppm, with an asymmetry (η) of 0.31. The individual average shielding components are $\sigma_{11} = -210$ ppm, $\sigma_{22} = -169$ ppm, and $\sigma_{33} = 14$ ppm. The values from the

spectra at the two spin rates showed good agreement, especially considering that peak heights were used rather than integrated peak areas.

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[20] *Crystal data:* **4**·$CH_2Cl_2$, $C_{33}H_{20}Br_4Cl_6O_8P_4$, $M$ = 1200.71, trigonal, space group $R\bar{3}$, $a$ = 49.520(7), $c$ = 9.009(2) Å (hexagonal axes), $V$ = 19.132(5) nm$^3$, $Z$ = 18, $D_x$ = 1.876 Mg m$^{-3}$, λ (Mo-$K_\alpha$) = 71.073 pm, μ = 4.36 mm$^{-1}$, absorption correction: ψ scans, min. trans: 0.58, max trans: 0.83, $F$(000) = 10512, $T$ = −100°C. *Data collection and reduction:* Colourless prism 1.0 × 0.50 × 0.50 mm, Siemens P4 diffractometer, 2θ range 6–50°, 11964 intensities, 7493 independent ($R_{int}$ = 0.058). *Structure solution and refinement:* The structure was solved by direct methods and refined anisotropically on $F^2$ (program system: G. M. Sheldrick, *SHELXL-93*, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. The final $R(F)$ value was 0.055 with $wR(F^2)$ = 0.146 for all reflections. $S$ = 1.07; max Δ/σ < 0.001; max Δρ = 1.2 e Å$^{-3}$ in the solvent region. The chlorine atoms of the solvent are disordered and were refined as two positions. Full details of the crystal structure determinations (except structure factors) have been deposited under the number CCDC-100083 at the Cambridge Crystallographic Data Centre. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: int. +44(0)1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk].

[21] The X-ray crystal structure of **5** was determined. The calix[4]resorcinol framework was as expected and displayed the cone conformation. The methyl groups were directed outwards from the framework. However, large regions of poorly resolved electron density precluded satisfactory refinement. Crystal data: monoclinic, space group $P2_1/m$, $Z$ = 2 (mirror symmetry), $a$ = 11.183(2), $b$ = 20.392(3), $c$ = 11.355(2) pm, β = 104.673(10)°.

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